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Author(s)	谷村, 克己
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MECHANISM
OF
STORAGE AND RELEASE OF RADIATION-INDUCED ENERGY
IN
ALKALI HALIDES

by
Katsumi TANIMURA

Department of Nuclear Engineering
Faculty of Engineering
Osaka University
Suita, 565
Japan

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INTRODUCTION

[1·1] Radiation Damages in Solids

The sharp developement of the nuclear physics thirty years ago has given the possibility that man utilizes the nuclear reactions as a new energy source, and has given scope to some connected areas of the research. These areas have now been systematized, under the aim of utilization of atomic energy, as the " nuclear engineering ".

This field of engineering has involved several characteristic problems which must be newly solved, though it is sure that the nuclear engineering has based on achievements of other fields of engineering and science which are established earlier.

Radiation damage is one of the most important subjects which nuclear engineering must clarify. Nuclear reactions, fission as well as fusion, always accompany radiations extending from the high-energy photon to heavy charged particles involving fission fragments. This situation has brought forward the problem of behaviours of materials under radiations.

Here radiation damage is defined to involve all phenomena resulted by the interaction between materials and radiations as well as the radiation-induced changes in properties of materials, and materials are restricted to crystalline solids.

Let us now pay our attention to defect formation by radiation; this is one of the main phenomena of solids under the radiation, andthis is the origin of changes in properties of solids.

Following three generic classes of defect formation process can be distinguished; electronic process, elastic collisions, and radiolysis.1) The electronic process includes all changes in electronic states owing to absorption of radiation energy, but does no formation of defects of crystaline lattices. Elastic collisions are the process where atoms and ions are displaced due to momentum and energy transfer from irradiating particles. Radiolysis process involves creation of defects of lattices which originates from an electronic excitation followed by a series of reactions.

In general, these entire range of defect formation processes results in extremely complex radiation effects. One of the useful approaches in understanding the mechanism of radiation damages has been " the method of analysis ", namely the simple act of choosing to work on solids which are chemically and structurally simple.2)

In this work on radiation damages, from this view point, alkali halide crystal which is the typical ionic crystal and is one of solids with most simple structure is adopted as a "solid", and radiations are limited to ionizing radiation at low temperature. This combination and restriction make radiolysis dominant in defect formation, and some aspects of radiation effects relatively simple. Thus this work concerns damages by radiolysis in a nesrly ideal ionic crystal.

[1·2] Color Centers in Alkali Halide Crystals

The ionizing radiation damages in insulaters has been studied for some 40 years. This type of study in alkali halides has been known as color center physics, since the radiation-induced defects in this solid cause optical absorption from ultra-violet(uv) to visible light regions which were transparent before irradiation.

The main reason for which this subject has been studied by many workers for a long time is following; this gives considerable insights into the interactions between electrons (or holes) and other electrons, phonons or nuclei in insulating solids, because of applicability of a wider range of experimental approaches and techniques and of enabling workers to compare theory and experiment more deeply for clearer understanding.

The study under the aim of technological application of color centers has also been made. Color centers are now widly used in dosimetry and have a potentially wide application in information storage and processing devices.3) Since such area of studies is, however, far from the aim of this work, further descriptions on the applied research given here.

The research of color centers except the technologically oriented application can be distinguished into following categories;

1) study on phenomena under irradiations,
2) study on properties and configurations of created defects,
3) study on defect annihilation process,
4) study on effects of radiation-induced defects on bulk properties of crystals.

The first category aims now to clarify defect formation mechanism and luminescent phenomena. The second is the study to understand the states of localized electrons and holes associated with, in most cases, lattice defects. The third involves the studies on the phenomena such as thermoluminescence (TL) and thermally stimulated conductivity (TSC) which take place during annealing of irradiated crystals. In the fourth category, the object of study is the interactions of radiation-induced defects with other species involved in the host crystal.

Brief reviews on the first, third and fourth categories of research will be given later in the appropriate parts of this thesis, to make clear the present problems in these fields, since these three are mainly investigated in this work.

In the second category of color-center research, properties of excited states of defects in alkali halides have been currently studies, though this work does not concern these properties. On the other hand, the most properties of the ground states and the configurations of typical simple color centers are well understood so far. In the following part of this section, these establishments are summarized in the sense that what types of defects are created by ionizing radiation at low temperature.

In Fig.1·2·1 are sketched some of defects which have close correlation with this work, and a few comments for these defects will be given later.

The first result which should be stressed is the fact that the Frenkel defects are created by radiolysis. The initial evidence is the discovery and establishment of the configuration of the H center based on the electron paramagnetic resonance (EPR) and optical absorption measurements.4-6) The H center is essentially the dihalide molecular ion located in one anion site, as illustrated in Fig.1·2·1. This assignment strongly indicates that the interstitial halogen atom is produced together with its complementary center, the F center, at least at low temperature.

More powerful evidence that Frenkel defects are created by radiolysis comes from simultaneous measurement of the expansion of a crystal and its increase in lattice constant. When Frenkel pairs are formed, equal changes in the macroscopic size and the lattice constant of a crystal should be observed. 7) Balzer et al. have demonstrated that the percentage increase in lattice constant and macroscopic size is the same at all temperatures up to room temperature. 8) The typical example of their measurements are shown in Fig.1·2·2. Their study thus has established that the radiolysis in alkali halides results in the formation of Frenkel defects.

Now, two types of Frenkel pairs are well known; one is the neutral Frenkel pair consisting F and H centers mention-

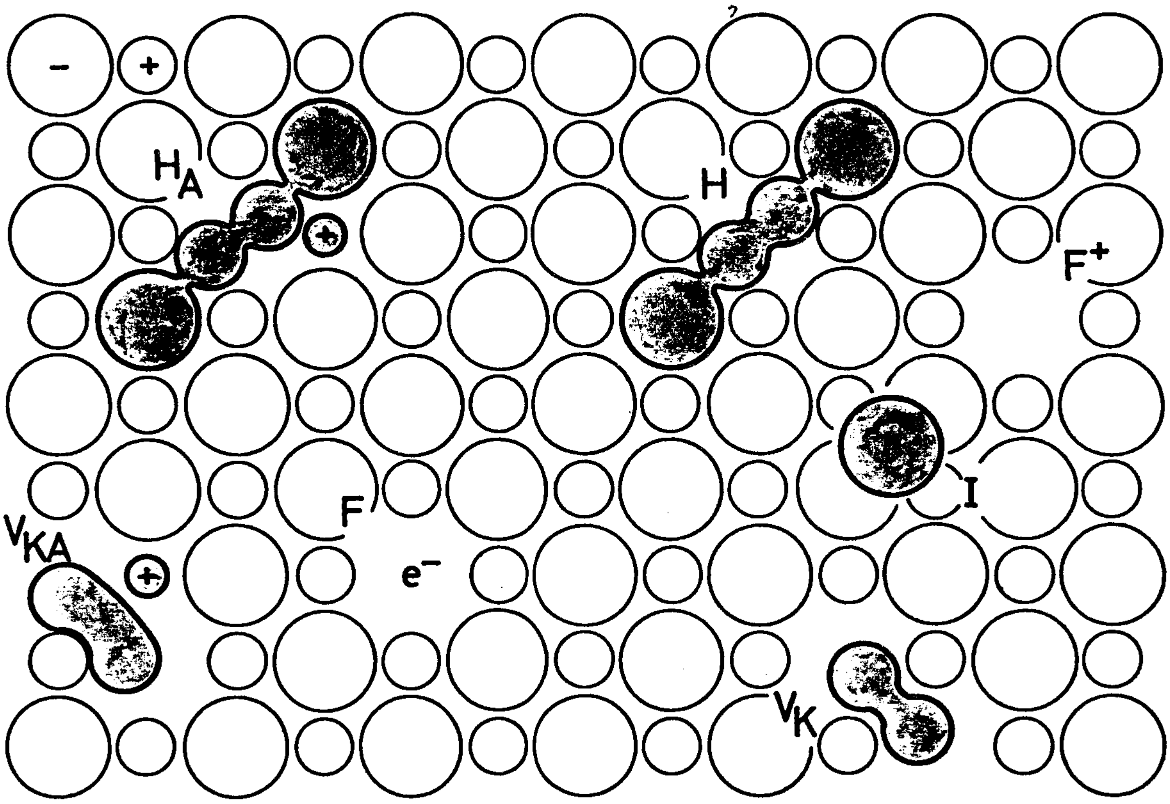


Fig.1.2.1. Schematical lattice configurations of simple defects in the anion sub-lattice of alkali halides with NaCl structure. Only defects which have close correlation with this work are sketched. An anion vacancy is abbreviated here mainly as F^+ instead of the older notation of α, based on the notation of Sonder and Sibley.[1)]

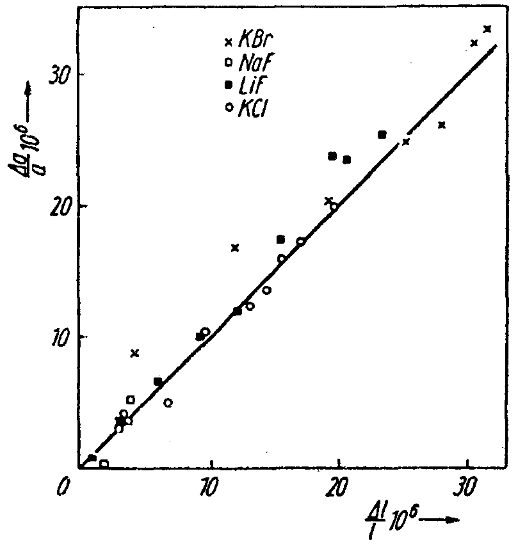


Fig.1·2·2. Relative lattice parameter and length changes for alkali halides x- ray irradiated at room temperature. (from ref.8)

ed above, and the other is the charged Frenkel pair which consists of an interstitial halogen ion, the I center, and a halogen vacancy, the F$^+$ center.

Theoretical lattice calculation 9) has suggested that the I center is an interstitial halogen ion situated at the center of the cube formed by four cations and four anions. However, Lohstöter et al. have concluded that the I center is a cube-oriented defects, based on their experimental results of diffuse x-ray scattering.10) The configuration of the I center has not been clearly established so far.

These halogen interstitial atoms and ions can be trapped by nearest neighboring alkali impurity ions to form the H$_A$ and I$_A$ centers.11-15) The configuration of the H$_A$ center associated with a Na$^+$ ion in KCl has been identified by EPR studies.12) The configuration is also sketched in Fig.1·2·1. The model of the I$_A$ center has not yet been established, as that of the I center has not.

Another interesting and important defect, which accompanies no defects of lattices, is the V$_K$ center. This is essentially the self-trapped hole in perfect crystals. The

EPR study has established its configuration of that the V_K center consists of two nearest-neighbor <110> halide ions which trapped a hole.[16) The V_K center associated with an alkali impurity ion, the V_{KA} center, is also formed.[17,18) It is noted that the formation of a self-trapped hole must accompany trapping an electron by some other defects, such as impurity.

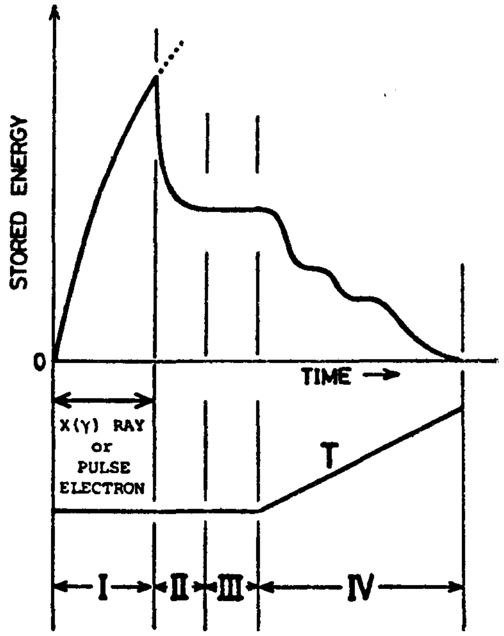
The self-trapped hole does play an essentially important role on the radiolysis in alkali halides.

[1·3] Outline of This Work

The view point of the author on the inonizing-radiation damages in alkali halides is followings. The defect formation due to irradiation results in the changes in electronic and lattice states which accompany the increase of total energy of the crystal. In other words, the defect formation is the radiation-energy storage in the form of lattice energy. This stored energy is the fundamental cause of the radiation-induced changes in properties of the crystal, and thus the recovery of the changes in properties originates from the release of stored energy due to defect annihilation.

Based on the view point, the ionization damages can be divided into four regions as shown in Fig.1·3·1. The region I involves defect formation process through which the radiation-energy is stored. After some transient phenomena(the region II), an "excited" state is formed. Properties of the excited state compared with those of ground state, i.e. the state before irradiation, are called radiation damage in a narrow sense(the region III). By external stimulation, for example by heat, the stored energy is released due to defect annihilation which accompanies the recovery of radiation-induced changes in properties (the region IV).

One of the main part of this work concerns the defect formation mechanism. Following sequence of processes can



- I IONIZATION-DAMADE PROCESS
  - Ionization
  - Hole Relaxation and Exciton Formation
  - Decay of Exciton
    - 1) Radiative Decay (Luminescence)
    - 2) Non-Radiative Decay
      - i) phonon creation
      - ii) defect formation
- II TRANSIENT PHENOMENA
- III PROPERTIES OF AN " EXCITED " STATE
  - (Radiation-Induced Changes in Properties)
- IV DEFECT ANNIHILATION AND RELEASE OF STORED-ENERGY
  - Release of Stored-Energy
    - 1) Phonon (Stored-Energy)
    - 2) Photon (Thermoluminescence)
  - Thermally Stimulated Conductivity
  - Thermally Stimulated Electron Emission

Fig.1.3.1. Distinction of the ionization damages present study concerns. The study on the region II is not involved in this thesis. Typical distinguishable phenomena in each region are mentioned in the figure.

be distinguished at the region I;

1) ionization, or creation of free electrons and holes,
2) hole relaxation and exciton formation,
3) decay of the exciton.

Since the first and second processes are considered to take place within very short time, less than 10^{-16} sec and 10^{-12} sec, respectively, direct observations of them are not possible at present. These processes have been treated only theoretically and/or by speculations based on the results of post irradiation. Our detailed experimental study on the region I, thus, is limited to the third process, or the decay of created excitons.

Two types of exciton decay take place; one is the radiative decay and the other is the non-radiative one. It is generally accepted that color-center formation is taking place through non-radiative decay of an exciton. Therefore, properties and behaviours of excitons are one of the subjects studied in this work.

It is also possible to distinguish radiolysis in alkali halides into following sequences; one is the dissociation of an exciton, and the other is the secondary reactions of created primary interstitials. The latter process is important to understand the color-center formation at temperatures where the primary interstitials are not thermally stable; the interaction of these interstitials with other imperfections to form variety of complex interstitial centers is the dominant reaction at the temperatures. The secondary reactions of created interstitials is the second subject which is investigated here.

The third concerns the mechanism of release of stored energy or defect annihilation (the region III). In general, stored-energy is released in two ways; in the form of light and of heat. The former is thermoluminescence and the latter is the release of "stored energy" in a narrow sense. The special interest lies in thermoluminescence, since it involves the conversion of lattice energy into the energy of electronic excitation which results in the emission of photons. Thus the mechanism of thermoluminescence has the reverse property of radiolysis. This has been studied for pure, or non-activated, materials.

As one of properties of an "excited" state(the region IV), radiation induced changes in mechanical property, hardness, of alkali halides have been studied. This subject is a typical one of studies in the fourth category mentioned before and has been known as radiation hardening. In the study of radiation hardening, the main interest is the interaction of radiation induced defects with dislocations crystals involve. Through the analysis of the interaction, one can know the mechanism of dislocation dynamics in the typical ionic crystals, and furthermore, some properties of the defects responsible for hardening.

The characteristic feature in experimental approach of this work is the application of method of INTERNAL PERTURBATION due to impurities. The main interest here is not the behaviours of the impurity in crystals itself, but the intrinsic process of crystals which can be cleared through the insight of impurity-effects in radiolytic behaviours. For this purpose, the "ideal" impurity is the one which does not drastically disturb the intrinsic processes and reactions, but does give the effective changes in radiolytic phenomena which can be observed experimentally. In this work, thus, the foreign alkali ions are used as such an impurity.

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2

EXPERIMENTAL METHOD

[2·1] Samples

Alkali halide single crystals used in this work are the pure crystals of KBr, KCl, NaCl, and KI, and crystals doped with alkali impurity ions and/or electron-trapping impurities such as NO_2^-, Ag^+, and Tl^+.

Pure specimens were obtained from crystal blocks purchased from Harshaw Chemical Co. Doped ones were all grown by the Kyropoulos method in dry nitrogen atmosphere, using powders purchased from Nakarai Chemical Co, or Merch Co. Assays of used KBr and KCl powders are shown in Table 2.1.1. The NaCl powder is one with a purity of 99.99%.

Lithium halide powders, which usually involve crystal water, were doped to the melt, after desiccation of powders in vacuum.

Li^+ impurity ions tend to aggregate. In order to disperse them again, Li^+-doped crystals were heated to 500 C and rapidly cooled to room temperature, before irradiation.

Concentration of impurities were determined by the semiquantitative spectrographic analysis with ± 10 % error, which was performed by Matsushita Electric Co.

Table 2.1.1. Assays of KBr and KCl powders used in this work.

	KCl	KBr
Solubility in water	To pass test	To pass test
Free alkali	To pass test	0.007%
Sulfate	0.002%	0.005%
Phosphate	0.001%	0.002%
Iodide		To pass test
Heavy metals	0.0005%	0.0004%
Iron	0.0003%	0.0005%
Barium	0.001%	0.002%
Magnesium	0.0005%	0.001%
Sodium	To pass test	0.0012%
Calcium	0.001%	0.001%
Arsenic		0.0005%
Total Nitrogen	0.001%	0.001%
Maximum	99.5%	99.8%

[2·2] Cryostat

Two different types of cryostats were used for the optical absorption and emission measurements at low temperature near liquid-helium temperature. These stainless steel cryostats were made in Torisha Lab. under the idea of the author.

One cryostat (Cryo.I) has the sub-tank with a needle valve for liquid-helium supply from the main-tank and with a heater. This structure makes it possible to keep a given temperature of the sample holder constant in the range from 6 K to 80 K.

The Cryo.I has also three pairs of light paths, which gives fairly an advantage for luminescence measurements described later.

The other cryostat (Cryo.II) is one for the optical absorption and emission measurements below 4.2 K. Samples can be cooled down to 1.7 K through thermal conduction, when the liquid-helium tank is evacuated with a rotary pump.

For the effective radiation shielding, infrared absorbing visible transmitting filters (CS1-75) and quartz plates are placed on the light paths of the radiation shield.

Temperature was measured by Allen-Bradley carbon resistor and/or Au:Fe - Chromel thermocouple.

Another cryostat (Cryo.III), whose optical-arrangement is similar to that of Cryo.I, was also used for the optical absorption and emission measurements above 80 K.

[2·3] Measurement and Control of Temperature

Temperature, except below 4.2 K, was mainly measured by Au:Fe - Chromel thermocouple, thermoelectromotive force of which shows an excellent linearity as a function of temperature between 4 K and 70 K, and between 90 K and 300 K. The linearity involves the advantage in the isochronal annealing experiments.

Two different patterns of temperature control were carried out; one is the isochronal pulse annealing where a fixed temperature remains unchanged for a given interval, and the other isochronal annealing where the heating rate is kept constant.

In the former, difference between the out put of a thermocouple and the voltage of a fixed value generated by a proper circuit was d.c. amplified, and the difference which was less than 1/100 of a fixed value of voltage was kept unchanged by proper dropping of liquid nitrogen or liquid helium to the sample holder. This treatment gave the heat pulse to the sample with a sharp initial rise and final drop and with a constant value between them.

In the case of isochronal annealing, the heating rate was kept constant within ± 0.05 deg/min, using a programable temperature controller (Shinku Riko HPC-5000VL) with a Au:Fe - Chromel thermocouple as the sensor.

[2·4] Stationary Measurements of Optical Absorption and Emission

Figure 2.4.1 shows the schematic diagram of the apparatus for the luminescence measurements. Luminescence resulted by x-ray excitation and by the excitation of a given color centers due to optical illumination were measured.

Samples were excited by x ray, generated by Toshiba x-ray tube (AFX-61A-W), through a KBr filter with a thickness of 0.2 mm, in order to prevent soft component of the x ray from the prominent coloration.

Monochromatic light was obtained from the white light of a Xe lamp (Ushio UXL-500D in UL-501C) and of D_2 lamp (Shimazu 33-86-35) through a Shimazu-Baush and Lomb grating monochromator or appropriate optical filters

Luminescence from a sample was detected by a HTV R-292 photomultiplier which was placed behind the exit slit of

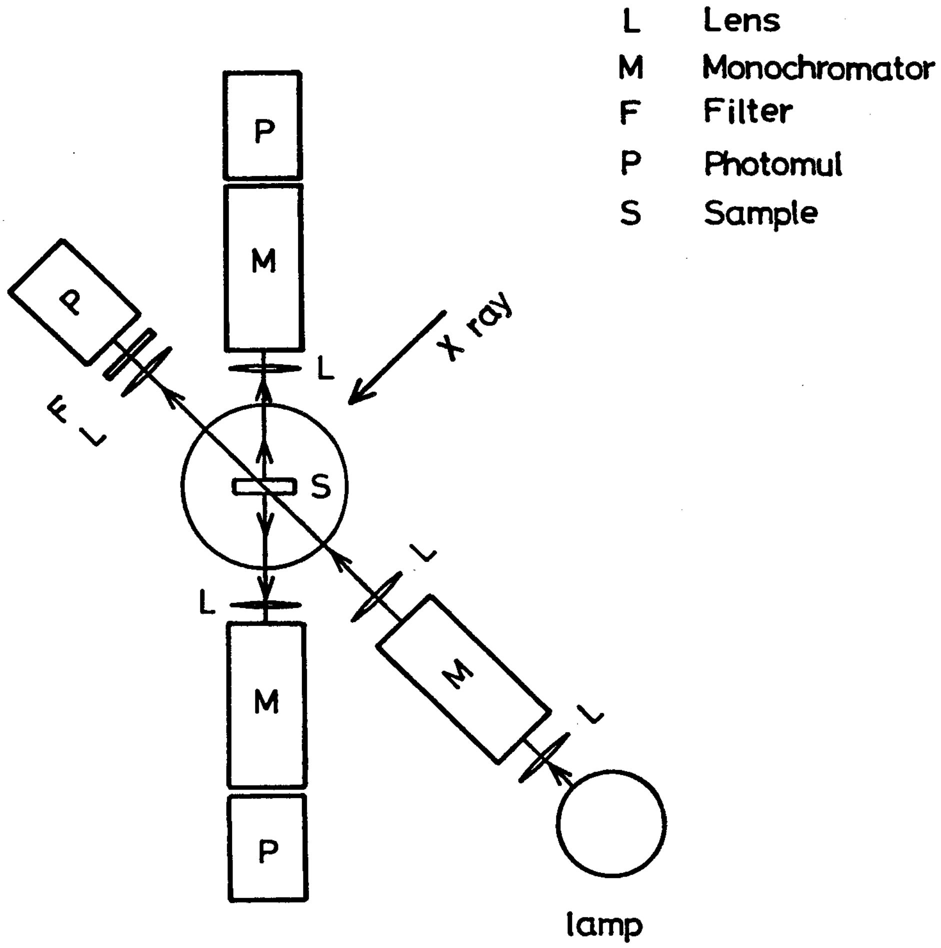

Fig.2.4.1. Schematic diagram of the apparatus for stationary luminescence measurements. Diagram for a continuous recording of the optical density is also shown.

the grating monochromator. Photomultiplier out put vs. wavelength was recorded by an X-Y recorder (Yokogawa Type 3077).

The spectral sensitivity of the detector system including the collective lens, the grating monochromator and the photomultiplier was calibrated, using a rhodamine B quantum counter.

Optical absorption spectra of irradiated crystals were measured by a Shimazu SV-50A spectrophotometer.

For a continuous recording of the optical density at a fixed wavelength in the isochronal annealing experiments, a Shimazu-Bausch and Lomb grating monochromator with a tungsten filament lamp was used as a light source and the transmitted intensity was measured with a HTV R-207 photomultiplier tube. The photomultiplier out put was recorded together with the thermoelectromotive force of a thermocouple by a multi-pen recorder (Rika Denki B-361).

[2·5] EPR Measurement

EPR measurements of irradiated alkali halides were also employed to obtain annealing behaviours of the paramagnetic color centers. Samples with dimensions of 2 X 2 X 15 mm^3 in a evacuated quartz tube were irradiated by Co-60 γ ray in liquid nitrogen.

EPR was measured by a JEOL-JM-PE-3 from 80 to 250 K, using a variable-temperature cabity.

[2·6] Mechanical Test

All the test were done in $\langle 100 \rangle$ compression using Tensilon testing machine with cross head speed of 0.03 cm/min.

Measurements were made at liquid-nitrogen temperature or at a given temperature from 4.2 K to 250 K.

The measurements at 77 K were performed as follows:

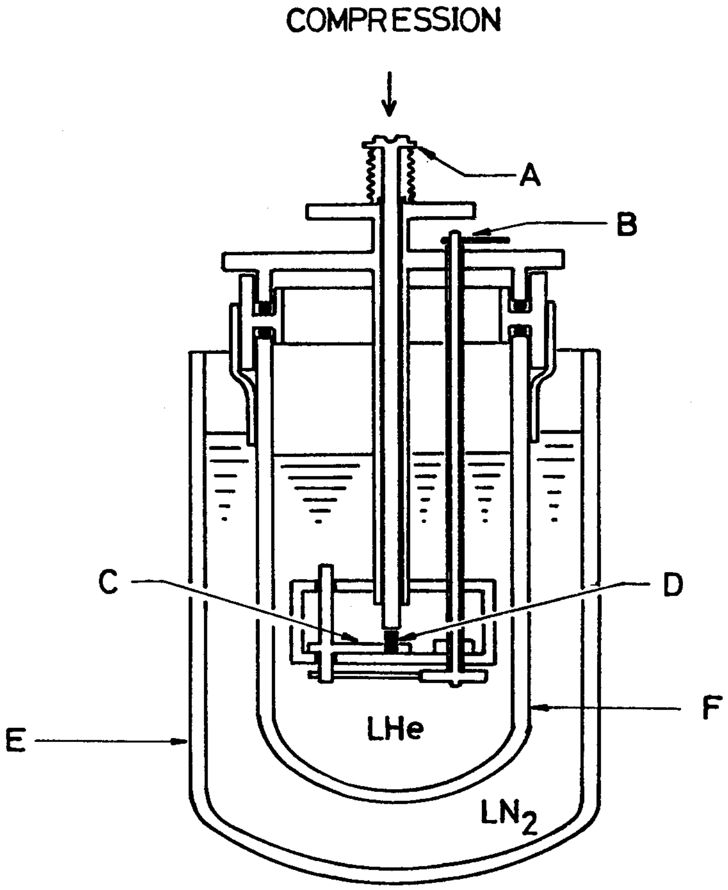

Fig.2.6.1. Experimental apparatus for low temperature (below 77 K) mechanical test:
A; compression rod, B; rotating rod for sample exchange, C; sample holder, D; specimen, E; outer dewar, F; inner dewar, respectively.

After irradiation, specimens were transferred to the precooled jig of the machine which remained immersed in liquid nitrogen under safety dim light.

The low-temperature test below 77 K were made using the special jig shown in Fig.2.6.1, as following procedures:

1) Six specimens irradiated at 77 K were set to the sample holder of the jig in liquid nitrogen,
2) next the jig was transferred, with a bath filled with liquid nitrogen, quickly into the inner dewar which was precooled by the outer dewar filled with liquid nitrogen,
3) then liquid helium was poured into the inner dewar before the temperature of the specimens rose up to 100 K.

Temperature of the specimens were measured by a Au:Co-Cu thermocouple.

[2·7] Transient Optical Absorption and Emission Measurements

Figure 2.7.1 shows the experimental arrangements for measuring the transient optical phenomena.

The electron pulse was generated with a Febetron Model 707, operated at an energy of 2 MeV, at a peak current of 1000 A. The waveform of the electron pulse is shown in Fig.2.7.2.

In order to obtain electron pulses with various intensities, 3 mm thick copper plates with different numbers and sizes of holes were placed between the electron tube of the Febetron 707 and the specimen. The specimen was separated from the copper plates by 10 cm, in order to make the electron intensity uniform at the position of the specimen.

Typical examples of the osciloscope traces for absorption and emission measurements are shown in Fig.2.7.3.

In the case of luminescence measurement, emitted light

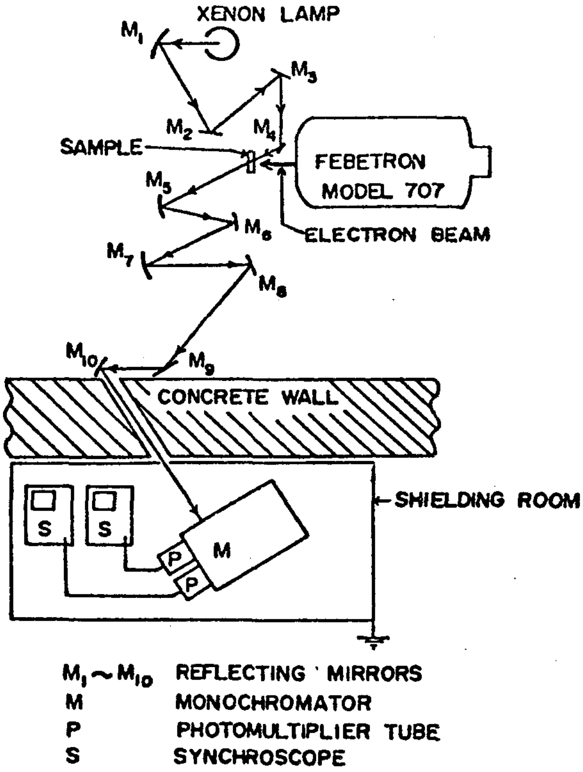

Fig.2.7.1. The experimental arrangements for measuring transient optical absorption and emission of crystals by an electron pulse irradiation.

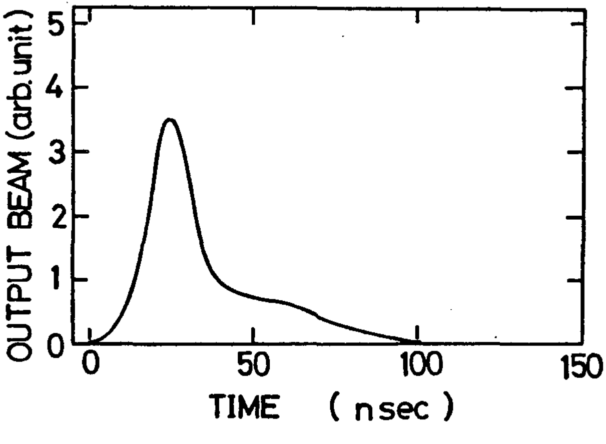

Fig.2.7.2. The waveform of the electron pulse obtained from Febetron 707.

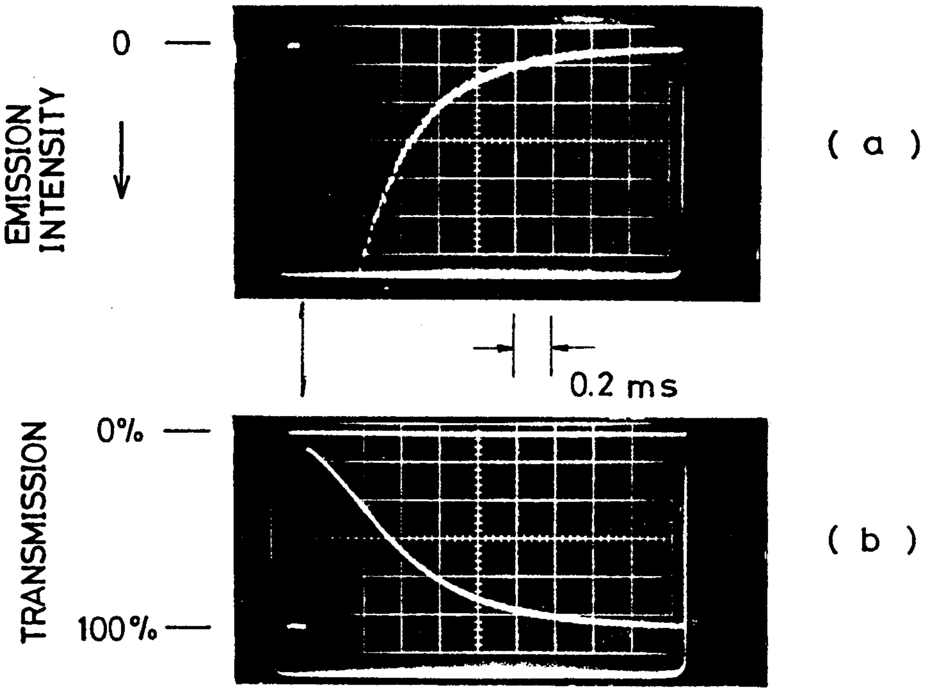

Fig.2.7.3. Oscilloscope traces of decay curve of the triplet emission at 390 nm (a), and of transmission change at 600 nm (b) in a NaCl crystal, induced by a single-electron pulse at 5 K. The time scale of one division in abscissa is 0.2 msec.

was guided into the shielding room by the reflecting mirrors (M_5 - M_{10}). The guided light was passed through a monochromator (Shimazu GE-100) and detected with two photomultipliers (EMI 6256 B) placed at two exit slits adjusted at two wavelengths. The out put signals of the two photomultipliers were recorded with two oscilloscopes (Iwatsu SS-112).

In the case of transient absorption measurement, the light from a Xenon Arc Lamp (Ushio UXL-150D) was incident on a specimen through the reflecting mirrors (M_1 - M_4). The emergent light was transmitted into the shielding room similarly as the emitted light. The changes in intensity caused by the electron pulse were detected with photomultipliers and recorded with oscilloscopes.

By employing the two-channel detector system, the absorption or emission changes at two wavelengths induced by a single pulse were compared. This procedure eliminates the possible error caused by the fluctuation of the intensity of the electron pulses produced by the Febetron.

3

RELAXATION AND DISSOCIATION OF THE EXCITON

[3·1]

INTRODUCTION

> Current knowledge on the relaxation and dissociation of an exciton in alkali halides is briefly reviewed in order to make the present problems in this field clear. In the first place, the electronic structure of the self-trapped exciton is summarized. Then, the precursor of the Frenkel pair, the exciton state responsible for the color center formation is discussed, based on the experimental results of recent works. Finally, we briefly sketch an overall plan of the contents of this chapter.

§1 Electronic Excitation (The Self-Trapped Exciton)

When alkali halide crystals are subjected to ionizing radiation, they luminesce if the temperature is low enough. The luminescence which is apparent to have no correlation with any impurity in a crystal, intrinsic luminescence, was first observed by Van Sciver and Hofstadter(1955),1) and by Teegarden(1957).2)

The clear assignment of the origin of intrinsic luminescence, however, has been first made by Kabler3) and by Murray and Keller.4) These workers have established that the intrinsic luminescence is due to the electron-hole recombination in which the hole is in the form of the self-trapped hole, the V_K center.

The lowest energy-absorption peaks in the absorption with considerable structure in the ultraviolet absorption region (a typical example is shown in Fig.3.1.1) has been shown to result in the creation of excitons on halogen ions.5-7) The emission spectra due to uv light excitation in the exciton-absorption band are closely related to the spectra resulting from x-ray irradiation, or the recombination of an electron with a V_K center. An example of emission spectra due to uv-light excitation is shown in

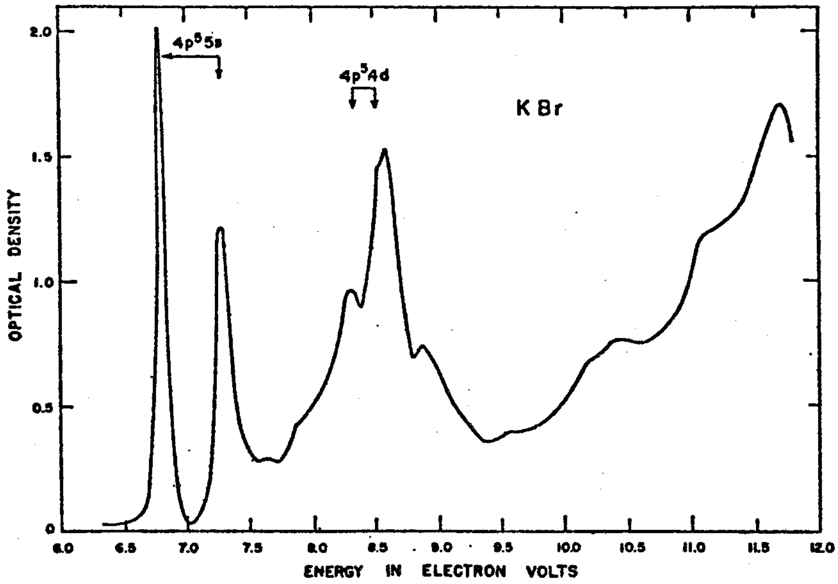

Fig.3.1.1. Optical absorption spectrum of thin film of KBr deposited on LiF substrate. Measurement was made at 10 K (from ref.7).

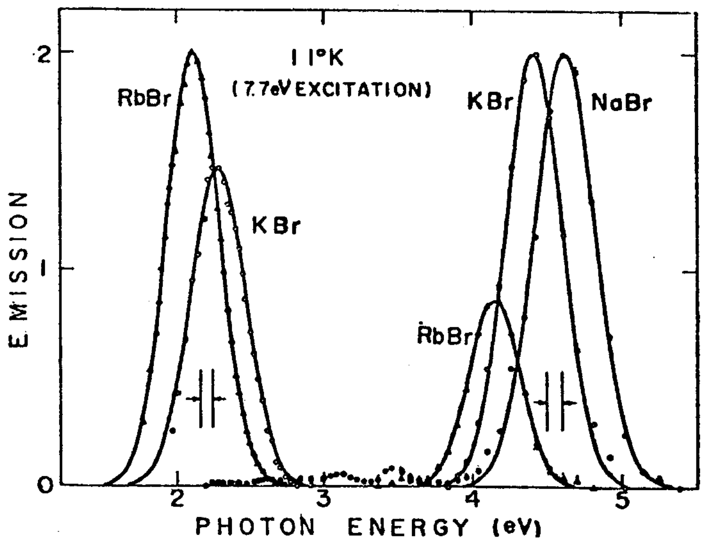

Fig.3.1.2. Luminescence spectra of alkali bromide crystals induced by illumination in the fundamental absorption region at 7.7 eV and measured at 11 K. Solid lines represent calculated Gaussian curves (from ref.8).

Fig.3.1.2.$^{8)}$

This result indicates that an exciton on a halogen ion forms the state of an electron trapped by a V_K center through lattice relaxation. Thus the term " self-trapped exciton " (STE) is appropriate to describe the initial state of intrinsic luminescence.$^{9)}$ The STE is hereafter abbreviated as (V_Ke).$^{10)}$

The electronic structure of (V_Ke) has been extensively studied mainly by Kabler and his cowarkers, through experiments of luminescence,$^{3,7,9)}$ magnetic circular dichroism (MCD),$^{11)}$ electron paramagnetic resonance (EPR),$^{12)}$ and optical absorption.$^{13,14)}$

Figure 3.1.3(a) shows schematical energy diagram for (V_Ke). The notation of the levels has been designated in terms of the irreducible representation for $D_{\infty h}$ and D_{2h}. The x,y,z axes for D_{2h} stands for the set shown in Fig.3.1.3(b). Arrows indicate the transitions within the (V_Ke), which have been observed so far.

In most alkali halides, two emission bands are observed; one is σ-polarized (σ emission), and the other π-polarized (π emission) with the lower transition energy than the former. It has been shown that the radiative lifetime of σ emission is the order ot 10^{-9} sec, whereas that of π emission varies from 10^{-3} sec to 10^{-6} sec.$^{9)}$ The relatively longer lifetime of π emission have suggested that the initial state of the emission is a triplet state.

This has been confirmed by the works on EPR and MCD.$^{11,12)}$ According to the notation of Fuller et al.$^{13)}$ the π emission in KBr thus arise from the electronic transition of $A1s\sigma_g;{}^3\Sigma_u^+ \rightarrow A\sigma_u 4p;{}^1\Sigma_g^+$, where A represents the out most electronic configuration of the bromine molecular ion, Br_2^-, of $(\sigma_g 4p)^2(\pi_u 4p)^4(\pi_g 4p)^4(\sigma_u 4p)$. The multiplicity forbiddenness in this transition is broken by mixing due to halogen spin-orbit (s-o) coupling of $C1s\sigma_g;{}^1\Pi_u$ into $A1s\sigma_g;{}^3\Sigma_u^+$, where C stands for the configuration of $(\sigma_g 4p)^2(\pi_u 4p)^3(\pi_g 4p)^4(\sigma_u 4p)^2$.

Song et al. have shown from their theoretical work that

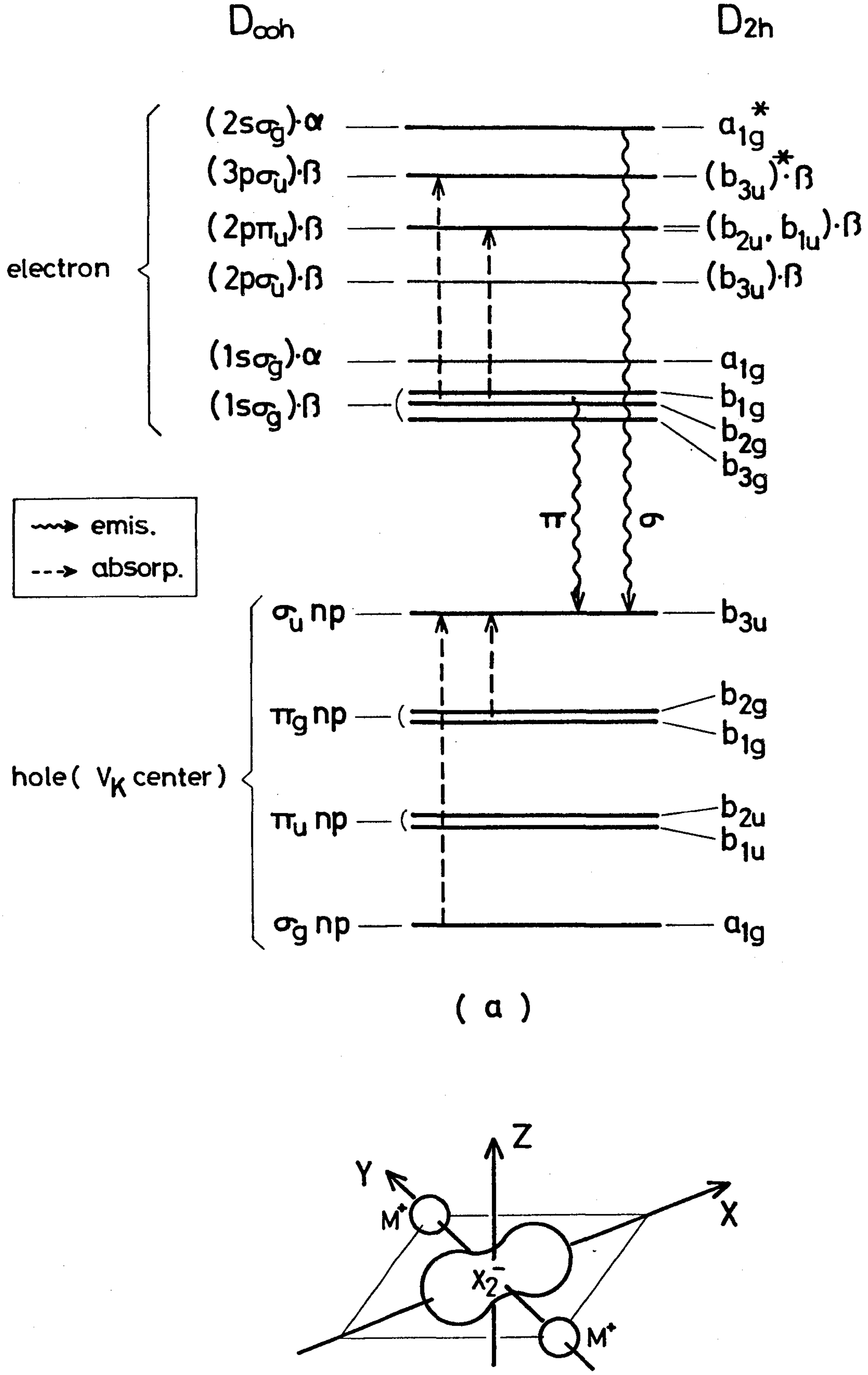

Fig.3.1.3. (a): Single electron state description of STE in alkali halides. α and β indicate singlet and triplet states of levels. Arrows show the optical transitions which have been observed. (b): The coordinate set of the exciton for D_{2h} symmetry.

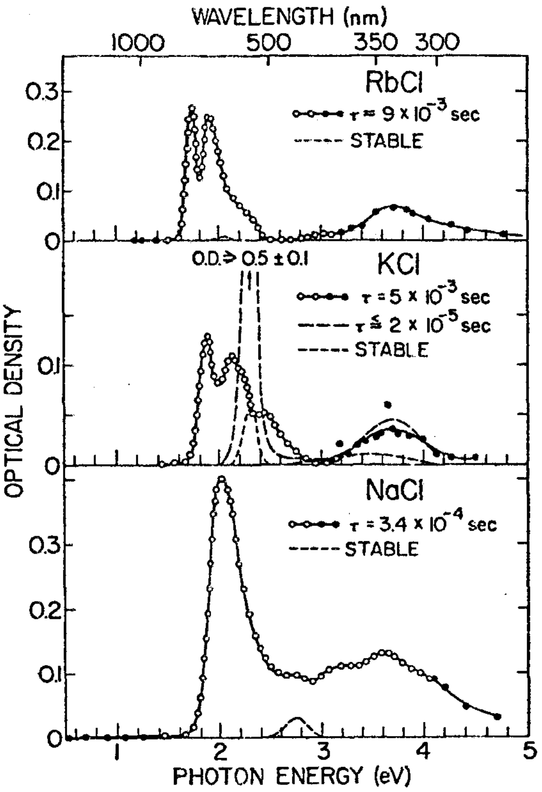

Fig.3.1.4. Time resolved absorption spectra for chlorides at 9 ± 3 K. The solid curves and data points indicate that part of the initial absorption which decays with the lifetime of the lowest triplet state of STE. Dashed curves indicate that part of the initial absorption which is due to F and hole centers (from ref.14).

the initial state of σ emission is $A2s\sigma_g;{}^1\Sigma_g^+$. Corresponding transition is dipole-allowed.

The luminescence corresponding to the transition from $A1s\sigma_g;{}^1\Sigma_u^+$ to $A\sigma_u4p;{}^1\Sigma_g^+$ has not been observed. The mechanism of absence of such an emission band has not been known yet.

In this thesis, the initial states of σ and π emissions are written as (V_Ke)$_\sigma$ and (V_Ke)$_\pi$, respectively, and the notation in terms of the irreducible representation shown in Fig.3.1.3(a) is used when nescessary.

Transient optical absorption due to (V_Ke)$_\pi$ has been studied by Kabler et al.[13,14] A typical example of their resuls, for clolides, is shown in Fig.3.1.4.

They have assigned the absorption in the 3 - 4 eV range to hole transition within the STE and that in the 1 - 3 eV range to excitations involving the electron trapped by X_2^- of STE, where X stands for halogens. Based on the features of the absorption due to electronic excitations that sharp edge in the near infrared, and a gradual decline toward higher energy, Kabler et al. have interpreted the absorption in terms of Rydberg sequence converging to the conduction band edge.

The doublet structures are evident in salts except NaCl. In their earlier works,[13,14] the doublet has been attributed to the transitions to $A2p\sigma_u$ and $A2p\pi_u$ from $A1s\sigma_g$, respectively. More recently, Williams has shown that the doublet bands are more favored to correspond to the transitions, $A1s\sigma_g;{}^3\Sigma_u^+ \rightarrow A2p\pi_u;{}^3\Pi_g$ and $A1s\sigma_g;{}^3\Sigma_u^+ \rightarrow A3p\sigma_u;{}^3\Sigma_g^+$, respectively.[16]

It is also shown that three sub-levels of the lowest triplet state of STE, which can be ignored in usual cases, plays the important role in luminescence below 4.2 K.[17,18]

Thus the electronic structure of relaxed exciton, especially of the lowest triplet state, has been understood very well. The present questions of the exciton physics in alkali halides concerns the mechanism of relaxation of the unrelaxed exciton, hot exciton, and mechanism of the non-radiative decay involving defect formation process.

§2 Dissociation of an Exciton (Excitonic Mechanism of Color Center Formation in Alkali Halides)

Other important and interesting phenomenon which is resulted by ionizing radiation is the color-center formation due to radiolysis. The mechanism has been studied for a long time, and various models has been proposed so far.[19-27]

Experimental results that uv irradiation[28,29] to alkali halides, involving two-photon absorption of laser light,[30,31] creates lattice defects, together with results that the energy required to form a pair of F and H centers is 20 - 100 eV,[32,33] indicate that the single ionization or the formation of an exciton is responsible for the radiolysis.

The first model of excitonic mechanism of defect formation has been proposed by Pooley,[22] by Hersh [23] and by Lushchik,[24] independently. The fundamental experimental results on which the model is based is the complementary behaviour between the color-center formation rate and the luminescence efficiency of π emission of exciton. Fig.3.1.5 is such a result obtained by Konitzer and Hersh for KI crystal.[29] The formation rate of F and V_2 center increases above 90 K where the luminescence intensity decreases owing to the competitive process of radiative decay and non-radiative transition via thermal activation. The configuration coordinate diagram of the lowest triplet state of an exciton in KI is shown in Fig.3.1.6.[22]

It has also been known that the formation yield of charged Frenkel pair is larger than that of neutral Frenkel pair in the case of conventional x-raying to KBr and others at low temeprature.

Pooley,[22] based on these experimental results, have proposed the following model: Energy,(E_{fi}^{0} $+\Delta_1$) in Fig.3.1.6, which is given to two halogen ions of (V_Ke) through non-radiative decay makes an ion start a replacement collision sequence along a <110> line, when the energy is unequally shared by two ions. Pooley mechanism thus

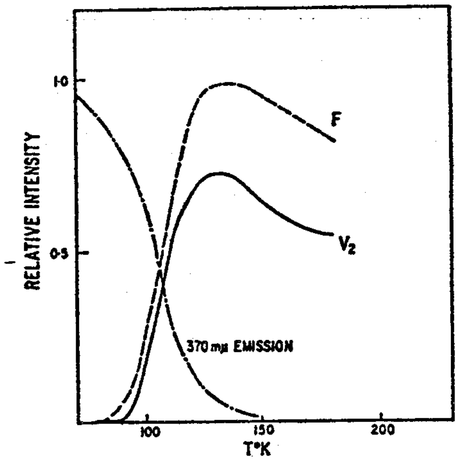

Fig.3.1.5. Temperature dependence of V_2- and F-center formation rate and of triplet emission intensity in KI (from ref.29).

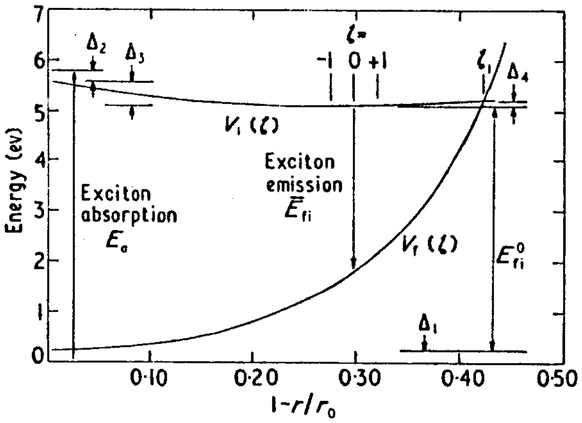

Fig.3.1.6. Energies of electron-hole pair states in KI as a function of relative separation r/r_0 of two iodide ions. (from ref.22).

involves the consequence that time constant of color-center formation, growth time, is the same as the lifetime of (V_Ke)$_\pi$.

A direct method to check the reliability of Pooley mechanism of defect formation is to observe the growth time of color center formation. This has been done using pulsed-beam of high energy electron,[32) or pulsed laser light.[31)

Figure 3.1.7 shows the transient absorption of KBr induced by a single pulse, which was measured at 50 n sec after the end of pulse at 8 K.[32) It is evident that F and H centers are dominant as the product of radiolysis. This result tends to indicate that the primary defects due to dissociation of an exciton is the neutral Frenkel pair consisting F and H centers, which is consistent with the theoretical conclusion obtained by Smoluchowski et al.[34)

The growth time of the F center (as well as F^+ center in KBr) is less than 3 n sec in KBr,[32) and is 11 p sec in KCl,[31) respectively. These are very shorter than the lifetimes of lowest triplet states in these salts, 1.0 X 10^{-4} sec in KBr and 5.0 X 10^{-3} sec in KCl, respectively.

These experimental results are the direct evidences that Pooley's model of excitonic mechanism is not adequate at least in KBr and KCl crystals.

Recent works have presented another experimental evidences that the exciton state responsible for the F-center formation, (V_Ke)$_F$, is different from (V_Ke)$_\pi$ as well as (V_Ke)$_\sigma$.

Karasawa and Hirai[35) have studied the F center formation and intrinsic luminescence below 4.2 K, and have found that these behaves independently in KBr and in KCl: The formation yield of the radiative STE is almost constant, whereas the yield of the F center decreases with an activation energy of a few meV with decreasing temperature.

Another one is given in this chapter, (Chap.[3·4]) from the study of impurity effects on behaviours of the exciton in KBr. It will be shown that the formation yield of (V_Ke)$_F$ is suppressed by an alkali impurity ion, whereas

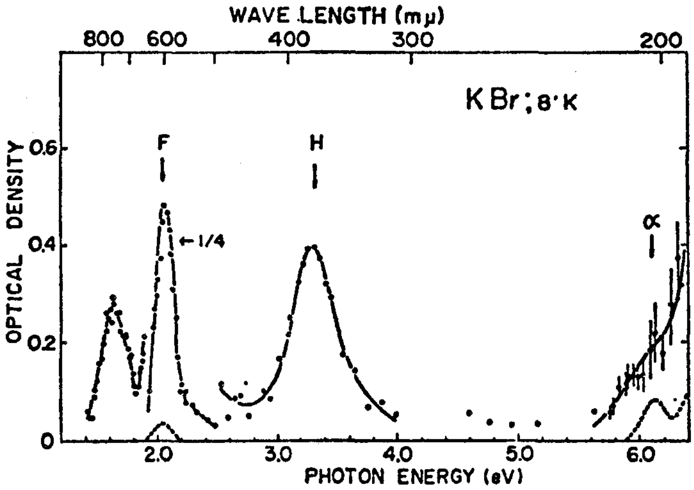

Fig.3.1.7. Transient (solid curve) and stable (broken curve) absorption spectra in a KBr crystal by an electron pulse. The transient absorption was measured at 50 n sec after the end of pulsed irradiation at 8 K. (from ref.32).

those of radiative STE's are not affected.[36)]

These results indicates that (V_Ke)$_F$ is the different from the states responsible for intrinsic luminescence.

Thus experimental works after the first excitonic mechanism model was proposed have revealed that such a model are not adequate in alkali halides except KI and other crystals which color poorly at low temperature. Now the main problem in defect formation mechanism concerns the exciton state responsible for the formation of F - H pairs, or the dissociation process of an exciton in KBr, KCl and others.

Several important results on the properties of (V_Ke)$_F$ has been obtained.

First, it has been demonstrated that the (V_Ke)$_F$ is at a higher energy than (V_Ke)$_\pi$ by the author and co-workers,[37)] and by Purdy and Murray,[38)] independently. They observed that the thermal annihilation of a pair of F and H centers produces π-emissions for both KCl[38)] and KBr.[37)] These results indicate that a stable pair of F and H centers has an energy higher than (V_Ke)$_\pi$. The details will be shown later (Chap.[5·3]).

Second, there are some pieces of experimental evidence which indicates that (V_Ke)$_F$ has close correlation with a triplet state of STE. Karasawa and Hirai[18)] have shown the competitive process of (V_Ke)$_F$ and the lowest triplet state in KBr, which is thermally controlled by an activation energy of 13.7 meV. Williams[16)] have recently shown that the (V_Ke)$_F$ is closely related to an excited state of $A1s\sigma_g;{}^3\Sigma_u^+$ in KCl by the cascade excitation. The author[39)] has pointed out that the luminescence yield of the π emission for several alkali halides is anti-correlated with the formation yield of the F center, based on the Rabin-Click plot[40)] of these quantities.

Recently, three new excitonic mechanism models have been proposed by Kabler,[25)] by Itoh and Saidoh,[26)] and by Toyozawa.[27)] These models involve a higher excited state of STE as the precursor of a Frenkel pair.

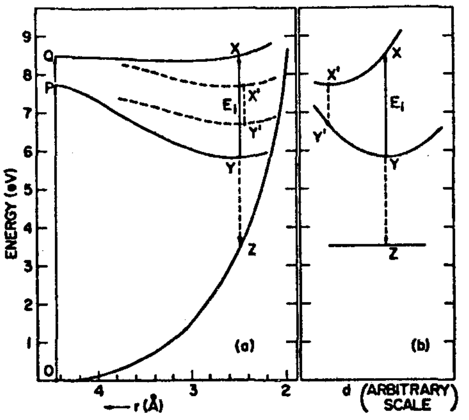

Fig.3.1.8. Semiquantitative configuration coordinate diagrams for the STE in KCl. Coordinate r is the approximate internuclear spacing of the Cl_2^- core, and d represents schematically the displacements of all other ions. (from ref.14).

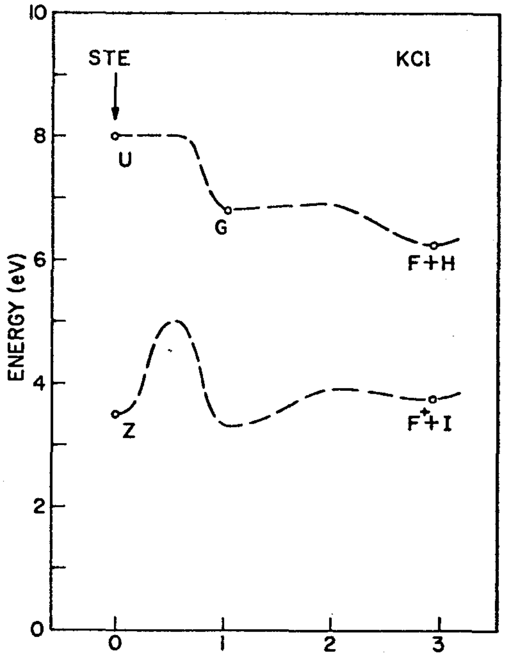

Fig.3.1.9. Schematic potential curves describing possible defect formation in KCl by relaxation of some arbitrary STE state via an odd-parity local mode z. (from ref.25).

Kabler's model is based on the current knowledge of the STE as described in the previous section. His model is essentially the X_2^- translation model of STE at point U which is considered to occur just below the absolute minimum in the configuration space of the highest excited state of SET.[25] The configuration coordinate diagrams for STE, on which his model is based, and the potential curves describing possible defect production are shown in Figs.3.1.8 and 3.1.9, respectively. The initial state of color-center formation in Kabler's model has not been conclusively indicated.

Toyozawa has assumed that the $A2p\sigma_u;{}^{1,3}\Sigma_g^+$ is the precursor of the F center.

On the other hand, Itoh and Saidoh have assumed that the state having an excited X_2^-, Π_g or Π_u, is responsible for the F - H production, based on their recent works on replacement collision sequence of created interstitial halogen.

In spite of these medels, the structure of $(V_Ke)_F$ is not established exactly at present. The process of the formation of Frenkel pairs is of great interest, since the electron-hole recombination takes place by a non-radiative process where the electronic-excitation energy is converted to kinetic energy with a momentum of halogen interstitials. The problem is the typical model of radiolysis in radiation damages.

§3 Outline of The Work in This Chapter

The aim of the work reported in this chapter is to obtain further knowledge of the properties and behaviour of an exciton from the experimental study by means of internal perturbation method.

We begin with the study of luminescence in KBr crystals containing Na^+ impurity ions. The origin of the supplementary emission band situated at 2.9 eV in the crystal is assigned to be radiative decay of the relaxed exciton trapped by a Na^+ ion, (V_Ke $)_{Na}$, after identification of the $V_{KA}(Na^+)$ band in KBr. The effects of the impurity ion on some properties of the V_K center is discussed. Quantum efficiency of the luminescence from (V_Ke $)_{Na}$ and its formation yield are also discussed.

Next the properties and electronic structure of the self-trapped exciton associated with an alkali impurity ion, (V_Ke $)_A$, are extensively studied by means of pulse electron irradiation as well as conventional x-raying.

It is clearly shown that luminescence due to (V_Ke $)_A$, the π_A emission, originates from the lowest triplet state similar to (V_Ke $)_\pi$. The changes in properties of (V_Ke) when it is trapped by an alkali impurity ion are discussed in terms of perturbation due to the ion.

After having cleared the structure of (V_Ke $)_A$, the effects of formation of such a perturbed exciton on other excitonic products, color-center formation and intrinsic luminescence are studied. It is shown that (V_Ke $)_A$ is formed through the selective interaction between (V_Ke $)_F$ and alkali impurity ions in KCl and KBr. Thus formation of (V_Ke $)_A$ results in the suppression of the F-center formation yield, and gives no effect on formation yields of radiative STE's, (V_Ke $)_\sigma$ and (V_Ke $)_\pi$. Relaxation process of an hot exciton and the formation mechanism of (V_Ke $)_A$ are discussed.

After having established close correlation between (V_Ke $)_F$ and (V_Ke $)_A$, temperature dependence of relaxation rate of (V_Ke $)_F$ from the hot exciton and of dissociation probability of (V_Ke $)_F$ into F - H pair are investigated from the measurement of formation yield of (V_Ke $)_A$ between 1.7 and 80 K in KBr and KCl. The dependence of these quantities is discussed based on the experimental results, together with results of formation yield of the F center obtained by Karasawa and Hirai.35)

Then the interaction between an exciton and a Li^+ ion in NaCl is studied. The different mechansim of the interaction from that in KBr and KCl is established in this salt. The mechanism of the interaction, which forms (V_Ke)$_{Li}$ in NaCl, is well interpreted in terms of hopping motion of the lowest triplet state of STE, (V_Ke)$_{\pi}$.40) The difference in excitonic behaviour between NaCl and KBr is discussed in connection with defect formation mechanism in these salts.

Finally, based on the establishment in the preceding chapters, relaxation of the hot exciton is discussed, and it is shown that the (V_Ke)$_F$ is the higher excited triplet state of an exciton.

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[3·2]

LUMINESCENCE FROM (V_Ke)$_A$ IN KBr CRYSTALS

Luminescence of KBr containing foreign alkali ions has been studied. First the interaction between self-trapped hole and a Na^+ ion is studied to make the properties of the $V_{KA}(Na^+)$ center clear. The V_{KA} center has a σ-polarized absorption band at 3.35 eV, and decays thermally at 200 K with an activation energy of 0.63 eV. Then identification of the origin of the 2.9-eV emission band in KBr:Na is made, based on the measurement of luminescence due to the recombination between an electron and the V_{KA} center. The 2.9 eV emission arises from the radiative decay of (V_Ke)$_A$ in KBr. Discussions are made on some properties of V_{KA} center and of (V_Ke)$_A$.

§1 Introductory Remarks

The role of monovalent cation impurity such as Na^+ or Li^+ for defect formation in alkali halides has been mainly investigated in terms of the secondary reactions of halogen interstitials or their interaction with the impurity.

Little attention has been payed on the effects of such types of impurity on the exciton behaviour so far. As discussed in Chap.[3·1], exciton plays the essential role in the low-temperature luminescence in alkali halides. Therefore, it is effective to see the change in luminescent phenomena due to impurities, in order to know whether alkali impurity affects the excitonic behaviour or not. Thus the first work in this chapter concerns the luminescence in alkali halides containing alkali-impurity ion.

Valbis has first observed that the alkali impurity causes characteristic emission bands under x-ray or uv light excitation at low temperatures.$^{1)}$ For example, KBr containing Na^+ ions shows the 2.9 eV-emission band together with singlet (4.42 eV) and triplet (2.27 eV) emissions. Nakai et al.[2] have proposed that the emission should have the origin in the ($V_{KA}{}^{+}$ e) system, but the clear identification has not been done yet.

As the first attempt of the study on the relaxation and dissociation of an exciton by means of the internal perturbation due to impurity, the origin of the supplementary emission band is investigated.

§2 Results and Discussions

In order to check the Nakai's model, it may be decisive to measure directly the emission spectrum caused by the recombination of a V_{KA} center with an electron. The V_{KA} center has been studied by EPR by Schoemaker in alkali chlorides.[3] The optical property and others in KBr crystals, however, have not been known yet. Then the properties of the $V_{KA}(Na^{+})$ center in KBr are first studied.

(2·1) The $V_{KA}(Na^{+})$ center in KBr

Though it is a dominant EPR center at 80 K, the V_K and/or V_{KA} center hardly formed by ionizing radiation. This is because the charge neutrality in a crystal; the formation of self-trapped holes needs electron-trapping centers.

For the enhancement of the formation of V_{KA} centers, NO_2^- ions were doped in the present study, which are known to be an effective electron-trapping center.[4]

Figure 3.2.1 shows the optical absorption spectra of a KBr:NO_2^- before and after x-ray irradiation. One can see in the spectrum of un-irradiated crystal a group of absorption bands which arranges with almost the same energy separation (0.07 eV) and with small absorption coefficients. The bands with fine-structure are clearly due to the NO_2^- ion added in the crystal. Details of these bands are not discussed here.

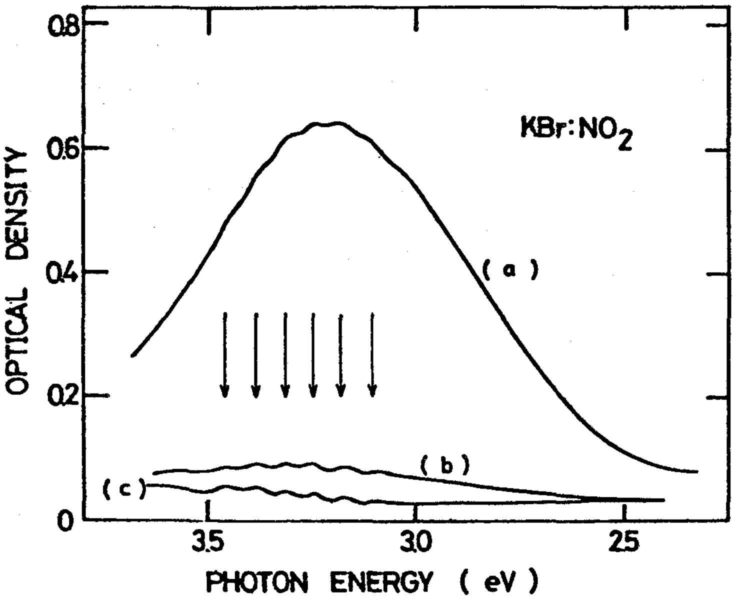

Fig.3.2.1. Optical absorption spectra of KBr:NO_2. Curves (a) and (c) are the spectra of after x-rayed and of before irradiation, respectively. Curve (b) is the spectrum of the sample which was warmed up to 170 K after irradiation. Arrows show peak positions of weak-absorption bands associated with NO_2^- ion. All measurements were made at 80 K.

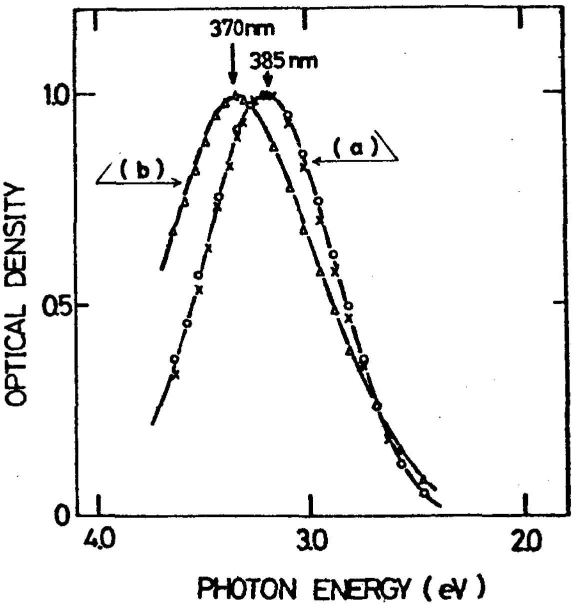

Fig.3.2.2. Optical absorption band of the V_K center, curve(a), and of the V_{KA} center, curve(b), respectively. Open circle of curve(a) is the anisotropic absorption, and cross is the difference between curves(a) and (b) in Fig.3.2.1. The triangle of curve(b) represent the band which decayed above 170 K in KBr:NO_2:Na

The main change in the spectrum due to irradiation is the induction of the broad band situated at 385 nm. The fine-structures of the broad band may be due to simple superposition of bands closely connected with NO_2^-, since the peak position and optical densities of the bands due to NO_2^- hardly change by the irradiation or by thermal treatments. The group of small absorption bands is neglected hereafter.

The principal defect formation process with ionizing radiation in this sample proceeds as follows:

$$Br^- \longrightarrow Br^\circ + e$$
$$NO_2^- + e \longrightarrow NO_2^{2-}$$
$$Br^\circ + Br^- \longrightarrow Br_2^- \; (V_K).$$

The band at 385 nm may, therefore, mainly due to these radiation products.

Delbecq et al. have shown that the Br_2^- center has an anisotropic absorption band at 3.22 eV with a halfwidth of 0.73 eV, which has been assigned to the transition from ${}^2\Sigma_u^+$ to ${}^2\Sigma_g^+$.[4)]

In fig.3.2.2 is shown an anisotropic absorption band which was introduced by <110>-polarized 400 nm light. The band is the same as that obtained by Delbecq et al. In the figure, the difference in spectra between before and after warming as irradiated sample up to 170 K is also shown. It is evident that the spectrum is essentially the same as the anisotropic one. The result indicates that the NO_2^{2-} contribute little to this absorption band region. Thus the 385-nm band can be treated as a pure V_K band below.

Figure 3.2.3 shows the absorption spectra of $KBr:NO_2:Na$. The peak position of the broad band at around 3 eV in as irradiated crystal is 392 nm, and band shape is not identical with that in $KBr:NO_2^-$.

When as-irradiated sample is warmed up to 130 K, the peak position and the band-shape changes to be the same as those in $KBr:NO_2$. The thermal treatment involves the decay of one component of the broad band, which accompanies

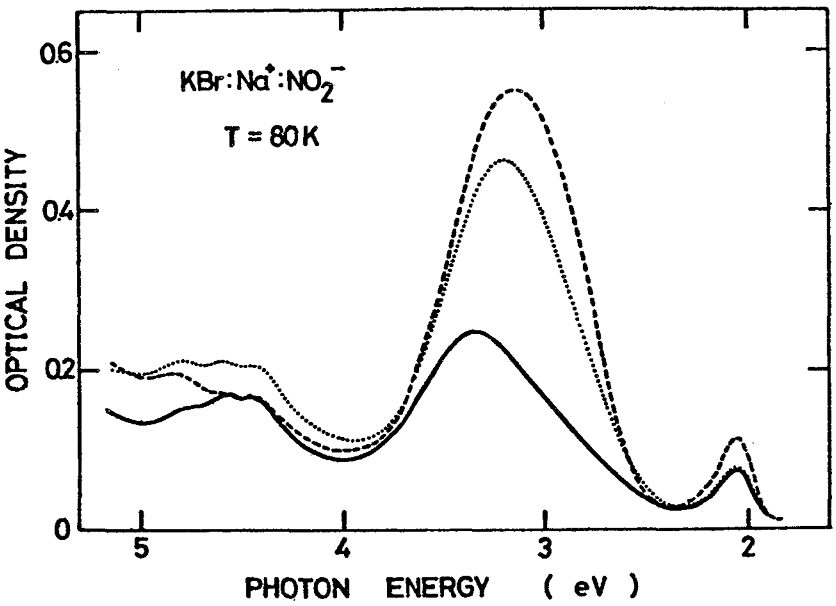

Fig.3.2.3. Optical absorption spectra of an as-irradiated KBr:NO_2:Na crystal (broken line), of after warming the irradiated sample up to 130 K (dotted line), and to 170 K (solid line), respectively. These spectra were obtained by subtracting from the measured absorption curves the one measured prior to the x irradiation.

simultaneously the decrease in the optical density of the F band and the increase in that of V_4-envelope. Therefore, the component is supposed to be due to one of interstitial centers, such as the H_{A1} center.[6)]

The 385-nm band in a sample warmed up to 130 K after irradiation also showed the <110>-type dichroism, and the anisotropic absorption spectrum is essentially the same as that in KBr:NO_2. This result may indicate that the 385 nm band in a KBr:NO_2:Na is also the V_K band.

The solid line in Fig.3.2.3 indicates the absorption spectrum measured at 80 K, after warming an irradiated sample up to 170 K. The absorption band, peaking at 370 nm, appears. Such a band is not observed in Na^+-free crystals in which the V_K band disappears almost completely when sample was warmed up to 170 K, as shown in Fig.3.2.1.

For the analysis of these annealing behaviours of the band, isochronal pulse annealing experiments were carried out, and results are shown in Fig. 3.2.4. The glow curves of these crystals are also shown in the figure.

In KBr:NO_2, the V_K band decays thermally around 160 K, which is accompanied by a strong glow peak. This glow peak may be due to the recombination of holes with NO_2^{2-} centers.[7)] On the other hand, the 385-nm band in KBr:NO_2:Na decreases with distinct two stages; one around 160 K and the other at 200 K. The first stage involves the peak shift of the absorption band from 385 nm to 370 nm, and the second annealing stage corresponds to the thermal decay of the 370-nm band. The glow curve of the sample with Na^+ impurity ions has two peaks, as shown in Fig.3.2.4.

In Fig.3.2.5, the result of annealing experiments on the EPR signal for V_K and $V_{KA}(Na^+)$ centers in KBr:NO_2:Na is involved. The V_{KA} center is enhanced when the V_K center decays thermally, and it decays at about 200 K, probably due to the thermally induced separation of Br_2^- from a Na^+ site. The decay temperature of the V_{KA} center is the same as that of 370 nm absorption band.

One can conclude, from these experimental results, that

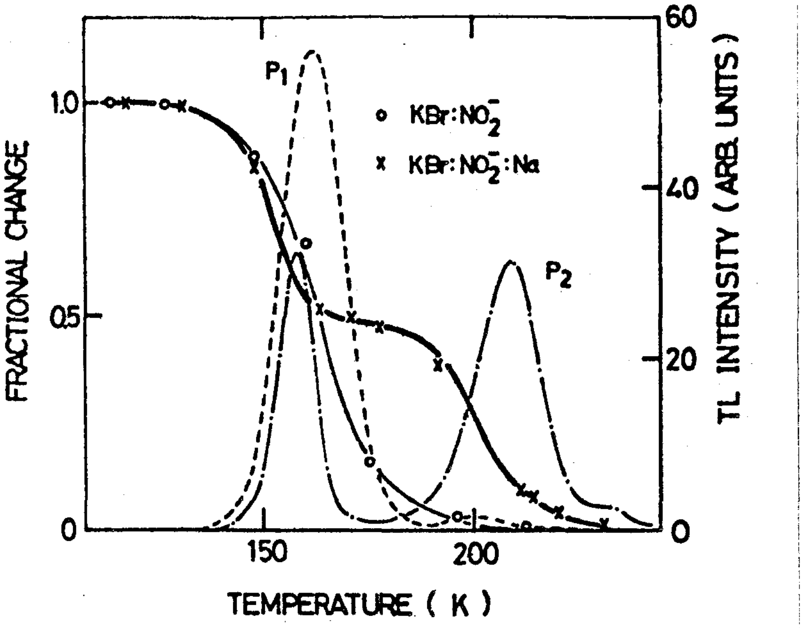

Fig.3.2.4. Annealing curves of 385-nm band in $KBr:NO_2$, open circle, and in $KBr:NO_2:Na$, cross, respectively. Broken and chain lines are respectively the glow curves of irradiated $KBr:NO_2$ and $KBr:NO_2:Na$.

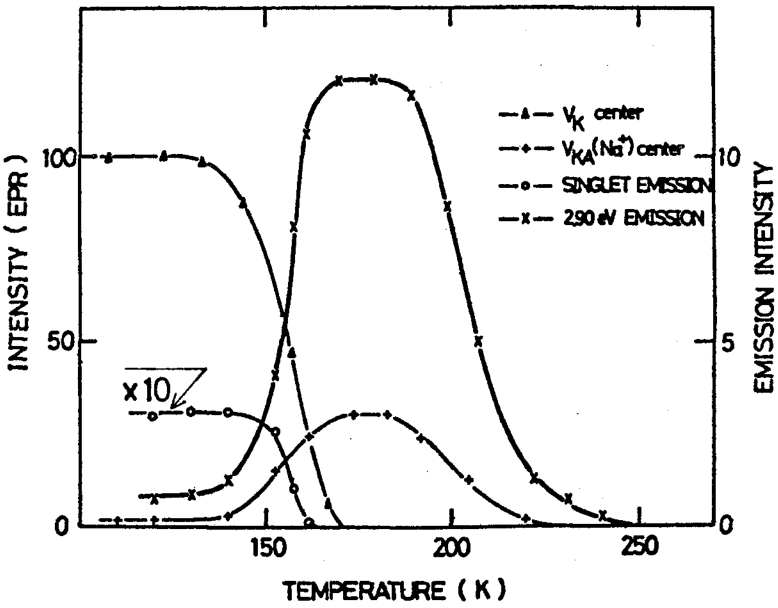

Fig.3.2.5. Annealing curves of V_K and $V_{KA}(Na^+)$ centers in $KBr:NO_2:Na$ measured by EPR. Samples were irradiated at 77 K with Co-60 γ ray. The relative intensities of the centers are given in arbitrary units. The figure also involves the "annealing-temperature dependences" of σ-emission and 2.9-eV emission intensities in an irradiated $KBr:NO_2:Na$ crystal, induced by the release of F-electron at 80 K.

the 370-nm band in KBr:NO_2:Na is due to the $V_{KA}(Na^+)$ center.

The glow curve around 160 K has been attributed to thermal migration and subsequent recombination of the V_K center, as mentioned above. Optical illumination at 80 K with 400-nm light to a KBr:NO_2:Na irradiated at 80 K and subsequently warmed up to 180 K resulted in the re-generation of the glow peak at 160 K, when the sample warmed again. Corresponding changes in optical absorption spectrum are that the peak position initially situated at 370 nm, shifted to longer-wavelength side after optical illumination at 80 K. The peak position again recovered after the re-generated glow peak.

These behaviours may be due to following reactions: The absorption of photons brings the V_{KA} center into an excited state, a fraction of which results in the separation of Br_2^- from a Na^+ ion (V_K center re-generation), and re-appearance of the 160-K glow peak is originated from the thermal decay of such optically created V_K centers.

The 370-nm band due to V_{KA} centers shows <110>-type dichroism at 80 K, though the optical conversion from V_{KA} to V_K centers makes it difficult to obtain the accurate anisotropic absorption spectrum of the V_{KA} center.

Since NO_2^{2-} centers is considered to have no absorption bands in the V_K-band region as discussed before, the spectrum of thermally decayed 370-nm band may represent the absorption spectrum of the V_{KA} center. In Fig.3.2.2, the spectrum is also shown, which may correspond to the transition from $^2\Sigma_u^+$ to $^2\Sigma_g^+$ in the V_{KA} center.

The shift of the peak energy to higher-energy side and the broadening of the halfwidth of the V_{KA} band in KBr are similar to those in KCl crystals obtained by Schoemaker.3)

(2·2) Assignment of the origin of 2.9-eV emission band in KBr:Na crystals

Figure 3.2.6 shows the emission spectra of a KBr:Na crystal excited by x ray at 6 K and at 80 K. The presence of Na^+ ions causes a supplementary emission band situated

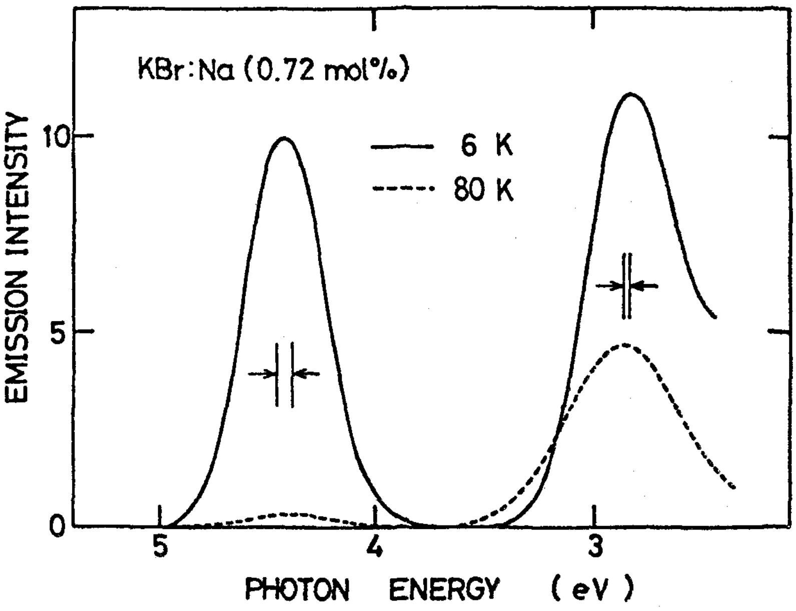

Fig.3.2.6. The x-ray excited emission spectra of KBr:Na(0.72 mol%) at 6 K and at 80 K.

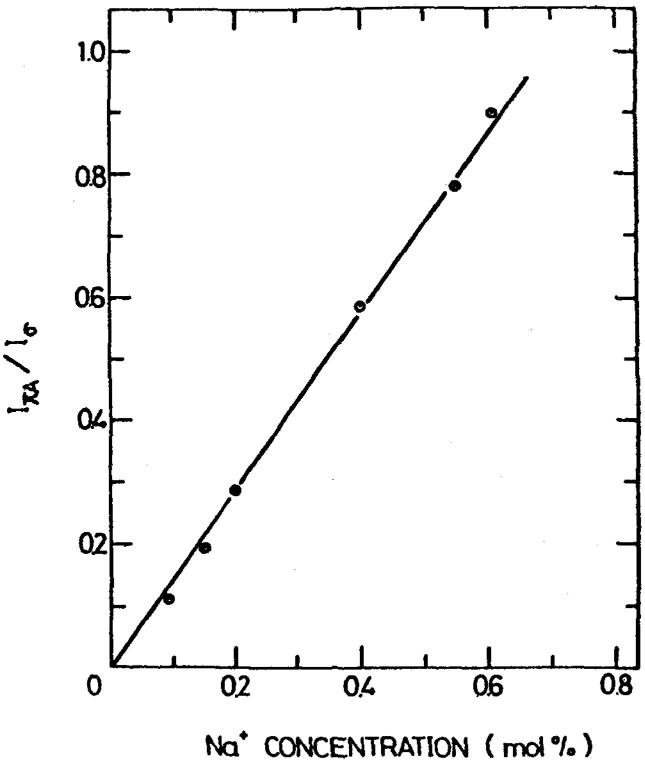

Fig.3.2.7. Na$^+$-concentration dependence of the ratio of the intensity of the 2.9-eV emission band to that of σ-emission band at 6 K.

at 2.9 eV besides intrinsic emission bands at 4.42 and 2.3 eV. The luminescence yield of the new band is comparative to those of intrinsic ones at 6 K, and it is dominant at 80 K where intrinsic luminescence is almost quenched thermally

It is clear that this new emission band is closely related to a Na^+ ion from the result shown in Fig.3.2.7, where the ratio of the intensity to that of intrinsic σ-emission band is plotted against Na^+ concnetration (C_{Na}). The ratio increases linearly with increasing C_{Na}.

Since the intensity of σ-emission band hardly changes irrespective of C_{Na}, the result shown in Fig.3.2.7 indicates that the intensity of the 2.9-eV emission band is in proportion to C_{Na}.

Then we identify the origin of the 2.9-eV emission.

By conducting a proper treatment based on the results obtained in preceding paragraph, we can obtain a sample which contains V_{KA} centers and F centers, but no V_K centers.

The broken line in Fig.3.2.8 is the emission spectrum introduced by F-light illumination at 6 K of KBr:NO_2:Na, which was previously annealed at 170 K after x-ray irradiation at 80 K. It is clear, from Fig.3.2.4, that such a sample does not contain V_K centers.

The emission spectrum consists of the main peak situated at 2.9 eV, accompanied by a very weak band at 4.25 eV. In the figure, the spectrum by the x-ray excitation of KBr:Na at the same temperature is also shown for comparison. One can see that the 2.9-eV bands are essentially the same for both.

Thus it can be concluded that the 2.9-eV emission originates from the (V_{KA} + e), or the relaxed exciton trapped by a nearest neighboring Na^+ ion. Hereafter, we abbreviate such an exciton as ($V_K e$)$_A$.

Further support for the assignment that the 2.9-eV emission is caused by ($V_K e$)$_A$ is obtained from the following experimental results.

In Fig.3.2.5 is shown the change of the intensity of 2.9-eV emission band which was introduced by the F-light il-

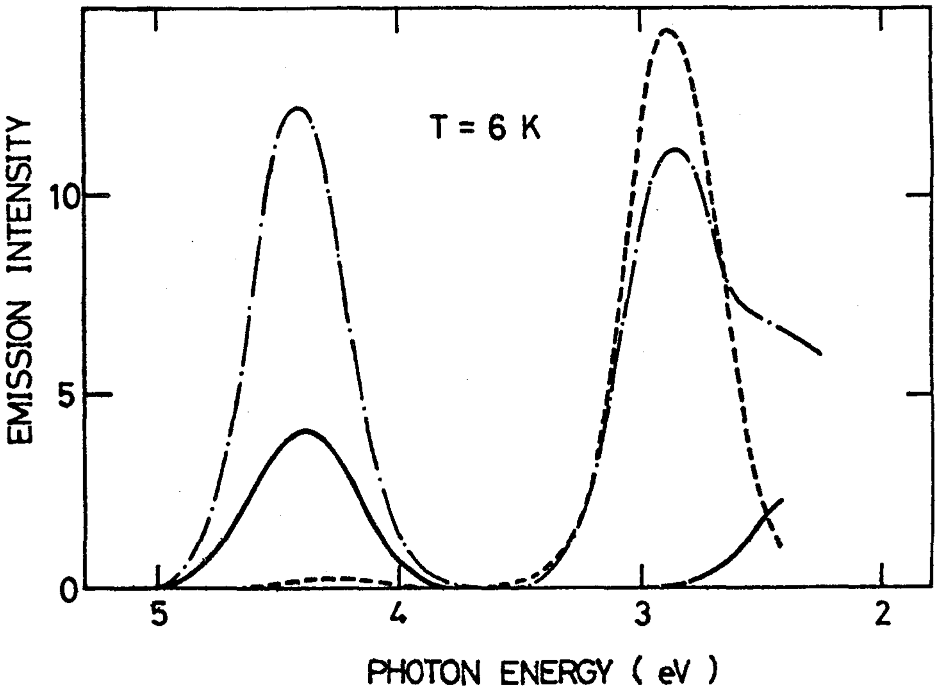

Fig.3.2.8. Emission spectra of recombination luminescence in KBr crystals at 6K. Broken and solid curves are respectively the spectra due to recombination of the $V_{KA}(Na^+)$ center in KBr:NO_2:Na, and of the V_K center in KBr:NO_2 with electrons released by the F-light illumination. These samples were prepared to involve about the same F-center concentration, and to have only one type of hole centers. The chain line is the spectrum of KBr:Na(0.61 mol%) excited by x ray.

lumination at 80 K. In this experiment, the sample was first irradiated with x ray at 80 K, then it was annealed at a given temperature for 5.0 min and cooled down to 80 K, and immediately the luminescence under the F-light illumination was measured.

The intensity increases between 150 and 165 K where the V_K center (and the σ emission) diminishes, and decreases between 190 and 220 K with thermal decay of the V_{KA} center.

Since the luminescence is measured at the same temperature, the intensity of the emission is proportional to the number of luminescence centers. The number of released electrons may be substantially identical in each measurement, since the F center is hardly bleached by F-light illumination after thermal treatment. Thus the main cause of the change in the number of luminescence center is due to the change in the number of hole centers, the V_K or $V_{KA}(Na^+)$ center.

The results above described lead us to the conclusion that the 2.9-eV emission has the origin in the radiative decay of the (V_Ke)$_A$ system, or the relaxed exciton trapped by a nearest neighboring Na^+ ion in KBr, as proposed by Nakai et al.[2)]

It is interesting to note that the emission spectrum of the (V_Ke)$_A$ consists of only one dominant band, whereas that due to (V_Ke) involves two bands.

Polarisation experiments, which were carried out using a KBr:NO_2:Na containing arranged V_{KA} centers, have revealed that the 2.9-eV emission is π-polarized. (Details of the experiment will be described in Chap.[3·3].) We will hereafter call, therefore, the 2.9-eV emission " π_A emission ". Detailed study on the electronic structure of (V_Ke)$_A$ will be done later.

(2·3) Discussions

(a) Effect of the Na^+ ion on optical property of Br_2^-

As shown in previous section, the $V_{KA}(Na^+)$ center has a σ-polarized absorption band at 3.35 eV. The peak energy is higher than that of the V_K center by 0.13 eV. First the shift is discussed.

The association of a Na^+ ion with a V_K center may give two types of main changes to Br_2^-; one is the change in symmetry surrounding the center, and the other is that on internuclear distance, R, of Br_2^- molecular ion.

As suggested by Schoemaker,[3)] the V_{KA} center may have a smaller R than that of the V_K center. Shift of the energy levels of a X_2^- with changing R, though schematic, has been considered by Känzig and Woodruff.[8)] Their result is shown in Fig.3.2.9(a). In the figure, E_v indicates the energy of σ-polarized absorption at uv region. E_v increases slightly with decreasing R. The H center is an essentially the X_2^- molecule ion which is situated at one anion lattice site.[8)]

It is reasonable to conclude that the internuclear distance of X_2^- in the V_{KA} center is shorter than that in the V_K center but is longer than that in the H center.

E_v of the H center in KBr is 3.26 eV at about 4 K and it hardly depends on temperature. The V_{KA} center, however, has E_v of 3.35 eV, which is fairly higher than that of the H center. Therefore, it may not be possible to explain the shift of the peak position in terms of change in internuclear distance only.

One can explain the larger blue shift of the σ-polarized absorption energy in V_{KA} center in terms of mixing between σ_g and π_u in C_{2v} of symmetry.

For the $V_{KA}(Na^+)$ center, the symmetry of the Br_2^- and surroundings becomes C_{2v}, whereas that of the V_K center is D_{2h}.

In Fig.3.2.9(b), the change is shown of molecular orbitals of X_2^- with changing symmetry. In C_{2v}, a_{1g} and b_{1u} orbitals in D_{2h} have the same representation of a_1. Furthermore, as shown in Fig.3.2.9(a), the energy level of b_{1u}($\pi_u$in $D_{\infty h}$) becomes low with decreasing R. Since R of X_2^- in the V_{KA} center is considered to lie between the distances of V_K and H centers, the levels of b_{1u} and a_{1g} may be close each other in the V_{KA} center.

In such a case, the orbitals with the same representation could interact each other. Therefore, two orbitals with the representation of a_1 may become linear combinations between a_{1g} and b_{1u}. Such an interaction may affect energy level of a_1 in "bonding" state to make it lower. Thus it can be expected that E_v, which corresponds to the transition between a_1 and b_1^* in Fig.3.2.9(b), becomes higher than that of X_2^- in D_{2h} symmetry.

The $a_1 \rightarrow b_1^*$ transition is allowed by the optical dipole moment of b_1, which is parallel to the axis of X_2^- also in C_{2v}.

(b) Effect of the Na^+ ion on thermal property of Br_2^-

In order to analyse the thermal stabilities of V_K and V_{KA} centers, it is worth while to evaluate their activation energies for disappearence, which can be obtained from the glow peaks.

It is known that the glow peak is represented by the following simple rate equation;[9)]

$$I(T) = -(dn/dT) = \frac{s}{\beta} n^x \exp(-E/kT) \qquad (3.2.1)$$

where I is the TL intensity, β heating rate, n the concentration of trapped carriers, s the frequency factor, x the order of kinetics, E the activation energy, respectively.

The order of kinetics for either P_1 or P_2 in Fig.3.2.4 was found to be unity, since the TL intensity decreased exponentially at a given temperature which was kept constant.

The activation energies were calculated using various area methods developed for mono-moleculer process.[10-15)] These methods are based on the shape of glow peak. Owing to the different approximations each method involves, the evaluated values of activation energy by these methods are not always the same.

In order to eliminate the possible error caused by the fluctuation of evaluated values, following procedure was carried out in the determination of activation energy.

1) Glow peaks were measured with several different

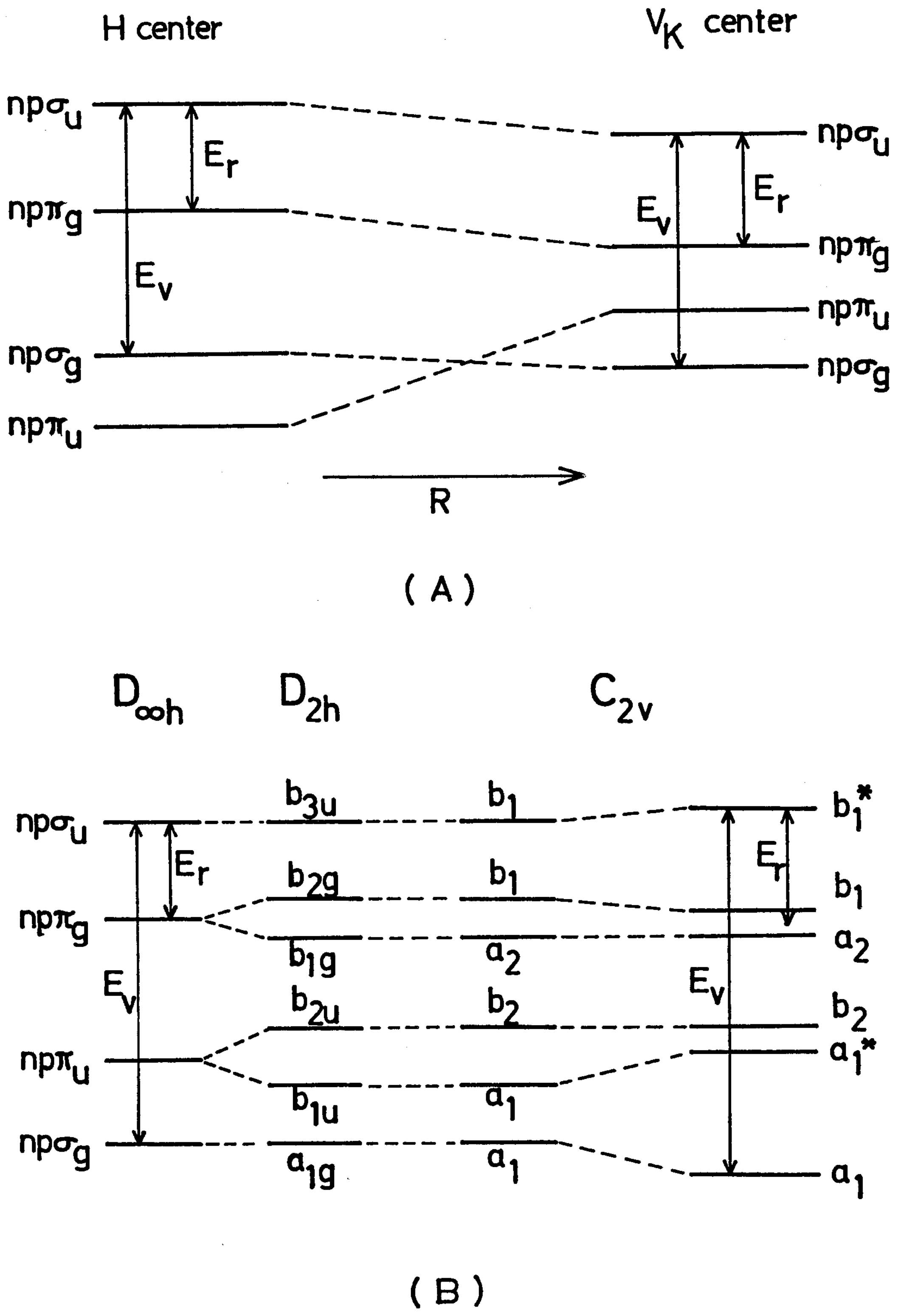

Fig.3.2.9. (a): Shift of energy levels of X_2^- molecule ion with increasing internuclear distance. E_v and E_r are the energies of uv and infrared absorption bands, respectively(After Känzig and Woodruff, ref.8). (b): Schematic energy diagram for molecular orbitals of X_2^- in different symmetry. The notation of levels has been designated in terms of the irreducible representation for a given symmetry. The coordinate set for D_{2h} and C_{2v} is the same as that shown in Fig.3.1.3(b).

heating rates.

2) Evaluation were made for these glow peaks by seven different formula, and results were plotted against the temperatures which give the peaks of glow curves.

3) Frequency with which evaluated results appear within the range of ± 0.02 eV of a fixed value of energy were plotted against the fixed value of energy.

4) The energy with largest value of frequency was determined to be the activation energy of the process.

Fig.3.2.10 shows the plots for the P_1 due to thermal decay of the V_K center in $KBr:NO_2$.

Thus determined activation energies for disappearance of V_K and V_{KA} centers in KBr are listed in Table 3.2.1.

It is seen that the $V_{KA}(Na^+)$ center is thermally more stable by about 0.3 eV compared with the V_K center. Thermal decay of the V_{KA} center may involve following two processes; one is the separation of Br_2^- from Na^+ ion and the other is the migration of the hole which follows the recombination with impurity ion (NO_2^{2-}). The difference of 0.3 eV in activation energy may have the origin in the former process, since the latter of the V_{KA} center may be the same as that of the V_K center.

Higher thermal stability of the V_{KA} center may be pertially due to its geometrical structure.

Delbecq et al. have shown that the disorientation temperature of the Cl_2^- center in various chlorides increases linearly with increasing Cl - Cl distance in the host lattice in the salt.16) In the plot of the temperature vs. Cl - Cl distance, the extrapolation of the straight line pertaining to the plot intersects with the abscissa at 2.4 Å which is very close to the Cl - Cl distance in the free Cl_2^-.

These results suggest that a hole jump for the migration occur when the internuclear distance of the V_K center becomes nearly equal to the distance between X^- at the next neighbor in the salt.

R of a V_K center is, in general, shorter than the distance between adjoining anions. The enlargement of the

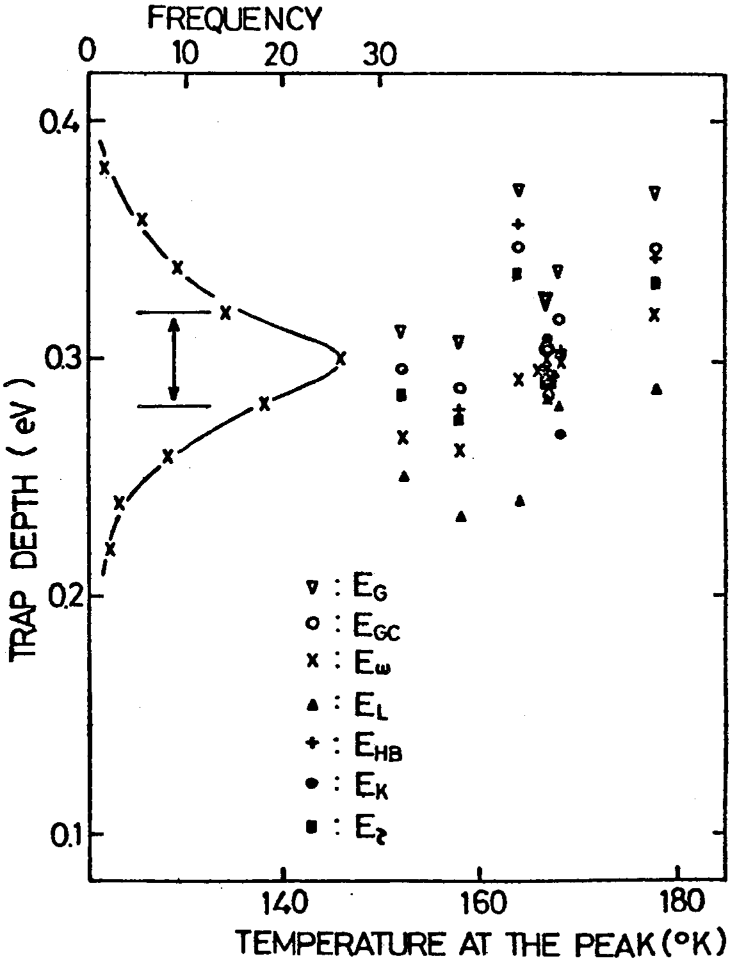

Fig.3.2.10. Plot of the activation energies evaluated from a glow peak (P1 in KBr:NO_2) vs. the temperature which gives the maximum glow intensity. Different symbols correspond to the values calculated using different formulas of several authors: E_g is the value using the formula by Grosswiener, E_ω by Chen, E_L by Lushchik, E_{HB} by Halperin and Braner, E_K by Keating. And E_{GC} and E_τ are ones by versions of E_G and E_{HB} by Chen, respectively.

Table 3.2.1. Optical and thermal properties of V_K and V_{KA} centers in KBr

	E_v (eV)	halfwidth (eV)	T_d* (K)	E** (eV)
V_K	3.22[a)]	0.73[a)]	163	0.34
$V_{KA}(Na^+)$	3.35	0.91	202	0.63

*) T_d (decay temperature) is defined as the temperature which gives the maximum-decay rate in the isochronal pulse annealing curves.

**) E (activation energy for disappearance) was obtained from glow peaks.

a) after Delbecq et al (ref.5)

internuclear distance for the jump may, therefore, come from the vibrational motion along the molecular axis, which may be induced by thermal excitation of the molecular ion.

The higher thermal excitation is considered to be nescessary for the $V_{KA}(Na^+)$ than for the V_K center in order to give rise to the enlargement, since R may be shorter in in the $V_{KA}(Na^+)$ center.

(c) On luminescence yield of π_A emission

In Fig.3.2.7, one can see that the yield of the π_A emission is very high in comparison with the Na^+ content in a sample. Here the high luminescence yield of the emission is discussed.

It is believed generally that the self-trapping process of the hole takes place within a very short time to form the V_K center. Since this self-trapped hole, the V_K center, can migrate only above 150 K in KBr, as shown above, the thermal migration of the center is not active at low temperature such as 6 K. Therefore, the probability of forming the $V_{KA}(Na^+)$ center at low temperature may be about the same as that finding a Na^+ ion in KBr crystals, i.e. the impurity concentration.

The (V_Ke)$_A$ state, if this is formed only through the electron-capture by created V_{KA} centers, may also has the similar formation probability as that of the V_{KA} center.

Assuming, now, that a (V_Ke)$_{Na}$ is formed when one of the six nearest neighboring Br^- ions of a Na^+ ion is excited, π_A-emission intensity, $I_{\pi A}$, is expressed by

$$I_{\pi A} = \eta_{\pi A}\ 6N_oC_{Na} \tag{3.2.2}$$

where $\eta_{\pi A}$ is the quantum efficiency of the π_A emission from the (V_Ke)$_A$, and N_o the number of excited Br^- ions by x ray per unit time, respectively.

In order to estimate the value of N_o, we pay our attention to the σ emission of pure (V_Ke). When the relaxation probability of the hot exciton into the $A2s\sigma_g;{}^1\Sigma_u^+$ is written by $1/\tau_{hs}$, the intensity of the singlet emission, I_σ, is represented by

$$I_\sigma = \eta_\sigma(1/\tau_{hs})N_o \qquad (3.2.3)$$

where η_σ is a quantum efficiency of the σ emission from (V_Ke)$_\sigma$. Then following equation is deduced;

$$I_{\pi A}/I_\sigma = (\eta_{\pi A}\tau_{hs}/\eta_\sigma)6C_{Na}. \qquad (3.2.4)$$

If it is further assumed that the hot exciton state is the same as that of the V_K center just after an excited electron is trapped, one can obtain experimentally the value of $\eta_{\pi A}\tau_{hs}/\eta_\sigma$ from following considerations.

Figure 3.2.8 shows the emission spectra of (V_Ke) in KBr:NO_2 and of (V_Ke)$_A$ in KBr:NO_2:Na generated by the F-light illumination at 6 K. In these measurements, two samples were prepared to have about the same concentration of the F center, N_F, and to have only one type of trapped hole centers, V_K in KBr:NO_2 and V_{KA} in KBr:NO_2:Na, respectively.

It was confirmed that the kinetics of the luminescence by the F-light illumination is mono-molucular process, at least for the time region not so long, for both samples. Therefore, following equation;

$$-(dN_F/dt) = KI_FN_F = I_\sigma/(\eta_\sigma/\tau_{hs}) \qquad (3.2.5)$$

can be applicable for σ emission, where K is a constant and I_F the intensity of the F light in the present experiment, respectively. The similar equation is also written for the π_A emission.

We should consider the self-absorption for the emitting light by the color centers the sample involves, for more accurate estimation.

In order to treat the effect, it is assumed that the distribution of the color centers is random within the colored layer with a thickness of x_o. Then the intensity of the F light depends on the distance, x, from the surface as $I_F(x) = I_F(0)\exp(-\alpha_F x)$. When the emission intensity at a distance x is written as $I_\sigma(x)$, the observed emission intensity $(I_\sigma)_{obs.}$ is given by

$$(I_\sigma)_{obs} = \int_0^{x_0} dx\ I_\sigma(x)\exp(-\alpha_\sigma x) \qquad (3.2.6)$$

where α_σ is the absorption coefficient of the sample at the wavelength of the emitting light.

From eqs.(3.2.5) and (3.2.6), together with similar equations for π_A emission, the next relation;

$$\frac{(I_{\pi A})_{obs}}{(I_\sigma)_{obs}} = \frac{\eta_{\pi A}}{\eta_\sigma/\tau_{hs}} \frac{\alpha_F+\alpha_\sigma}{\alpha_F+\alpha_{\pi A}} \frac{1-\exp\{-(\alpha_F+\alpha_{\pi A})x_0\}}{1-\exp\{-(\alpha_F+\alpha_\sigma)x_0\}} \qquad (3.2.7)$$

is obtained, since $I_F(0)$, N_F and K are about the same for both emissions.

Substituting these values which are obtained experimentally, one can find the value of $\eta_{\pi A}\tau_{hs}/\eta_\sigma$ is about 1.5 ± 0.5.

The results shown in Fig.3.2.7, however, indicates that the proportionality constant is about 10^2, whereas the constant obtained from eq.(3.2.4), using the value obtained above, is at most 10.

This contradiction indicates that the $(V_Ke)_A$ state is formable more effectively than the case we assumed above. Another mechanism, therefore, should exist in the formation of $(V_Ke)_A$ in KBr crystals.

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[3·3]

ELECTRONIC STRUCTURE OF THE RELAXED EXCITON ASSOCIATED WITH AN ALKALI IMPULITY IN KBr

Several properties of $(V_K e)_A$ in KBr crystals have been investigated by means of optical absorption and emission measurements caused by x-ray excitation or pulsed electron irradiation. The 2.75-eV emission band in KBr:Li is assigned to be due to radiative decay of $(V_K e)_{Li}$. It is also found that both the emission band at 2.9 eV due to $(V_K e)_{Na}$ and the 2.75 eV band are π-polarized. The broadening of the halfwidth of these emission bands with raising temperature is described in terms of strong interaction formula; $H(T) = H_0 \coth^{1/2}(2h\nu_e/kT)$. The value of ν_e is 2.3×10^{12} sec^{-1} for $(V_K e)_{Na}$ and $(V_K e)_{Li}$. The transient absorption corresponding to the transitions to higher excited states from lowest excited states of $(V_K e)_A$ in KBr crystals has newly observed at 1.75 and 1.6 eV for $(V_K e)_{Li}$ and 1.65 and 1.5 eV for $(V_K e)_{Na}$ at 80 K, respectively. Association of $(V_K e)$ with a foreign alkali ion results in shorter lifetimes (2.5×10^{-5}sec for $(V_K e)_{Na}$ and 1.5×10^{-5}sec for $(V_K e)_{Li}$, respectively), in a remarkable blue shift in emission energy, and in a change in quenching behaviour of decay time, especially in frequency factor. These changes are discussed in terms of the perturbation to $(V_K e)$ of an alkali impurity ion.

§1 Introductory Remarks

Existence of the relaxed exciton trapped by an alkali impurity has been confirmed in the previous chapter. Few discussions were made there on some properties of such a exciton, $(V_K e)_A$.

In this chapter, electronic structure of $(V_K e)_A$ in KBr crystals has been extensively studied by various experimental techniques, which involves pulsed-electron irradiation.

Such a study concerns the assignment and understanding of an excited species in alkali halides. One of the main interests here is the changes in decay modes of an exciton when it is associated with a nearest neighboring foreign alkali impurity ion.

For this purpose, KBr crystals doped with Li^+ ion as well as one doped with Na^+ ions were used. This series of of impurities will cause systematical changes in properties of pure STE, which may give us better understanding of the role of impurities on changes in excitonic behaviours.

§2 Experimental Results

Fig. 3.3.1 shows the x-ray excited emission spectrum of KBr:Li(0.07 mol%) at 6 K and at 80 K. Luminescence yield of the emission band at 2.75 eV is comparative order to those of intrinsic luminescences at 6 K, and dominant at 80 K, respectively.

The intensity of the 2.75-eV emission band of KBr:Li increases with increasing Li^+ concentration at both 6 K and at 80 K, similarly as the 2.90-eV emission in KBr:Na.$^{1)}$ The emission band in KBr:Li is, therefore, tentatively assigned to be due to (V_Ke)$_{Li}$.

In order to obtain more information of the properties of the initial state of the emission band from (V_Ke)$_A$, polarization measurement similar as that made by Kabler for (V_Ke)$^{2)}$ was made. V_{KA} centers in alkali halides lie in the (100) plane with approximate <110>-molecular axis, as shown by Schoemaker.$^{3)}$ The anisotropy of the V_{KA} center makes it possible to measure poralization of the emission from (V_Ke)$_A$. The $V_{KA}(Na^+)$ center in KBr has a σ-poralized absorption band at 3.35 eV, as shown in the preceding chapter.

A $KBr:Na:NO_2$ crystal x-rayed at 80 K was warmed to 180 K.

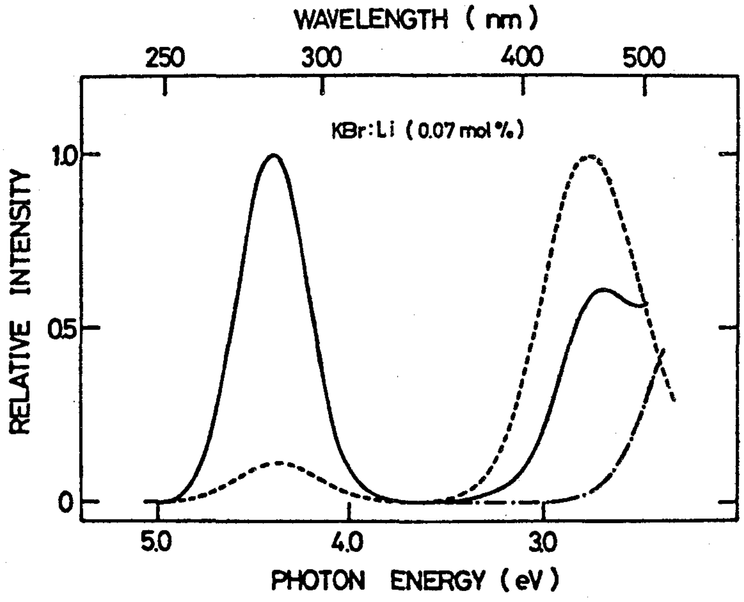

Fig.3.3.1. The x-ray excited emission spectra of KBr:Li (0.07 mol%) at 6 K, solid curve, and at 80 K, broken curve, respectively. The chain line is the tail of π emission of pure KBr at 6 K, and the σ emission is overlapped with the emission of KBr:Li. The intensity is normalized to unity at energy which gives the maximum emission intensity in a spectrum.

Such thermal treatments annihilate the V_K center and enhance the $V_{KA}(Na^+)$ center.[1] Then the V_{KA} center was oriented along the <0$\bar{1}$1> direction of the crystal by illumination of <011>-polarized 370 nm light at 6 K. Successive F band excitation results in the polarized emissions of 2.9-eV band and also of 4.4 eV band. The latter is identical with the σ emission of (V_Ke) in its peak position and band width.

The 4.4-eV emission was not observed when the illumination of 370 nm light was not made prior to F bleaching. It can be, therefore, concluded that the 4.4-eV emission is due to the recombination of an electron with the V_K center which is " regenerated " from $V_{KA}(Na^+)$ centers by the excitation with 370-nm light at 80 K. In this experiment, the polarization of 2.9-eV emission can be determined with " reference " of well-known σ-polarized emission of (V_Ke).

In Fig.3.3.2, we plot the intensities of the 2.9-eV and 4.4-eV bands as the analyzer is rotated relative to the crystal. Angle 0 of polarizer orientation indicates the <0$\bar{1}$1> direction, or the arranged V_{KA}-center axis. It is clear that the 2.9-eV emission band is π-polarized. The percent polarization calculated from the result is -36, which is higher than the value of π emission of (V_Ke).[2]

It is reasonable, therefore, that one calls the 2.9-eV emission band in KBr:Na $\pi_A(Na^+)$ emission, in the sense that the emission is π-polarized and associated with an alkali impurity ion. Similarly, the 2.75-eV emission is called $\pi_A(Li^+)$ emission.

The result that the π_A emission is π-polarized suggests that the initial state of the radiation is a triplet state.

The pulse-electron irradiation was employed to obtain the decay of the emission band and the transient optical absorption due to (V_Ke)$_A$. Since the π_A emissions exhibit nearly the same intensity at 80 K as 6 K, detailed study of the luminescence and optical absorption of (V_Ke)$_A$ was made at 80 K.

A typical example of the decay at the $\pi_A(Na^+)$-emission region is shown in Fig.3.3.3. The temperature is 80 K.

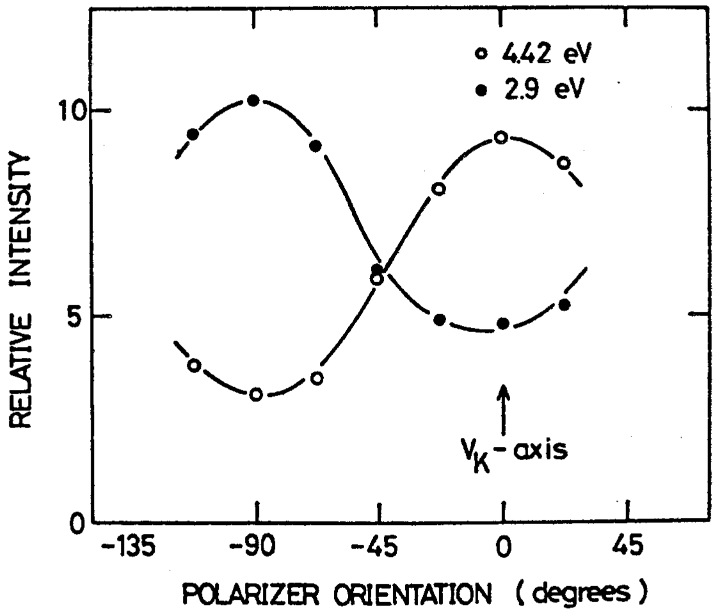

Fig.3.3.2. Relative emission intensities transmitted through a polacoat UV105, as a function of rotation angle of the analyzer. Emission was excited by optical illumination (λ>570 nm) in the F band at 6 K, after the axis-arrangement of the V_{KA} (and V_K) center by preferential optical bleaching.

The decay curve of the emission intensity at 415 nm involves a very fast-decay component whose decay time is less than 30 n sec and a slow component with the decay time of 11.8 μ sec.

Figure 3.3.4 shows the time-resolved emission spectra in KBr:Na(0.61 mol%). Open circle and closed one indicate the emission intensities at 90 nsec, I_{90}, and at 1.5 μ sec, $I_{1.5}$, after the pulse bombardment, respectively. The double circle are the differences in emission intensities of the two. The intensity at 1.5 μ sec after a pulse is producted by 2, for convenience.

The curve consisted of $I_{1.5}$ represents the emission spectrum whose decay time is 11.8 μ sec, and the one of double circles, or of the differences between I_{90} and $I_{1.5}$ is considered to represent the spectrum of fast-decay component. The difference in peak energies of the two emission bands is about 0.15 eV.

The decay time of the fast component is about three orders of magnitude shorter than that of the slow one, whereas the initial intensity of the former is roughly one order of magnitude larger. Therefore, the π_A emission excited by conventional x-raying corresponds to the slow component with the decay time of 11.8 μ sec at 80 K.

Similar results were obtained for KBr:Li crystals. The decay time of the $\pi_A(Li^+)$ emission is 13.0 μ sec at 80 K.

Figure 3.3.5 shows the transient optical absorption spectra which are seen in KBr containing alkali impurity and share the same decay times as those of π_A emissions. The peak energies of the absorption are 1.5 and 1.65 eV for KBr:Na, and 1.6 and 1.75 eV for KBr:Li. Since the lifetime of the lowest triplet state of pure STE, $(V_K e)_\pi$, in KBr is less than 10^{-7} sec at 80 K,[4,5] it is clear that these absorption peaks are not originated from pure STE.

To obtain further confirmation of the origin of these absorption bands, the Na^+ concnetration dependence was measured. The results are shown in Fig.3.3.6.

The absorption coefficient of 1.5-eV absorption band

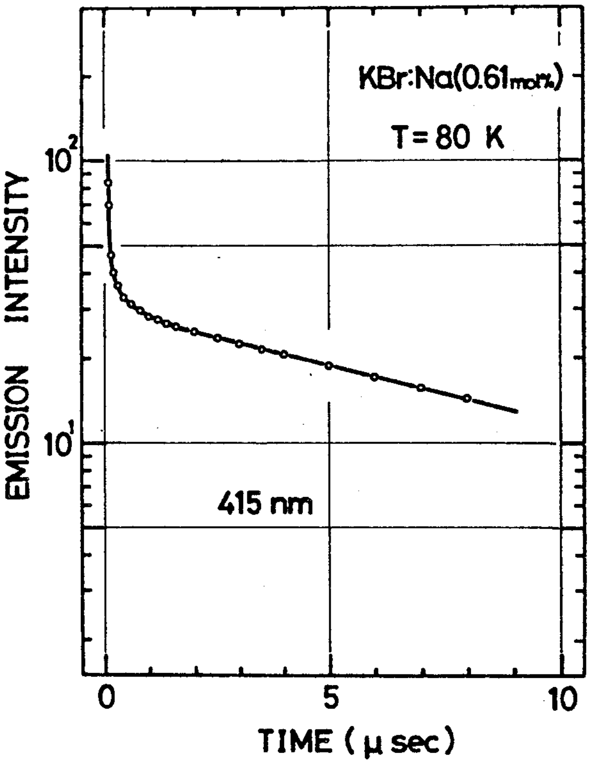

Fig.3.3.3. Decay of emission intensity at 415 nm region excited by a single electron pulse in KBr:Na at 80 K. The best fit between the data points after 1.5 μsec and an exponential-decay component was obtained when the decay time is 11.8 μsec.

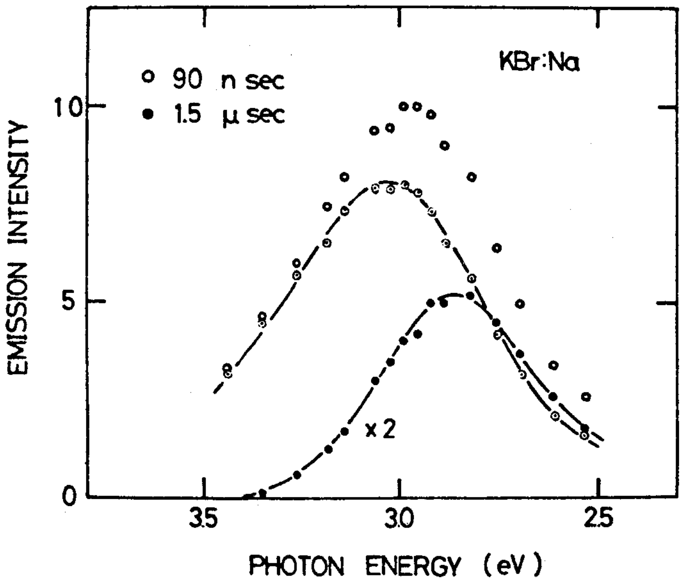

Fig.3.3.4. The time resolved emission spectra at π_A-emission band region in KBr:Na. Measurement was made at 80 K.

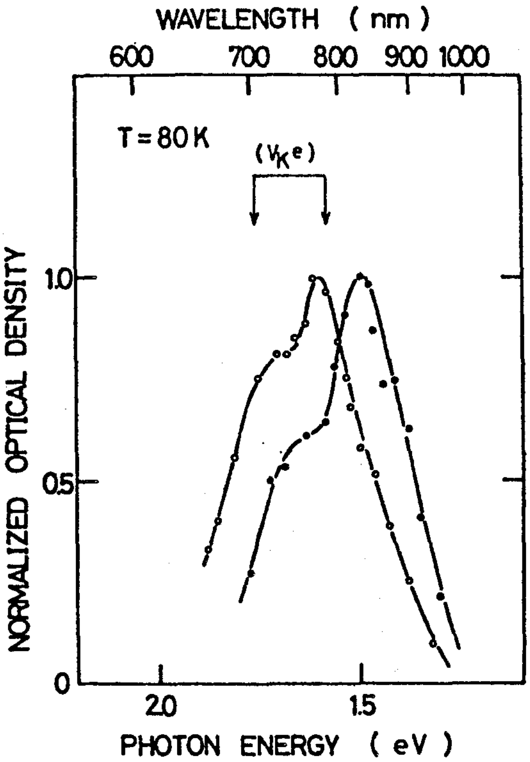

Fig.3.3.5. Transient absorption spectra of KBr:Na, solid circle, and of KBr:Li, open circle, respectively. Arrows indicate the peak positions of the absorption due to $(V_Ke)_\pi$ at 6K(ref.4).

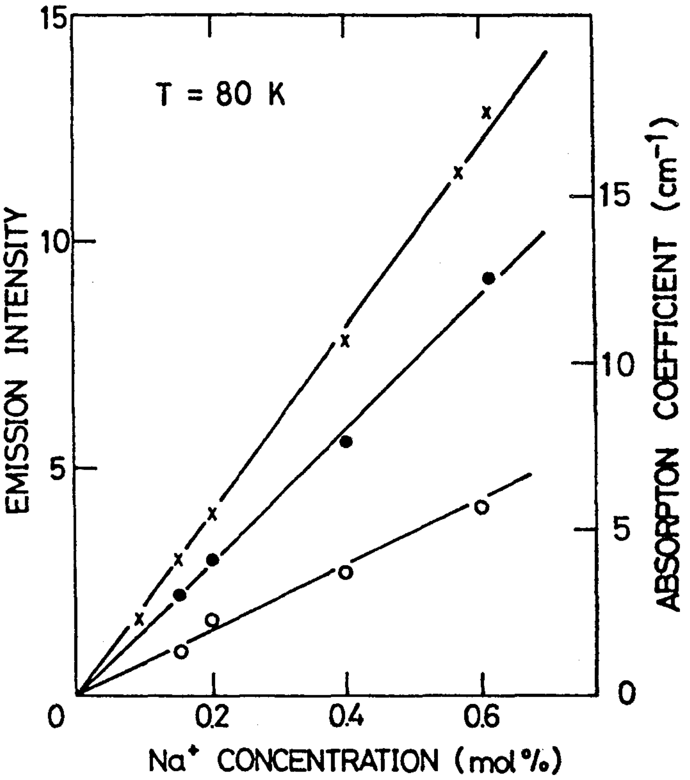

Fig.3.3.6. Na^+-concentration dependence of emission intensity of π_A emission excited by x ray, (x), and by pulse electron, (o), and of absorption coefficient of the transient absorption, (●), respectively. The emission intensity was measured at 415 nm, and the absorption at 825 nm, respectively.

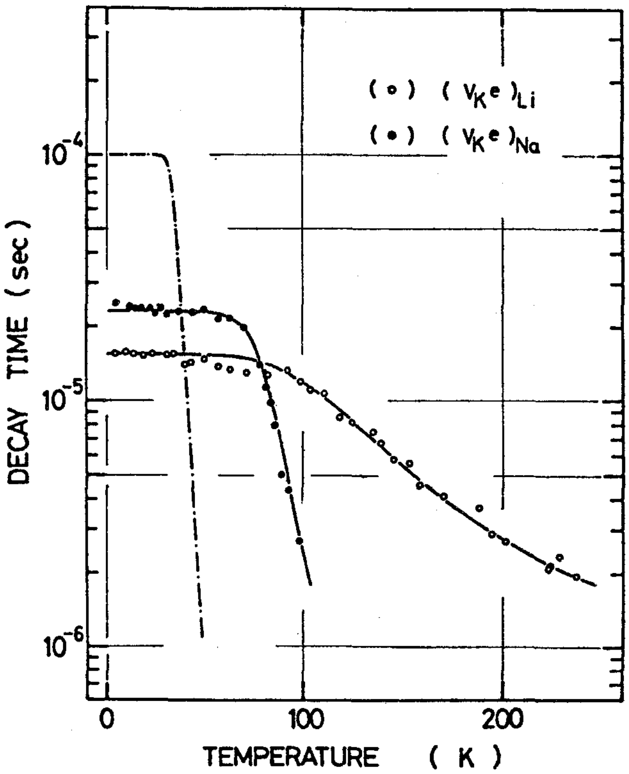

Fig.3.3.7. Temperature dependences of decay times of $\pi_A(Na^+)$ emission (•), and $\pi_A(Li^+)$ emission (o). The solid lines along data points are calculated curves by equation; $1/\tau = 1/\tau_0 + \nu\exp(-E/kT)$. The chain line is also the calculated curve for the quenching of decay time of π emission in pure KBr, using values of parameters obtained by Karasawa and Hirai (ref.5).

is in proportion to Na^+ concnetration as the emission intensity of 2.9-eV band is.

The agreement of the decay times of these absorption peaks with those of π_A emissions and the same linear dependence on impurity concentration confirm that these absorption bands correspond to the optical transition from the π_A state to higher excited states of STE trapped by an alkali impurity ion.

Measurements were made on temperature dependence of the decay time of π_A emissions. Results are shown in Fig.3.3.7, with that of π emission for comparison.[5)] The decay time of $\pi_A(Na^+)$ is 2.5×10^{-5} sec at 6 K, and is quenched thermally above 70 K. The decay time of $\pi_A(Li^+)$ exhibits the value of 1.5×10^{-5} sec at 6 K, and becomes shorter gradually above 60 K.

The temperature dependence of decay time, τ, can be represented in terms of the typical quenching pattern, i.e. $1/\tau = 1/\tau_0 + \nu\exp(-E/kT)$, where $1/\tau_0$ is the radiative transition probability and ν and E are frequency factor and activation energy for non-radiative decay via thermal activation, respectively. The values of ν and E, obtained by best fit of these data are 3.2×10^9 sec^{-1} and 0.075 eV for $\pi_A(Na^+)$, and 4.7×10^6 sec^{-1} and 0.048 eV for $\pi_A(Li^+)$, respectively.

The results shown in Fig.3.3.7 indicate that radiative lifetime and its quenching pattern are strongly affected by the alkali impurity ions with which (V_Ke) is accosiated; lifetime, τ_0, becomes short and ν is reduced in the order of (V_Ke $)_{Na}$ and (V_Ke $)_{Li}$.

The temperature-dependent broadening of the halfwidth of the π_A emission band excited by x ray has been also measured. Results are shown in Fig.3.3.8. The halfwidth of $\pi_A(Na^+)$ or of $\pi_A(Li^+)$ at 6 K is 0.49 and 0.47 eV, respectively. One can see that the pattern of bradening of the halfwidth with increasing tempersture is essentially the same for both cases.

The result can be described by the formula: $H(T) = H(0)\coth^{1/2}(h\nu_e/2kT)$. The solid curve in the figure is the

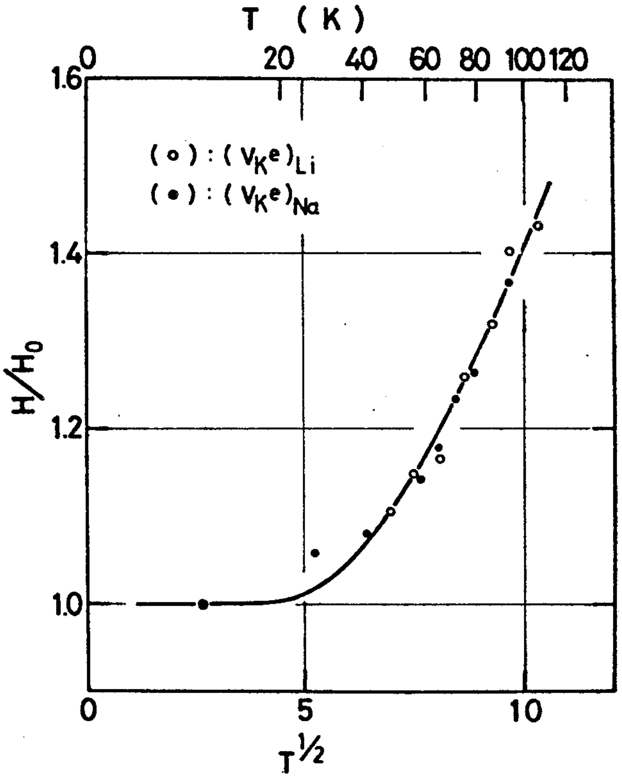

Fig.3.3.8. Temperature dependence of the halfwidth of the π_A-emission band in KBr crystals. Solid line represents the calculated curve of the function; $H(T) = H(0)\coth^{1/2}(h\nu_e/2kT)$, where the value of ν_e is $2.3 \times 10^{12} sec^{-1}$. H(0) is 0.47 eV for $\pi_A(Li^+)$ or 0.49 eV for $\pi_A(Na^+)$, respectively.

calculated curve with the value of 2.3 X 10^{12} sec^{-1} for ν_e. Agreement between the calculated curve and the experimental points is good.

The fact that the value of ν_e is the same for both $\pi_A(Na^+)$ and $\pi_A(Li^+)$ is very contrast to the strong dependence of the value of ν on the kind of alkali impurity of $(V_Ke)_A$. The different behaviours between ν_e and ν are discussed in the next section.

§3 Discussions

Results obtained for π_A states in KBr in the preceding section can be summalized as follows:

1) The emission band is π-polazied.
2) The lifetimes of $\pi_A(Na^+)$ and $\pi_A(Li^+)$ states are 2.5 X 10^{-5}sec and 1.5 X 10^{-5}sec, respectively,
3) Transient absorption peaks corresponding to the transition from π_A states to higher excited states are situated at 1.5 and 1.65 eV in KBr:Na and 1.6 and 1.75 eV in KBr:Li, respectively,
4) Temperature dependences of the decay times of π_A emissions depend strongly on the alkali impurity ion associated STE, whereas the dependence of the broadening of the halfwidth is essentially the same for both.

The π_A state possesses similar properties as those of $(V_Ke)_\pi$. It is, therefore, evident that the initial state of the π_A emission is the lowest triplet state of the self-trapped exciton associated with an alkali impurity ion in KBr.

The association of STE with an impurity ion results in changes in its optical and thermal properties. Various quantities of $(V_Ke)_A$ are listed in Table 3.3.1, with the corresponding values of $(V_Ke)_\pi$ for comparison.

Principal changes are followings;

1) Lifetime becomes shorter,
2) the emission energy shows a remarkable blue shift

Table 3.3.1. Various quantities in transitions of ($V_K e$)$_A$. Corresponding values of ($V_K e$)$_\pi$ and the F^+(α) center are also shown for comparison. Peak energies, E_{em}, and half width, W, of the emission bands, thermal activation energies for decay-time quenching, E_q, and the peak energies of transient optical absorption, E_{ab}, are given in units of eV. Lifetime of a state, τ_0, and frequency factors for decay-time quenching, ν_q, and for the halfwidth broadening, ν_e, are given in units of sec and sec^{-1}, respectively.

	E_{ab}	E_{em}	W	τ_0 ($X10^{-5}$)	E_q	ν_q	ν_e ($X10^{12}$)
($V_K e$)$_{Na}$	1.5 1.65	2.90	0.49	2.5	0.075	$3.2 X 10^9$	2.3
($V_K e$)$_{Li}$	1.6 1.75	2.75	0.47	1.5	0.048	$4.7 X 10^6$	2.3
($V_K e$)	1.58 1.77[a]	2.27[b]	0.40[b]	10[c]	0.050[c]	$1.3 X 10^{11}$[c]	—
F^+(α)	—	2.47[d]	0.52[d]	—	—	—	2.9[d]

a) R.T.Willians and M.N.Kabler (ref.4)

b) M.N.Kabler (ref.2).

c) T.Karasawa and M.Hirai (ref.5).

d) T.Timusk (ref.13).

and absorption energies are almost the same and/or slightly red shifted, and

3) the frequency factor for thermal quenching of decay time is significantly dependent on impurity.

The Li^+ ion has a smaller ionic radius, so that perturbations to (V_Ke), which occurs through lattice disorder surrounding it, may be greater for Li^+ than for Na^+. The degree of changes in some properties are, in fact, in the order of (V_Ke $)_{Na}$ and (V_Ke $)_{Li}$. For example, the lifetime and the frequancy factor in the probability of non-radiative decay are the case. The changes of them may be, therefore, closely related to the lattice disorder.

However, others, especially the differences in the peak energies of absorption and emission, are not. These results is supposed to indicate that the perturbation of a foreign alkali ion nearby STE does not take place only through the ionic disorder surrounding (V_Ke).

Below, we shall first discuss the change in lifetime, next the shifts in peak energies of absorption and emission, then temperature-dependent properties, and absence of σ emission in (V_Ke $)_A$. Finally, general features of (V_Ke $)_A$ are summalized with the comparison with those of pure (V_Ke) and of other perturbed excitons.

(3·1) Changes in radiative lifetime

The spontaneous emission probability between non-degenerate states $|k>$ and $|m>$ is[6)]

$$1/\tau_{km} = \frac{4e^2 n E_{km}^3}{4h^4 c^3} \left(\frac{\xi_{eff}}{\xi_o}\right)^2 <k|\mathbf{r}|m>^2 .$$

The value of τ_{km} has been obtained by Karasawa and Hirai[5)] to be 1.0 X 10 sec for (V_Ke $)_\pi$. Those of (V_Ke $)_{Na}$ and (V_Ke $)_{Li}$ are 2.3 X 10^{-5} sec and 1.5 X 10^{-5} sec, respectively. Assuming that the effective field ratio is about the same for each, the matrix element is roughly two or four times larger for $\pi_A(Na^+)$ or for $\pi_A(Li^+)$, respectively, than that of (V_Ke $)_\pi$.

The initial state of π_A emission, $|k\rangle$, may be linear combination between a triplet part $|t\rangle$ and a singlet part $|s\rangle$ the admixture of which mainly comes from halogen s-o coupling.[7)]

There may be two possibilities that make the matrix element large; one is supplementary admixture of another singlet state into the triplet state, and the other is the change in the value of $\langle s|r|m\rangle$ itself.

First, the former possibility is discussed. For (V_Ke)$_A$ the X_2^{2-} molecule ion is placed in a C_{2v} symmetry, whereas in D_{2h} for (V_Ke). Figure 3.3.9 shows the schematical energy diagram of pure (V_Ke) and of (V_Ke)$_A$. The ordinate of the figure represent the energy, though the scale is quite arbitrary. The notation of the one-electron level has been designated in terms of the irreducible representation for $D_{\infty h}$, D_{2h}, and C_{2v}.

For π emission, the important singlet part is considered to be the one which has the configuration of $\mathrm{Cl}1s\sigma_g;{}^1\Pi_u$ in terms of the representation for $D_{\infty h}$.[7)] The one-electron level, $1s\sigma_g$, in triplet state splits into three sub-levels of b_{1g}, b_{2g}, and b_{3g} in D_{2h}. The first two can be mixed with the levels of ${}^1\Pi_u$.

For π_A emission, the singlet part, ${}^1\Pi_u$,degeneracy of which are resolved into A_1 and B_2 in C_{2v}, can combine with the sublevels of the triplet state, A_1 and B_2. Furthermore, a state with the configuration of $(\sigma_g)(\pi_u)^4(\pi_g)^4(\sigma_u)^2(1s\sigma_g)$; ${}^1\Sigma_g^+$ in the representation for $D_{\infty h}$, which is A_1 in C_{2v} and is represented as A_1^* for convenience, could be combined with A_1 of a sub-level of the triplet state.

The degree of admixture between A_1^* and the sub-level of A_1 is determined mainly by the energy separation of these states.

One important changes, which may take place in (V_Ke)$_A$, is the reduction of the internuclear distance of two halogen ions. As discussed previously, the shorter nuclear separation results in the considerable lowering in the energy level of π_u, whose representations are b_2 and b_1 in C_{2v}.[8)] In such a case, the energy level of A_1^* is considered

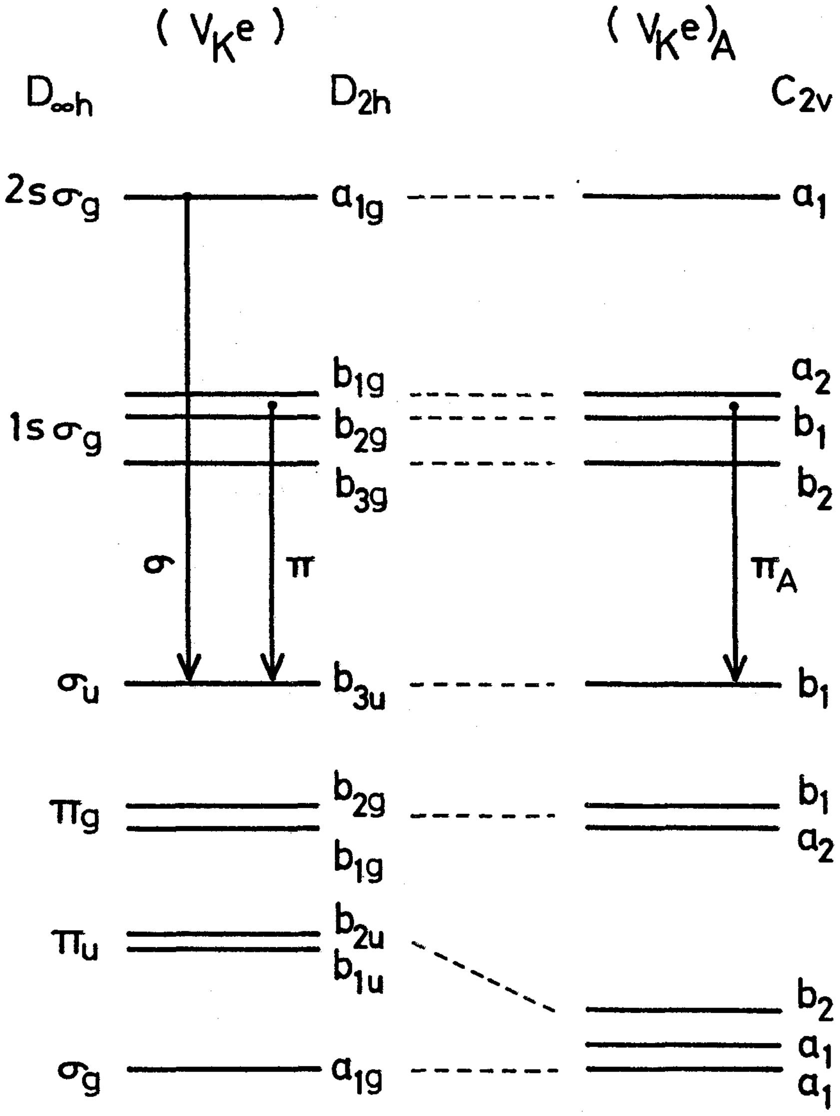

Fig.3.3.9. Schematic single electron state description of (V_Ke) and (V_Ke)$_A$. Sub-levels of lowest triplet state are designated in terms of the direct product of space representation and spacies of spin functions in each symmetry. Changes in internuclear separation of X_2^- and in symmetry are taken into account.

to be close to that of $^1\Pi_u$. Therefore, the contribution of a supplementary admixture of A_1^* to the larger matrix element may not be unplausible.

The possible recombination of A_2(B_{1g} in D_{2h}) with a sub-level of the triplet state may not be important, since the sub-level does not contribute to the radiative transition.

The possiblity that makes the matrix element itself large may be possible, too, which may come from the change in overlap of electron wavefunctions of two states.

As suggested by Schoemaker,3) the V_{KA} center has a smaller nuclear distance. Since the overlap of p orbitals of Br^- depends on the distance, it may be expected that the value of matrix element changes with changeing the nuclear separation. Thus the mechanism may be probable,too.

It has not been cleared here which possibility is important in the present case. Further investigation is nescessary to make clear the origin of the change in lifetime.

(3·2) Shift of transition energies

Association of (V_Ke)$_\pi$ with a foreign alkali ion gives a remarkable blue shift in emission energy and little changes in the absorption due to the transitions to higher excited states of the lowest triplet state.

This result indicates that a nearest neighboring alkali impurity ion mainly affect the electronic transition between levels involving the ground state. First we disscuss the changes in emission energies.

The energy level of the ground state of X_2^{2-} may be repulsive potential between two halogen ions. The presence of the nearest neoghboring cations may enhance the potential especially for smaller nuclear distance between two halogen ions. Replacing K^+ by Na^+ or Li^+ in KBr may reduce the repulsive potential. The smaller nucler distance of V_{KA} center compared with that of the V_K center is considered to be resulted by such a reason. Thus it is not unprobable that the level of ground state is lowered by the substitution of a host cation with one having smaller ionic radius.

Douglus9) has calculated the total energy change in replacing a mol of K^+ by Na^+ in KBr. It has been shown that overlap-repulsion energy is drastically reduced by 16.0 kilocal/mol, and that the total energy change is - 10.45 kilocal/mol, or is - 0.45 eV.

It is, therefore, reasonable to attribute the difference in the emission energy of π_A emission from that of emission in KBr, about 0.5 eV, to the reduction in energy level of the ground state.

The line of this argument involves the larger blue shift of $\pi_A(Li^+)$ than that of $\pi_A(Na^+)$. The experimental result is not, however, the case. This contradiction seems to indicate that the lowest triplet state is also affected by the impurity ion, though the degree of changes is, of course, considered to be smaller than that of the ground state. This problem will be discussed later in this paragraph.

We then discuss the transitions to higher excited levels from the lowest triplet state.

As seen in Fig.3.3.5, the peak positions of the doublet peaks of $(V_K e)_{Li}$ is about the same as those of $(V_K e)_\pi$, and the positions of $(V_K e)_{Na}$ show slightly red-shift. The relative strength of the doublet ansorption peaks of $(V_K e)_{Li}$ is about the same as that of $(V_K e)_\pi$, whereas the strength of $(V_K e)_{Na}$ changes considerably.

One can also see in Fig.3.3.5 that the doublet splitting of $(V_K e)_A$ does not very differ from that of $(V_K e)_\pi$. The doublet has been assigned to transitions from $A1s\sigma_g;{}^3\Sigma_u^+$ to $A2p\pi_u;{}^3\Pi_g$ and to $A3p\sigma_u;{}^3\Sigma_g^+$, respectively.10) If an alkali ion nearby STE affects the electronic states of these higher states, appreciable change in doublet splitting could be observed, since the level of $2p\pi_u$ should be perturbed more seriously than that of $3p\sigma_u$. The results in

Fig.3.3.5, thus, appear to favor that the excited states of (V_Ke)$_\pi$ are less perturved than its ground state by a foreign alkali ion.

The behaviour seems to be reasonable; the wavefunctions of electron in these excited states is considered to be considerablly extensive, so that the difference in the hole configuration between V_K and V_{KA} centers may be less important. The changes in the absorption of (V_Ke)$_A$ from that of (V_Ke)$_\pi$ may, therefore, originate from the change in the initial state, the lowest excited state.

Results shown in Fig.3.3.5 suggest that the changes in the lowest excited state are more serious in (V_Ke)$_{Na}$ than in (V_Ke)$_{Li}$. Such a type of perturbation, if it is true, is supposed to come not from the change in symmetry, or in the distortion of surrounding lattices, but from other mechanisms, since a Li^+ ion, not a Na^+ ion, should cause larger degree of the changes.

Stoneham$^{11)}$ has calculated the electronic state of a relaxed exciton by Hartree-Fock calculations, and shown that the atomic orbitals of alkali ions, especially s orbitals, are also important in the lowest excited state. In the present case of (V_Ke)$_A$, a metal ion of (MX)$_2$ compound is replaced by a ion with smaller quantum number of the orbitals. It is, therefore, expectable that the energy level of the lowest excited state varies, depending on the level and on the degree of admixture of the orbital of foreign alkali ions.

The lowest unoccupied atomic state, 2s for Li^+ and 3s for Na^+ may be of most importance. The eigen values of these orbitals in free ions have been calculated by Hartree-Foch-Slater ($X\alpha$) method. The results are shown in Table 3.3.2.

One can see that the value does not change in the order of Li^+, Na^+, and K^+, but that the value of 3s in Na^+ has the lowest one. Though these values must be modified, of course, in the crystaline field, the order in the levels may not change. Therefore, it is not unreasonable

Table 3.3.2(a): Eigenvalues of atomic states in free alkali ions calculated by Hartree-Fock-Slater ($X\alpha$) method. Values are given in atomic unit.

	Li^+	Na^+	K^+
1s	-2.254835	-38.189875	-128.992404
2s	-0.235062	- 2.349977	- 13.116703
2p	-0.161896	- 1.341782	- 10.564924
3s		- 0.244043	- 1.490007
3p		- 0.135122	- 0.898269
4s			- 0.208119
4p			- 0.123063

Table 3.3.2(b): Total energy, T.E., Hartree-Foch value, E_{HF}, kinetic energy, K.E., potential energy, V, nuclear attraction energy VZ, electron repulsion energy, VE, and exchange-correlation energy, VX of lowest unoccupied atomic state of free alkali ions. (atomic unit).

	T.E.	E_{HF}	K.E.	V	VZ	VE	VX
2s(Li^+)	-.60408	-.27328	.37025	-.60531	1.30513	.77624	-.07643
3s(Na^+)	-2.02824	-.30625	.60082	-.84486	4.35105	3.63061	-.12442
4s(K^+)	-2.81104	-.27159	.63913	-.84725	5.98962	5.26930	-.12693

to expect that the change in energy level of the lowest excited state is most serious not in (V_Ke)$_{Li}$ but in (V_Ke)$_{Na}$.

From the data indicated in Table 3.3.1, it can be seen that the difference in emission energy and that in absorption energy between (V_Ke)$_{Li}$ and (V_Ke)$_{Na}$ is about 0.1 eV. It appears that the larger blue shift in emission energy is compensated by the larger red shift in absorption energy. This behaviour could be undersood, if the $\pi_A(Na^+)$ state is energetically higher than the $\pi_A(Li^+)$ state by about 0.1 eV. Such a situation is supposed to be possible.

The calculation of the electronic state of (V_Ke)$_A$ may give the answer the question why a Na^+ ion affects the lowest excited state of (V_Ke).

(3·3) Changes in quenching pattern of decay time

Measurements of temperature-dependent properties of color centers give us informations on the interaction of an electron with phonons. For many cases in alkali halides, the interaction has been well interpreted in terms of strong interaction.

In the present problems, the broadening of the half-width of the emission band is analyzed well with the formula; $H(T) = H_0\coth^{1/2}(h\nu_e/2kT)$.[12] This result indicates that the strong interaction is also applicable to (V_Ke)$_A$.

The value of ν_e obtained here is essentially the same and is 2.3×10^{12} sec^{-1} for both (V_Ke)$_{Li}$ and (V_Ke)$_{Na}$. This value is close to that of emission of the α center, which is also a perturbed exciton,[13] and is comparable to that of the frequency of LO-phonon in KBr.

The distortions surrounding the imperfections such as Li^+, Na^+ and an anion vacancy are considered to be different significantly. For example, the degree of the lattice relaxation due to surrounding Li^+ in KBr is about two times larger than that due to Na^+ ion, according to the calculation of Douglus.[9] The similarity of the value of ν_e's for (V_Ke)$_{Na}$, (V_Ke)$_{Li}$ and also the α center, therefore, indicates that the phonon mode responsible for the broadening of halfwidth of an emission band is not sensitive to the localized displacement of ions nearby the center.

According to the arguments of Williams and Kabler,[4)] the phonon mode responsible for the broadening of the spectra is breathing mode which reflects the displacements of all ions surrounding the center (external mode). Such a mode may not be very sensitive to the distortion at the localized region.

Temperature dependence of decay time also gives us information on phonon interacting with an electron. As shown in Fig.3.3.7, the temperature dependence can be described adequately in terms of the competitive process of two channels which are the radiative decay with the probability of $1/\tau_0$ and the non-radiative transition with the temperature-dependent probability of $\nu\exp(-E/kT)$.

Ikezawa and Kojima[14)] have shown that the frequency factor ν for (V_Ke) is of the order of ν_e. But, present result shows that ν is essentially different from ν_e; ν of (V_Ke) is drastically reduced when it associates with a foreign alkali ion, and it, furthermore, depends strongly on the kind of impurity ion. This behaviour of ν is very much in contrast to that of ν_e. The result may suggest that the phonon mode which is responsible for the non-radiative decay is not the same as that resulting in the broadening of the halfwidth.

As discussed above, the latter might be the external mode of vibration. There may be the different type of vibration, internal mode of X_2^{2-}.[4)] It has been suggested that the internuclear distance of X_2^- becomes shorter in V_{KA} centers. The thermal properties of a V_{KA} center also shifts from those of a V_K center; the decay temperature of the V_{KA} center is higher, whereas the disorientation temperature becomes lower.[3)] Therefore, it may be expected that the internal mode of vibration strongly depend on the configuration of X_2^- in STE. Thus the internal mode of the core of STE might be responsible for the non-radiative transition of (V_Ke) and (V_Ke)$_A$.

Detailed mechanism of non-radiative decay of an exciton has not been revealed so far, and the physical meaning of the parameters determining the quenching pattern of decay time may not be very clear. The present results, the essentially different behaviours of ν_e and ν, may be interesting and may give something for clear understanding of the mechanism of non-radiative decay of an exciton.

(3·4) The emission band with fast decay time

One of the significant difference in properties of (V_Ke)$_A$ and pure (V_Ke) in KBr is the absence of the σ emission of (V_Ke)$_A$. In (V_Ke), the σ emission takes place at 4.40 eV, as well as π emission at 2.27 eV in KBr.[2)] As clearly shown in Chap.[3·2], the (V_Ke)$_A$ has only one dominant emission band which is π-polarized, π_A emission.

It has been identified that the σ emission corresponds to the transition from $A2s\sigma_g;\ {}^1\Sigma_u^+$ to $A\sigma_u np;{}^1\Sigma_g^+$.[15)] Such a transition is also dipole-allowed in (V_Ke)$_A$ where the X_2^{2-} is placed in a C_{2v} symmetry, as shown in Fig.3.3.9. The experimental result that the σ emission of (V_Ke)$_A$ is not observable, therefore, indicates that the population of the initial state of such a transition is suppressed in this system. The mechanism of this suppression has not been cleared here. It may be supposed that the mechanism has close correlation with that through which some alkali halides, such as KCl and NaBr, do not possess the σ-emission band.

In (V_Ke)$_A$, the emission band whose decay time is very fast is observed at the triplet-emission (π_A) band region, as shown in Fig.3.3.4. Such a band with similar decay time is observed at 6 K as well as 80 K. The decay time less than 30 n sec may indicate that the emission is due to the dipole-allowed transition. The peak position of this emission band situates at about 3.0 eV which is close to and slightly higher than the peak energy of π_A-emission band.

These results suggest a possibility that the fast component originates from $A1s\sigma_g ; {}^1\Sigma_u^+$.

Onodera and Toyozawa have obtained the exchange energy of 0.26 eV for unrelaxed exciton in KBr.[16)] On the other hand, Marrone et al.[17)] have shown that the energy for the lowest excited state of the relaxed exciton is 0.0076 eV, based on their EPR study. The exchange energy depends, in the first approximation, on the average distance between an electron and a hole, and decreases exponentially with increasing the distance. The wavefunction of an electron in lowest excited state of $(V_K e)_A$ is considered to be more close-packed than in $(V_K e)$, since the hole may be more locarized due to smaller nuclear separation of X_2^- in $(V_K e)_A$. It may be, therefore, expected that the value of exchange energy for $(V_K e)_A$ lies between values of unrelaxed exciton and of $(V_K e)$.

The value of 0.17 eV, the difference in the peak energies of the fast component and of the π_A emission, may not be unplausible for the exchange energy for $(V_K e)_A$.

Of course, the clearer assignment of the origin of the fast-decay emission band at 3.0 eV needs further detailed study, though the above-mentioned model is supposed to be a possibility.

(3·5) General features of $(V_K e)_A$ as a perturbed exciton

Discussions on the decay mode of $(V_K e)_A$, made in the previous paragraphs in this section, have revealed the following characteristics, comparing with that of $(V_K e)$; $(V_K e)_A$ has larger radiative-transition probability and has less probability of non-radiative transition, which comes from the larger activation energy and from smaller frequency factor. The $(V_K e)_A$ thus tends to deexcite radiatively.

This property of $(V_K e)_A$ is very contrast to that of

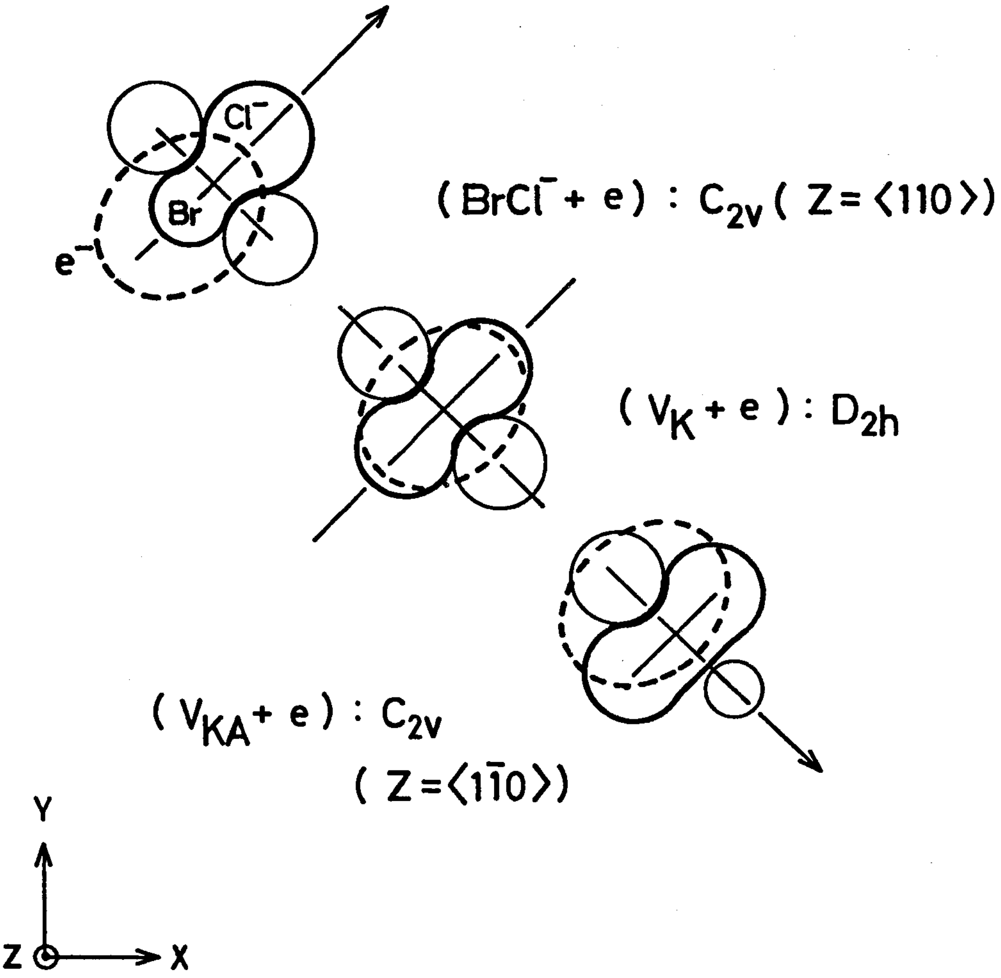

Fig.3.3.10. Schematic morphology for (V_Ke), (V_Ke)$_A$, and ($BrCl^-$+ e) in (100) plane. Broken circles represent approximately the distribution of an electron in each system. Arrows in (V_Ke)$_A$ and ($BrCl^-$+ e) indicate the direction of perturbation to pure (V_Ke).

another perturbed exciton, the heteronuclear exciton such as ($ClBr^-$+ e).

Schematic models of these excitons are sketched in Fig.3.3.10. The symmetry of (V_Ke) is D_{2h}, and that of (V_Ke $)_A$ as well as ($ClBr^-$+ e) becomes C_{2v}. However, the perturvation to (V_Ke) is along a <110> direction for ($ClBr^-$+ e), whereas that is along a $\langle 1\bar{1}0\rangle$ for (V_Ke $)_A$.

(V_Ke) possesses two decay modes, radiative decay and non-radiative one, which involves dissociation of an exciton or defect formation, though the relative ratio of the probabilities of these modes depends strongly on the kind of the salt.

Keller and Patten[18)] have found that ($ClBr^-$+ e) in KCl crystals is roughly an order of magnitude more effective in dissociation than intrinsic (V_Ke). Maki et al.[19)] have also obtained the similar result. This is considered to be because of the asymmetric-energy pertition for the mixed V_K-center recombination due to the perturbation to a $\langle 110\rangle$ direction, halogen axis, along which replacement collision sequence of an interstitial takes place.

In intrinsic (V_Ke), such an asymmetric pertition of energy could be occur, though the probability is supposed to be smaller owing to its higher symmetry of D_{2h}.

In the system of (V_Ke $)_A$, however, asymmetricity along not to $\langle 110\rangle$ but to $\langle 1\bar{1}0\rangle$, metal axis, is emphasized, as shown in Fig.3.3.10. In this system, thus, the probability of aymmetric partition of energy for effective creation of interstitials is considered to be fairly lowered, which may be accompanied by the higher probability of radiative decay.

Thus, it is expected that the formation of (V_Ke $)_A$ in alkali halides results in the decrease of color-center formation rate at low temperature. This effect will be studied in the next chapter.

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[3·4]

EFFECTS OF THE ALKALI IMPURITY ON THE RELAXATION OF AN EXCITON IN KBr AND KCl

Study on defect formation and luminescence in KBr and KCl crystals containing alkali impurities have been performed by means of measurements of optical absorption and emission due to x-ray or pulse electron irradiations at low temperatures. The most important finding is that the alkali impurity suppresses the the colorability, enhances the emission from (V_Ke)$_A$, but gives no effects on the intrinsic luminescence. The suppression of the defect formation is shown, quantitatively, to be due to the formation of (V_Ke)$_A$. It is proposed that the formation of (V_Ke)$_A$ takes place through the selective interaction between the exciton state responsible for the creation of F - H pairs and the impurity ion. A model for the relaxation of an exciton and the origin of the selective interaction are discussed based on results obtained in this study.

§1 Introductory Remarks

One of the most important present problems in the field of color center physics concerns the properties of the exciton state as precursors of F - H pairs.[1-3]

In the earliest excitonic mechanism model by Pooley and by Hersh, color centers were considered to be formed from the relaxed exciton which is also responsible for the intrinsic luminescence.[4,5] Recent studies on defect formation have shown, as discussed in Chap. [3·1], that the exciton state responsible for the color-center formation, (V_Ke)$_F$ is a higher excited state different from the states which result in intrinsic luminescence. Several new excitonic mechanisms have been proposed based on the recent understanding.[1,6,7]

Then our attention should be focused on the relaxation of the hot exciton, through which paticular states of the exciton such as (V_Ke)$_\sigma$, (V_Ke)$_\pi$, and (V_Ke)$_F$ are formed. Here we study the relaxation of an exciton in terms of internal perturbation due to the alkali impurity.

In previous chapters, we have identified the origin of the 2.9-eV emission band to be due to radiative decay of the (V_Ke)$_A$, i.e. the exciton trapped by a nearest-neighbor alkali-impurity ion. The electronic structure and other properties of (V_Ke)$_A$ have also been studied. It has been clearly shown that the formation efficiency of (V_Ke)$_A$ is very high, comparing with the consequence of statistical consideration. This means that (V_Ke)$_A$ is formable quite effectively during irradiation process which involves the relaxation of hot excitons. Another important property of (V_Ke)$_A$, which has been revealed in Chap.[3·3], is that the perturbed exciton tends to de-excite radiatively.

Taking account of these interesting establishments of preceding chapters, it may be fully expected that color-center formation is affected when (V_Ke)$_A$ is formed.

The role of alkali impurity such as Na^+ or Li^+ for defect formation in alkali halides has been mainly investigated in terms of the secondary reaction of halogen interstitials or their interaction with the impurity. Little attention, however, has been payed on the effects of such impurities on the behaviour and properties of excitons so far.

One should, at this point, reconsider the role of the alkali impurity for defect-formation process from a more general approach involving not only interaction process of created interstitials, but also dissociation of an exciton.

From such a point of view, we study in this chapter defect formation in KBr:Na and other similar systems, paying main attention to the correlation between coloration and luminescence by x-ray or pulsed electron beam irradiations. Results obtained here have revealed some important features in relaxation of the hot exciton and in properties of (V_Ke)$_F$ in KBr and KCl crystals.

§2 Experimental Results

(2·1) Effects of alkali impurity on x-ray induced colorability and luminescence

Figure 3.4.1 shows the radiation-induced absorption spectra of KBr containing Na^+ ion of different concentrations. The heights of both F and H bands decrease with increasing C_{Na}. In the H-band region, the shift of peak position toward low-energy side is noticeable. The heights of F^+ band and of the band due to the interstitial bromine ion (I and I_A bands) also decrease. The Na^+ ion, which enhances the formation of F and F^+ centers at LNT, suppresses the colorability at low temperature where primary interstitials are stable.

In order to obtain the correlation between the formation yields of F and F^+ centers and the luminescence intensity, measurements were made of the changes of both quantities as a function of the Na^+ concnetration. The results are shown in Fig.3.4.2. One can see that the yields of both F and F^+ centers decreases linearly with increaseing C_{Na}, though the rates are not equal. The intensity of π_A emission band increases in proportion to C_{Na}, within the present range of the impurity concnetration. One could notice the following two characteristic features; the complementary behaviour between the decrease of colorability and the enhancement of intensity of the π_A emission band, and the constancy of the intensities of singlet and triplet emissions irrespective of the Na^+ concnetration.

Therefore, it is clear that the existence of the π_A emission band, i.e. the formation of (V_Ke $)_A$, plays an important role in the suppression of the colorability at 6 K.

It has been shown in Chap.[3.3] that (V_Ke $)_{Li}$ is also formed in KBr crystals containing Li^+ impurity ions. It is expected that the Li^+ ion gives the similar effects as those of Na^+ ions on the color center formation, since the (V_Ke $)_{Li}$ has similar properties as the (V_Ke $)_{Na}$. In Fig.3.4.3 formation yield of the F center and the intensities of luminescences are plotted against the Li^+ concentration. We see

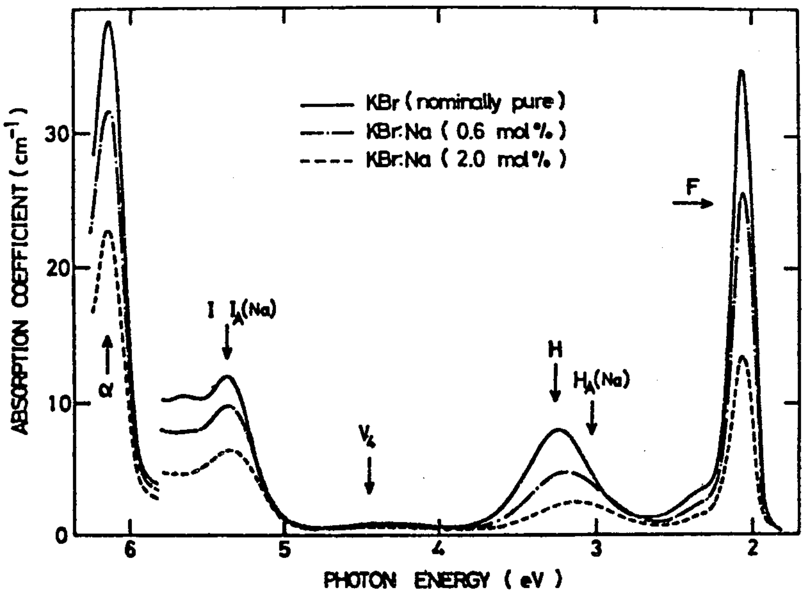

Fig.3.4.1. Optical absorption spectra of KBr crystals induced by the 30-min x-ray irradiation at 6 K. The irradiation time was shortened to 8 min for successful measurement of the F^+(α) band.

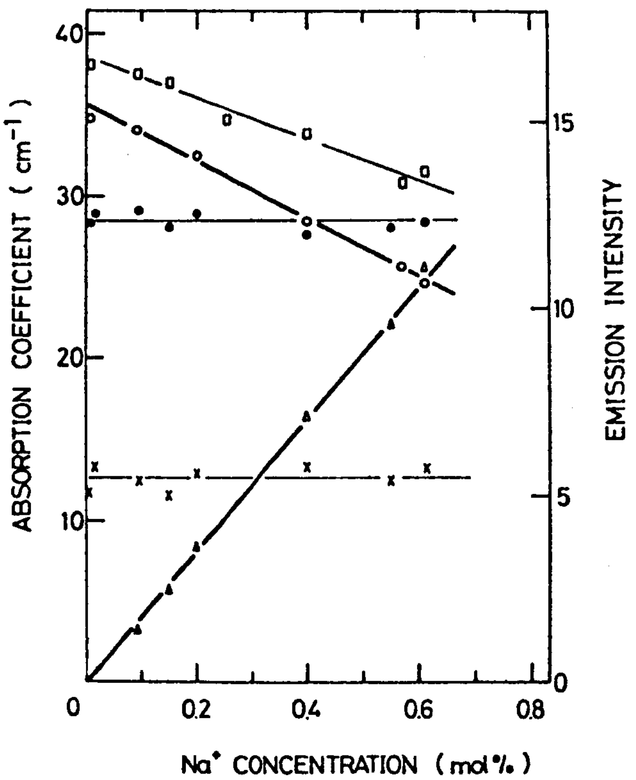

Fig.3.4.2. Na^+-concentration dependence of the yields of the F center (o), and of the F^+ center (□), and dependence of intensities of singlet (●), triplet (x), and π_A (Δ) emissions, respectively. All measurements were made at 6 K.

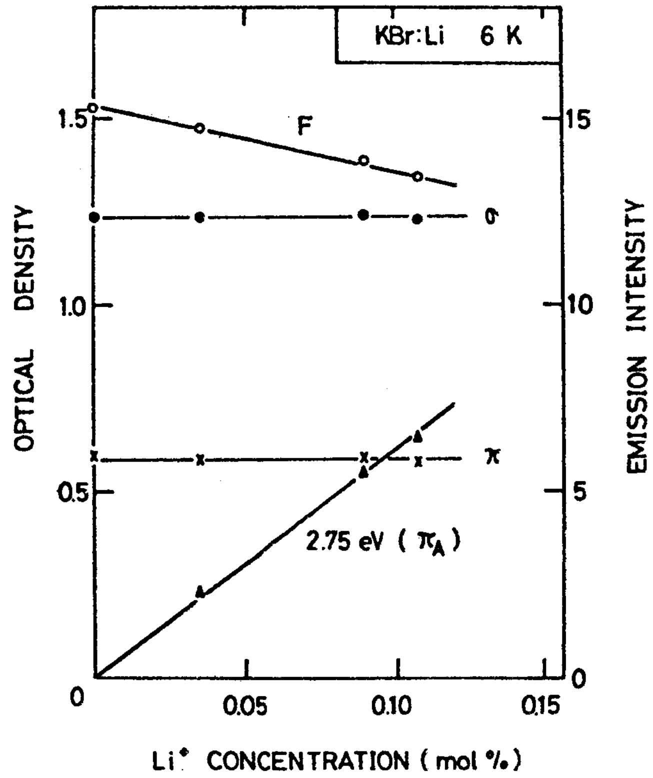

Fig.3.4.3. Li^+-concentration dependence of the yield of the F center and of the intensities of σ-, π-, and π_A-emission bands of KBr crystals at 6 K. Irradiation time for the measurement of the F-center yield is the same as that for KBr:Na system.

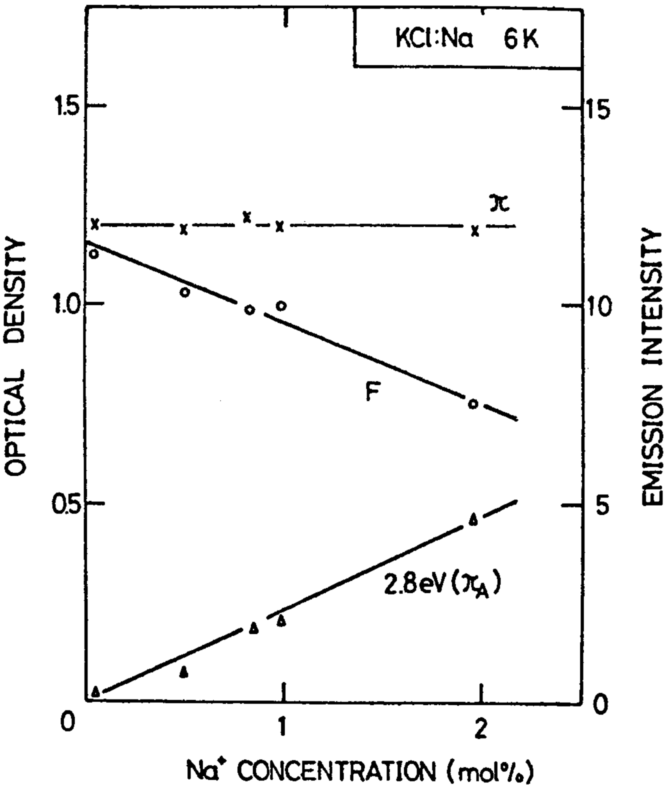

Fig.3.4.4. Na^+-concentration dependence of the yield of the F center and of the intensities of π- and 2.8-ev emission bands in KCl crystals at 6 K.

the similar behaviours of these quantities as those in KBr:Na in also KBr:Li system.

However, it should be pointed out that the changes in these quantities per unit impurity concentration is larger in KBr:Li than in KBr:Na.

Figure 3.4.3 shows the results of similar experiments carried out to the KCl:Na system. Again the similar results were obtained. In KCl:Na, the supplementary emission band appears at about 2.8 eV upon the x-ray excitation at 6 K. This emission band may be due to the exciton associated with Na^+ ions.9) The emission intensity increases following the decrease of the yield of the F center with increasing Na^+ concentration, though the relative intensity compared with that of π emission is fairy weak.

Thus, alkali-impurity ions in KBr and in KCl crystals affect the radiolytic behaviours at low temperature, to suppress the defect formation, to enhance the intensity of the emission band due to $(V_K e)_A$, but to give no effects on intrinsic σ and/or π luminescences.

(2·2) Effects of the impurities on dynamical process; experiments by pulse-electron irradiations

In order to obtain more informations on the effects of the impurities on color-center formation, the pulse electron irradiation was employed. First, the dynamical recombination process of formed F and H centers at 5 K was measured.

In Fig.3.4.5, the result of KBr:Li(0.07 mol%) is shown and is compared with that obtained by Kondo et al. for pure KBr.8) One can see that both are essentially the same; most fraction of the F center produced by a pulse decays, owing to the dynamical recombination with the H center. This result indicates that the dynamical recombination is hardly affected by alkali impurity ion at 5 K.

Second, the effects of Na^+ ions on the radiolytic behaviours in KBr at 80 K were studied. Since the primary interstitials, the H center and the I center, are not stable

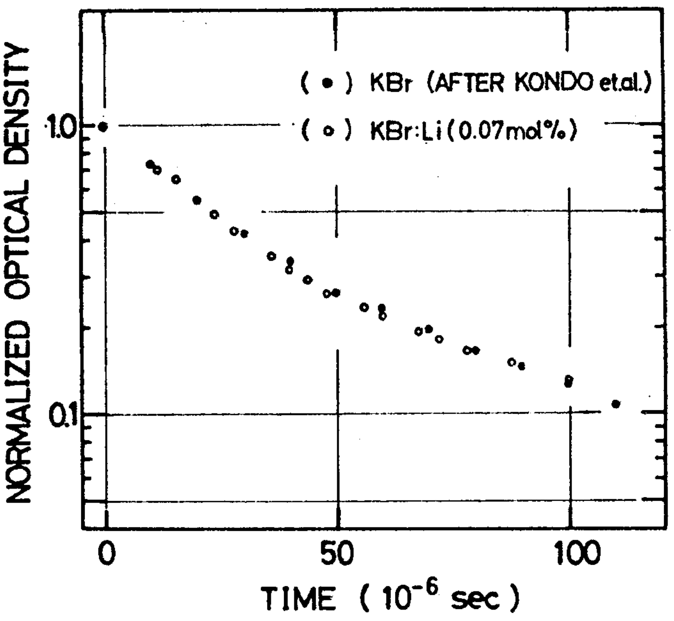

Fig.3.4.5. Semi-logarithmic plot of the decrease of the optical density at the F band in a KBr:Li(0.07 mol%) after the pulsed electron irradiation at 5 K. Similar result of pure KBr crystal, obtained by Kondo et al.(ref.8), is also shown for comparison.

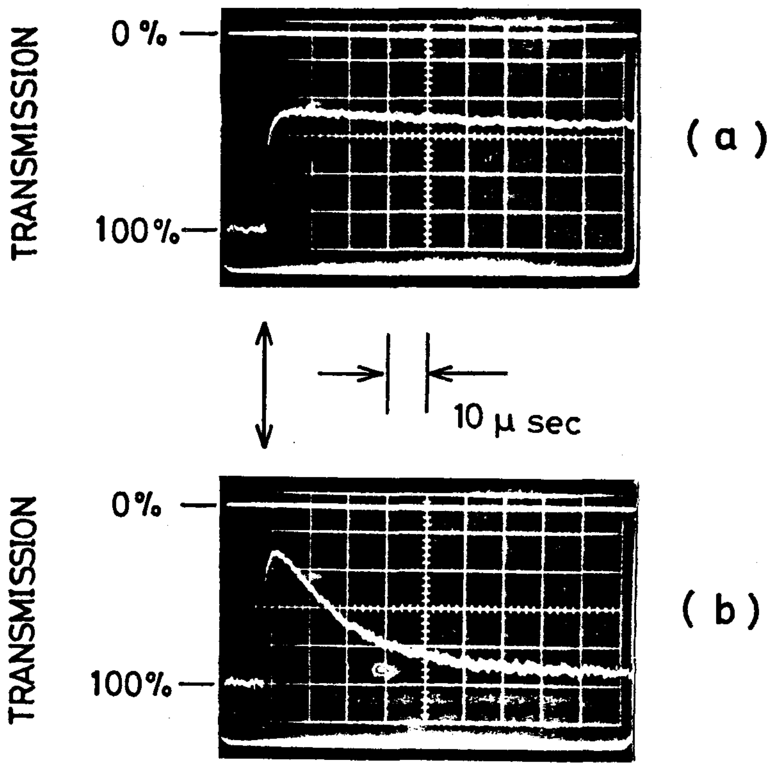

Fig.3.4.6. Oscilloscope traces of transmission changes at 610-nm, (a), and 765-nm, (b) regions in KBr:Na(0.70 mol%) induced by a single electron pulse at 80 K. Measurements were made simultaneously for the same sample and the same electron pulse.

at this temperature, observation of the same impurity effects as those at 6 K is possible only by the pulse radiolysis technique.

Upon the pulse electron bombardment, the transient absorption bands due to (V_Ke $)_{Na}$ as well as the F band was observed. Typical examples of the results are shown in Fig.3.4.6.

Curve(a) in Fig.3.4.6 shows the change in transmitting light through the F band in a KBr:Na(0.70 mol%). The intensity slightly increases upto 60 μsec after the pulse bombardment and remains almost unchanged at longer times. Since the life time of the H center at 80 K is the order of 10^{-2} sec, thermal recombiantion of the H center is not important in this time region. Curve(b) shows the change in transmitting-light intensity at 765 nm in the same sample. The decay time of the absorption band, calculated from the data is 1.1×10^{-5} sec. From this decay time, it is evident that the transient absorption band is due to (V_Ke $)_{Na}$(see Chap[3.3]). The slight increase of the transmitting light, or the decrease in optical density, upto 60 μsec in Curve(a) is due to the overlapping of the absorption band of (V_Ke $)_{Na}$.

Figure 3.4.7 shows Na^+ concentration dependences of the absorption coefficients of the F band afer 60 μsec, $\alpha_{60}(F)$, and that of (V_Ke $)_{Na}$ at t=0, α_m, in KBr:Na crystals. In the figure, the dependences of intensities of σ and π_A emission bands excited by x ray at 80 K are also included. One can see that $\alpha_{60}(F)$ decreases and α_m of (V_Ke $)_{Na}$ increases with increasing C_{Na}. The σ emission intensity, which is reduced to 1/200 compared wuth the intensity at 6 K, remains unchanged at 80 K, too. The effects of the Na^+ impurity ion on radiolytic phenomena in KBr at 80 K is thus essentially the same as those at 6 K.

3 DISCUSSIONS

(3·1) Secondary reactions of defects and suppression of colorability

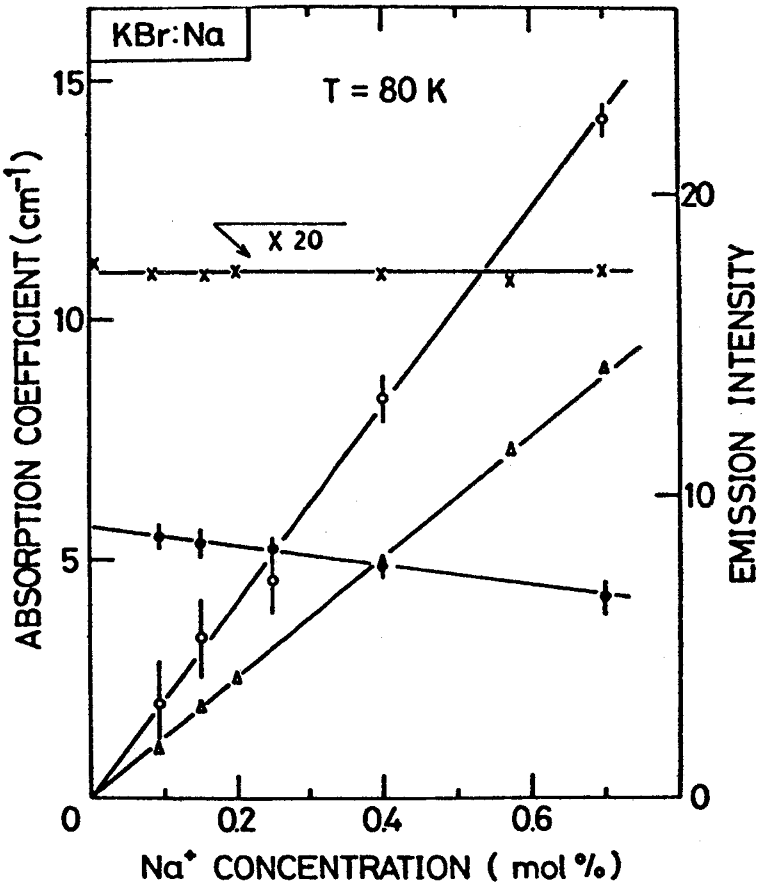

Fig.3.4.7. Na^+-concentration dependence of the absorption coefficients of the F band at 60 μsec after pulse bombardment (●), and of the transient absorption band (828 nm) due to (V_Ke)$_{Na}$ at t=0 (o), and the dependence of σ- (x) and π_A- (Δ) emission intensities, respectively. The intensity of the σ-emission band is maltiplied by 20, for convenience.

In discussiing the suppression of defect formation in the present case, we can consider the following sequence of defect-formation process;[7)] one is the dissociation of an exciton, and the other is the secondary reactions of created defects. First, we shall consider several possible secondary reactions which might cause the suppression.

1. Interaction of replacement sequence with Na^+ ion

Kondo et al.[8)] have shown that the primary defect created by ionizing radiation is a pair of an F center and an H center. Dynamic behaviours of the energetic H center in alklai halides have been extensively studied by Saidoh, Itoh, and their cowarkers. At temperatures as low as 6 K the thermal migration of the H center is not active,[10)] and the main mode of motions may be adiabatic replacement sequence. Saidoh et al.[11,12)] have shown that the replacement sequence attractively interacts with a Na^+ ion to form an H_A center. Therefore, the Na^+ ion may not act for the replacement sequence as does the I^- ion in KBr, which is considered to reflect back the moving interstitial atom as shown by Hirai.[13)] Thus the interaction of the replacement sequence with Na^+ ions may not be responsible for the suppression of the F center formation.

Kondo et al.[8)] have also shown from their study by pulse electron irradiation, that only 1/50 of the initial F centers remains stable at 10 K, and they attributed the bleaching to the recombination of a pair with short distance. As shown in the previous section, the Li^+ ion hardly afftects this dynamic recombiantion process. It may be, therefore, also impossible to attribute the suppression of the colorability by the Na^+ ion to this transient bleaching effect.

2. Conversion from the neutral Frenkel pair into charged pair

Next, it is nescessary to consider the conversion reaction of a F - H pair into an I - F^+pair: Such a reaction could exist, since the primary product is shown to be the former, though the details of the reaction are not known.

One possible type of such reactions may be capture of an electron from the F center by the H and/or the H_A center during irradiation.[14)] The ratio of the formation yield of the H_A center to that of the H center increases with increasing C_A, since the probability of finding a impurity ion along the interstitial collision sequence increases. This is, probably, the cause of the shift of peak position of the H-band region shown in Fig.3.4.1.[11,12)]

The conversion reaction can be a cause of the decrease of the yield of the F center only when the H_A center captures an electron more effectively than the H center: Effective conversion of the pair in the form of F - H_A centers might result in the further decrease of the F center corresponding to the increase of C_A. Saidoh and Itoh[15)] have shown that the $H_A(Na^+)$ center cannot be converted into $I_A(Na^+)$ center by capturing an electron from the F center, although the $H_A(Li^+)$ center can. The I and F^+ bands should be enhanced with decreasing the F-band height, if the conversion reaction is active. Hoever, the yield of the I- and F^+-center production also decreases with increasing C_{Na} as shown in Fig. 3.4.1 in the case of KBr:Na system. Thus the conversion reaction also cannot be the main cause of the decrease of the yield of the F center, though the reaction might give some effects in KBr:Li system.

3. Optical bleaching by π_A emission

Another possibility should also be considered, which is the optical bleaching effects by the luminescence during irradiation.[16,17)] The intensity of the π_A emission increases with increasing C_{Na}, and the π_A emission band appreciably overlaps with the H and H_A absorption bands. The decrease of the yield of defect formation by alkali impurity ion might be due to the reabsorption of the emission by H and/or H_A centers, which results in the excitation of the centers and the succeeding recombiantion with F centers.

This optical bleaching effect can be, however, also disregarded in view of the following experimental results: An optical illumination with the similar band shape and intensity as that of the π_A emission during or after x-ray irradiation was made on a nominally pure KBr. The illumination caused little change in the yield of each color center. The light even with the intensity, two orders of magnitude larger than that of the π_A emission of KBr:Na(0.61 mol%), bleached at most a few percent of the H and F centers produced by irradiation, and no appreciable decrease was observed in the heights of F^+ and I bands. On the contrary, the suppression of the colorability by Na^+ impurity correlated with the considerable decrease in the yield of the F^+-center production as shown in Fig.3.4.2. Therefore, the main origin of the suppression in the present case cannot be ascribed to the optical bleaching by the π_A emission.

Thus, we can conclude that the secondary processes of the created color centers are not responsible for the suppression of the F-center formation. Above discussions together with the result that the formation of $(V_Ke)_A$ is closely related to the suppression of the F center formation focus our attention on the dissociation process of an exciton, or relaxation of the hot exciton.

(3·2) Relaxation of exciton in alkali halides containing alkali impurities

The complementary behaviour between F center formation yield and the π_A-emission intensity shown in Figs.3.4.2, 3, and 4 indicate that teh formation of $(V_Ke)_A$ plays an important role in the suppression of colorability. This relationship is, however, very qualitative, since the formation yield of $(V_Ke)_A$ is measured by its emission intensity. In order to obtain more quantitative and decisive correlation between the decrease of the formation yield of the F center and the formation yield of $(V_Ke)_A$, we shall focus our attention on the results of pulse-radiolysis experiments where the formation yield of $(V_Ke)_A$ is measured by means of optical absorption.

Since the lifetime of the H center for thermal recombination is not active in the time region of 10^{-4} sec, $\alpha_{60}(F)$ in

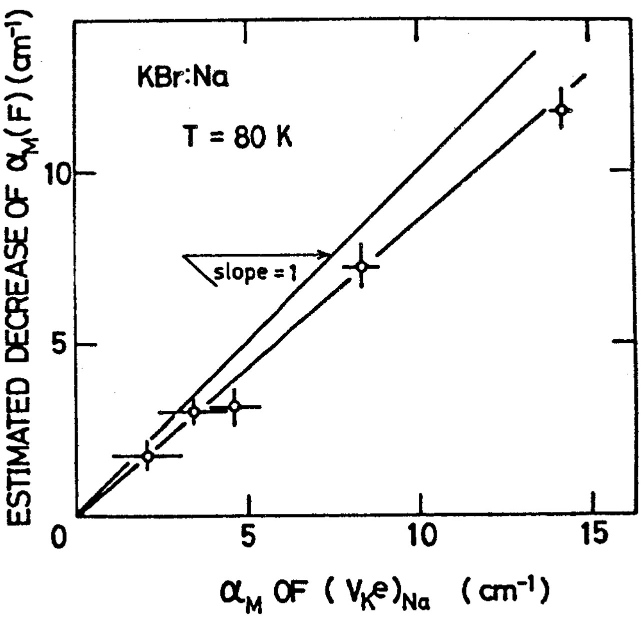

Fig.3.4.8. Plot of the decrement from that in pure KBr in the estimated maximum absorption coefficient of the F band, α_M, vs. α_M of the 828-nm band in the KBr:Na crystals.

Fig.3.4.7 is considered to represent the total number of surviving interstitial halogen atoms in the forms of H and H_A centers after the dynamical recombination process which takes place within less than 10^{-7} sec after the pulse electron bombardment at 80 K. The meaningful values which we can compare each other are, however, the absorption coefficients at t=0, α_M. Unfortunately, optical density of the F band at t=0, $(O.D)_0$, was not obtained in the present experiments, since the dynamical recombiantion of the F center at 80 K was not observable by the present experimental system. Karasawa and Hirai have measured $(O.D)_0$ in KBr between 1.8 and about 80 K, and have compared it with the optical density at 500 sec after the pulse bombardment, $(O.D)_{500}$.[18] The ratio of $(O.D)_0$ to $(O.D)_{500}$ is about 11 at 76 K. The value of optical density at 60 μsec after electron bombardment obtained present experiment may be essentially the same as $(O.D)_{500}$ of Karasawa and Hirai.[18] Therefore, it is possible to estimate $(O.D)_0$ from the present data with assistance of the data obtained by them.

In Fig.3.4.8, decrease in estimated value of absorption coefficient, α_m is plotted against the increase in that of $(V_Ke)_{Na}$ in crystals with different Na^+ concentration. The results shown in the figure indicate that the decrease in absorption coefficient of the F band at t=0 in a given KBr:Na crystal is about the same as the height of absorption coefficient of the $(V_Ke)_A$ band in the crystal. Since the oscillator strengthes of F and $(V_Ke)_A$ bands are considered to be about the same,[1] one can conclude that the suppressed concentration of the F center by Na^+ ions is about the same as that of formed $(V_Ke)_{Na}$. This is the direct evidence that the suppression of the F center formation is due to the formation of $(V_Ke)_A$.

Two types of reactions may be possible for the formation of the $(V_Ke)_A$; (i) one is the interaction between an exciton and a impurity ion, and (ii) the other is the interaction of a hole with the ion followed by the subsequent electron trapping. If the $(V_Ke)_A$ is formed mainly through the latter reaction, the intensity of the intrinsic luminescence should be also suppressed corresponding to the increase of the π_A emission intensity, since the increment of the formation probability of the V_{KA} center with increasing C_A may result in the decrease of the number of V_K center to form the exciton state.

Kondo and Hirai[19)] have shown that a small amount of Ag impurity suppresses the formation of H and F centers in KCl at 10 K. They attributed the suppression to the trapping of an electron by the impurity, which may result in the decrease of the probability of electron-hole recombaintion to form the exciton state. In such a case, intensity of intrinsic luminescence should also be suppressed.

As shown in Figs.3.4.2,3, and 4, the alkali impurity ion gives no effect on the intrinsic luminescence, at least within the present range of the impurity concnetration. These results rule out the possibility that the formation of the ($V_K e$)$_A$ would take place mainly through the interaction of a hole with a impurity ion. From the same reasons, the possibility that the hot exciton itself would be trapped by a impurity ion is also disregarded. The present results strongly indicate that the alkali impurity ion in KBr and KCl interacts " selectively " with the state of the exciton which is responsible for the F-center formation.

In the earliest excitonic-formation mechanism model,[4,5)] the same state is responsible for the defect formation and intrinsic luminescence. These models cannot explain the present results. According to the very recent model proposed by Toyozawa,[6)] the adiabatic instability at the $2p_z$ state of the electron trapped by the V_K center is responsible for the F-center formation and the 1s state for the intrinsic luminescence. And the origin of the occurrence of two channels (defect formation and intrinsic luminescence) are whether the relaxation follows the adiabatic potential or the transition to the 1s state occurs. It may not be possible that this model explain the result that only the exciton state which results in the defect formation is affected by a alkali impurity ion.

Karasawa and Hirai[18)] have measured the yield of the F center and the intrinsic luminescence of KCl and KBr below 4 K, and found that the yield of the F center decreases with decreasing temperature with an activation energy of a few meV, while the intensity of intrinsic luminescence is almost constant. Their results that the behaviours of the F-center formation and of the intrinsic luminescence are independent of each other may suggest that the exciton state responsible for each phenomenon is essentially different.

The results and discussions above described lead us to suggest the following model of the relaxation of an excion: The exciton splits, with a fixed ratio which might depend only on the salt, into different two states; one is responsible for defect formation, and the other for intrinsic luminescence, and a " turning point " between two channels lies just after a hot exciton is formed.

In the light of this model, the features of the present results are well described in the following reaction: After the splitting, (V_Ke)$_F$ interacts selectively with an alkali impurity ion to form the (V_Ke)$_A$ which release energy in terms of the π_A emission.

Here, it is worth considering the model proposed by Itoh and Saido.[7)] In their model, the cause of the splitting into two channels lies in the relaxation of the hole in an exciton; the exciton with a V_K center in a Π_g state (Π_g exciton) is responsible for the F-center formation, and that in a Σ_u state (Σ_u exciton) for the intrinsic luminescence, respectively. The relaxation of the hole into Π_g or Σ_u state is considered, presumably, to take place with a given ratio. Since the V_K center in a Π_g state is energetically higher than that in a Σ_u, the Σ_u exciton may be more deeply self-trapped. Thus the perturbation of the Π_g exciton by a impurity ion may be more serious, and the Π_g exciton would be selectively attracted by the ion. This model thus can explain the characteristic features of the relaxation of an exciton as revealed above. In their model, however, one question remains unsolved. Keller and Patten[20)] have shown that the H center can be formed by the recombination of an electron with the V_K center in KCl crystal. In their study, the V_K center must be in the state of Σ_u. This result does not appear to be consistent with Itoh's model.

(3·3) On formation process of ($V_K e$)$_A$ in KBr and KCl crystals

In this paragraph, we shall discuss the formation process of ($V_K e$)$_A$, i.e. the interaction between ($V_K e$)$_F$ and an alkali impurity ion in some details.

Since the impurity ion hardly affetcs the dynamical recombaintion process of created H and F centers as shown in previous section, the concentration of the formed F center by present stationary irradiation, $(n_F)_s$, may be proportional to that of ($V_K e$)$_F$, $n[V_K e]_F$. From the complementary behaviour of the F-center formation yield and the formation yield of the ($V_K e$)$_A$ state, following equation is reasonably written;

$$(n_F)_s = AP_D(n[V_K e]_F - n[V_K e]_A), \qquad (3.4.1)$$

where P_D is the dissociation probability of ($V_K e$)$_F$ into F-H pair, A is a constant, and $n[V_K e]_A$ is the concentration of ($V_K e$)$_A$, respectively.

From the proportionality of $n[V_K e]_A$ to the impurity concentration, C_A, and from the selective interaction between ($V_K e$)$_F$ and an impurity ion, the $n[V_K e]_A$ may be expressed as follows;

$$n[V_K e]_A = n[V_K e]_F \, V^* \, C_A, \qquad (3.4.2)$$

where V^* is a parameter with a dimension of volume, which may represent the degree of exciton - impurity interaction. Then the $(n_F)_s$ is written as a function of C_A in the following form;

$$(n_F)_s = A \, P_D \, n[V_K e]_F \, (1 - V^* C_A). \qquad (3.4.3)$$

One can estimate, from eq.(3.4.3), the value of V^* based on the results shown in Figs.3.4.2, 3, and 4. Obtained values for KBr:Na, KBr:Li, and KCl;Na are listed up in Table.3.4.1.

It is seen that the value of V^* depends not only the kind of the impurity but on the salt itself: The value for KBr:Li is about two times larger than that for KBr:Na, and V^* in KCl:Na is less than a half of that in KBr:Na.

It has been shown by Saidoh and Itoh that the H_A(Li) center can convert into I_A(Li) center by capturing an electron of the F center.15) If such a reaction is the case during x-ray irradiation, the value of V^* for KBr:Li may involve some ambiguity. Taking account of such a situation, the ratio of V^* for KBr:Li to that for KBr:Na is about the same as the ratio of the missmachings of Li^+ in KBr to those of Na^+ in the salt.21) Therefore, it may be clear that V^* involves the factor representing the probability of capturing an axciton which may mainly come from the disorder in the lattice by an impurity ion. This factor is hereafter represented by Σ^*.

Then we will compare the value of V^* in KCl:Na with that in KBr:Na. The disorder of Na^+ ions in KCl is about the same as (or rather larger than) that in KBr crystal, as seen in Table.3.4.1. However, the value of V^* in KCl:Na is so smaller than that in KBr:Na. This result suggests that not only the lattice disorder by an impurity ion, but also the properties of the exciton in a salt are important for the exciton - impurity ion interaction studied here. The properties may reflect the " mobility " of the exciton in the motion toward the impurity site to form ($V_K e$ $)_A$. Taking into account such a property, V^* should be represented as a product of Σ^* and μ^*, the latter of which reflects the motional property in a salt.

The smaller V^* in KCl crystal may be reasonable, since the V_K center, which is the core of a exciton, in KCl is more deeply self-trapped than in KBr.22) Though detailed mechanism of the exciton - impurity interaction are not clear, results and discussions above suggest that the exciton state

Table 3.4.1. Interaction volume between (V_Ke)$_F$ and the alkali-impurity ion, V^*, determined from the decrease in F-center production yield in KBr and KCl. Some related quantities are also shown for reference.

	V^*		distortion of	T_d of
	6K	80K	n.n. ions$^{a)}$	V_K center$^{b)}$
KBr:Na	50 (35)$^{c)}$	35	-0.03958	160 K
KBr:Li	110	–	-0.06162	
KCl:Na	18	–	-0.04256	210 K

a) Results of calculations by Douglas (ref.21).

b) T_d is the decay temperature. After Schoemaker (ref.22).

c) The value of V^* determined from the decrease in F^+-center formation yield.

which is responsible for the F-center formation involves motions in its relaxation process.

Two possible types of motions of an exciton in alkali halides have been considered so far; one is the hopping motion of the self-trapped exciton which is stimulated thermally,23) and the other is the coherent diffusion of an unrelaxed exciton.24) In order to obtain more informations on the behaviours of the exciton in the present case, we discuss here the temperature dependence of interaction volume, V^*, in KBr:Na crystals.

In Fig.3.4.9, replot was made of the Na^+ concentration dependences of formation yields of the color centers and the ratio of the yield of π_A emission to that of intrinsic σ emission at 6 and 80 K. The value of V^* can be evaluated from these plots using eq.(3.4.3).

The value obtained from date of the formation yield of the F center is 50, whereas that of the F^+ center is 35 at 6K, respectively. Ritz and Kabler25) have shown that the concentration of the produced F^+ centers to that of F centers depends on the duration of the irradiation as well as others. The Difference of the values of V^*'s may be due to this effect, since the x-ray dose under which the yields of the two centers were measured are different from each other. Since the conventional x-raying which was applied to obtain yields of color centers in this study involves various processes of defect formation, it is not decisive which value of V^*'s is more accurate. However, it may not be unreasonable to conclude that the value of V^* at 6 K in KBr:Na is the avelage of these two, about 40.

The decrease of the formation yield of the F center, which was obtained by pulse electron irradiation at 80 K is well described by eq.(3.4.3) with V^* of 35. This value is coinside with that obtained from data of F^+ center at 6 K.

On the other hand, one can estimate the temperature dependence of V^* also from the luminescence data involved in Fig.3.4.9. In the figure, the intensity ratio between π_A and σ emissions, $(I_{\pi A})_0/(I_\sigma)_0$, is the value which is based

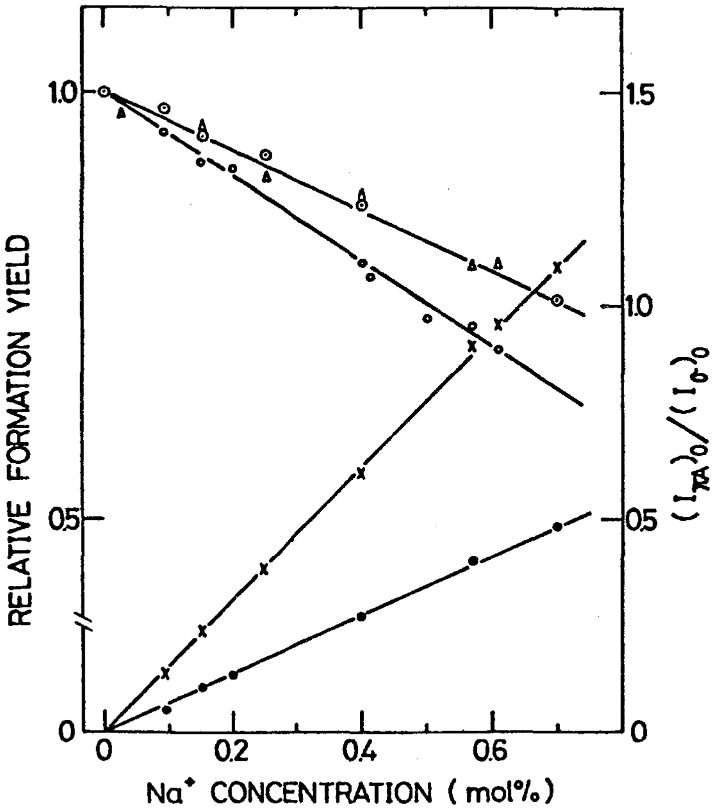

Fig.3.4.9. Na^+-concentration dependence of the relative formation yields of F (o) and F^+ (Δ) centers at 6 K, and of the F center at 80 K (⊙), and the dependence of the ratio of ($I_{\pi A}$)$_0$/(I_σ)$_0$ at 6 K (x) and at 80 K (●), respectively. Formation yields at 6 K were obtained from the x-ray irradiation data (Fig.3.4.2), and the yield at 80 K from pulse-irradiation data (Fig.3.4.7), respectievly. ($I_{\pi A}$)$_0$ as well as (I_σ)$_0$ represents the emission intensity of each emission band corrected in terms of the luminescence efficiency at the temperature.

on the emission intensities corrected in terms of temperature dependent luminescence efficiencies. Therefore, the ratio is supposed to represent that of concentrations of both luminescence centers.

When the relaxation probabilities of hot excitons into $(V_K e)_\sigma$ and $(V_K e)_F$ are written as $1/\tau_{hs}$ and $1/\tau_{hf}$, respectively, the intensity ratio can be expressed, using eq.(3.4.2), as follows;

$$\frac{(I\pi_A)_o}{(I_\sigma)_o} = \frac{\eta_{\pi A}/\tau_{hf}}{\eta_\sigma/\tau_{hs}} V^* C_{Na} \qquad (3.4.4)$$

where $\eta_{\pi A}$ and η_σ are the quantum efficiencies of π_A and σ emissions, respectively.

It is clear that the ratio at 80 K is smaller than that at 6 K. This reduction is considered to come from that of $1/\tau_{hf}$: Karasawa and Hirai$^{26)}$ have shown that the formation yield of $(V_K e)_F$ at 80 K is reduced to about a half of that at 6 K in KBr.

Taking the decrease of $n[V_K e]_F$ into account, the value of V^* at 80 K becomes nearly equal to the value at 6 K. This indicates that V^* hardly depends on temperature.

Based upon these results for V^*, it can be concluded that the V^* in KBr crystals hardly depends on the temperature from 6 K and 80 K. This conclusion may rule out the possibility that the mobility of an exciton in the exciton-impurity interaction originates from thermally induced motion of self-trapped exciton. It appears to favor that the motion of $(V_K e)_F$ has adiabatic nature.

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[3·5]

FORMATION OF (V_Ke)$_A$ BETWEEN 1.7 AND 80 K IN KBr AND KCl

Behaviour of (V_Ke)$_F$ between 1.7 K and 80 K have been studied by means of measurement of the formation yield of (V_Ke)$_A$ in KBr and KClcrystals. It has been clearly shown that the formation yield of (V_Ke)$_F$ is constant below 4.2 K and decreases above 25 K, as concluded by Karasawa and Hirai. Dissociation probability of (V_Ke)$_F$ into F-H pair is constant irrespective of temperature above 25 K, and decrease below 4.2 K with decreasing temperature. Some speculations on the behaviour of (V_Ke)$_F$ are given

§1 Introductory Remarks

In Chap.[3·3], the electronic structure and other important features of (V_Ke)$_A$ has been cleared. In Chap.[3·4], the effects of the formation of (V_Ke)$_A$ on other radiolytic behaviours has been studied. Results of these works have led us following important conclusions; (1) (V_Ke)$_F$ is essentially different from those states which result in intrinsic luminescences, (2) the hot exciton splits into these different two states not complementary but with a fixed ratio, and (3) only (V_Ke)$_F$ interacts selectively with an alkali impurity ion to form (V_Ke)$_A$, which reduces colorability.

The results obtained previous chapters give us a possibility that one can know, to some extent, the properties of (V_Ke)$_F$ by means of measurements of behaviours of (V_Ke)$_A$.

So far, the properties of (V_Ke)$_F$ has been studied mainly by measuring colorability or the change in optical absorption corresponding to formed F and/or H centers, η_F. It may be clear that the η_F is combined with (V_Ke)$_F$ through an unknown factor which represents the dissociation probability of (V_Ke)$_F$ into F - H pair, P_D. In the case where P_D is constant irrespective of various variables on which the changes of η_F are measured, temperature, impurity concentration, and so on, η_F certainly represents the behaviours of (V_Ke)$_F$. If not so, however, η_F may not be an exact observables of (V_Ke)$_F$, though meaningful one.

On the other hand, since (V_Ke)$_A$ is correlated with (V_Ke)$_F$ directly as shown in Chap.[3·4], measurement of formation yield of (V_Ke)$_A$ is more powerful to know the behaviours of (V_Ke)$_F$ when P_D changes.

In this chapter, based on above results and considerations, temperature-dependent behaviour of (V_Ke)$_F$ is studied by means of measurement of that of (V_Ke)$_A$ between 1.7 and 80 K. First, the formation yield of (V_Ke)$_F$ above 6 K is discussed, and is to be shown that P_D is constant and η_F and (V_Ke)$_A$ give the same information on (V_Ke)$_F$. Next, the results below 4.2 K are considered. It will be shown that in this temperature region, P_D decreases with decreasing temperature, whereas the formation yield of (V_Ke)$_F$ is constant. Some speculations are given based on these results.

2 Results and Discussions

(2·1) The π_A emission between 6 and 80 K

Figure 3.5.1. shows the temperature dependence of the emission intensity of the singlet and π_A emissions which were excited by x ray. The change in intensity of singlet emission is well analyzed by the function;

$$I(T) = I_o\{ 1 + \tau_o\nu\exp(- E/kT) \}^{-1} \qquad (3.5.1)$$

where $1/\tau_o$ is the radiative transition probability, and I_o the intensity at T = 0, and E and ν are constants, respectively. The value of E obtained by best fit to the data is 0.025 eV which is essentially identical to that obtained by Ikezawa and Kojima[1)]

This behaviour of the singlet emission indicates that

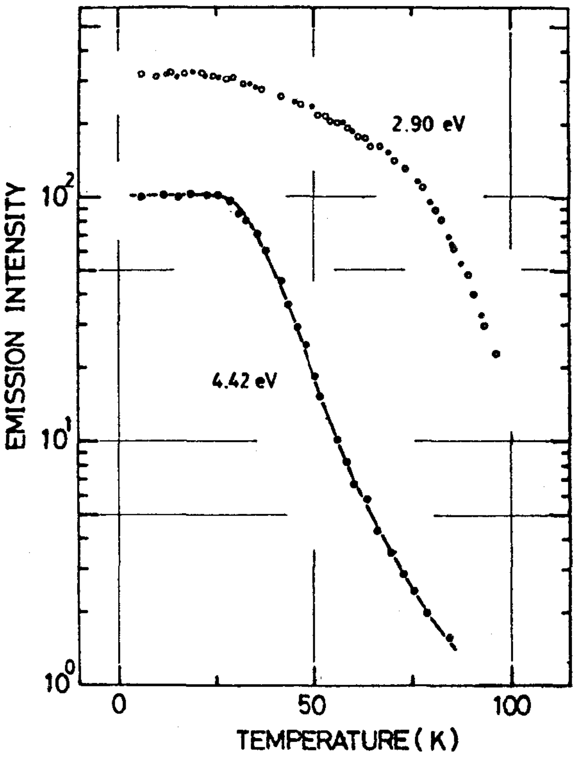

Fig.3.5.1. Temperature dependence of σ- and $\pi_A(Na^+)$- emission intensities. The π_A-emission intensity was measured at 2.9 eV. In the data of the 2.9-eV emission, open circles and solid ones are the intensities measured during warming up and cooling down the sample, respectively.

the formation yield of (V_Ke)$_\sigma$ is not temperature-dependent, though the luminescence efficiency depends on temperature.

On the other hand, the intensity of the π_A emission does not show the typical quenching pattern; it decreases gradually between 25 and 70 K, and falls off rapidly above 70 K. Recently, it has been shown that coloration suppresses the intensity of intrinsic emissions in KI.$^{2)}$ The open circles in the figure is data point which was measured buring warming up a sample, and the dotts are ones during cooling down the sample. If the decrease in intensity originates in coloration, these two types of data must show the " hysteresis ", since the coloration is not removed by cooling down the sample. Thus, good agreement of two types of data points seen in Fig.3.5.1 excludes the possibility that the decrease is due to the coloration, and shows that the gradual decrease in intensity is an essential phenomena.

In order to make clear the behaviour of the π_A emission, the temperature dependence of the luminescence efficiency of (V_Ke)$_A$ was studied by two different methods; one is the measurement of the decay time of the π_A emission, and the other is measurement of the luminescence originated from the recombination of $V_{KA}(Na^+)$ centers with electrons.

In the measurement of recombination luminescence, the sample which contains V_{KA} centers and F centers but no V_K centers was prepared by similar treatments described in Chap.-[3·2]. After the treatments, temperature of the sample was cooled down to 6 K, and the luminescence under F light illumination was measured at a given temperature. It can be concluded that the concentration of created (V_Ke)$_A$ due to recombination for each measurement may be substantially identical in this experiment, based on following reasons:

(1) Thermal decay of the V_{KA} center by warming up the crystal up to 110 K is not active, since the decay temperature of the center is higher (~200 K),

(2) number of released electron may be essentially the same, since the properties of the excited F center does no change up to 100 K,$^{3)}$ and the intensity

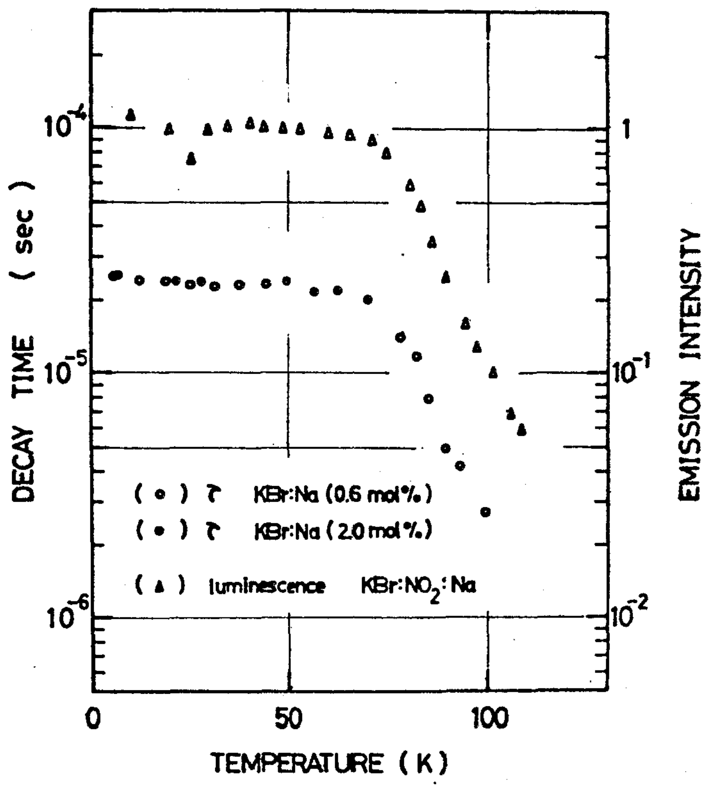

Fig.3.5.2. Temperature dependence of decay time of $\pi_A(Na^+)$ emission and of the emission intensity due to recombination of the V_{KA} center and an F-electron the latter of which was released by optical illumination.

of exciting light is the same for each measurement,

(3) the intensity of the F light is so weak that it hardly bleach the F and V_{KA} centers during a series of the measurements.

Thus the results of recombination luminescence may represent the luminescence efficiency of (V_Ke $)_A$.

The intensity of recombination luminescence is almost constant up to 70 K, then drops sharply above 70 K. This result can be explained in terms of two competitive process desrcibed by eq.(3.5.1).

The temperature dependence of the decay time of π_A emission also shows the quenching pattern; the time becomes shorter only above 70 K, whereas it remains unchanged below the temperature. Results shown in Fig.3.5.2, therefore, indicates that the luminescence efficiency of the (V_Ke $)_A$ follows the normal thermal quenching. Then it is clear that gradual decrease of the intensity excited by x ray between 25 and 70 K has the origin in the change of formation yield of the (V_Ke $)_A$.

Karasawa and Hirai have shown that η_F in KBr decreases with increasing temperature above 25 K.[4) In Fig.3.5.3, I compared the dependences of $n[V_Ke]_{Na}$ obtained in this study with that of η_F obtained by Karasawa and Hirai. One can see that these two quantities show the same temerature dependence.

Karasawa and Hirai have explained the decrease of η_F in terms of following model. In their study, η_F and the yield of $^3\Sigma_u^+$, η_T, compete with each other above 25 K, and their behaviours are well represented following set of equations,

$$\eta_F = (1/\tau_{FF})/(1/\tau)$$

$$= [1 + (\tau_{FF}/\tau_{HT})\exp(-E/kT)]^{-1}, \qquad (3.5.2)$$

$$\eta_T = C + (1 - \eta_F), \qquad (3.5.3)$$

where τ_{FF}, τ_{HT} and C are constants. According to their interpretation, the thermally controlled competition takes place upon the relaxation of hot exciton; $1/\tau_{FF}$ is relaxation probability of hot exciton into (V_Ke $)_F$ and $(1/\tau_{HT})\exp(-E/kT)$ is that into $^3\Sigma_u^+$, respectively, and another relaxation channel

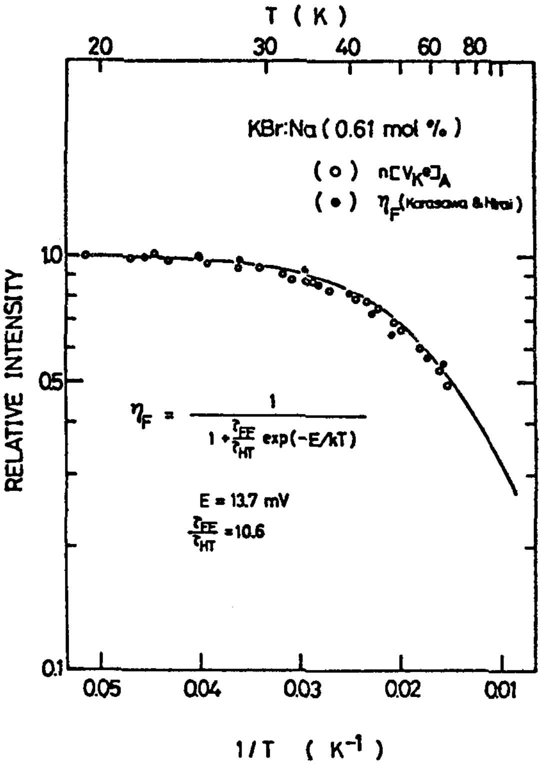

Fig.3.5.3. Temperature dependence of formation yield of ($V_K e$)$_A$ and of the F center in KBr crystals. The solid line is the calculated curves by eq.(3.5.2), using the values of parameters obtained by Karasawa and Hirai (ref.4).

with a constant probability into $^3\Sigma_u^+$ also exists.

However, another interpretation of the competition process, therefore the meaning of constants in eqs.(3.5.1) and 2, is certainly possible, where the transition of relaxed (V_Ke)$_F$ into $^3\Sigma_u^+$ occur by thermal activation. Based on the latter model, the formation yield of (V_Ke)$_F$ is not temperature-dependent, and the temperature-dependent η_F in eq(5.3.2) corresponds to P_D of (V_Ke)$_F$. Therefore, only from the measurement of η_F, it may be impossible to clearly show which of two processes, the relaxation of the hot exciton or the dissociation of (V_Ke)$_F$ is temperature-dependent.

However, the results obtained here may be able to determine which process is responsible for the competition. As discussed in Chap.[3·4] formation yield of the $(V_Ke)_A$ is represented as

$$n[V_Ke]_A = n[V_Ke]_F\ V^*\ C_A, \qquad (3.4.2)$$

and the interaction of (V_Ke)$_F$ and an impurity ion takes place before (V_Ke)$_F$ creates F - H pair, and possibly before the transition of (V_Ke)$_F$ into $^3\Sigma_u^+$, if the transition is the case. It has also been shown that V^* hardly depend on temperature. Therefore the temperature dependecne of $n[V_Ke]_A$ should represent the dependence of $n[V_Ke]_F$. It is evident in Fig.3.5.3 that the temperature dependence of $n[V_Ke]_A$ is well described by eq.(3.5.2).Thus one can safely conclude that the formation yield of (V_Ke)$_F$ itself is temperature dependent. And the agreement of the behaviours of $n[V_Ke]_A$ and η_F indicates that P_D is constant above 6 K.

(2·2) The π_A emission below 4.2 K

(V_Ke)$_A$ and η_F behaves with same way above 6 K, as discussed previous section. This indicates that P_D is constant irrespective of the temperature in this resion. Karasawa and Hirai have measured the formation yield of the F center below 4.2 K, and found that it decreases with decreasing temperature.5) They have argued this phenomena in terms of Toyozawa model on the F center formation,6)

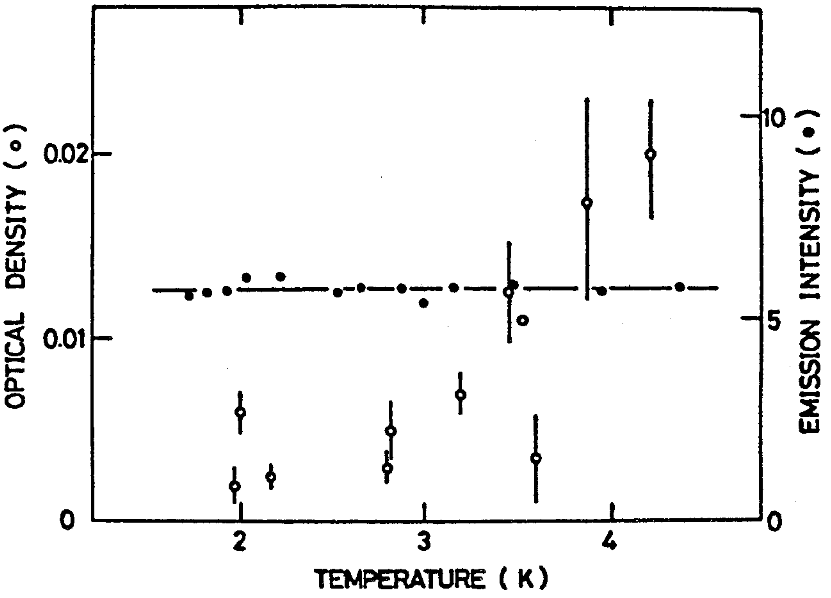

Fig.3.5.3. Temperature dependence of emission intensity of (V_Ke)$_A$ and of η_F below 4.2 K in KCl crystals. Values of η_F are ones obtained by Karasawa and Hirai (ref.5).

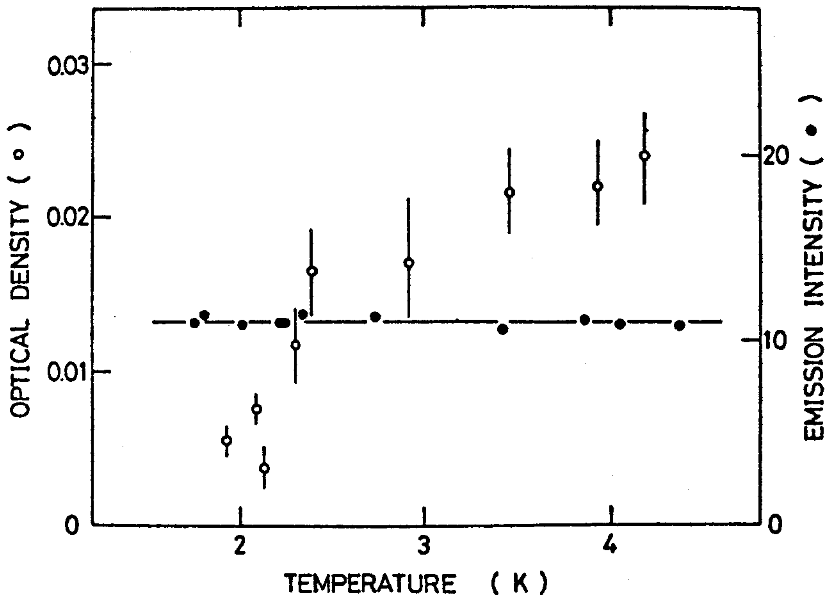

Fig.3.5.5. Temperature dependence of emission intensity of (V_Ke)$_A$ and of η_F below 4.2 K in KBr crystals. Values of η_F are ones obtained by Karasawa and Hirai (ref.5).

and reached the conclusion that the decrease has its origin in the decrease of P_D owing to the potential bariour at the dissociation process. However, the evience that (V_Ke)$_F$ is constantly formed below 4.2 K is absent in their work, and alternative possibility of the decrease of η_F, i.e. the decrease of the formation yield of (V_Ke)$_F$ itself is the origin in the decrease in η_F, survives yet. It is therefore, very meaningful to measure the formation yield of (V_Ke)$_A$, since it directly represents the yield of (V_Ke)$_F$.

Figs.3.5.4 and 5 show temperature dependence of luminescence yield of π_A emission in KCl and in KBr, respectively. Figures also involves η_F which is obtained by Karasawa and Hirai. The luminescence yields of intrinsic luminescences are almost constant, as shown by them. Results shown in the figures indicate that the formation yield of (V_Ke)$_A$, or (V_Ke)$_F$, is constant below 4.2 K. Therefore, it is evident that the decrease of η_F below 4.2 K is due to the decrease of P_D, as concluded by Karasawa and Hirai.

This behaviour of (V_Ke)$_F$ is very interesting. How is the energy of (V_Ke)$_F$ exhausted at low temperature?

It is generally acceptable that that (V_Ke)$_F$ is a higher excited state of STE. Bradford et al. have shown that time constant of the F center formation is 11 p sec in KCl.[7) This means that (V_Ke)$_F$ is coupled with phonons very poorly, or the stokes shift of (V_Ke)$_F$ is very small. Such a greater energy gap between (V_Ke)$_F$ and the ground state of STE may make the non-radiative decay of (V_Ke)$_F$ in terms of phonon creation less probable. However, the constancy of the luminescence yield of σ or π emission in KBr as well as in KCl below 4.2 K indicates that the energy of (V_Ke)$_F$ is not spent in terms of intrinsic luminescence.

Recently, Lushchik et al. have observed " edge emission " in alkali iodides at low temperature.[8) Such a emission might be correlated with the radiative decay of (V_Ke)$_F$, though they have assigned it to be the radiative decay of mobile one-center type excitons. The detailed study on the edge luminescence below 4.2 K may give useful and interesting informations on the relaxation of a exciton.

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[3·6]

EXCITON - Li^+ ION INTERACTION IN NaCl CRYSTALS

Effects of Li^+ impurity ion on the behaviour of excitons in NaCl crystals have been studied by means of measurements of optical absorption and emission due to pulse electron irradiation as well as conventional x-ray irradiation. The (V_Ke)$_{Li}$ is formed at 80 K as is formed in KBr and in KCl. (V_Ke)$_{Li}$ has a radiative lifetime of 2.8 X 10^{-4} sec, and this is quenched thermally above 150 K with typical quenching pattern. The peak energy of the emission band in 3.32 eV. The (V_Ke)$_{Li}$ has the similar transient absorption band at 2.14 eV as that of $^3\Sigma_u^+$. These properties have been briefly discussed. The formation of the (V_Ke)$_{Li}$ in NaCl is temperature dependent, and the mechanism is described well in terms of hopping motion of the lowest triplet state of STE. Li^+ ions give no effects on formation yield of the F center as well as luminescent phenomena at 6 K. This essentially different behaviour of Li^+ impurity ions in this salt from that in KBr has been discussed in connection with the defect formation mechanism.

1 Introductory Remarks

The effects of alkali impurities on the relaxation of an exciton in KBr and KCl crystals have been studied in the previous chapters. Alkali impurity ions having smaller ionic radii in these salts suppress the colorability in terms of the formation of (V_Ke)$_A$ which spends the energy radiatively. The intrinsic luminescence or the exciton states responsible for the radiations are not affected by the ions. The formation of (V_Ke)$_A$ takes place through the selective interaction between (V_Ke)$_F$ and the ions, and the interaction volume hardly depends on temperature.

These crystals studied above show higher F center formation efficiency at low temperature, and very short time constant of the F-center formation ($<10^{-9}$ sec).[1,2]
Therefore, these do not belong to the materials Pooley mechanism was applicable.[3]

It has been shown that the radiolytic behaviours of the NaCl crystal at low temperature are significantly different from those of KBr and KCl.[3,4] For example, the formation yield of the F center is very small at temperatures near liquid helium temperature, and it increases with increasing temperature, which is in reverse to that of KBr and KCl.[3] These differences may suggest that the properties and/or behaviours of excitons in NaCl are different comparing with those in KBr and KCl.

Thus, it is interesting and meaningful to study the properties of an exciton in NaCl crystals with the same method that was applied to KBr and KCl. In this chapter, radiolytic behaviours in NaCl has been investigated in terms of internal perturbation due to Li^+ impurity ion.

§2 Experimental Results

(2·1) Luminescence and F-center formation by x-ray irradiation at low temperature

The x-ray excited emission spectrum of NaCl:Li(1.2 mol%) at 6 K is compared with that of pure NaCl in Fig.3.6.1. There are no differences in the spectra within the limit of experimental resolution, and the supplementary emission bands related to Li^+ ion are not observable at 6 K in this salt.

Figure 3.6.2 shows the Li^+-concentraion dependence of the intensity of excitonic luminescence and the yield of the F center at 6 K. At this temperature, the yield of the F center as well as luminescence intensity is almost constant irrespective of the Li^+ concentration up to 1.2 mol%, which is the very contrast to the results in KBr:Na and

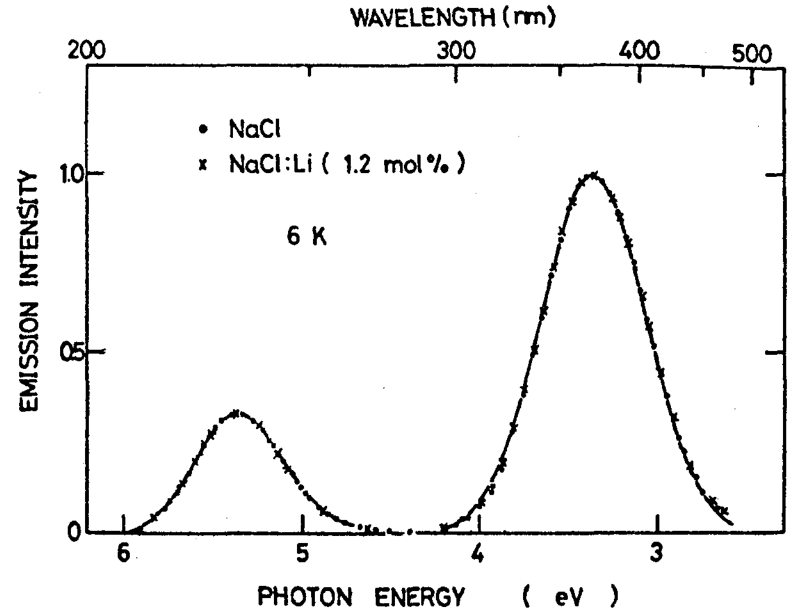

Fig.3.6.1. Emission spectra excited by x ray in NaCl and in NaCl:Li (1.2 mol%). The intensity is normalized to unity at the maximum of the 3.35 eV. Solid curves represent calculated Guassians with parameters obtained by Ikezawa and Kojima(ref.6).

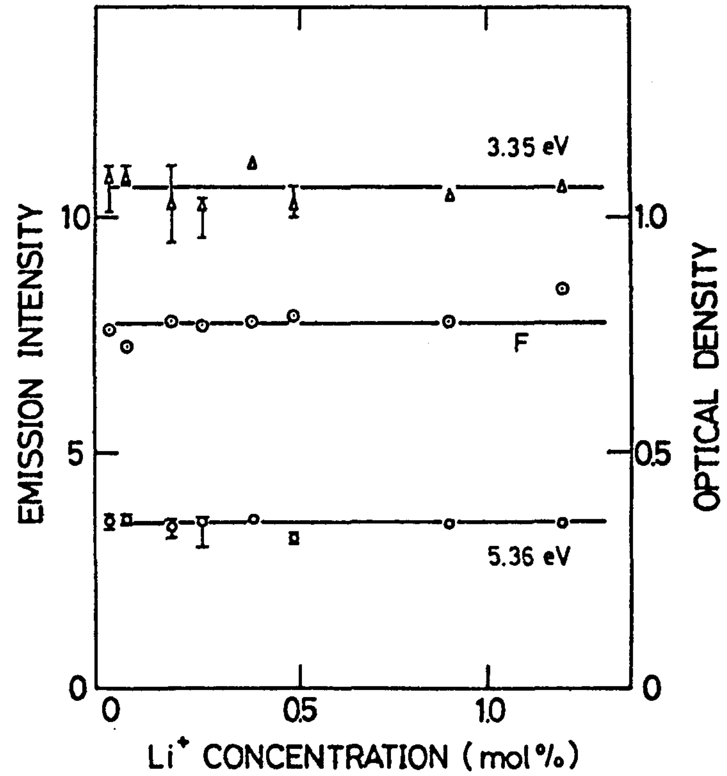

Fig.3.6.2. Li^+- concentration dependence of the formation yield of the F center and of the intensities of intrinsic luminescence. The F center were produced by x-ray irradiation (50 KV 40 mA) for 90 min at 6 K.

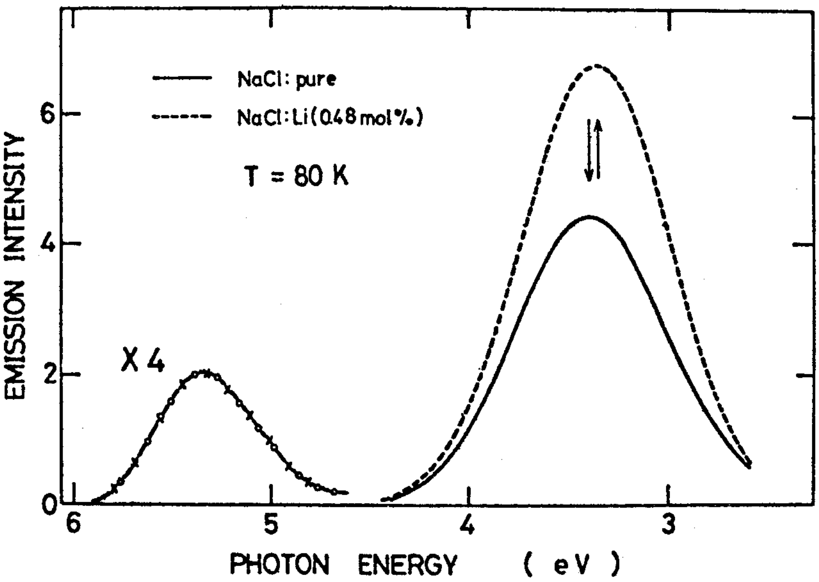

Fig.3.6.3. Emission spectra excited by x ray at 80 K of NaCl and NaCl:Li(0.48 mol%), respectively. Arrows indicate the peak position of emission band in each sample. Symbols (o) and (x) indicate the σ-emission bands of NaCl and NaCl:Li, respectively.

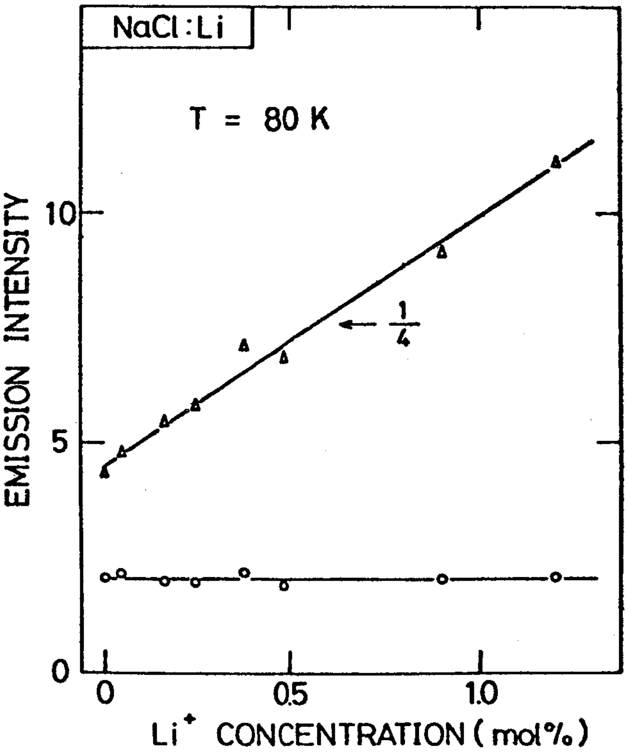

Fig.3.6.4. Li^+-concentration dependence of emission intensities at 5.35 eV (o), and at 3.40 eV (Δ), respectively. The intensity at 3.40 eV is reduced to 1/4 for convenience.

others.[5)]

Though the formation yield of the F center is not affected by Li^+ ions, absorption spectrum at the H-band region is affected; the optical density of the H band, peaking at 3.86 eV, decreases, whereas that of another absorption band at 3.30 eV increases with increasing Li^+ concentration. This change is supposed to be due to the formation of $H_A(Li^+)$ centers.

These results suggest that the interaction between an exciton and the impurity ion seen in KBr or KCl does not take place in NaCl at 6K, although the interstitial atom interacts with impurity ions attractively.

Figure 3.6.3 shows the x-ray excited emission spectra of pure NaCl and of NaCl:Li(0.48 mol%) at 80 K. Presence of Li^+ impurity results in the increase in emission intensity at the region of π-emission band and in the shift of peak position to longer wavelength side.

In Fig.3.6.4, the intensities of emission bands are plotted against Li^+ concentration. The intensity of the band around 3.4 eV increases with increasing the impurity concentration, whereas that of σ-emission band does not change. Thus the Li^+ ion affects the luminescence at 80 K, though it hardly does at 6 K.

The band at about 3.4 eV in all NaCl:Li crystals used in this study can be resolved into two gaussians; one is the triplet emission band at 3.4 eV and the other is the band situated at 3.32 eV with the halfwidth of 0.76 eV.

(2·2) Measurements by pulse-electron irradiation

For clearer understanding of the Li^+ effects in NaCl, pulse electron irradiation was employed. First, in order to prove above divisions of emission band at about 3.4 eV meaningful, measurement was made on the time-resolved emission spectrum of NaCl:Li.

Typical example of the decay curve of NaCl:Li above 80 K is shown in Fig.3.6.5. Pure NaCl has only one com-

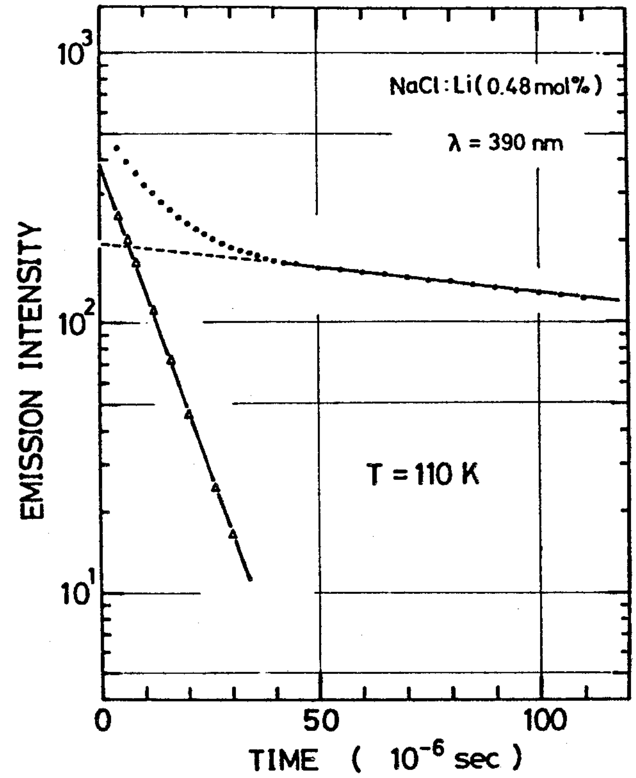

Fig.3.6.5. Decay of emission at 390 nm in NaCl:Li(0.48 mol%) following a single pulse of electron. Open circles are data points, and the triangles indicate the resolved fast component with decay time of 1.0 X 10^{-6}sec. Decay time of slow component is 2.8 X 10^{-4}sec. Measurement was made at 110 K.

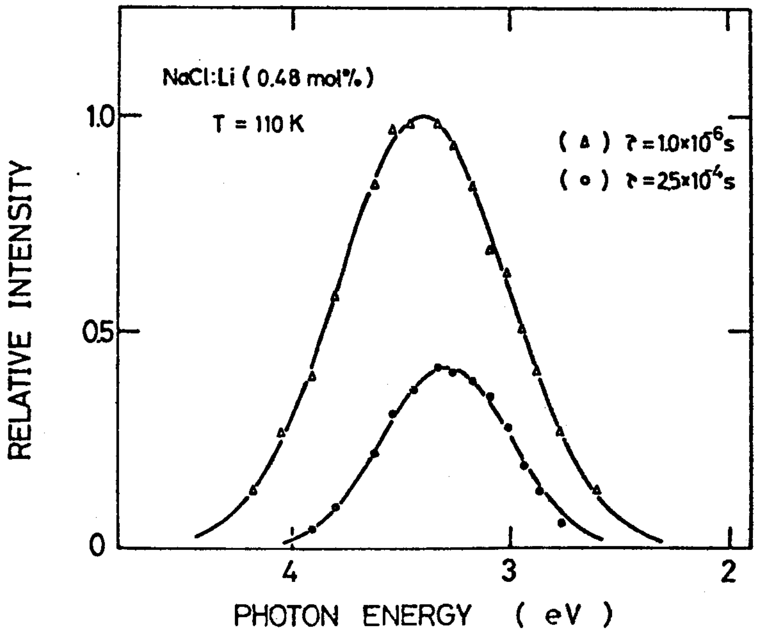

Fig.3.6.6. Time-resolved emission spectra of NaCl:Li(0.48 mol%) at 110 K.

ponent whose decay time is 1.0×10^{-6} sec at 110 K in this spectral region, whereas NaCl:Li has another one of 2.5×10^{-4} sec together with the same one of pure NaCl.

This slow component is characteristic to Li^+ impurity ion; the relative ratio of the emission intensity at $t = 0$ to that of fast component increases with increasing Li^+ concentration.

Figure 3.6.6 indicates the time-resolved emission spectra of a NaCl crystal. Two peaks shareing different decay time are clearly separable, and these band shapes are essentially the same as those obtained by Gaussian separation of x-ray excited spectra.

The emission band, peaking at 3.40 eV and having the decay time of 1.0×10^{-6}sec at 110 K, is due to the lowest triplet state of STE, since the peak position and the decay time are identical with those obtained by other workers.6,7) The band at 3.32 eV with decay time of 2.5×10^{-4} sec at 110 K is tentatively assigned to be due to $(V_K e)_{Li}$ in NaCl, based on the impurity-concentration dependence of the emission intensity.

As discussed in Chap.[3·3], the relaxed exciton trapped by an alkali impurity in alkali halides, possesses the characteristic absorption bands corresponding to higher excited states, the higher quenching temperature of the decay time, and so on. In order to confirm the assignment that the 3.32 eV emission band is due to $(V_K e)_{Li}$, temperature dependence of decay time, τ, and the transient optical absorption bands were measured.

Figure 3.6.7 shows the result of temperature dependence of τ, and Fig.3.6.8 indicates the transient absorption spectrum shareing the same decay time of the 3.32-eV emission band at 80 K.

The decay time of 3.32 eV-emission band quenches thermally above 150 K this temperature dependence of τ is well analysed by the well known equation; $1/\tau = 1/\tau_0 + \nu \exp(-E/kT)$. The best fit of pertaining data points is obtained when the values of E and ν are 0.22 eV and 1.5×10^{10} sec^{-1}, respec-

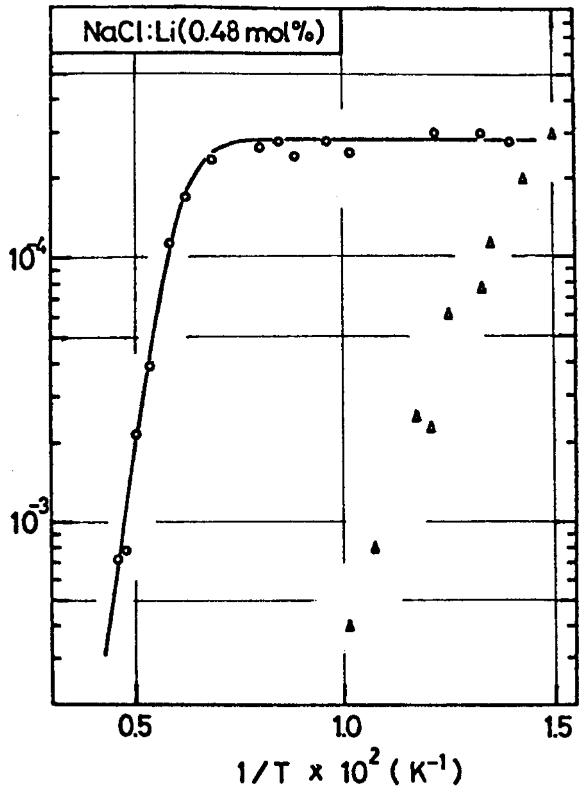

Fig.3.6.7. Temperature dependence of decay times of (V_Ke $)_A$ (o), and of $^3\Sigma_u^+$, (Δ) in NaCl crystals, respectively. The solid line along open circles is the calculated curve of equation; $\tau = \{ 1/\tau_0 + \nu ecp(-E/kT) \}^{-1}$.

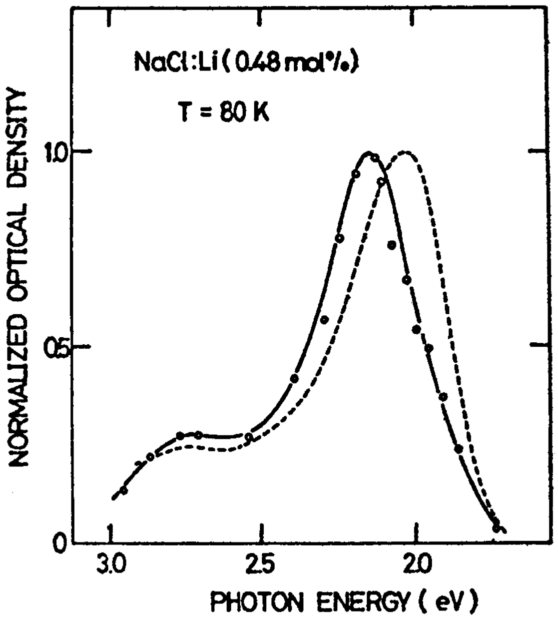

Fig.3.6.8. Transient absorption spectrum due to (V_Ke $)_{Li}$, solid curve. The broken curve is the spectrum of the lowest triplet state of STE in NaCl at 9 K, obtained by Fuller et al.(from ref.8).

tively. The obtained activation energy for thermal quenching is more than two times larger, and the value of the frequency factor is about two orders of magnitude samller, than those of ${}^{3}\Sigma_{u}^{+}$ in NaCl.[6)] These changes in E and ν are very similar to those of (V_Ke)$_A$ in KBr crystals.

Transient absorption spectrum shown in Fig.3.6.8 is similar to that of ${}^{3}\Sigma_{u}^{+}$ in NaCl obtained by Fuller et al.(broken line in the figure).[8)] This result is a powerful evidence that the 3.32-eV emission band is due to the lowest triplet state of (V_Ke)$_{Li}$. The main absorption band of (V_Ke)$_{Li}$ has the peak energy of 2.14 eV at 80 K. It is clear that the absorption energy of (V_Ke)$_{Li}$ in NaCl shows the blue shift, whereas that of (V_Ke)$_{Na}$ in KBr shows red shift.

(2·3) The formation yield of (V_Ke)$_{Li}$ from 6K to 90 K

Above results clearly show that the (V_Ke)$_{Li}$ system is also formed in NaCl crystals, at least at 80 K. As mentioned in (2·1), however, no significant changes originated from the Li^+ ion in the luminescent phenomena were observed at 6 K. The peak energy of the emission band of (V_Ke)$_{Li}$ in NaCl shows slight red shift from the peak position of π-emission band, which makes us difficult to clearly show that no (V_Ke)$_{Li}$ are formed or not at 6 K, from the spectral resolution only.

The luminescence yield of π-emission region at 80 K is reduced to 15% of that at 6 K in pure crystal. On the other hand, the reduction is suppressed and about 2/5 are survives at 80 K in NaCl:Li(1.2 mol%). Such a temperature-resistive emission intensity may come from the formation of (V_Ke)$_{Li}$ in samples containing Li^+ ions.

From the results, one can expect that the contribution of (V_Ke)$_{Li}$ to the emission intensity at the band region is as much as 25% of the luminescence yield at 6 K, if (V_Ke)$_{Li}$ is formed at the temperature as is formed in KBr crystals. Therefore, the increase in emission intensity may be fully detectable at 6 K.

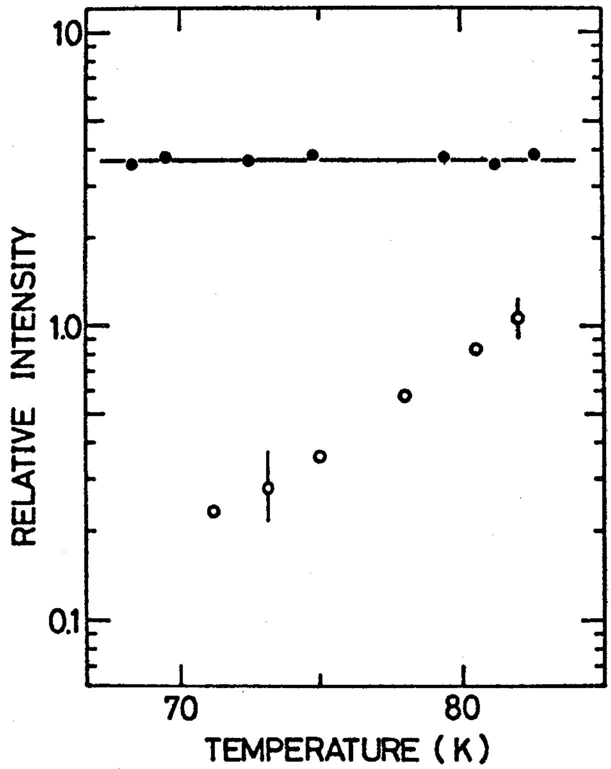

Fig.3.6.9. Temperature dependence of the emission intensity of π emission in pure NaCl at t=0, (●), and of intensity ratio of π_A emission to π emission at t=0 in NaCl:Li(1.2 mol%), (o), respectively. The intensity at t=0, $(I)_o$, was extrapolated, based on the decay-curve analysis.

The constancy of the emission intensity shown in Fig.3.6.2 rules out the possibility that the (V_Ke)$_{Li}$ is formed, from the same mechanism as that in KBr at 6 K in NaCl.

Thus it appears that the Li^+-effects on exciton behaviour is temperature-dependent in NaCl crystals. To make the problem clear, temperature dependence of formation yield of (V_Ke)$_{Li}$ was measured by pulse irradiation experiments.

In a decay curve of an emission intensity, the intensity at t = 0, $(I)_o$, should be in proportion to the concentration of a luminescence center populated by a pulse at any temperature. One can, therefore, estimate the formation yield of a center when measurements are made on $(I)_o$.

In Fig.3.6.9 are shown results of such measurements on pure NaCl and a NaCl:Li(1.2 mol%). Closed circles in the figure are the intensities of π emission of a pure crystal, $(I_\pi)_o$. One can see that the intensity is constant at the temperatures, which indicates that the formation yield of $^3\Sigma_u^+$ of an exciton remains unchanged irrespective of change in temperature. This result is the same as that obtained by Karasawa and Hirai.$^{7)}$ However, the $(I_\pi)_o$ in the sample containing Li^+ ions decreases at the temperature region where τ decreases owing to thermal quenching. The open circle in Fig.3.6.9 is the ratio of the intensity of (V_Ke)$_{Li}$, $(I_{\pi A})_o$ to that of $^3\Sigma_u^+$. It is evident that the formation yield of (V_Ke)$_{Li}$ relative to that of $^3\Sigma_u^+$ increases with increasing temperature, compensating the decrease of $(I_\pi)_o$.

This behaviour of (V_Ke)$_A$ in NaCl is essentially different from the temperature dependence of formation yield of (V_Ke)$_{Na}$ in KBr discussed in Chaps.[3·4] and [3·5]. Thus a different mechanism in exciton interaction with an alkali impurity ion may be responsible for the formation of (V_Ke)$_{Li}$ in NaCl crystals.

§3 Discussions

(3·1) Electronic structure of (V_Ke)$_{Li}$ in NaCl

First the properties of (V_Ke)$_{Li}$ are discussed. It has been identified that the 3.32 eV emission band in NaCl:Li is due to the radiative decay of (V_Ke)$_{Li}$. From its slow radiative lifetime of 2.8 X 10^{-4} sec, and the transient absorption spectrum silimar to that of $^3\Sigma_u^+$, it is apparent that the initial state is a triplet state. (V_Ke)$_A$ in KBr has no σ-polarized emission band as shown in Chap.[3.4].The constancy in the emission intensity and in the band shape of singlet emission band in NaCl:Li crystals, as shown in Figs.3.6.3 and 4, suggest that also (V_Ke)$_{Li}$ in NaCl has no singlet emission band, whereas (V_Ke) in NaCl has both.

The quenching energy and frequency factor of (V_Ke)$_{Li}$ for thermal quenching of its decay time change from those of $^3\Sigma_u^+$ with the same way as the corresponding ones of (V_Ke)$_A$ in KBr do.

However, it should be noticed that the shift of peak energy of emission of of absorption spectrum of (V_Ke)$_{Li}$ in NaCl is qualitatively different from that of (V_Ke)$_A$ in KBr: The energy of emission band shows a little red shift whereas that of absorption band shows a blue shift, which is reverse of those shifts of (V_Ke)$_A$ in KBr. Since lattice distortions surrounding substituted Li^+ ion is about the same degree as ones due to Na^+ ion in KBr, according to the calculation of Douglus,⁽⁹⁾ the different pattern of peak shifts between (V_Ke)$_{Li}$ in NaCl and (V_Ke)$_A$ in KBr may be due to other changes which impurity ions introduce.

Possible one concerns the change in energy levels of lowest unoccupied orbitals of alkali ions. As discussed previously, s orbitals of alkali ions closest to a X_2^- plays an important role for electronic states of an exciton.⁽¹⁰⁾ According to the calculation with the Hartee-Fock-Slater model (Xα method) calculation, both 2s of Li^+ and 3s of Na^+ have lower eigen values than that of K^+, though 2s of Li^+ has higher one than that of 3s of Na^+(see Chap.[3·3]). In the case of (V_Ke)$_A$ in KBr, the eigen value of a vacant s orbital of a foreign alkali ion, Li^+ or Na^+, is therefore, lower than the value of host cation. On the other hand, the situation is reverse in (V_Ke)$_{Li}$ in NaCl. This difference may be responsible for different type of peak shifts of (V_Ke)$_A$ in the two materials. Apart from the different behaviour, it should be emphasized that (V_Ke)$_{Li}$ in NaCl has very similar properties as those of (V_Ke)$_A$ in KBr.

(3·2) Mechanism of formation of (V_Ke)$_{Li}$ in NaCl: Hopping motion of triplet exciton

As concluded in the previous section, the formation yield of (V_Ke)$_{Li}$ in NaCl increases, corresponding to the decrease of the yield of $^3\Sigma_u^+$, with increasing temperature. This increase must be based on the different type of motion of excitons from that in KBr and KCl crystals, since features of exciton - impurity interactions in two types of salts are essentially different. In KBr crystals, the formation of (V_Ke)$_A$ is closely related not to $^3\Sigma_u^+$, i.e. (V_Ke)$_\pi$ but to (V_Ke)$_F$, and the formation yield of (V_Ke)$_\pi$ is not affected by the added impurity ion. And the interaction volume for (V_ke)$_{Na}$ in KBr crystals, defined in eq.(3.4.2), behaves as temperature-independent. In NaCl crystals, to the contrary, (V_Ke)$_{Li}$ appears to be formed, temperature-dependently, from lowest triplet state of the exciton. These results suggest that the thermally stimulated motion of $^3\Sigma_u^+$ is a main origin of the formation of (V_ke)$_{Li}$ in NaCl crystals.

Such a motion, hopping motion of self-trapped exciton, had been considered so far only theoretically.11) But the result obtained in this study suggests that the hopping motion is, in fact, the case in NaCl crystals. Below, we consider the motion rather quantitatively.

Song has studied the motion of STE by means of small polaron treatment of continum model.11) His result of hopping probability, $W_{R\to R'}$, is

$$W_{R\to R'} = (\pi/4h^2E_akT)^{1/2}|J|^2 \exp(-E_a/kT), \quad (3.6.1)$$

where E_a is an activation energy and J is the transfer energy for a self-trapped exciton between two adjacent sites R and R'.

In the present case, there is no significant delay in the formation of (V_Ke $)_A$ as seen in Fig.3.6.7,which indicates that the formation of (V_Ke $)_A$ takes place within very short time. Then the interaction volume for (V_Ke $)_{Li}$ may be expressed as follows;

$$V^* = A\, W_{R\rightarrow R'}\Sigma^* \tag{3.6.2}$$

where Σ^* is a facter representing a probability capturing an exciton of Li^+ ion and A is a constant. The formation yield of (V_Ke $)_A$ is thus

$$n[V_Ke]_{Li} = n[V_Ke]_\pi\, V^*\, C_{Li} \tag{3.6.3}$$

where n[ ] is a concentration of the indicated exciton state at t=0. Experimenally obtained values, $(I)_o$, are now

$$\begin{aligned} (I_{\pi A})_o &= (1/\tau_o)_{\pi A}\, n[V_Ke]_\pi\, V^*\, C_{Li}, \\ (I_\pi)_o &= (1/\tau_o)_\pi\, n[V_Ke]_\pi (1 - V^* C_{Li}). \end{aligned} \tag{3.6.4}$$

Thus the $(I_\pi)_o/(I_{\pi A})_o$ should satisfy the following relations, if the present models are relevant;

$$(I_\pi)_o / (I_{\pi A})_o = (\tau_o)_{\pi A}/(\tau_o)_\pi (1/V^* C_{Li} - 1). \tag{3.6.5}$$

The ratio between the radiative lifetimes of (V_Ke $)_{Li}$ and (V_Ke $)_\pi$ is about unity, as shown before. In the present range of temperatures, V^* is approximated as $V^* = B\exp(-E_a/kT)$, since the important factor in eq (3.6.1) is the exponential term. B is also a constant. Then eq (3.6.5) becomes

$$(I_\pi)_o/(I_{\pi A})_o + 1 = (1/B)\exp(- E_a/kT). \tag{3.6.6}$$

The values corresponding to right side of eq.(3.6.6) obtained from the results in Fig.3.6.9 were plotted against reciprocal temperatures in Fig.3.6.10. The straight line obtained by least square fit gives an E_a of 0.049 eV. In Fig.3.6.10 the agreement between the data points and the model considered here is good, which indicates that the formation of (V_Ke $)_{Li}$ in NaCl is due to the hopping motion of the lowest triplet state of STE. The obtained value of activation energy is less than 1/5 of the minimum value obtained theoretically.

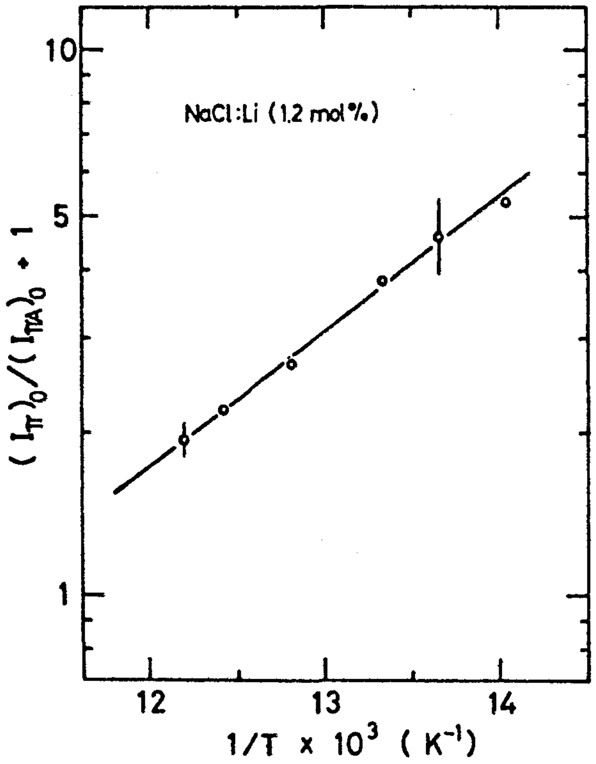

Fig.3.6.10. Plot of $(I_{\pi})_0/(I_{\pi}A)_0 + 1$ vs. reciprocal temperatures. The straight line gives the value of E_a of 0.049 eV.

(3·3) Li^+ effects in NaCl at 6 K

Finally let's consider the role of Li^+ ion on the defect formation in NaCl crystals. As clearly shown above, the $(V_K e)_{Li}$ is mainly formed in terms of hopping motion of $^3\Sigma_u^+$. E_a of 0.049 eV makes such a motion impossible at 6 K, which means that $(V_K e)_{Li}$ is not formed at 6 K, at least by the motion of $^3\Sigma_u^+$. This conclusion is confirmed by the experimental results shown in Figs.3.6.1. and 2, where not only the emission intensity, but also the band shape of π emission from $^3\Sigma_u^+$ are not affected by Li^+ ion.

The constancy of the formation yield of the F center irrespective of the Li^+ concentration, shown in Fig.3.6.2, also means that no $(V_K e)_{Li}$ formation occur at 6 K, which has the same origin in the formation of $(V_K e)_A$ in KBr or in KCl crystal. This is the case of $V^* = 0$ in eq.(3.4.3).

Apparently, Σ^* in V^* of Li^+ ion in NaCl is non-zero, as discussed in the preseding part of this section. The factor μ^*, which representing the mobility of an exciton may be zero in NaCl at 6 K. The $W_{R\to R}'$ in KBr crystals, if exists, may not so different from that in NaCl, since the thermal property of the V_K center in both crystals are very close.12) Therefore, the motion of $(V_K e)_F$ to form $(V_K e)_A$ in KBr may be adiavatic.

Above results and consideration lead us to the conclusion that $(V_K e)_F$ in NaCl does not have the motional property as that $(V_K e)_F$ in KBr has.[#]

So far, some different properties of $(V_K e)_F$ in NaCl from those in KBr or in KCl have been reported. Fig.3.6.11 is the temperature dependences of the F-center formation yields in alklai halides.14) One can see the different behaviours of NaCl comparing to the behaviour of KBr or KCl especially at low temperatures where the formation yield in NaCl decreases

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[#] Recently, Kondo and Kanzaki have reported that an electron in relaxed excited state of the F center is more strongly coupled with LO-phonons in NaCl than that in a potacium halides.13) This mode of coupling contribute to the effective mass of polaron state. Therefore, such a behaviour might be related to the present results in NaCl.

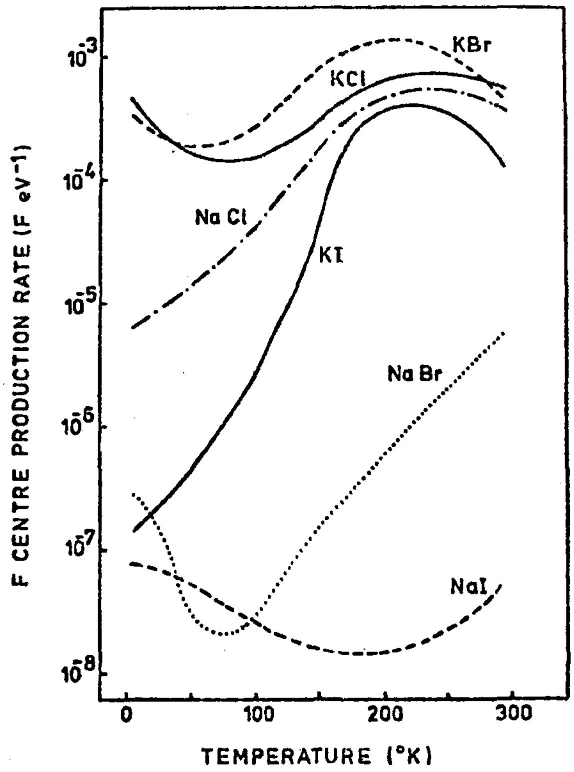

Fig.3.6.11. Temperature dependence of the F-center production efficiency in alkali halides (from ref.14)

with decreasing temperature. Energy necessary for the formation of one Frenkel pair is so high in NaCl cpmparing with that in KBr or in KCl.

Another important difference in the properties of (V_Ke)$_F$ concerns the time constant of the F center formation. Kondo et al. has shown that the time constant in NaCl is about 1.0 X 10^{-6}sec,4) whereas those in KBr and KCl are less than 10^{-9}sec.1,2)

These different properties of (V_Ke)$_F$ in NaCl, together with the present results of exciton - impurity interaction, suggest that the (V_Ke)$_F$ in NaCl crystals is essentially different state from that in KBr or KCl. Therefore, different mechanism of the F center formation from that in KBr etc. might be relevant in NaCl crystals.

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[3·7]

SPIN STATE OF THE PRECURSORS OF THE FRENKEL PAIRS

An essential property of the precursor of Frenkel pairs, the spin state of (V_Ke)$_F$ is discussed, based on the establishments of the work in the preceding chapters. It is clearly shown that (V_Ke)$_F$ is a higher excited state of triplet exciton.

§1 Introductory Remarks

Based on the results and conclusions obtained in the preceding chapters, we here discuss some properties of the precursor of Frenkal pairs. The question we will solve here is that: Is (V_Ke)$_F$ a triplet state or singlet one ?

It has been shown in Chap.[3·4] that the relaxation of an exciton, hot exciton, into a particular relaxed state takes place with a fixed ratio which might depend on the kind of salts. Significant differences are supposed to exist in the relaxation channels between KBr and NaCl: Results in Chap[3·6] may indicate that the state of (V_Ke)$_F$, which results, in KBr, in the F-center formation with very short time constant, and in the formation of (V_Ke)$_A$ at 6 K, is not formed in NaCl crystals.

Analysis of these characteristic features in relaxation of an exciton leads us to believe that (V_Ke)$_F$ is a higher excited triplet state of an exciton.

§2 Rabin-Klick diagram for production yields of the F center, σ and π emissions

F-center formation yield as well as the efficiency of intrinsic luminescence strongly depends on the kind of alkali halides. This fact indicates that relaxation probabilities of the hot exciton into responsible relaxed states depend on the unknown factor each salt possesses. First, lut us consider the dependence from a broader view-point.

Rabin-Klick diagram[1)] is one of powerful methods with which we can see the outline of the dependence of yields excitonic products on kind of salts.

Rabin and Klick[1)] measured the energy consumed per F center in various alkali halides, and introduced some system in their data by plotting the energy against S/D, where S is the space for the interstitial along a <110> direction, and D is the diameter of the halogen atom. The results obtained by Rabin and Klick for the F center production at 4 K are shown in Fig.3.7.1, together with recent data by Ikezawa et al.[2)] and by Huges at al.[3)]

On the other hand, Pooley and Ranciman[4)] have measured the x-ray or electron excited luminescence in all alkali halide crystals. Their results enable us to evaluate the energy required per 1 photon for most intrinsic emissions. Evaluation was made, taking the difference in halfwidths of the emission bands into account. Results are also plotted against S/D in Fig.3.7.1.

It should be pointed out that the production yield of the π emission for several alkali halides is anti-correlated with the production yield of the F center; at smaller S/D the production yield of the F center is smaller and that of the π emission is larger.

It should also be noticed that the yield of the σ emission depends very little on the kind of alkali halides whenever it is observed.

Apparently the relaxation of a hot exciton into $(V_K e)_\sigma$ depends little on other process, but $(V_K e)_\pi$ and $(V_K e)_F$ are correlated until they finally become uncorrelated.

Anti-correlation between the formation yields of the F center and π emission, together with the constancy of that of σ emission, suggests that $(V_K e)_F$ is a triplet state of an exciton.

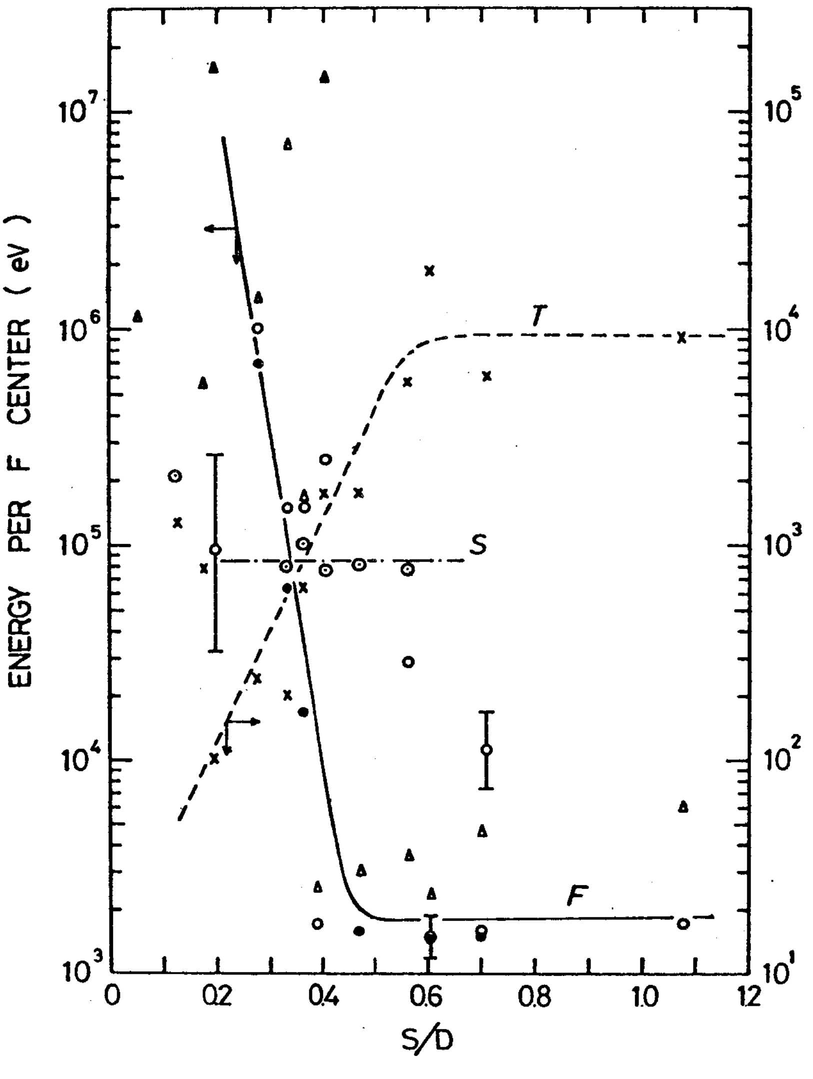

Fig.3.7.1. Energy required to form an F center (•, o, and Δ), a photon of σ emission (⊙), and a photon of π emission(x) by ionizing irradiation versus S/D. Solid, chain, and broken lines with capital letters of F, S, and T indicate overall dependence on S/D of the F center, singlet, and triplet emissions, respectively. Data for the F center are taken from Rabin and Klick(ref.1), (•), Ikezawa et al.(ref.2), (o), and Hughes et al.(ref.3), (Δ), respectively. Optical data are taken from Pooley and Rancimann (ref.4).

§3 Relaxation of an exciton in KBr and in NaCl

Now we discuss the suggestion that (V_Ke)$_F$ is a triplet state rather quantitatively, based on the results of investigations by means of internal perturbation due to impurity.

It has been shown in Chap.[3·4] that the hot exciton relaxes into particular states, (V_Ke)$_\sigma$, (V_Ke)$_\pi$, and (V_Ke)$_F$, with a fixed probabilities. Based on this conclusion and on the results shown in Fig.3.7.1, one may consider such a model of exciton-relaxation that is shown in Fig.3.7.2.

Hot exciton, first, splits into two states; singlet and triplet states with a fixed probabilities of s and t, respectively. Singlet exciton reaches, through relaxation, the state of (V_Ke)$_\sigma$ which de-excites in terms of σ emission. On the other hand, triplet exciton has another " turning point " where they separate into (V_Ke)$_\pi$ and (V_Ke)$_F$ with probabilities of e and d, respectively. It has been clearly shown that (V_Ke)$_F$ forms (V_Ke)$_A$ through a selective interaction with alkali-impurity ions, if they are involved in the crystal.

Results shown in Fig.3.7.1 may indicate that the probabilities of e and d strongly depend on the kind of salt. This can be confirmed by the results obtained in Chaps.[3·4] and [3·6].

As discussed in Chap.[3·6], the formation of (V_Ke)$_F$ in NaCl is quite improbable at 6 K. However, the formation probability of (V_Ke)$_F$, d, is supposed to be very large,in KBr since (V_Ke)$_A$ is formed with a high efficiency at 6 K.

Figure 3.7.3 shows the emission spectra of x-ray excited luminescence in KBr and NaCl, under the same experimental conditions.

One can see that the emission intensity of σ-emission in each crystal is about the same, whereas the intensity of π-emission of KBr is very weak comparing that of NaCl.

Since the non-radiative transition probability can be negligiblly small at low temperature such as 6 K, the emission intensities of these emission band is considered to be

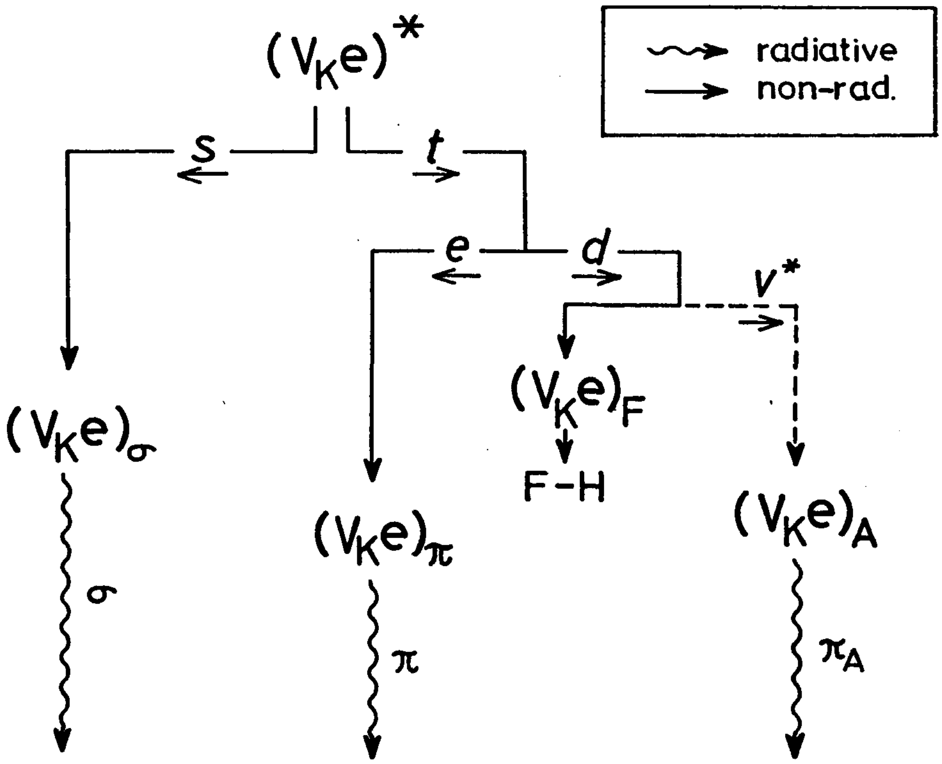

Fig.3.7.2. Possible relaxation channel of the hot exciton in alkali halides. The ordinate of the figure represents schematically the energy of the electron-hole pair.

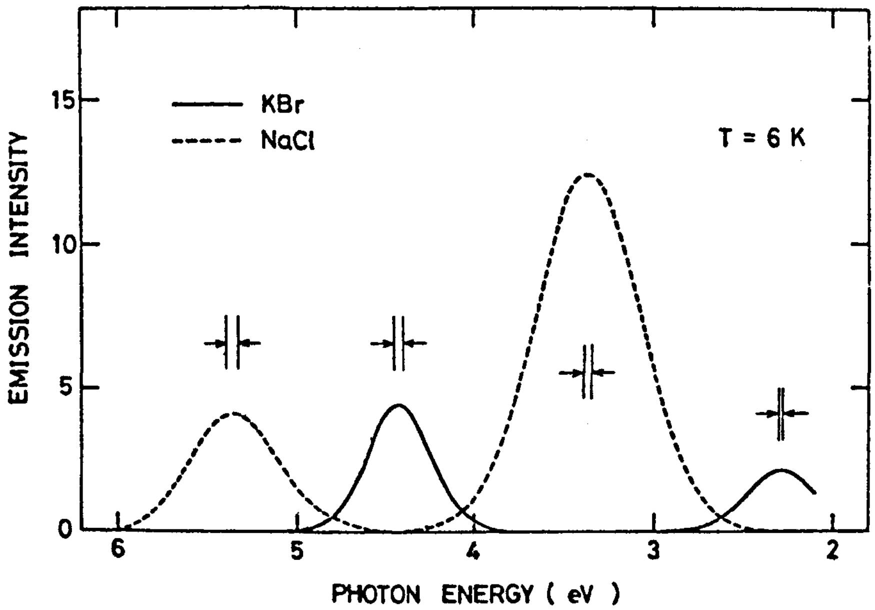

Fig.3.7.3. The x-ray excited emission spectra of KBr and NaCl. Measurements were made under the same experimentsl conditions.

in proportion to the concentration of populated these radiative exciton states.

As mentioned above, the formation probability of (V_Ke)$_F$ in NaCl is so small, that the value of d could be neglected in this salt. Then tha relative ratio of emission intensities of σ- and π-emission bands may give the ratio between s and t.

From the results shown in Fig.3.7.3, one can ontain that the value of s/t is about 1/3.

It has been shown that KI colors poorly at low temperature,$^{5)}$ which suggests that d is very small also in KI. The emission-intensity ratio between σ- and π-emission bands in KI is again about 1/3, from the results of Pooley et al.$^{4)}$

The formation of a hot exciton due to ionizing radiation is supposed to take place in terms of recombination of an conduction electron with a self-trapped hole. It may be, therefore, natural that the ratio of formation probabilities of singlet and triplet states is 1/3.

On the other hand, π-emission intensity is weaker than σ-emission intensity in KBr, which may come from relatively larger value of d in Fig.3.7.3. Then we discuss the value of s/t in KBr crystals.

As clearly shown in Chaps.[3·4] and [3·5], (V_Ke)$_F$ in KBr forms another state of exciton, (V_Ke)$_A$, through a selective interaction with an alkali-impurity ion. The following relation has been established;

$$n[V_Ke]_A = n[V_Ke]_F \, V^* \, C_{Na}. \qquad (3.4.2)$$

The value of V^* in KBr:Na system is about 50. If one write the quantum efficiencies of σ and π_A emissions as η_σ and $\eta_{\pi A}$, respectively, following equation is deduced;

$$\frac{I_{\pi A}}{I_\sigma} = \frac{\eta_{\pi A}}{\eta_\sigma}\,\frac{n[V_Ke]_A}{n[V_Ke]_\sigma}$$

$$= \frac{\eta_{\pi A}}{\eta_\sigma}\,\frac{n[V_Ke]_F}{n[V_Ke]_\sigma}\, V^* \, C_{Na} \qquad (3.7.1)$$

where $I_{\pi A}$ and I_σ are the intensities of π_A- and σ-emission bands, respectively.

The plot of $I_{\pi A}/I_\sigma$ vs. C_{Na}, which has been done in Fig.3.2.7, gives

$$\frac{\eta_{\pi A}}{\eta_\sigma}\,\frac{n[V_Ke]_F}{n[V_Ke]_\sigma}\,V^* = 140 \pm 10 \qquad (3.7.2)$$

Under a reasonable assumption that both quantum efficiencies are about unity, one can obtain, with the value of V^*,

$$\frac{n[V_Ke]_F}{n[V_Ke]_\sigma} = 2.8 \qquad (3.7.3)$$

Emission-intensity ratio between π and σ emissions in KBr indicates that $n[V_Ke]_\pi/n[V_Ke]_\sigma = 0.5$.

It is evident that $t = e + d$ in Fig.3.7.2. Thus the value of s/t in KBr is about 1/3, as similaly in NaCl and KI.

Above results and discussions lead us to believe that $(V_Ke)_F$ in KBr is a triplet state, and that about 80% of triplet exciton relaxes in $(V_Ke)_F$ in KBr, whereas little does in NaCl and KI.

Since it has been demonstrated that $(V_Ke)_F$ is at a higher energy than $(V_Ke)_\pi$,[6,7] it can be safely concluded that $(V_Ke)_F$ is a higher excited triplet state.

This conclusion we have deduced here is consistent with the recent experimental results by Karasawa and Hirai[8] and by Williams.[9] The mechanism of the dependence of d on the kind of alkali halide is the problem we must solve in future.

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4

MOTIONS AND REACTIONS OF THE PRIMARY HALOGEN INTERSTITIALS

[4·1]

INTRODUCTION

Recent knowledge on the behaviour of primary interstitials in alkali halides is briefly reviewed. In the first place, the modes of interstitial-motions are discussed. Next the recent results on temperature dependence of the dynamic-interstitial motion are summalized. Then discussions are made on the interaction of interstitials with other imperfections. Finally, we briefly sketch a outline of the work in this chapter.

§1 Modes of Interstitial Motions

The interstitial-halogen atom in which the de-excitation energy of an exciton is imparted exhibits a so-called replacement collision sequence through which the interstitial separates from the original lattice site where an F center is formed. At the end of the sequence, the H center is formed, if the temperature is low enough.

Following experimental results are the evidences for that the created interstitial halogens possess a mode of motions which takes place at low temeprature where thermally induced migration of interstitials is not active:

1) The EPR experiment indicates that the H center and the F center are separated by about ten lattice spacings,[1)]

2) and, Itoh and Saidoh[2)] have shown that the $H_A(Na^+)$ center is formed at liquid helium temperature with high efficiency which need about 10 lattice distance of the H-center displacement.

Such a mode of motions, dynamic motion, is considered to be an adiabatic process different in nature from thermal migration described later,[3)] and may be most probablly in the form of crowdion motion along a fixed <110> direction.

The structure of the replacement collision sequence has not been cleared so far. Itoh and Saidoh[4)] have proposed that an excited state of the H cneter, Π_g or Π_u, is responsible for the sequence, based on their experimental results of temperature dependence in dynamic motion of the interstitial halogen atom.

At higher temperature, the H center becomes mobile owing to the thermally induced migration.

In most cases, the annealing of the H center takes place at steps. Behr et al.[5)] have found that the annealing of the H center in KCl has two stages at 32 K and at 45 K. Detailed analysis has been performed by Saidoh and Itoh[6)] for the annealing behaviour of the H center in KBr. The H center in this salt also shows distinct two annealing stages.

In both crystals, the first stage and the second one are described by the first-order and the second-order reactions, respectively.

It has been concluded that the first annealing stage is due to the recombination of correlated F - H pairs, and that the second stage corresponds to the thermal migration of the H center.

The mechanism of the thermal migration of the H center has not been very clearly understood. It is to be noted that the migration of the H center must involve atomic motion, whereas the migration of the V_K center is the motion of only the hole. The thermal migration of the H center is considered to be a random-walk process, since the frequency for re-orientation of the H is larger than jump frequency for the migration.

The migration process of the H center has been studied theoretically by Smoluchowski et al.[7)] They concluded that the likely saddle-point configuration for the migration of an H center along a <110> is an X_3^{2-} molecule-ion with its center at a face-centered position and spread out over two nearest neighbor halogen sites of the normal lattice.

It may be also considered that the migration of an H center occurs when the separation of the X_2^- ion of the H center becomes large enough for one of the halogen atoms to form a new bond with a neighboring halogen ion.³⁾

Though the mechanism of motion of interstitial halogen atom have not been made very clear, two different modes of motions, replacement collision sequence and thermal migration, could be distinguished.

§2 Temperature Dependence of The Interstitial-Dynamic Motion

Temperature dependence of the dynamic motion of interstitial halogens is the problem of great interest: Such a behaviour of interstitials has close correlation with the dependence of the formation yield of Frenkel pairs on temeprature.8)

Saidoh, Itoh, and their co-workers have extensively studied the interaction of the interstitials with other imperfections in alkali halides.

In their recent studies on the dynamical motion of interstitials, they have employed pulse-electron irradiation, where the H_A center as well as di-H center (V_4 center) are formed within a much shorter time than the lifetime of thermal migration of the H center. The formation yields of these complex centers, which are characterized in terms of interaction volume, increase with increasing temperature above 80 K.8) A typical example of their results are shown in Fig.4.1.1.

Saidoh et al. have attributed the temperature dependence of the interaction volume to the temperature-dependent change in the range of the dynamical motion of the primary interstitials, and have pointed out that the range, L, of the dynamic motion of the interstitial halogen may be expressed as

$$L(T) = L_o + L_1 \exp(-E_d/kT) \qquad (4.1.1)$$

where E_d is an activation energy and L_o and L_1 are constants.

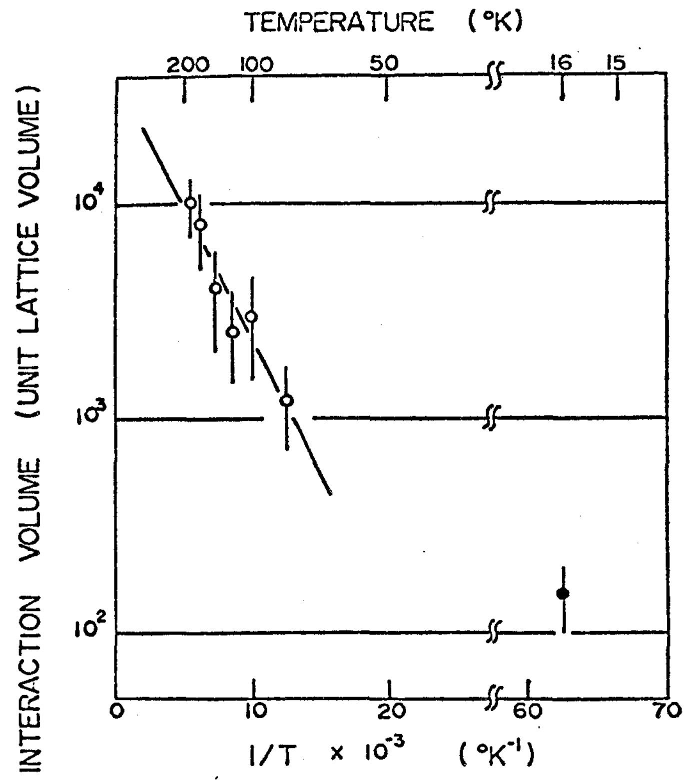

Fig.4.1.1. Temperature dependence of the interaction volume of the replacement collision sequence with a Na$^+$ impurity ion in KBr. (from ref.8).

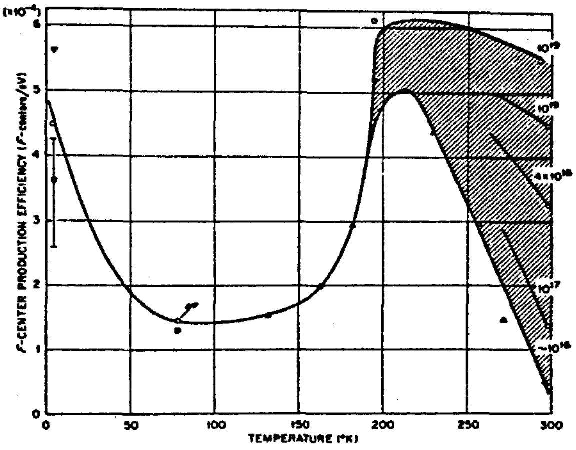

Fig.4.1.2. Radiation production efficiency for F centers in KCl at different temeoratures. (from ref.9).

One important consequence of their model is the successful explanation of the temperature dependence of the Frenkel-pair formation efficiency above 100 K.

The dependence of this efficiency has been one of the very interesting problem in color center formation in alkali halides, which has been studied by many workers for a long time.[9)]

Figure 4.1.2 shows a plot of F center production efficiency vs. temperature in KCl.[9)] It should be pointed out that the efficiency is based on measurements of stably produced color centers after irradiation.

The decrease in the efficiency below 50 K has been shown to be due to the thermal migration of the H center resulting in the recombination between the Frenkel pairs during irradiation.[10)] The remarkable rise in efficiency between liquid-nitrogen temperature and 200 K was not well understood before Saidoh et al. have proposed following model.

Under the assumption that a stable Frenkel pair is formed if the range of a dynamic sequence exceeds a critical value, r_o, Saidoh et al.[8)] have deduced the following probability with which Frenkel pairs are formed;

$$p = \exp\{\ r_o/\ L_o + L_i \exp(-E_d/kT)\ \}. \qquad (4.1.2)$$

Figure 4.1.3 shows the comparison of the experimental production yield with eq.(4.1.2) for KCl. Good agreement between them is evident.

Recently, Dienes and Smoluchowski[11)] suggested a model based on an analysis of the stochastic aspects of the random walk and ascribed the increase of the interaction volume to the increase of the frequency of the rotational motion of the H center.

Another possibility of the increase has been proposed by Townsend.[12)]

It is, however, sure that the interaction of primary interstitials with other imperfections becomes dominant at higher temepratures where primary interstitials are not stable. It is also acceptable that the modes of inter-

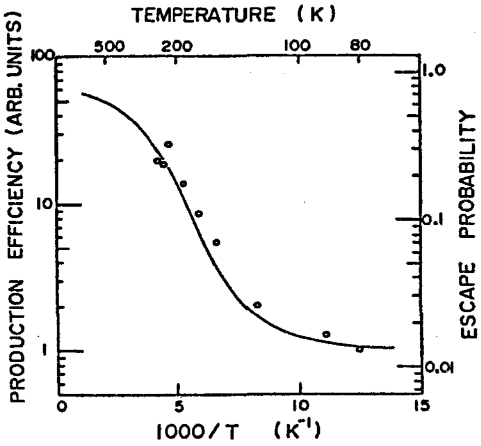

Fig.4.1.3. Temperature dependence of the F center formation efficiency in KCl. Open circles show experimental data. The solid curve shows the best fit of the experimental results to eq.(4.1.2). (from ref.8).

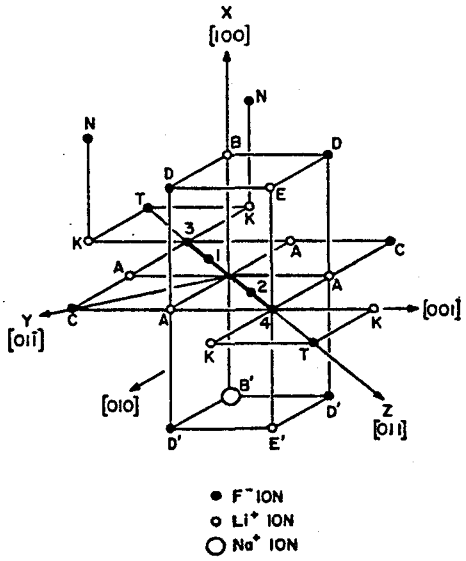

Fig.4.1.4. The lattice model of the $H_A(Na^+)$ center in LiF crystal. (from ref.21).

stitial-motions are fairly complicated at such temperature regions. This situation may result in the formation of a variety of complex interstitial centers.

§3 Interaction of Primary Interstitials with Other Imperfections

The study on the interaction of halogen interstitials with other imperfections such as impurities is very important in order to understand the defect formation process at higher temperatures where primary interstitials, the H and I centers, are mobile, since the secondary reactions, aggregation and/or stabilization by other imperfections become dominant at such temperature regions.9)

Interstitial aggregation, or mutual interaction among primary interstitials, has been studied by several workers with several methods.6,13,14) It has been indicated6) that the di-H center, which has the absorption band in the V_4-envelope in KBr, is formed through the interaction between two thermally migrating H centers. Details of aggregation mechanism and the nature of higher aggregate-interstitial centers are, however, far from being well understood.

The interstitial interaction with other imperfections, especially with impurities, has been studied more extensively. In the course of such works, it has been shown that interstitial stabilization takes place, which depends on several factors such as nature of the interaction (electrostatic and/or elastic),3) size, shape and concnetration of impurities,15,16) temperature of the crystal,17) and so on.

The interstitial interaction with impurities, in general, results in the formation of various defects of different configurations which have several characteristics. Furthermore, the formation of these defects is accompanied, in most cases, with the F-and/or F^+-center enhancements at " early stage " of coloration.

Thus the observation of these resulting phenomena may give us useful informations on the mechanism of the interaction of interstitials with these impurities.

It is well known that a monovalent cation impurity such as Na^+ or Li^+ is an effective and important trap for halogen interstitials in KBr and KCl at about 80 K.

It has been shown that the Na^+ impurity enhances x-ray coloration in KBr at 80 K.[15,18] In the crystal, enhancement of the F- and F^+- center production is accompanied by the growth of the V_1 and 5.4-eV bands, respectively, and this has been attributed to interstitial-atom and -ion stabilization by the impurity ion.

Delbecq et al. have shown that the V_1 band in KCl is due to an H center stabilized at n.n. site of a Na^+ ion, the $H_A(Na^+)$ center,[19] and the similar model has been assumed for the V_1 band in KBr so far.

On the other hand, the role of alkali impurity ions with larger ionic radii than that of host cations has been less understood so far.

Giuliani has shown that the Rb^+ ion in KBr does not affect the production efficiency of F and F^+ centers at 80 K, and has concluded that such a type of impurity ion does not result in the interstitial stabilization.[15]

Following two reports, however, suggest that impurity ions with larger ionic radii affect formation rate of coloe centers and that it can interact attractively with the H center.

1) Still and Pooley have shown that the formation yield of the F center in KCl is suppressed by Rb^+ ions at 5 K.[20]

2) Dakss and Miether have found that the H_A center associated with a Na^+ ion in LiF, and that this $H_A(Na^+)$ center is thermally more stable than the intrinsic H center.[21]

Figure 4.1.4 shows a lattice model of the $H_A(Na^+)$ center in LiF.[21] The lattice configuration is different from that of the $H_A(Na^+)$ center in KCl[19]: In the former case, the Na^+ ion is situated at the nearest-neibor site in a direction perpendicular to the molecular axis of the F_2^-, whereas, in the latter case, the Na^+ ion lies in the {001} plane containing the H center and is in a nearest-neighbor position to the central nuclei of the Cl_4^{3-} molecule ion, as shown in Fig.1.2.1.

As shown by Peisl et al.22,23) the H center, which is essentially neutral to the lattice, accompanies the anisotropic lattice distortion in KBr and KCl. The elastic interaction is, thus, considered to play an important role in the interaction of the H center with other imperfections. It is, therefore, supposed that the most important part of the secondary reactions of the created interstitials concerns the interaction, whose nature is elastic, of the H center and other imperfections.

Theoretical calculation on the interaction has been made by Dienes at al.14) by Bachmann and Peisl,22) and by Diller.24)

The mechanism of the H center interaction, however, has not been understood very clearly, in spite of current knowledge based on theoretical and experimental works. The clarification of this mechanism is of great importance for full understanding of defect formation process, especially at higher temperatures.

§4 Outline of The Work in This Chapter

The aim of the work reported in this chapter is to make clear the elastic-interaction mechanism of the primary interstitials with other imperfections. The alkali-impurity ion has been adopted as the imperfection. This type of impurity is considered to be the best " target " with which the H center interacts elastically, since the main effect of such a type of impurity to the lattice is the distortion around the substitutional ion.

The main interest here is whether the different modes of motions of primary interstitials cause any difference in the elastic interaction between interstitials and impurities, or not.

We begin with the study on interstitial centers trapped by a pair of Na^+ ions in strongly Na^+-doped KBr. The new optical absorption band due to H_{AA}-type centers is identified. It is shown that the effects of impurity pairs become important in the crystal containing a few mol% on impurity ion.

After having established the condition where impurity pairs are negligible, the H center interaction with a Na^+ ion in KBr is studied mainly in terms of Na^+ concnetration dependence. In order to see the effects of difference in mode of interstitial motion, both the γ-ray irradiation at 77 K and the irradiation at 6 K with subsequent thermal annealing were employed.

Composite structure of the V_1 band induced by γ-irradiation at 77 K has been analyzed to indicate that two different types of centers, H_{A1} and H_{A2} centers, are mainly responsible for the absorption band. These are attributed to the complex centers consisting of an H center and a Na^+ ion formed during thermal migration and during dynamic motion of interstitial atoms, respectively, based on the analysis of the Na^+ concnetration dependences of formation yields of these centers. Proposed model is discussed in terms of eleastic interaction of the H center with a Na^+ ion.

Then the interaction of the H center with a Rb^+ ion in KBr crystals is investigated. It is shown that the $H_A(Rb^+)$ center can be formed only during thermal migration of the H center. Association energy between an H center and a Rb^+ ion is 0.022 eV. Formation efficiency of Frenkel pairs at 6 K are suppressed by Rb^+ ions in KBr.

These experimental results are discussed based on the calculation of the elastic-interaction energy between the H center and a Rb^+ ion.

The anisotropy of the elastic interaction of the H center can well explain the experimental results obtained here. Calculated elastic interaction energy suggests that the lattice configuration of the $H_A(Rb^+)$ center in KBr is the same as that of $H_A(Na^+)$ center in LiF.

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[4·2]

HALOGEN-INTERSTITIAL CENTERS TRAPPED BY A PAIR OF Na^+-IMPURITY IONS IN KBr CRYSTALS

A detailed analysis has been made of the thermal annealing of the V_1 and I_A bands in strongly Na-doped KBr crystals. Two components (406 and 415 nm) exist in the V_1-band region in such crystals, and decay thermally at 140 K and at 170 K, respectively. The 415-nm component, which increases with decreasing peak height of 406-nm one and shows a <110>-type dichroism, has been assigned to be H_{AA} and/or $H_{A'A}$ band. The 5.4-eV band shows distinctive two thermal annealing stages at 110 and 150 K. Thermally more stable component has been attributed to the interstitial halogen ion trapped by a pair of impurity ions.

§1 Introductory Remarks

Much work has been done on the interaction of interstitials with monovalent cation impurities such as Na^+ and Li^+.[1-6] The interaction, in general, results in the formation of interstitial-complex centers, or in the stabilization of primary interstitials by impurity ions.

The stabilization depends on the concentration of impurities,[1] degree of interaction,[2] and temperature of the crystal,[3] so that various types of defects of different configurations are formed, which may have characteristic thermal stability and optical absorptions.

Giuliani has shown that the V_1 band in KBr has two components peaking at different wavelengths and having different thermal stability.[5] He has suggested that these are given by two different configurations of a pair consisting an interstitial halogen and a Na^+ ion.

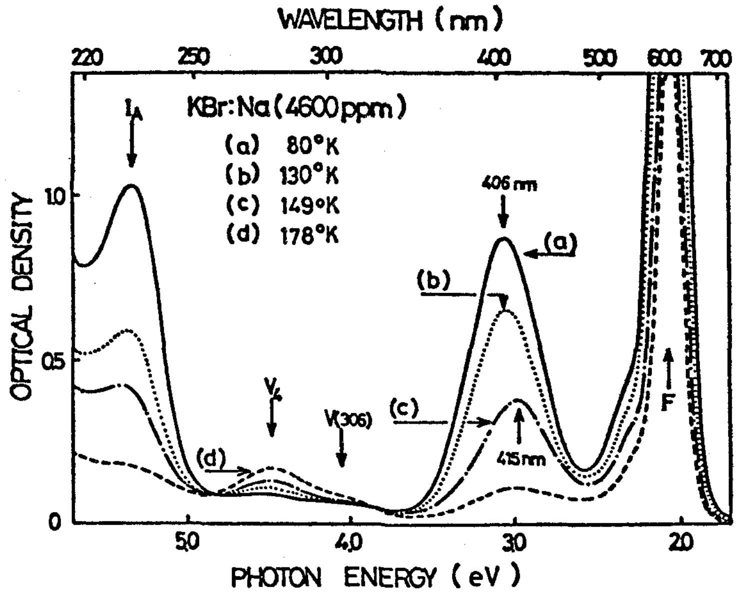

Fig.4.2.1. The absorption spectrum of KBr:Na(2.0 mol%) γ-irradiated at 77 K for 40 hr with a dose rate of 2.5 X 10^5 r/hr and measured at the same temperature [curve(a)], and spectra after warming the sample to 130 K[curve(b)], 149 K[curve(c)], and 178 K[curve(d)], respectively. Measurements were made at 77 K.

It has been shown, from EPR study, that two other H type centers (H_{AA} and $H_{A'A}$ centers) are formed which are interstitial atoms stabilized by pairs of impurity ions in strongly Na^+- doped KCl. Optical properties of such centers, however, have not been known so far.

It may be possible that the H center trapped by a pair of impurity ions is responsible for the composite structure of the V_1 band in KBr.

As the first attempt in the research of this chapter, optical absorption study was performed on the V_1 and the 5.4-eV bands in strongly Na^+-doped KBr crystals.

§2 Experimental Results

In Fig.4.2.1, curve(a) shows the optical absorption spectrum of KBr:Na(2.0 mol%), γ-irradiated at liquid-nitrogen temperature, and curves(b), (c), and (d) are obtained after warming the irradiated sample up to 130, 149, and 178 K, respectively.

Few V_4 and V(306) bands were formed, probably owing to interstitial trapping by Na^+ impurities.

The V_1 band, which is associated with the complex of Na^+ ions and interatitial halogens,[2,6] peaks initially at 406 nm and appears to show distinctive three annealing stages.

For further analysis of annealing behaviour, detailed isochronal pulse annealing experiments were carried out, and the results are shown in Fig.4.2.2.

The annealing curves of the V_1 band, measured as a change in optical density at 406 nm, is made up of three stages: In the first stage (below 120 K), a small fraction of the band decays, about a half of the band decays with a shift of the peak position from 406 to 415 nm between 120 and 160 K (second stage), and the band disappears below 200 K, leaving the peak position of 415 nm unchanged (third stage).

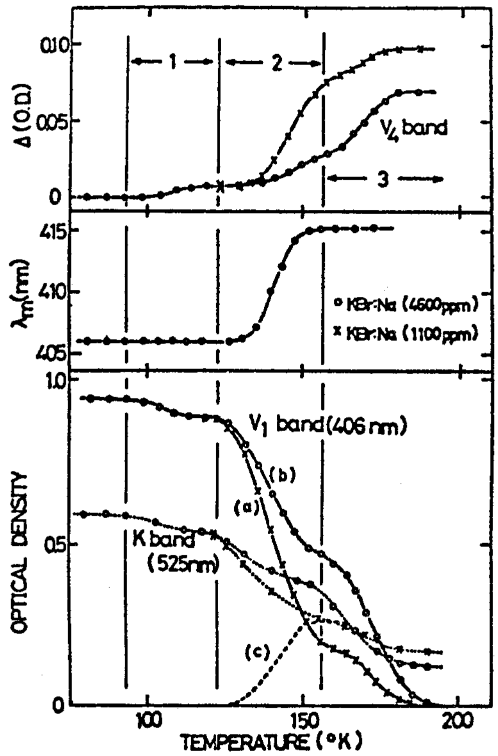

Fig.4.2.2. Isochronal pulse annealing curves of the F and V_1 centers and the growth of the V_4 center in KBr:Na(0.6 mol%),(x), and KBr:Na(2.0 mol%),(o). The value of the former sample are normalized with respect to that for the latter at 123 K. Δ(O.D) is the increase of the V_4 band. Curves(a) and (b) represent annealing curves of V_1 bands in these two samples, and curve(c) is the difference between the two. λ_m is the peak position of the V_1 band in KBr:Na(2.0 mol%).

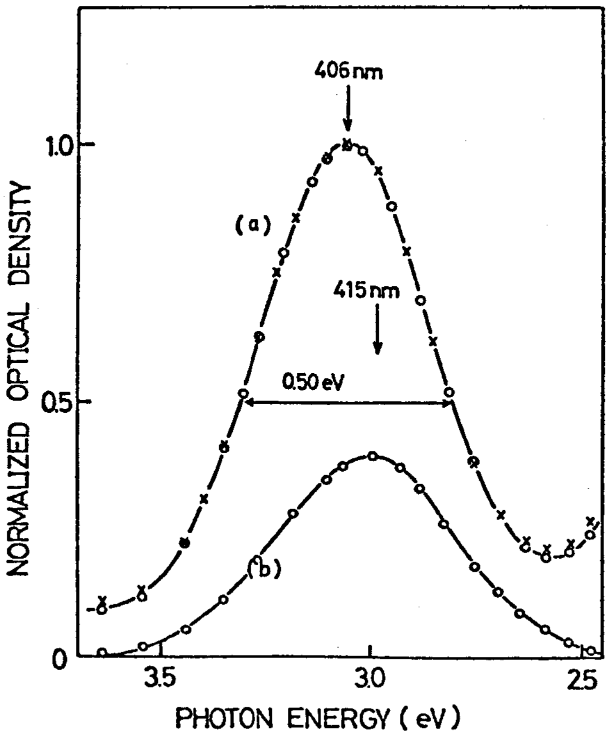

Fig.4.2.3. Comparison of 406-nm bands in two samples. (o) and (x) represent the spectra of KBr:Na(2.0 mol%) and KBr:Na(0.6 mol%),(a). Curve(b) is the <110> anisotropic absorption spectrum in KBr:Na(2.0 mol%).

In KBr:Na(2.0 mol%), the decrement of the V_1 band in the first stage is comparable with that in the second stage. On the other hand, in KBr:Na(0.6 mol%), the 406-nm band decays mainly in the stage around 140 K (curve (a) in Fig.4.2.2).

In Fig.4.2.3, the comparison was made on the shape of the V_1 bands in two samples which were warmed up to 120 K and measured at 80 K. It can be seen that the shape is the same for each crystal.

Figure 4.2.4 shows the results of dichroic bleaching experiment for the 415-nm band with polarized light at 80 K. It is clear that the absorption band is caused by the transition which arise from a center with symmetry axis along <110> direction. The anisotropic-absorption spectrum caused by the polarized light is shown in Fig.4.2.3 (curve (b)).

Figure 4.2.5 shows the results of isochronal pulse annealing experiments for the absorption band situated at about 5.4 eV. This band, which is enhanced by Na^+ impurity as shown in the inset of the figure, decays thermally in two stages. The first stage is seen for each sample, whereas the second one can be seen in the samples having larger impurity concentration. It is also evident that the fraction decayed at the second stage increases with increasing Na^+ concnetration. The shift of the peak position during thermal annealing was hardly observed.

The annealing curve of α band in KBr:Na(2.0 mol%) was also measured. It was found that the annealing curve has similar two stages as those of 5.4-eV band.

§3 Discussions

(3·1) The V_1 band and H_{AA}-type centers

The annealing behaviour of the V_1 band in strongly Na^+-doped KBr is rather complicated, though it can be divided

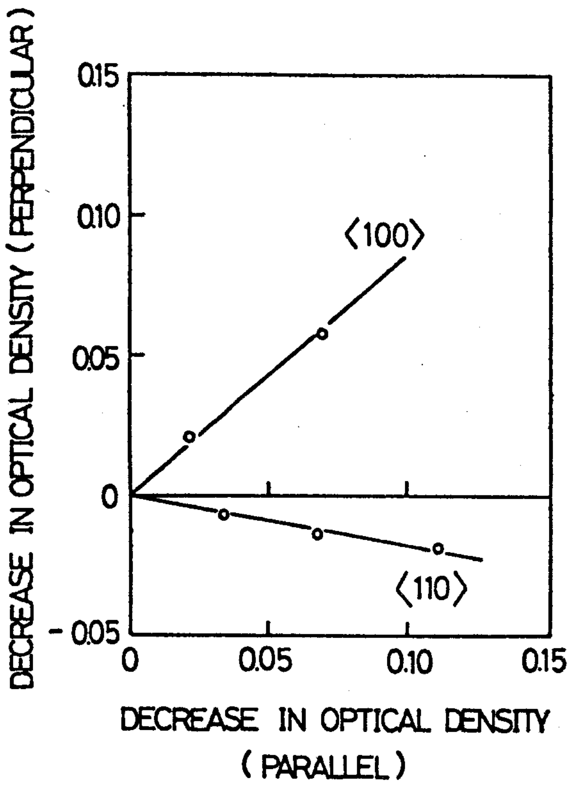

Fig.4.2.4. The results of dichroic bleaching experiments of the 415-nm band in KBr:Na(2.0 mol%). The abscissa is the decrease of the optical density measured with light polarized parallel to the bleaching light and the ordinate is the changes in the perpendicular component.

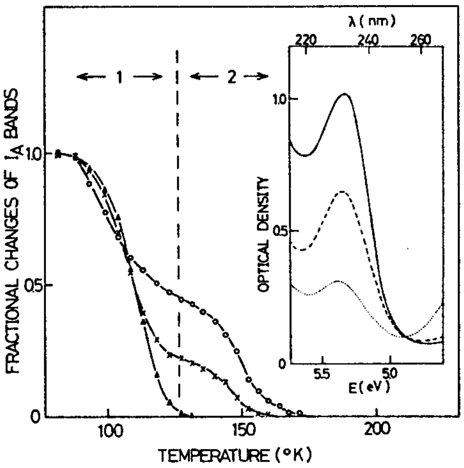

Fig.4.2.5. Thermal annealing of the I_A band in KBr:Na crystals. (▲), (x), and (o) show the annealing curves of the samples containing 0.09, 0.60 and 2.0 mol% of Na$^+$ ions, respectively. The inset shows the I_A band induced by γ-irradiation in the first(dotted line), the second (broken line), and the third sample(solid line), respectively.

into three stages, as shown in Fig.4.2.2.

The first stage may not be due to electron release from F^- ot other otraps, but may be to thermal decay of the center repsonsible for this band: The former mechanism should result in the growth of F centers and in the decrease of not only the V_1 center but of other interstitial-atom centers such as V_4 center. As seen in Fig.4.2.2, this stage is, however, is accompanied by F-center decay and V_4-center growth.

This stage is, therefore, considered to be due to the thermal decay of an interstitial centers consisting of an H center and Na^+ ions. The center responsible for this first annealing stage will be discussed in the next chapter, and further descriptions are not given here.

The peak shift of the V_1 band in the second stage is characteristic of strongly doped specimens, and such a type of peak shift was not observed in samples with lower doping concentration(<0.6 mol%).

In principle, the annealing behaviour at the second stage in strongly doped specimans may be due to

a) the growth of 415-nm band with the decay of 406-nm band, or

b) coexistence of 406-nm and 415-nm bands in as-irradiated sample, which decay thermally in second and third stages, respectively.

Hypothesis (b), however, can be ruled out from following experimental results:

1) V_1 bands in two samples, containing 2.0 and 0.6 mol% of Na^+ ions respectively, which were warmed up to 120 K after irradiation, have the same shape, as shown in Fig.4.2.3. If 415-nm component exists in the sample, the band shapes in two specimens should be different from each other, since the contents of this component in two samples are not the same;

2) the decaying spectrum in the second stage of KBr:Na(2.0 mol%) did not remain the same in shape, which means that thermally-induced changes of the absorption spectrum

in the V_1 band region are not solely the decrease of 406-nm band at this stage.

Therefore, it can be concluded that 415-nm band grows with the decrease of 406-nm component in the second stage around 140 K, and that the former decays thermally in the third stage.

Thus the annealing curve of the V_1 band may be resolved into two components; one is a decaying component due to thermal decay of 406-nm band and the other a growing one (represented by curve (c) in Fig.4.2.2) due to the growth of 415-nm band.

The 406-nm band in KBr:Na crystals is considered to be $H_A(Na^+)$ band, since the peak position and the thermal stability agree with the results for $V_1(Na^+)$ band obtained by Saidoh and Itoh.6)

When an H_A center decays thermally, an interstitial atom is ejected into a 'normal' interstitial site. Such ejected atoms may result in the recombination with F centers to restore the perfect lattice and in the recombination with other defects to convert them into thermally more-stable form, for example the V_4 center.

In KBr:Na(0.6 mol%), a major fraction of the growth of V_4 band and that of the decrease of F band occur simultaneously with the decrease of H_A band in the second stage (120 - 150 K). On the other hand, changes of both V_4 and F bands in the second stage are less than those in the third stage in KBr:Na(2.0 mol%). This behaviour can be explained in terms of interstitial trapping by impurity-pairs.

Since the Na^+ concentration in KBr:Na(2.0 mol%) is so high, that the considerable amount of impurity pairs is supposed to be formed. The pair is the more effective trapper for interstitials than a single impurity ion.1) In such a case, it is expected that the growth of V_4 band and the decrease of F band will be suppressed owing to the effective trapping of interstitials by impurity pairs, and that a new absorption band corresponsing to the H_{AA} type centers will be appear during the H_A-decay process (the second stage).

Following considerations lead us to believe that 415-nm band is due to an interstitial atom trapped by a Na^+-impurity pair:

1) This band is closely related to an interstitial halogen atom, in view of the facts that this band grows when the H_A center decays thermally and that the thermal decay of this 415 nm band is accompanied by the growth of V_4 band and the decrease of the F band.

2) This band is characteristic of strongly Na^+-doped specimens, so that the band is considered to be related to impurity complex. In the range of 2.0 mol% of impurity concentration, most probable and dominant impurity complex is the pair.

3) The peak position of 415 nm may not be unreasonable for H_{AA} type centers, since to a first approximation the interstitial atom-type defects, such as H, H_A and H_{AA} centers, belong to the same chemical species, and hence would be expected to possess absorption bands situated at roughly the same wavelength. In KBr crystals, the H center has a σ-polarized absorption at 380 nm which corresponds to the transition from σ_g to σ_u.7) In the case of H_A centers, H center perturbed by a Na^+ impurity ion, the corresponding absorption may be at 406 nm, whereas the Br_2^- in the H_{AA}-type centers is supposed to be more perturbed 1) and hence would have absorption at a lightly longer wavelength.

4) This band shows <110> dichroism at 80 K. This anisotropic spectrum is shown in Fig.4.2.3. This results agrees with that from EPR observation of H_{AA} centers in KCl:Na.1)

(3·2) The 5.4-eV Band and I_{AA}-type centers

As shown in Fig.4.2.5, the 5.4-eV absorption band in strongly Na^+-doped KBr has supplementary annealing stage at 150 K.

In general, F^+ centers decay at different temperatures in the range 100 - 300 K, when irradiation was made at 80 K.

Most likely, much of the low-temperature annealing of the F^+ center is due either to electron release by F^- or other traps or to interstitial-vacancy recombination.[8)]

F^+ centers in KBr are enhanced by Na^+ impurity ion owing to the interstitial ion, Br_i^-, stabilization by the impurity, which results in the formation of the I_A center responsible for the 5.4-eV absorption band.

In a crystal containing nominally 1 mol% of NaBr, F^+ centers almost completely decay thermally in two distinct stages as the sample is warmed at 190 K.[2)] Giuliani has concluded that in these two stages the mobile entities are the interstitials.

The first annealing stage around 110 K is concluded to be due to the thermal decay of the I_A center, since the stage can be seen in crystals where impurity pairs are negligible.

The second annealing stage is also due to the decrease of absorption band situated at 5.4 eV. Similarity of peak position of the band as those of I and I_A bands and the simultaneous decrease of the α band indicate that the band, which decay around 150 K, is due to the interstitial bromine ion.

The ion is considered to be associated with higher aggregate of Na^+ ions, since the crystals where the formation of impurity pairs are negligiblly small do not have the annealing stage at 150 K. Most probable aggregete may be a pair.

Thus one can conclude that the absorption band responsible for the second annealing stage is due to the I_{AA}-type centers.

Na^+ impurities give a large thermal stability for Br_i^- as well as interstitial atom. On the other hand, optical absorption of Br_i^- is hardly affected by nearest neighboring Na^+ ions. This means that the electronic levels of I centers are perturbed little by the lattice distortion Na^+ ion should cause which gives the significant thermal stability for an interstitial halogen ion.

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[4·3]

THE INTERACTION OF THE INTERSTITIAL BROMINE ATOM WITH A Na^+ ION DURING DEFECT-FORMATION PROCESS IN KBr CRYSTALS

The interaction of interstitial bromine atom (Br_i^o) with a Na^+ impurity ion during defect-formation process has been studied in KBr crystals through the systematical analysis of the composite structure of the V_1 band and the formation yield of the F center in terms of the Na^+ concentration (C_{Na}) dependence. The formation yield of the F center at 80 K, as a function of C_{Na}, reaches a maximum at about 0.12 mol% of C_{Na} and decreases gradually for higher C_{Na}. This behaviour of the F center has been shown to have close correlation with the composite structure of the V_1 band. Three different centers, H_{A1}, H_{A2}, and V(410) centers, are responsible for the V_1 band. Optical and thermal properties of these centers have been cleared. The Na^+-concentration dependence of the formation yield of the complex center consisting of an H center and a Na^+ ion which is formed through the interaction of replacement sequence of Br_i^o with a Na^+ ion, (H_A)$_d$ center, is descrived by $n[(H_A)_d] = A\{1-\exp(-v_dC_{Na})\}/(1-V^*C_{Na})$. On the other hand, that of the complex center formed through the interaction of the thermally migrating H center with a Na^+ ion, (H_A)$_t$ center, is expresses by $n[(H_A)_t] = KC_{Na}\exp(-v_tC_{Na})$. The formation yields of the H_{A1} and H_{A2} centers show similar C_{Na} dependences as those of (H_A)$_t$ and (H_A)$_d$ centers, respectively. Thus the different modes of motions of Br_i^o result in the formation of the complex centers with different properties, through the interaction with a Na^+ ion in KBr. Mechanism of the interaction of Br_i^o with different mode of motion with a Na^+ ion is discussed in terms of the elastic interaction between them.

§1 Introductory Remarks

Behaviour and properties of interstitial halogens could be investigated in terms of their interaction with proper " targets " which are doped in pure crystals.

The alkali impurity is supposed to be the best one of such targets, since the main effect the impurity gives to the crystal is considered to be the lattice distortion around it. On the other hand, the H center, the primary interstitial halogen, is neutral to the lattice, and accompanies the significant lattice distortion.[1] Thus we can know the properties of the interstitial atom, in elastic nature, through its interaction with alkali impurity.

It is well known now that Na^+ as well as Li^+ is an effective and important trapper for halogen interstitials at about 80 K. When one supposes that the interaction between an H center and a Na^+ ion at 80 K is so simple process that it results in the formation of only one type of the complex center, following consequence may be expected that the formation yield of the F center, which is determined mainly by the number of trapped H centers by the impurity, increases monotonically, even if not linearly, with increasing Na^+ concentration, C_{Na}. This idea is, however, not the case at least in KBr crystals: the yield of the F center at 80 K depends, in subtle way, on C_{Na},[2] and the V_1 band, which is mainly due to the products of the H center-alkali impurity interaction,[3-5] has the composite structure.[6,7]

It has been shown, in the preceding chapter, that the formation of H_{AA}-type centers results in the composite property of the V_1 band in KBr which has significantly higher doping concentration of Na^+ ions. The structure, however, does exist in the sample where impurity pairs are negligible, as have been shown by Giuliani[6] and by the author,[7] which suggests that the interaction of the H center with a Na^+ ion in KBr is somewhat complicated process.

However, the origin of the composite structure is far from being well understood so far. The study on this

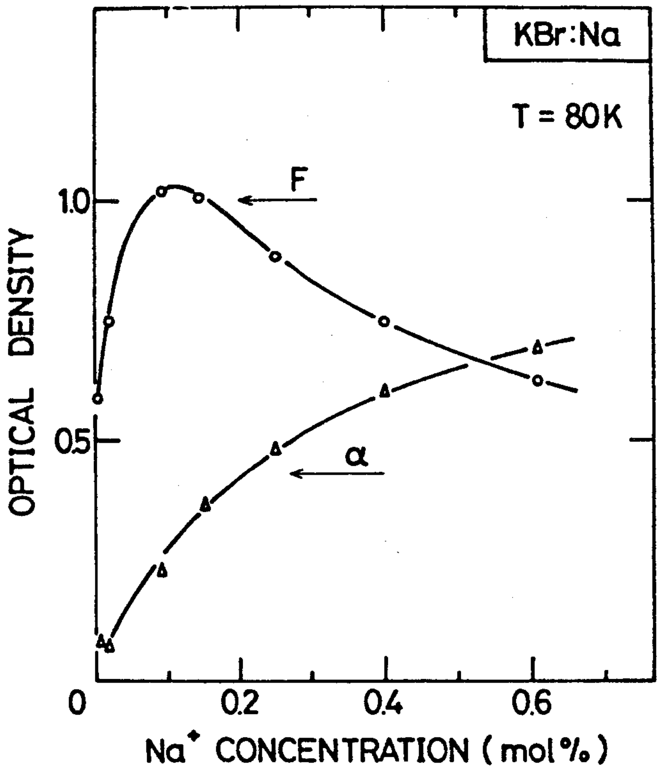

Fig.4.3.1. Na$^+$-concentration dependence of the formation yields of the F and α (F$^+$) centers induced by x-ray irradiation at 80 K in KBr crystals.

problem is, therefore, significantly important for the clarification on the interaction of interstitial bromines with Na^+ ions.

In this chapter, the mechanism of the interactions, which form the complex center consisting an interstitial atom and a Na^+ ion and result in the " enhancement " of the F-center production, is studied through the systematical analysis of these resulting phenomena in terms of Na^+-concentration dependence.

2 EXPERIMENTAL RESULTS

(2·1) Formation yield of the F center in KBr:Na crystals

Fig.4.3.1 shows the Na^+ concentration dependences of x-ray induced formation yields of the F and α cneters in KBr:Na crystals under a fixed dose of x rays at 80 K. One can see that the yield of the α center increases monotonically with increasing C_{Na}. Therefore, the generally used term, enhancement, is adequate to call the dependence of the yield in the case of α centers. But the formation yield of the F center depends in subtle way on C_{Na}; it reaches a maximum at about 0.12 mol% of C_{Na} and then decreases gradually. This result suggests that the interstitial atom interacts with impurity ion through some complicated mechanism.

In Fig.4.3.2 formation yields of α and F centers which were produced by x-ray irradiation at 6 K, and the fractions of them, which remains in the crystals warmed up to 80 K after irradiation at 6 K, were plotted against C_{Na} of the samples. The decreases in formation yields of both centers due to x raying at 6 K with increasing C_{Na} have been discussed in Chap.[3.4]. The rests of these centers after warming up samples show, respectively, similar dependences as those of the formation yields of the centers by x raying at 80K shown in Fig.4.3.1, though the formulas describing the Na^+ concentration dependences are not exactly the same.

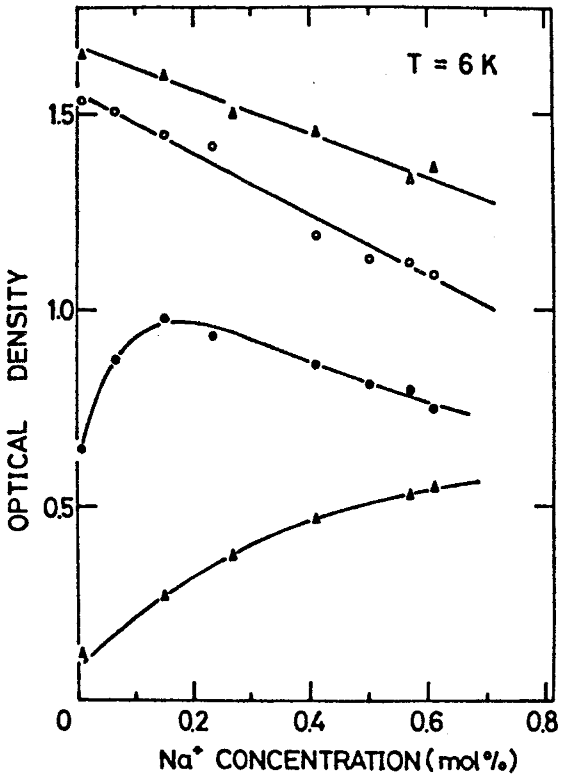

Fig.4.3.2. Na^+-concentration dependecne of the formation yields of the F (o) and α (Δ) centers induced by x-ray irradiation at 6 K and of the rests of the F (●) and α (▲) centers after warming irradiated samples up to 80 K, respectively. Measurements were made at 6 K.

The decrease in the yield of the F center at 6 K accompanies the decrease in the total number of formed interstitial halogen atoms. In the present experiments, the absorption band of the V_4-envelope, mainly due to di-H centers was hardly observed in all samples. Therefore, most Br_i^o type defects are in the form of H and H_A centers.* Fig.4.3.3 shows absorption spectra at the H-band region of pure KBr and of a KBr:Na(0.50 mol%). The band shape in pure KBr is well described by a gaussian with a peak energy of 3.24 eV and the halfwidth of 0.47 eV. These values are essentially the same as those of the H band obtained previously.8) The absorption spectrum of a KBr:Na is considered to be composed of bands due to H and H_A centers. If one divides it into two gaussians, one of which is the H band, the best fit with data points can be obtained when another one has a peak energy of 3.06 eV and the halfwidth of 0.50 eV, as shown in Fig.4.3.3. The new band of a gaussian in shape can be assigned to be the H_A band.

Such division of the absorption bands at about 3 eV in other KBr:Na crystals are applicable, which makes it possible to obtain the formation efficiencies of the H_A center at 6K. Fig.4.3.4 shows the Na^+ concentration dependence of the formation yield of the H_A center relative to that of total number of Br_i^o-type centers in KBr:Na system at 6 K. The total number of Br_i^o-type centers were evaluated here by adding the heights of resolved H and H_A bands, taking into account the differences in their oscillator strengths and halfwidths.8) It was confirmed that the evaluated number is in proportion to the height of the F bands in all samples used here. It is seen in Fig.4.3.4 that formation efficiency of the H_A center increases monotonically with increasing C_{Na}. The solid line in the figure is the calculated curve of

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* The notation of " H_A " means in this chapter the center consisting an H center and a Na^+ ion. This does not involve any model of the configuration of the center.

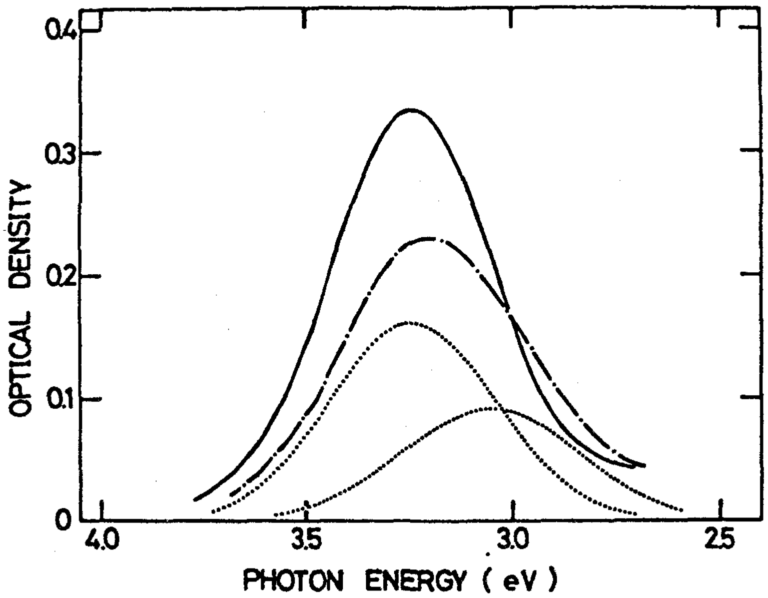

Fig.4.3.3. Optical absorption bands at H and V_1-bands region of pure KBr(solid curve) and of KBr:Na(0.50 mol%)(chain line), induced by x-ray irradiation at 6 K, respectively. The dotted curves show the resolved Gaussian peaks in the band of KBr:Na(0.50 mol%).

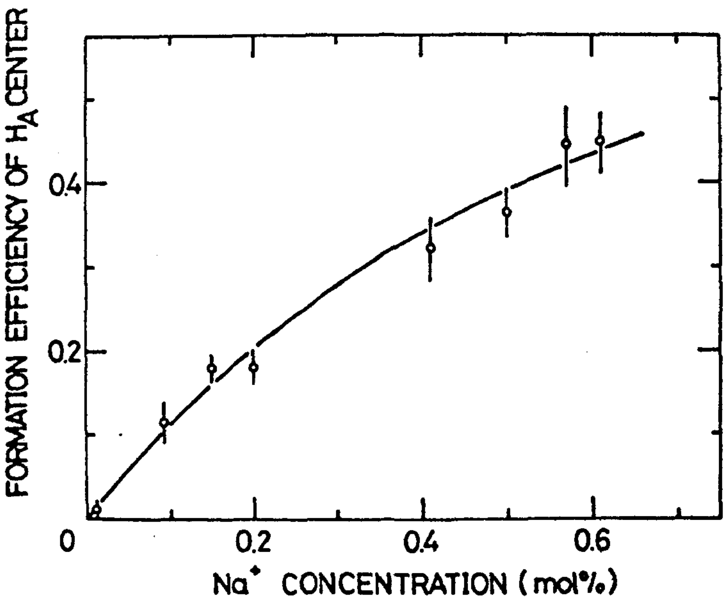

Fig.4.3.4. Na^+-concentration dependence of the formation efficiency of the H_A center at 6 K. The solid curve is the best fit of eq.(4.3.4) with values of 200 and 0.62 for v_d and B, respectively(see the text).

a saturating-exponential function. Details of the function is discussed later.

(2·2) Composite structure of the V_1 band

Figure 4.3.5 and 6 show the absorption spectra induced by γ-ray irradiation at 77 K in samples with different Na^+ concentrations. One can see followings; 1) the V_1 band is enhanced, whereas the V_4 -envelope [9)] is suppressed with increasing C_{Na}, and ii) the peak position and shape of the V_1 band are different for each sample.

In order to make the behaviours of the V_1 band more clear, we showed in Fig.4.3.7 changes of the peak position and " asymmetry "* both of which can well characterize the behaviour of the V_1 band in the present case. The peak position shifts from 417 to 406 nm, and asymmetry increases to approach unity, or become more symmetric, with increasing C_{Na}. The results indicate that the V_1 band in as-irradiated samples has a composite structure, and that the structure depends on the Na^+ concnetration.

It is, therefore, important for the full understanding of the composite structure of the V_1 band to clarify 1) what components compose this band, and 2) how these depend on the Na^+ concnetration.

1. Separation of the components of the V_1 band

We separate the components, making use of the differences in the thermal stabilities of them. Fig.4.3.8(a) shows the isochronal pulse annealing curves of the V_1 band measured at 410 nm in samples with different Na^+ contents, and (b) of the figure indicates the changes of the peak position during thermal annealing. All measurements were made at 80 K, and the peak heights of the V_1 bands before

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*) Asymmetry is defined here as (E_h-E_m)/(E_m-E_l) for a V_1 band, where E_m is the photon energy which gives the maximum peak height, and E_h and E_l are energies corresponding to a half maxima at higher and lower energy side of E_m.

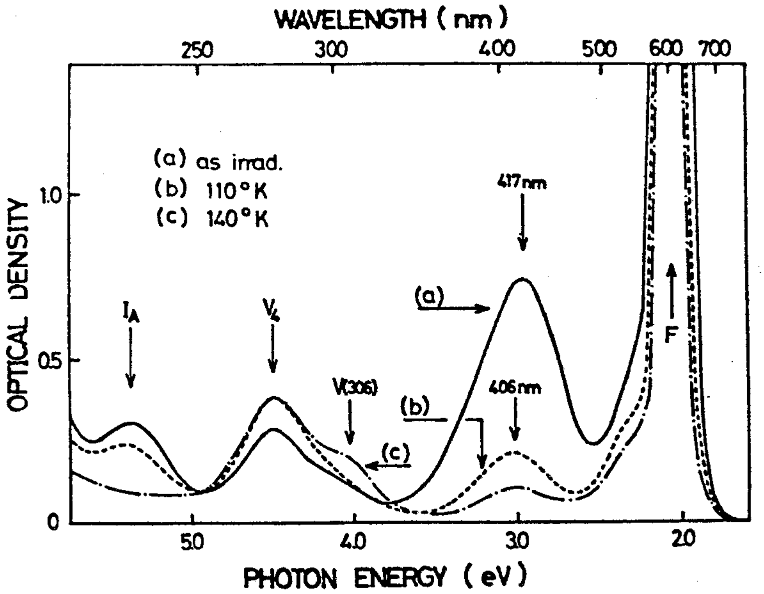

Fig.4.3.5. Optical absorption spectrum of KBr:Na(0.09 mol%) induced by γ irradiation at 77 K, and its changes due to warming the irradiated specimen up to gives temperatures. All measurements were made at 80 K.

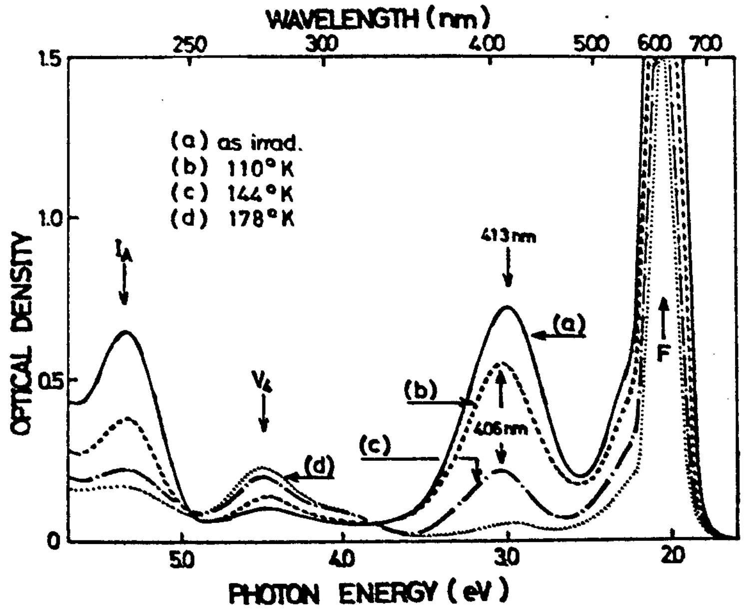

Fig.4.3.6. Optical absorption spectrum of KBr:Na(0.50 mol%) induced by γ irradiation at 77 K, and its changes due to warming the irradiated specimen up to given temperatures. All measurements were made at 80 K.

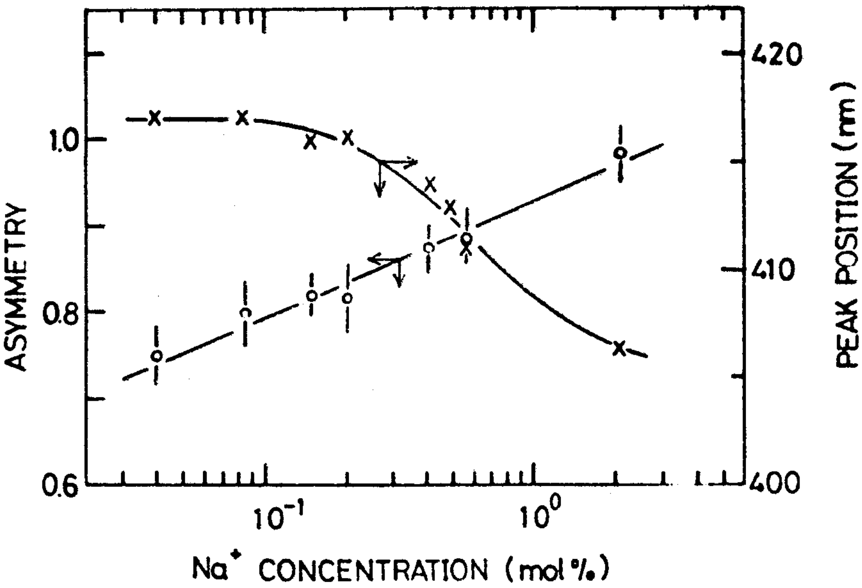

Fig.4.3.7. Na^+-concentration dependence of the peak position(x) and the asymmetry(o) of the V_1 band in KBr, respectively. Measurements were made for the as-irradiated samples at 80 K.

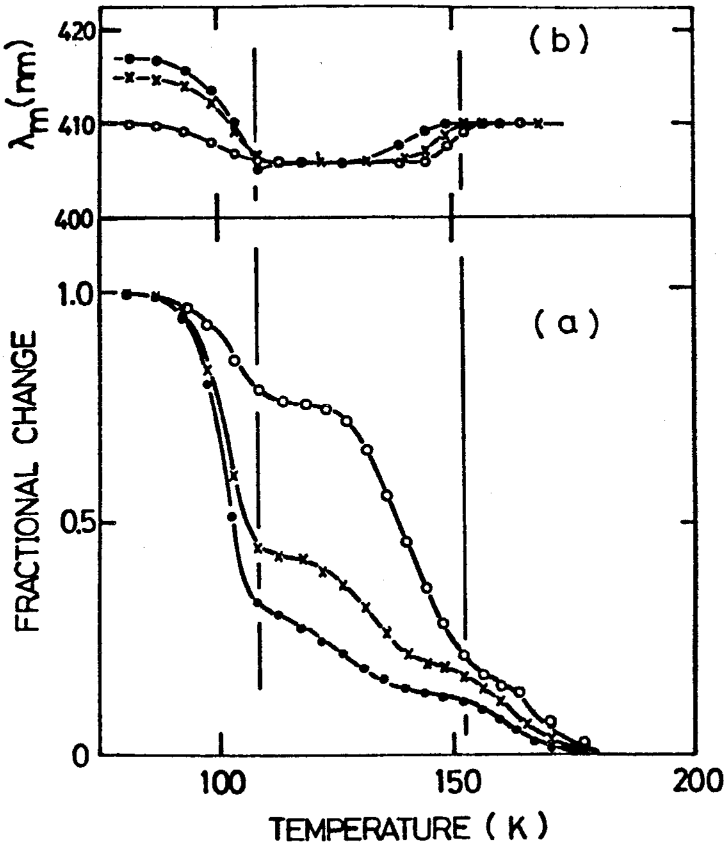

Fig.4.3.8. The isochronal pulse annealing curves of the V_1 bands, (a), and the accompanied changes of the peak position, (b), in KBr containing 0.04 mol% (●), 0.20 mol%(x), and 0.50 mol%(o) of Na^+ ions, respectively. λ_m indicates the peak position of the V_1 band in each sample. All measurements were carried out at 80 K.

annealing are normalized to unity, for comparison.

The V_1 band in each sample decays thermally through three annealing stages. In the first stage (80 - 110 K), the peak position shifts to short-wavelength side to 406 nm, while the position shifts to slightly longer wavelength side to 410 nm in the second stage around 140 K. The third stage corresponds to the decrease of the band with the peak position of 410 nm unchanged. The results show that the V_1 band is composed of three different centers, and that the relative yields of three centers depend on the Na^+ concentration.

It was found that these annealing stages of the V_1 band are accompanied with the simultaneous decrease of the F center and with the growth of other V centers, as seen in Figs.4.3.5 and 6. It is, therefore, clear that these centers consist of interstitial bromine atoms.

The centers responsible for stage 1, 2, and 3 are tentatively called the H_{A1}, H_{A2}, and V(410) centers, respectively.

In order to know the optical absorption spectra of these centers, the difference of spectra between before and after an annealing stage was examined. Results are shown in Fig.4.3.9. Curves(a) and (b) in the figure show the spectra for stage 1 and 2, respectively. The spectrum for stage 2, the H_{A2} band, is well represented by a Gaussian with a peak energy of 3.05 eV and the halfwidth of 0.51 eV. It can be concluded that the H_{A2} center has an absorption band at 3.05 eV. It was confirmed that the V(410) center has an absorption band situated at 3.02 eV with a halfwidth of 0.43 eV. However, the spectrum for stage 1 due to the H_{A1} center is complicated. The open circles, triangles, and crosses of curve (a) in Fig.4.3.9 indicate changes in absorption spectra of the V_1 band in KBr:Na(0.09 mol%), which were caused by warming the irradiated sample up to 107 K, by F light and by 420-nm light illumination at 80 K, respectively. It is evident that these are the same each other.

In the F-light bleaching experiment, a small fraction

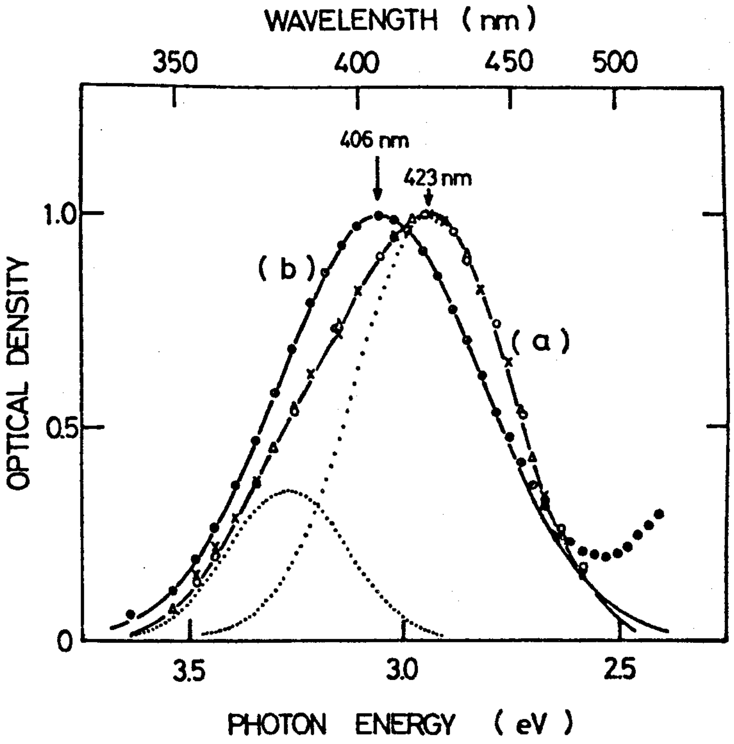

Fig.4.3.9. Optical absorption spectra of the H_{A1} center, curve(a), and of the H_{A2} center, curve(b), respectively. The dotted lines show the resolved two Gaussians of the H_{A1} band, peaking at 3.28 and 2.92 eV, respectively. Symbols;(o), (x), and (Δ) in curve(a) show the change in absorption spectrum produced by warming up to 107 K, by F light and by 420-nm light illuminations, for KBr:Na(0.04 mol%). (⊙) indicates the change by warming the irradiated sample, KBr:Na(0.50 mol%), from 110 to 150 K, and the solid line of curve(b) is a Gaussian peaking at 3.05 eV.

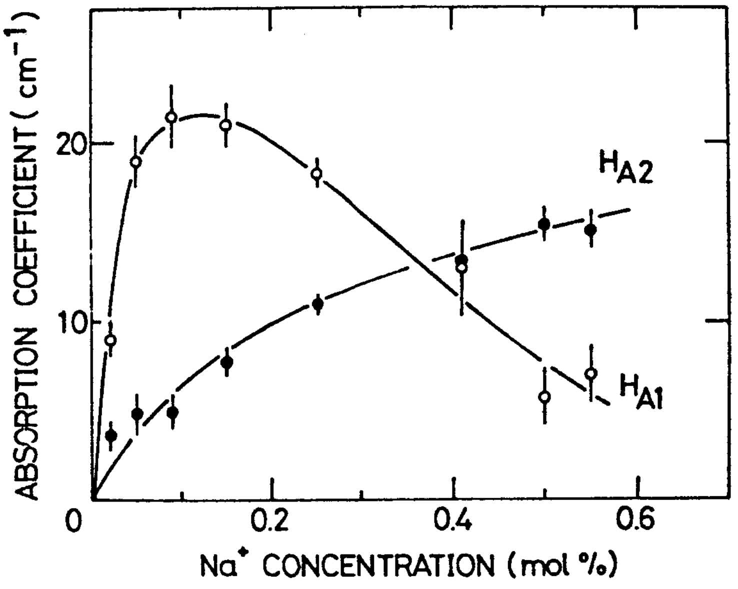

Fig.4.3.10. Na$^+$-concentration dependence of the formation yields of the H_{A1} and H_{A2} centers produced by γ irradiation at 77 K.

of the V_1 band decreases rapidly, and very gradually after that. The rapid bleached component has the broad absorption band situated at about 385 nm, which was assigned to be the V_K band. The difference in spectra shown in Fig4.3.9 is based on the data in the latter gradual bleaching stage, so this spectrum may not involve the band which comes from the V_K center.

This band is not symmetric, which may mean that the spectrum is superposed by several components. This spectrum can be resolved into two gaussians peaking at 3.28 and 2.93 eV, as shown in Fig4.3.9(dotted lines). These may be caused by the transitions in the same center*.

Above results lead us to believe that the V_1 band in KBr:Na crystals has four bands due to three different centers except the V_K center.

(2) Na^+ concnetration dependecne of formation yields of H_{A1} and H_{A2} centers

During the irradiation-induced growth of the V_1 band in a given sample, peak position and the shape of the band remains unchanged, which means that formation efficiencies of above mentioned three centers does not depend on dose. The efficiencies, however, depend on the Na^+ concentration for a fixed dose as seen in Fig.4.3.8. The height of each stage of the annealing curve of the V_1 band was plotted to the Na^+ concnetration in Fig.4.3.10.

The yield of the H_{A2} center increases monotonically with increasing C_{Na}. On the other hand, that of the H_{A1} center changes in complicated way, namely, it increases to the maximum value at about 0.1 mol%, and decreases at higher Na^+ concentration. The origins of the Na^+ concent-

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*) Giuliani has attrubuted in the paper 6) where he has first pointed out the composite structure of the V_1 band the decayed band around 100 K to the complex of 423 nm band and the V_K band. His conclusion may, however, not be correct in the author's opinion. It is proposed that the decayed band is doublet consisting of 3.28 and 2.93 eV components.

ration dependences of the formation yields of these centers are discussed in later.

It is clear that the V(410) center is a complementary defect to the F center, because the decay of the center is accompanied with the simultaneous decrease of the F center. However, in contrast to the H_{A1} and H_{A2} centers, the yield of this center does not seem to depend on the impurity concnetration. It is also sure that the band is not seen in irradiated pure KBr.

Figure.4.3.11 shows results of dichroic bleaching experiments of the V(410) bands at 80 K. The result shows that this band has a <100> symmetry axis. This symmetry is similar to those of di-H centers. 5)

The origin of the 410-nm absorption band was not cleared here. Further statements on the V(410) center will not be given hereafter.

3 DISCUSSIONS

(3·1) Reactions of Br_i^o during thermal migration

The production rate of the F center at 80 K depends in subtle way on C_{Na} as seen in Fig4.3.1. What causes such a behaviour of the F center with respect to C_{Na} ?

The formation of F-aggregate centers as well as of the impurity associated F centers (F_A centers)10) may affect possibly the number of formed " pure " F centers. These, however, are disregarded for the present irradiation condition from following reasons.

i) The F-aggregation is active only in near room temperature regions.11)

ii) The M band becomes appreciable in KBr at 77 K only in the case where the concentration of the formed F center amount as one order of magnitude higher as that in this study.8)

iii) In fact, no absorption bands were observed in infrared region, and the peak position and the shape of

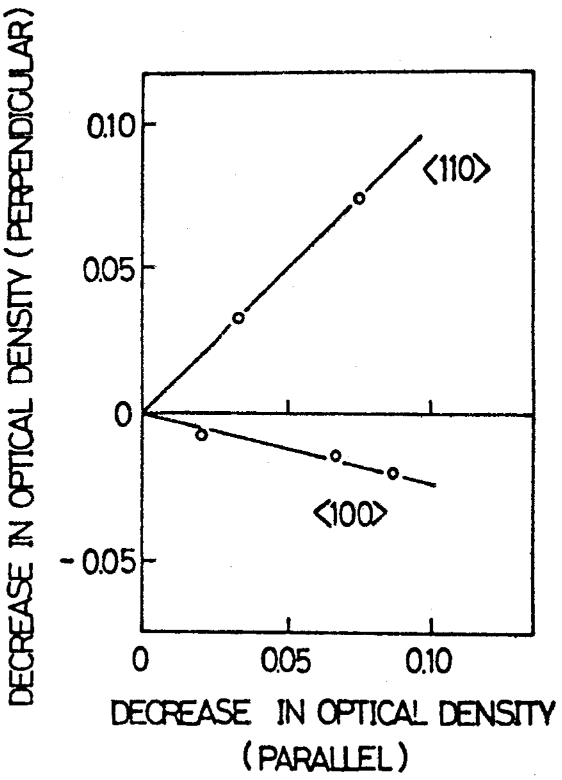

Fig.4.3.11. The results of dichroic bleaching experiments of the V(410) band in KBr:Na. The abscissa is the decrease of the optical density measured with light polarized parallel to the bleaching light and the ordinate is the changes in the perpendicular component.

the F band does not differ for all samples. Therefore, it is concluded that the behaviour of the formation yield of the F center shown in Fig.4.3.1 has the origin in the formation of its complementary centers.

It should be noticed here that the concentration of the F center in a sample which was x-rayed at 6 K and was warmed up to 80 K shows similar Na^+ concentration dependence as that of formation yield of F centers due to x-ray irradiation at 80 K. This result suggests that the reactions of H centers during thermal annealing of an irradiated sample play an important role for the behaviour of the formation yield of the F center.

In order to analyze the reactions during thermal annealing, it is convenient to divide F centers formed at 6 K into two groups of F_H and F_{HA}; these constitutes Frenkel pairs with H and H_A centers, respectively. Then the concentration of the initial F center, n[F], is written as

$$n[\,F\,] = n[\,F_H\,] + n[\,F_{HA}\,]. \qquad (4.3.1)$$

The value of $n[F_{HA}]$ is not considered to change by warming an irradiated crystal up to about 80 K, since the H_A center is thermally stable up to above 100 K.

The concentration of the F center at 80 K, therefore, becomes the sum of $n[F_{HA}]$ and the fraction of $n[F_H]$ which survives at 80 K; the latter is hereafter represented as $n[F_{Hs}]$.

It has been known that the H center thermally migrates in the lattices above the decay temperature ($\sim$ 40 K) and results in the recombination with F centers to restore the perfect lattice or in the association with imperfections to form more stable defects. In the present case, it is not unreasonable to think that the imperfections are Na^+ ions and the H center itself. Therefore, the defects which are formed by the reactions of thermally migrating H centers are the V_4 center (di-H center) and the H_A center.

In this chapter, the center consisting of a pair of the H center and a Na^+ ion formed by the reactions of thermally migrating H centers is represented by (H_A $)_t$, whereas that formed through the interaction of replacement collision sequence of Br_i^o with a Na^+ ion is represented by (H_A $)_d$, respectively.

Then $n[F_{Hs}]$ can be expressed as follows;

$$\begin{aligned} n[\ F_{Hs}\ ] &= \{\ P_f(H_A) + P_f(V_4)\ \}\ n[\ F_H\ ] \\ &= n[\ V_4\ ] + n[(H_A)_t] \end{aligned} \qquad (4.3.2)$$

where $P_f(H_A)$ and $P_f(V_4)$ are the probabilities of the H centers to form $(H_A)_t$ and V_4 centers during the thermal migration process, respectively.

Since the formation efficiency of the $(H_A)_d$ center at 6 K has been known, one can evaluate $n[F_{HA}]$, $n[F_H]$ and $n[F_{Hs}]$, based on the results shown in Figs.4.3.2 and 4. The Na^+ concentration dependence of $n[V_4]$ can be also obtained experimentally from measureing the increment of the peak height of the V_4 band after warming a sample up to 80 K. The $(H_A)_t$ center is hardly formed by thermal annealing in a pure KBr crystal, so that $n[F_{Hs}]$ may be equal to $n[V_4]$ in the crystal. The value of $n[(H_A)_t]$ can be obtained by subtracting $n[V_4]$ from $n[F_{Hs}]$ in a given sample.

Thus obtained $n[(H_A)_t]$ and $n[V_4]$ as well as $n[F_{Hs}]$ are shown in Fig.4.3.12. It is seen that the formation rate of the H_A center formed by thermal annealing of the H center increases with increasing C_{Na} to about 0.2 mol% of C_{Na}, and then decreases to higher C_{Na}'s. The function well describing the Na^+ concnetration dependence of the formation rate of the (H_A $)_t$ center is following;

$$n[(H_A)_t] = K\ C_{Na}\ \exp(\ -v_t C_{Na}\ ) \qquad (4.3.3)$$

as shown in Fig.4.3.13, where K and v_t are constants. The straight line pertaining to data points gives a value of v_t of 460 v_o (v_o is the volume of an ion-pair).

On the other hand, the formation efficiency of the (H_A $)_d$ center increases monotonically with increasing C_{Na}, as shown in Fig.4.3.4. Here the dependence of the formation yield of the (H_A $)_d$ center on Na^+ concentration is discuss-

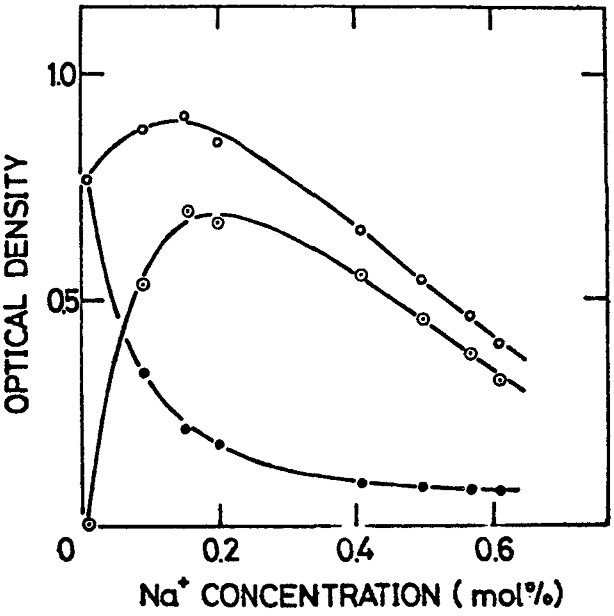

Fig.4.3.12. Na$^+$-concentration dependence of n[F_{HS}], (o), n[V_4], (●), and n[$(H_A)_t$], (⊙), obtained from results in Figs.4.3.2 and 4, respectively.

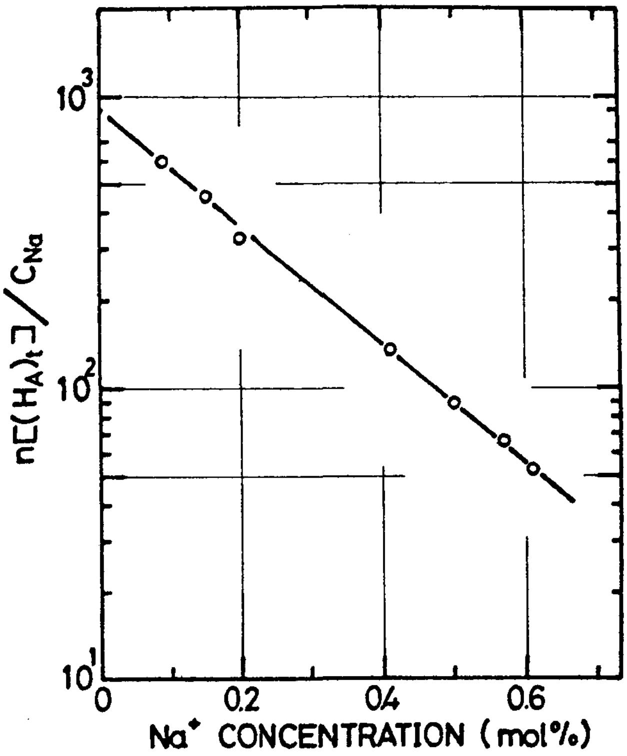

Fig.4.3.13. Plot of n[$(H_A)_t$]/C_{Na} vs. Na$^+$ concentration. The results show that the n[$(H_A)_t$] is well described, as a function of C_{Na}, by eq.(4.3.3). The straight line gives the value of 460 for v_t.

ed. As mentioned before, the solid curve in Fig.4.3.4 represents the following function;

$$n[(H_A)_d]/\ n[H]+n[(H_A)_d]=B\{1-\exp(-v_d C_{Na})\} \quad (4.3.4)$$

with the values of 200 v_o and 0.62 for v_d and B, respectively. On the other hand, it is evident that from Fig.4.3.2 n[F] is represented, as a function of C_{Na}, by

$$n[\ F\ ] = F_o(\ 1 - V^* C_{Na}\ ) \quad (4.3.5)$$

where F_o is a constant and V^* is the interaction volume defined in Chap.[3.4].Thus the formation yield of the (H_A)$_d$ center by the x-raying at 6 K can be written as

$$n[(H_A)_d] = A(\ 1 - V^* C_{Na})(\ 1 - \exp(-v_d C_{Na}))\ (4.3.6)$$

Above results and considerations lead us to the conclusion that the formation yields of the (H_A)$_t$ center and the (H_A)$_d$ center are expressed as functions of C_{Na} by eqs. (4.3.3) and (4.3.6), respectively. Physical meaning of these functions are discussed in the last paragraph, and here it is stressed that the difference in the motion of the Br_i^o results in the formation of the center consisting of an H center and a Na^+ ion whose formation yields depend on C_{Na} in different ways.

(3·2) The H_{A1} and H_{A2} centers in KBr:Na

It is revealed, from results described in (2·2), that irradiation at 80 K introduce at least two types of the centers apparently consisting of H centers and Na^+ ions, the H_{A1} and H_{A2} centers.

So far, configurations of three centers consisting of interstitial halogen atoms and monovalent cation impurities have been established. These are called H_A, H_{AA}, and $H_{A'A}$ centers. Detailed EPR studies have been done by Schoemaker et al. on such complex centers.3,12,13) In their studies, it has been shown that the H_A(Na), H_{AA}(Na), and $H_{A'A}$(Na) centers in KCl decay thermally at 110, 140 and 158 K, respectively. These temperatures are respectively close to the values of decay temperatures of H_{A1}, H_{A2} and V(410) centers in the present specimens. But following considerations rule out the possibility that these centers are the H_A, H_{AA}, and $H_{A'A}$ centers in KBr:Na crystals.

1) Thermal stability of interstitial halogen atom is considered to be determined mainly by the bonding nature of an atom and by the elastic conditions of lattices including that. These dominating factors may depend on the salt: According to Känzig and Woodruff,[13)] the H center in KCl decays thermally at 42 - 60 K, whereas the center in KBr at 20 - 40 K. Therefore, an assignment of a center from the similarity in thermal stability only may not be applicable to a center in the different salt.

2) The H_{AA} and $H_{A'A}$ centers, both of which are interstitial atom centers stabilized by impurity dimers, should become experimentally observable only for relatively higher doping concentration. Schoemaker[12)] has pointed out the probability of having impurity pairs is negligibly small for low doping concentrations($\sim$ 0.1 wt%). Even though the difference in distribution coefficients of Na^+ ions in KCl and KBr is taken into account,[14)] the formation probability of impurity pairs may be disregarded in the present sepecimens.

3) Tanimura et al. [7)] have studied the V_1 band in strongly Na^+ doped KBr(2 mol%) which should contain reasonable concentration of impurity pairs. In such a crystal, the absorption band at 415 nm has been assigned to be due to H_{AA} center in KBr. This H_{AA} band was not observed in the present specimens. Furthermore, annealing behaviour of the V_1 band in strongly doped samples is different from those in samples used in this work. These results indicate other centers except H_{AA}-type centers are responsible for the V_1 bands in the present samples.

Thus other models should be considered for the H_{A1} and H_{A2} centers.

In order to make clear the origin of the H_{A1} and H_{A2}

centers, let our attention focus on the Na^+ concentration dependences of the formation yield of these centers.

In Fig.4.3.10, one can see that the dependence of the yield of the H_{A1} center is similar to that of $(H_A)_t$ center shown in Fig.4.3.12. In fact, the dependence of the H_{A1} center can be described by eq.(4.3.3), as shown in Fig.4.3.14, though the value of v_t is not the same as that of $(H_A)_t$ centers.

On the other hand, the dependence of the H_{A2} center is similar to that of $(H_A)_d$ centers. The formation yield of the H_{A2} center can be represented by eq.(4.3.6): The solid curve in Fig.4.3.1 , where $n[H_{A2}]/(1 - V^* C_{Na})$ is plotted against Na^+ concentration, represents the calculated curve of eq.(4.3.6) with values indicated in the figure. The good agreement between the curve and data points is evident. Thus the formation yields of the H_{A1} and H_{A2} center have the same formula describing the Na^+ concentration dependence as those of $(H_A)_t$ and $(H_A)_d$ centers, respectively.

It should be also stressed here that the absorption band of the H_{A2} center is essentially the same as that of the $(H_A)_d$ center.

These results allow one to conclude that the H_{A1} and the H_{A2} center, produced by the irradiation at 77 K, are the complex centers consisting of an H center and a Na^+ ions formed by the reaction of thermally migrating H centers and by that of replacement collision sequence of Br_i^o, respectively.

(3·3) Thermal stabilities of Br_i^o trapped by a Na^+ impurity ions

In discussing the interstitial interaction with imperfections, one of the important factors may be the association energy of the interstitials with imperfections. One of the powerful methods to estimate the factor is considered to be thermally stimulated luminescence measurements.15) In order to discuss the association energies of the H_{A1} and H_{A2} centers, the activation energies for disappearance were

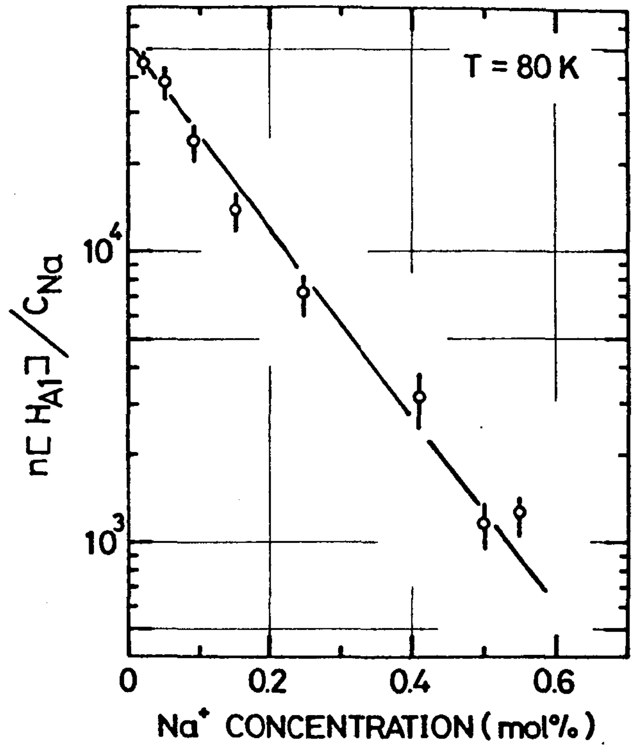

Fig.4.3.14. Plot of $n[H_{A1}]/C_{Na}$ vs. Na^+ concentration. The concentration of the H_{A1} center was estimated by the Smakula's equation.

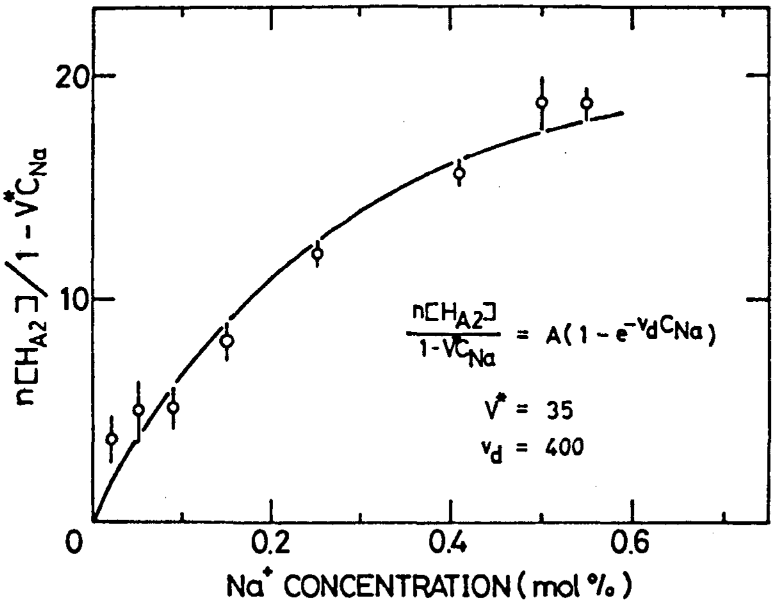

Fig.4.3.15. Plot of $n[H_{A2}]/(1 - V^*C_{Na})$ vs. Na^+ concentration. The ordinate is given in arbitrary unit. The solid curve is the best fit of the equation shown in the figure, with the values of parameters indicated. The value of 35 for V^* has been obtained in Chap.[3·4].

evaluated from the glow peaks.

Glow curves of KBr:Na crystals irradiated by γ ray at 77 K were measured. It has been confirmed that the thermal decay of the H_{A1} and H_{A2} centers accompany glow peaks at 102 K and 145 K, respectively (see Chap.[5.2]). The order of the kinetics of these glow peaks were confirmed to be unity for both cases, since the intensities of glow peaks decreased exponentially at constant temperatures.

The evaluated activation energies using several area methods16-20) are listed in Table 4.3.1, together with various parameters for these centers.

So far, the results for the thermal stability of the " V_1 center " in KBr crystals have been reported by several authors. Dutton and Maurer21) have evaluated the activation energy in Harshaw KBr* to be 0.23 eV from thermally stimulated conductivity(TSC) measurements. In their study, the TSC peak at 115 K was attributed to the thermal decay of the V_1 center. Saidoh and Itoh 5) have studied the annealing behaviour of the V_1 band in KBr:Na, and found that the maximum decay rate of the band occurs around 145 K with the activation energy of 0.30 eV. On the other hand, Ueta22) has obtained the value of 0.25 ± 0.02 eV for the V_1 center in " pure " KBr using pulse electron irradiation. One of the interesting facts in his study is that the V_1 center in a 0.3 % Na-doped KBr has a longer life time such as 26 μsec in contrast with 1.3 μsec in a " pure " crystal, though this was not discussed in detail there.

From experimental results obtained by the above mentioned several authors, together with the present results, one could see that the V_1 center is thermally more stable in the sample with considerable Na^+ doping concentration than in slightly doped (or nominally pure) ones. This

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*) It is supposed the the sample of "pure" KBr used in their study contained slight amount of Na^+ impurity, since the purity of the older crystals is not so good.

Table 4.3.1. Several properties of three centers responsible for the V_1 band in KBr:Na.

	decay temperature* (K)	trap depth** (eV)	peak energy (eV)	halfwidth (eV)	dichroism at 80 K
H_{A1}	102	0.23 ± 0.02	2.92 3.28	0.45 0.30	—
H_{A2}	140	0.27 ± 0.03	3.05	0.52	—
V(410)	170	0.3	3.02	0.43	<100>

*) This is defined here as the temperature which gives the maximum decay rate in isochronal pulse annealing curve.

**) The value was obtained by the similar procedure as described in Chap.[3·2].

may be attributed to the existence of two components in V_1 band, the H_{A1} and H_{A2} centers: The H_{A1} center with lower thermal stability is dominant in slightly doped KBr crystals, whereas the H_{A2} center is dominant in considerably doped ones.

There are some differences between the annealing behaviours of the H center and H_A centers. The H center decays at distinct two stages in KBr: the first stage is due to the recombination of a correlated F - H pair, whereas the second stage is due to the free migration of an H center, which is accompanied with the growth of the V_4 center.[23)] On the other hand, the H_{A1} center and the H_{A2} center can convert into the V_4 centers as well as recombine with the F center during their thermal decay in the same stage. This indicates that thermal decay of both H_{A1} and H_{A2} centers results directly in the free migration of Br_i^o. The thermal decay of these complex centers may involve following two processes; one is the separation of a Br_i^o from a Na^+- ion site and the other is the migration of freed Br_i^o. The difference of 0.04 eV in activation energy of two centers may have the origin in the former process. The fact that the H_{A2} center has higher thermal stability indicates that the association energy of a Br_i^o with a Na^+ ion in the H_{A2} center is larger than in the H_{A1} center.

(3·4) Discussions on interaction parameters

Above results and discussions have revealed that the the different modes of motions of interstitial bromine atoms results in the formation of the H_A centers with different configurations: The replacement collision sequence of Br_i^o interacts with a Na^+ ion to form the H_{A2}, or $(H_A)_d$, center and thermally migrating H centers result in the formation of the H_{A1}, or $(H_A)_t$, center through the interaction with a Na^+ ion, respectively.

The formation yield of the H_{A2} center depends on the Na^+ concentration with the function of eq.(4.3.6). The interpretation of the term of ($1 - V^{*}C_{Na}$) in the equation has been given in Chap.[3.4]. The problem is now the physical meanings of the term of ($1 - \exp(-v_d C_{Na})$) in eq.(4.3.6). This factor represents the formation efficiency of the (H_A)$_d$ center as shown in Fig.4.3.4.

The replacement collision sequence of Br_i^{o} has been extensively studied by Itoh and his coworkers.24) It has been proposed that the path-length of the sequence, L, can be expressed as

$$L(T) = L_o + L_1 \exp(-E_d/kT) \qquad (4.1.1)$$

where E_d is an activation energy and L_o and L_1 are constants. It has also been pointed out that the collision sequence is likely to be one-dimensional along a <110> direction.25) The formation process of the (H_A)$_d$ center thus concerns the interaction of a " test particle " moving one-dimenionally with " target particles (Na^+ ions) " in the lattice.

This process is considered to be essentially the same as a simple problem of analytical thermodynamics,26) where the probability, w(x), that a test particle will travel a distance x without collisions with targets is given by

$$w(x) = \exp(-N\sigma x) \qquad (4.3.7)$$

where N is the concentration of a target particle and σ is the collision cross section of a target with a test particle. If σ is considered to be a capture cross section, the probablility that a test particle is captured by targets is then ($1 - w(x)$).

Application of these formulas to the interaction of replacement sequence with Na^+ ions may not be unreasonable. Then N, σ, and x may correspond to the concentration of Na^+ ions, C_{Na}, interaction cross section of a Na^+ ion with a Br_i^{o}, and the pass length of the replacement sequence, respectively. Thus the term of ($1 - \exp(-v_d C_{Na})$) in eq.(4.3.6) is deduced, when $v_d = \sigma L$.

The value of v_d at 80 K is about two times larger than that at 6 K, which indicates that the collision sequence is tend to be easily trapped by a Na^+ ion at higher temperature. This increase in formation yield of the H_A center with increasing temperature has been discussed by several authors, and has been attributed to some different mechanisms.[24,27,28]

It is also considered that the increase has close correlation of the temperature dependecne of the formation yield of the Frenkel pairs;[24] the yield increases with increasing temperature above 100 K.[12] Two models based on experimental studies has been proposed to explain the increase of the F center formation yield. Itoh et al.[24] have attributed the increase to the thermally induced increase of path-length of the collision sequence which has temperature dependence of a formula shown in eq.(4.1.1). On the other ahnd, Sonder[29] have proposed a model where the efficiency of putting interstitial atoms into the lattice sites increases owing to the thermally induced increase in escape probability of X_i^o from the F center.

Present results and analysis for the formation yield of the $(H_A)_d$ center clearly show that the path-length, L, is in fact temperature-dependent and increases with increasing temperature, since the the interaction cross section, σ, is considered to hardly depend on temperature. Therefore, the present results support the Itoh's model for the temperature dependence of the formation yield of the F center.

However, other models on this phenomena[27,28] may be applicable at present. It is interesting to note that present data of v_d at 80 K is rather smaller than that of corresponding parameter obtained by Saidoh et al. by means of pulse radiolysis technique,[24] though the value at 6 K is essentially the same. The results may give some hints for clearer understanding of the behaviour of the temperature dependence of the replacement collision sequence of Br_i^o.

The formation yield of the H_{A1} center, or $(H_A)_t$ center depends on C_{Na} obeying eq.(4.3.3). The value of v_t

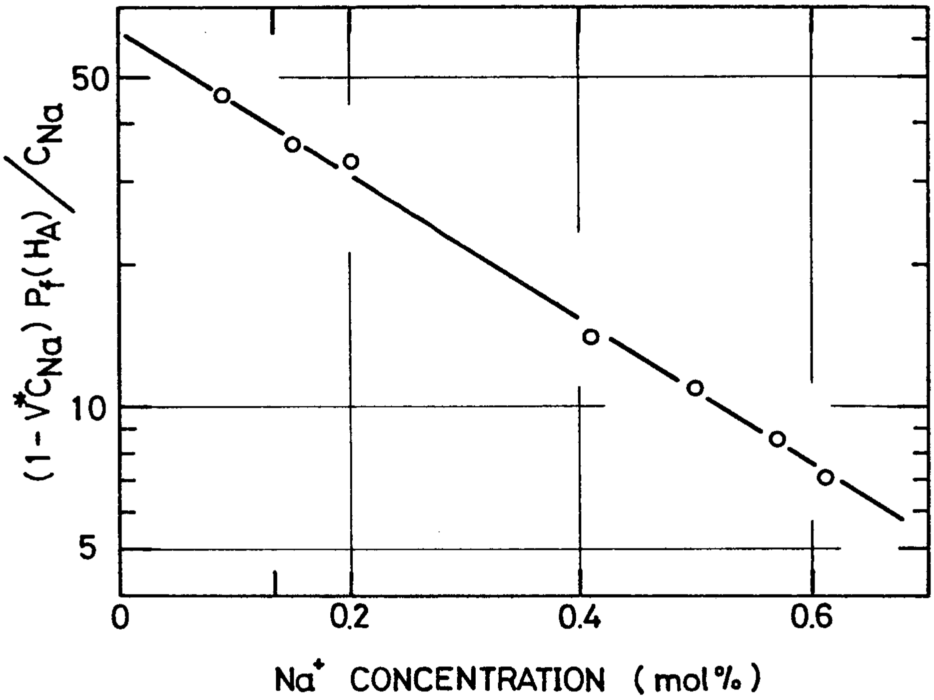

Fig.4.3.16. Na^+ concentration dependence of $P_f(H_A)$ in KBr:Na. This result indicates that $P_f(H_A)$ is adequately expressed by eq.(4.3.8). The straight line gives the value of 300 for v_a.

for the H_{A1} center produced by irradiation at 80 K, $v_t(80)$, is again larger than that, $v_t(6)$, of the (H_A)$_t$ center formed by thermal annealing after irradiation at 6 K. The difference between $v_t(80)$ and $v_t(6)$ is about the same as the difference between $v_d(80)$ and $v_d(6)$. This suggests that the v_t involves thermally induced increase in v_d. The differences between v_d and v_t at 6 and 80 K are about the same each other.

Taking into account these results, formation-probability of the (H_A)$_t$ cetner, defined in eq.(4.3.2) should have following form;

$$P_f(H_A) = D\, C_{Na} \exp(-v_a C_{Na})/(1-V^* C_{Na}), \qquad (4.3.8)$$

where D and v_a are constants, and it is expected that $v_a = v_t - v_d$.

Since $n[H]$ and $n[(H_A)_t]$ have been obtained experimentally for the irradiated samples at 6 K, $P_f(H_A)$ can be obtained, based on the results shown in Figs.4.3.2 and 12.

In Fig.4.3.16, C_{Na} dependence of $P_f(H_A)$ of the form of eq.(4.3.8) was examined. It is seen from the figure that eq.-(4.3.8) is adequate to represent the dependence of $P_f(H_A)$. The straight line in the figure gives a value of v_a of 300, which is very close to the difference between v_t and v_d, as expected.

The reason why $P_f(H_A)$ is expresses by eq.(4.3.8) was not cleared here. The complicated dependence of $P_f(H_A)$ on C_{Na} may suggest that the interaction of thermally migrating H centers with Na^+ ions to form (H_A)$_t$ center is a complicated process.

(3·4) Elastic interactions of H centers with different modes of motions with Na^+ ions

The most important result obtained in this study may be that the different types of motions of Br_i^0 result in the center consisting of an H center and a Na^+ ion with different configurations.

The nature of the interaction of the H center with an imperfections is considered to be elastic interaction, since the H center is essentially the neutral atom.

Dick[30)] has calculated the distortions introduced by Na^+ impurities in KBr. His results suggest that the 24 elementary cubes surrounding the unit cell with a Na^+ ion at its center could provide interstitial positions more stable than the normal ones. Therefore, more than one types of the H center stabilized by a Na^+ ion could be formed, though only one configuration of the H_A center has been established in KCl:Na crystals so far.

Shuey and Beyeler[31)] have obtained formulas by which the elestic interaction energy can be evaluated. Bachmann and Peisl [1)] have obtained the double force tensor of the H center in KBr, which describe the elastic interaction of defects. The tensor of a Na^+ ion in KBr has obtained by Saidoh, too.[32)]

Based on these results, the interaction energy of an H center with a Na^+ ion was calculated here. The results indicates that the interaction of the H center with an ion along <110> direction is attractive, whereas that along <001> is repulsive, respectively.

The main difference in the two types of motions of the H center, replacement collision sequence and thermal migration, may be that the former is an one-dimentional motion along a <110> direction, whereas the latter is a random-walk process with change its orientation. Therefore, in the interaction of collision sequence with a Na^+ ion only one mode of interaction along a <110> direction may be relevant. On the contrary, both modes of interactions may become important in the case of thermally migrating H centers.

From these results and discussions, together with the result of Dick, it may not be impossible that the different modes of motions on the interstitial halogen atom result in the formations of the H_A centers with different configurations through the elastic interactions with a Na^+ ion.

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[4·4]

THE H CENTER INTERACTION WITH A Rb^+ ION DURING IRRADIATION AND THERMAL ANNEALING IN KBr:Rb CRYSTALS

The role of Rb^+ ion on defect formation process has been studied in KBr crystals. The impurity ion suppresses the colorability by x-ray irradiation at 6 K. The H center trapped by a Rb^+ ion is formed only during thermal migration of the H center. The $H_A(Rb^+)$ center has an absorption band at 3.16 eV and decays thermally at 55 K, obeying the second order rate equation with an activation energy of 0.102 ± 0.005 eV. The elastic interaction energy between the H center and a Rb^+ ion has been calculated. Based on these calculated results, the interaction of the H center with a Rb^+ ion during dynamical motion and thermal migration has been discussed to clear the origin of the suppression of colorability at 6 K and the formation of the $H_A(Rb^+)$ center.

§1 Introductory Remarks

In this chapter, the role of the alkali impurity ion which has larger ionic radius than that of host cation on defect formation process is studied.

The secondary reactions of primary interstitials created by dissociation of an exciton is important to understand the defect formation mechanism at temperatures where the primary interstitials are not stable thermally: The interactions of these interstitials with other imperfections to form variety of complex interstitial centers are the dominant reactions at the temperatures.$^{1)}$

Two different modes of motions of interstitial halogen atom, X_i°, can be distinguished; one is the replacement collision sequence, which is the dynamical motions along a given ⟨110⟩ durection, and the other is the thermal migration of the H center which is considered to be a random walk process.[2] It has not been clear so far, whether the difference in modes of motions of the X_i° results in some differences in the interaction of it with other imperfections, or not.

Many works have been made on the role of the alkali impurities which have smaller ionic radius than that of host cation on the defect formation process, or on the interaction of these impurities with H and I centers.[3-7] It is now well known that these impurities stabilizes H and I centers to form H_A and I_A centers, which in most cases results in the enhancement of F and α center production at about 80 K.[4]

However, little works has been done on the role of the alkali impurity ions with larger ionic radii than those of host cations. The reason of this situation is that such a type of impurity is considered to give little effects on defect formation process. Giuliani has shown that the Rb^+ ion in KBr does not affect the production efficiency of F and F^+ centers and that the ion does not cause any V_1- and I- type bands at 80 K.[4] Following two reports, however, suggest that this type of impurity affects formation rate of color centers and that it can interact attractively with the H center. Still and Pooley have shown that the formation yield of the F center in KCl is suppressed by Rb^+ ion at 5 K.[8] Dakss and Mieher have found that the H_A center associated with a Na^+ ion in LiF, and that this $H_A(Na^+)$ center is thermally more stable than the H center.[9]

Thus the knowledge of such types of impurity on defect formation has been limited and it has not been known well. In order to make clear the role of alkali impurity which has larger ionic radius than that of host cations on the defect formation, or on the interaction with the H center, the colorability at 6 K and the annealing behaviours of F and H centers were studied in KBr:Rb system in this chapter.

§2 Experimental Results

In order to see the effects of Rb^+ ion on the defect formation at 6 K, the formation yields of color centers by x-ray irradiation were first obtained as a function of Rb^+ concnetration. Fig.4.4.1 shows the results for F and H centers. The formation yield of pure KBr crystals is normalized to unity. It is seen that the yields decreases linearly with increasing Rb^+ concnetration. It was observed that the peak heights of I and α bands are also decreased and no supplementary absorption bands were observed in all KBr:Rb crystals used here.

The x-ray excited emission spectrum were also measured. The emission band corresponding to π_A emission band which is seen in the case of KBr containing Na^+ or Li^+ was not observed. The emission intensity of intrinsic σ- or π-emission band is constant irrespective of Rb^+ concnetration. This result suggest that the suppression of the colorability by Rb^+ ion in KBr has different origin from that in KBr:Na -type system.

Fig.4.4.2 shows the annealing curve of F bands in pure KBr and in a KBr:Rb(1.0 mol%). For comparison, the decrements of the F band after warming irradiated sample up to 70 K with a constant heating rate of 2.4 deg/min are normalized to unity for both samples. It is clear that the annealing behaviour of the F band is strongly affected by Rb^+ ion; the main annealing stages in pure KBr are first and second atages at 29 and at 41 K, respectively, whereas that in a KBr:Rb is the third stages(47 - 65 K) which is scarcely observed in pure KBr.

The results indicate that the thermal decay of interstitial bromine atom centers to annihilate F centers through recombination takes place mainly at 47 - 65 K instead of below 50 K in KBr containing Rb^+ ions.

In order to know the origin of the third annealing stage of the F center in KBr:Rb crystals, the measurements were made on the change induced by warming up the irradiated crystal in absorption spectrum at the H band region. In

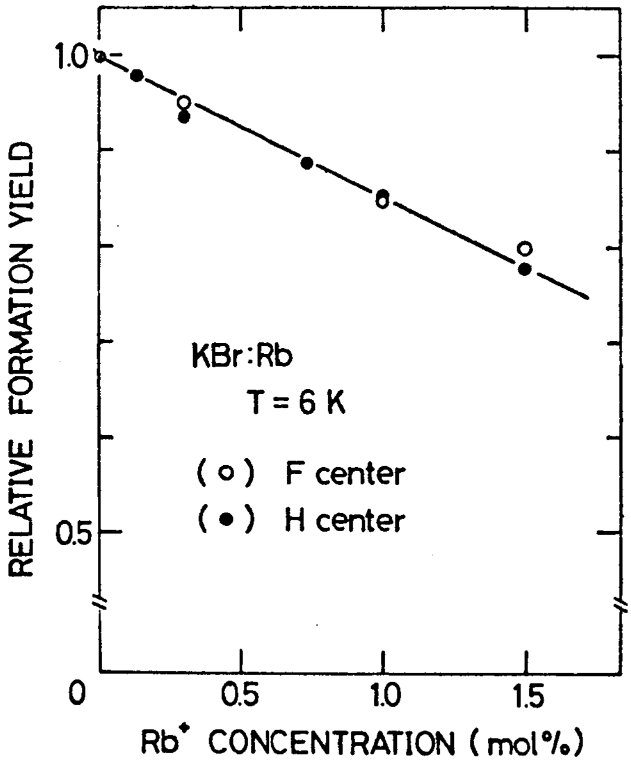

Fig.4.4.1. Relative formation yields of the H and F centers in KBr:Rb crystals as functions of Rb^+ concentration. Samples were irradiated by x ray for 10 and 40 min for measurements of the yields of F and H centers, respectively.

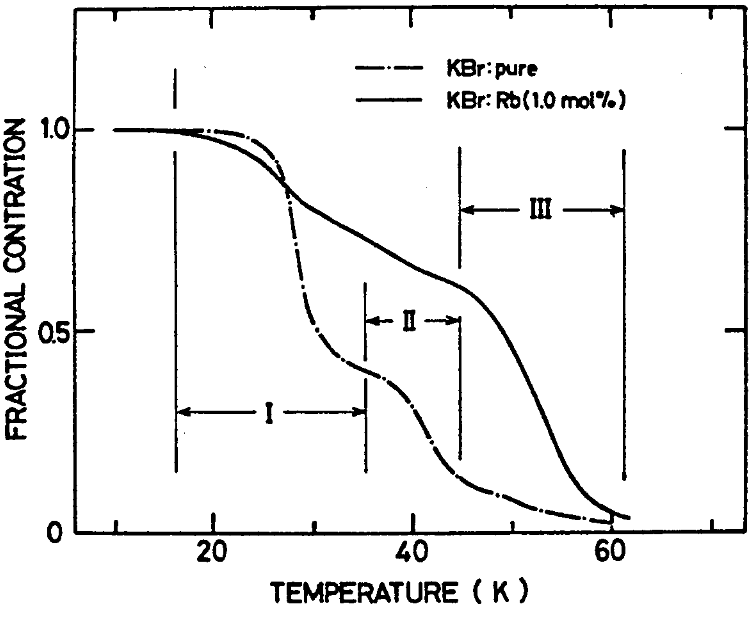

Fig.4.4.2. Isochronal annealing curves of the F center in pure KBr and KBr:Rb(1.0 mol%). Heating rate is 2.4 deg/min. The decrements of the F center due to warming irradiated specimens up to 70 K are normalized to unity for both cases

In Fig.4.4.3, the shapes of the absorption bands induced by x-ray irradiation at 6 K in pure KBr(open circle) and in a KBr:Rb(cross) are compared. No differences were observed. The shape of the band can be well represented by a Gaussian whose peak energy and a halfwidth are 3.25 and 0.47 eV, respectively. These values of parameters are essentially the same as obtained previously.$^{10)}$ This result suggests that no other components are involved in the H-band region in a KBr:Rb(1.5 mol%) as well as a pure KBr.

The broken and chain lines in Fig.4.4.3, respectively show the absorption spectrum of a pure KBr and a KBr:Rb(1.5 mol%) both of which were warmed up to 40 K after x-ray irradiation at 6 K and again cooled down to 6 K. The peak heights of these bands are relative to those of initial H bands in these crystals. Presence of Rb^+ ions causes following changes in spectrum after thermal treatment;

1) the peak height of the surviving band relative to that of the H band becomes higher, and
2) the peak position as well as shape of the absorption band varies.

The results indicate that the another H-like centers except the pure H center which decays thermally at the second stage is also responsible for the surviving absorption band in KBr containing Rb^+ ions.

The H band after thermal treatment in pure KBr is described by a Gaussian with peak energy and halfwidth of 3.24 and 0.56 eV, respectively. These values slightly change from those of the spectrum in as irradiated crystal. Assuming that the one component is the same in shape as this H band, the surviving absorption band of the KBr:Rb(1.5 mol%) can be divided into two Gaussians as shown in Fig.4.4.4. The new component has the peak energy and halfwidth of 3.16 and 0.47 eV, respectively. This band is tentatively called the $H_A(Rb^+)$ band.

Such a division was applicable for the absorption bands after the similar thermal treatments in all KBr:Rb crystals

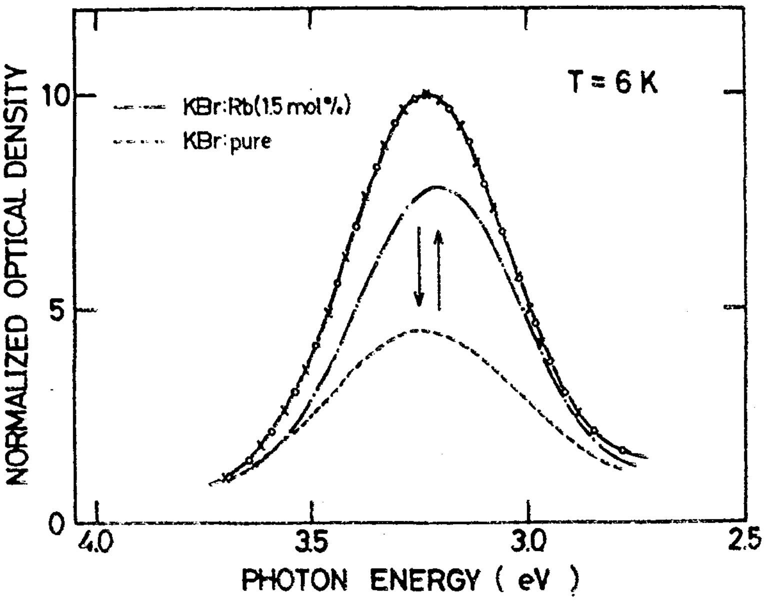

Fig.4.4.3. Optical absorption spectra of the H-band region in KBr crystals. Open circle and cross represent the spectra after x-irradiation at 6 K in pure KBr and in KBr:Rb(1.5 mol%), respectively. The heights of absorption peaks are normalized to unity at 3.25 eV of photon energy. The chain and broken lines are the spectra in samples which were warmed up to 40 K after x-rayed at 6 K. All measurements were made at 6 K.

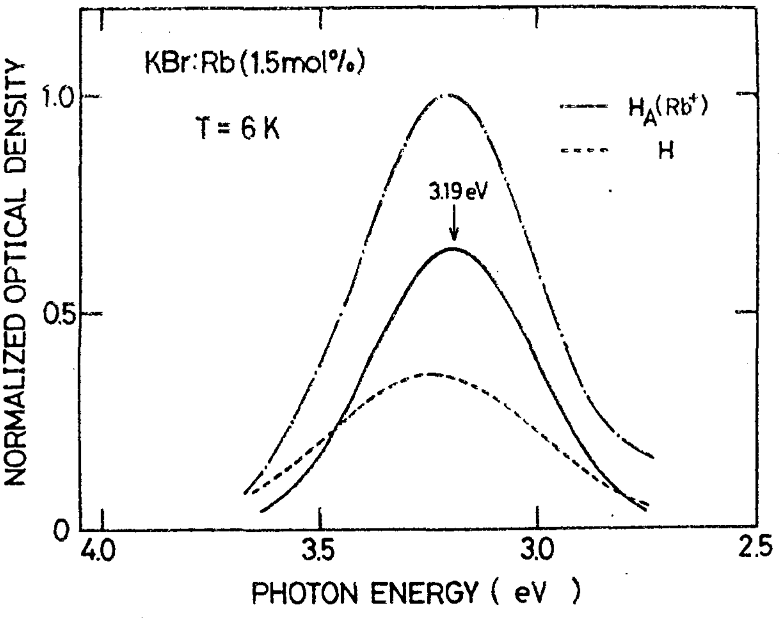

Fig.4.4.4. Optical absorption spectra at the H-band region in KBr:Rb (1.5 mol%) which was warmed up to 40 K after x-rayed at 6 K, and the resolved absorption peaks of Gaussians in Shapes. Measurement was made at 6 K.

used in this study. The ratio of thus obtained peak heights of the $H_A(Rb^+)$ band to those of the initially formed H bands, the formation efficiency of the $H_A(Rb^+)$ band by thermal treatment, is plotted against the Rb^+ content in Fig.4.4.5. One can see that the ratio increases with increasing Rb^+ concentration. Therefore, it is clear that the absorption band peaking at 3.16 eV is related to Rb^+ impurity ions.

In the figure, the ratio of the decrements of the F center by warming an irradiated crystal at 6 K up to 40 K to the initial F center concentration, the annihilation efficiency of the F center, is also plotted. The ratio decreases with increasing Rb^+ concnetration. The complementary behaviour of the formation efficiency of the $H_A(Rb^+)$ band to that of the annihilation efficiency of the F center indicates that the 3.16-eV absorption band is closely related with H center.

It is evident from results shown in Fig.4.4.5 that the H center which should recombine with F centers to annihilate them in pure KBr when samples were warmed up to 40 K, servives in the form of thermally more stable defects which is responsible for the 3.16 eV absorption band in KBr containing Rb^+ ions.

3 DISCUSSIONS

We can deduce the conclusion, based on the results obtained above, that the 3.16 eV absorption band is due to the $H_A(Rb^+)$ center, or the H center trapped by a Rb^+ ion in KBr.

The results that the shape of absorption band at the H band region in a KBr:Rb crystal irradiated by x ray at 6 K is the same as that in pure KBr suggests that the $H_A(Rb^+)$ center is not formed during irradiation at 6 K, and that the center is formed only in the thermal annealing process of irradiated crystals. First, the mechanism of formation of the $H_A(Rb^+)$ center is discussed in terms of elastic interaction between the H center and a Rb^+ ion.

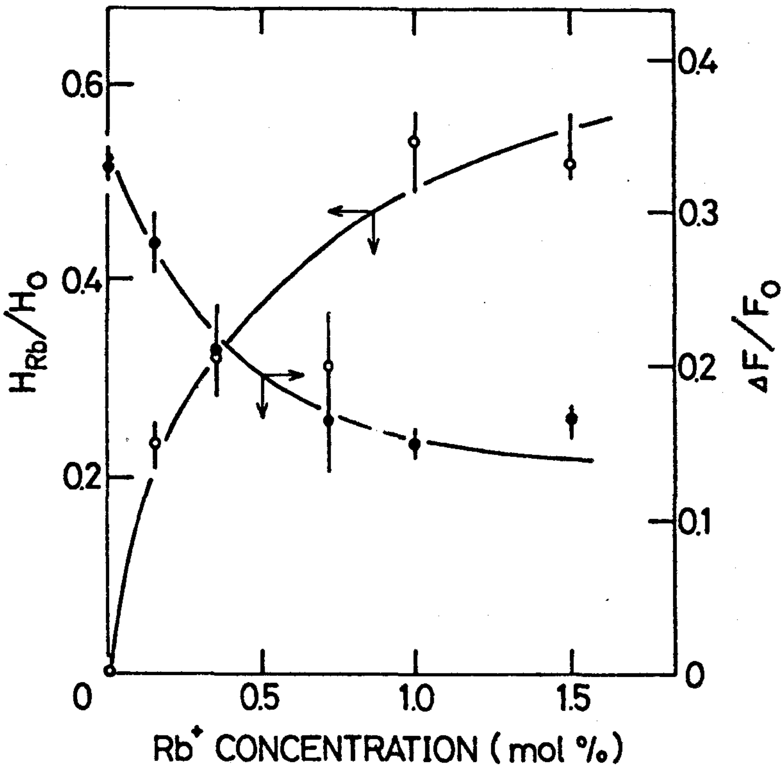

Fig.4.4.5. Rb$^+$-concentration dependence of the formation efficiency of the $H_A(Rb^+)$ center during thermal annelaing, (●), and of the annihilation efficiency of the F center, (o), respectively. These quantities are defined in the text.

(3·1) The formation of the $H_A(Rb^+)$ center

The main mode of motions of the interstitial halogen atom during irradiation at 6 K is considered to be the dynamical replacement collision sequence. 2) Since the range of the collision sequence may not be very large, only a small percentages of the interstitials will interact with other imperfections. Saidoh and Itoh have shown that the interaction of replacement collision sequence and a Na^+ ion in KBr at about 10 K takes place within the characteristic interaction volume of 150 v_o, where v_o is the ion-pair volume. 5) They have concluded that the interaction volume is the product of average range of replacement sequence, L, and the area of the interaction, S. Since the interaction between the collision sequence and a Na^+ ion is the elastic in nature, 6) the value of S may reflect mainly the distortion around the impurity. The degree of the distortion of nearest neighboring ions around a Rb^+ ion in KBr is about a half of that around a Na^+ ion, though the sign of the distortion is reverse.11) Therefore, it is not unplausible that the value of S for Rb^+ ions is about a half of that for Na^+ ions.

As a consequence of this conclusion, it can be deduced that about 50 % of created Br_i° with dynamical motions are in the " interaction volume " in the KBr crystals containing 1.0 mol % of Rb^+ ions.

If the interaction of the replacement collision sequence and Rb^+ ions is attractive, the considerable amount of the $H_A(Rb^+)$ center should be formed, which should result in the appreciable change in absorption spectrum in the H band region. Results shown in Fig.4.4.3 that no changes were observable in shape of the H band, therefore, indicate that the $H_A(Rb^+)$ center cannot be formed through the interaction of replacement sequence and a Rb^+ ion at 6 K, though the sequence is considered to have enough chances to encounter a Rb^+ ion.

Above results and considerations lead us to conclude that the attractive interaction between interstitial bromine and a Rb^+ ion in KBr to form the $H_A(Rb^+)$ center takes place only in the thermal-migration process of the H center.

In order to understand this interesting result, discussions are made below in terms of elastic interaction of the H center with a Rb^+ ion.

Shuey and Beyeler have obtained the interaction formula which makes it possible to calculate the elastic interaction energy between two defects with the double force tensor, P.12) The tensor of the H center in KBr has been obtained by Bachmann and Peisl, has the following form;13)

$$P = \begin{pmatrix} 7.9 & -0.7 & 0 \\ -0.7 & 7.9 & 0 \\ 0 & 0 & -4.4 \end{pmatrix} \text{X } 10^{-12} \text{ erg.} \qquad (4\cdot4\cdot1)$$

According to spherical-harmonic representation of Schuey and Beyeler, this Cartesian tensor of the H center is represented by following three components with non-zero values, P_s, P_0, and P_{2s}.

The tensor of Rb^+ ion which is substituted for Na^+ ion is isotropic, which allow to represent the tensor only by the scalor, P_s.

Then the equations to calculate the interaction energy between the H center and a Rb^+ ion along [001] and [110] orientations of the line of the centers become

$$E_{[001]} = \sqrt{\frac{3}{2}}\,\frac{P_0^H P_s^{Rb}}{4\ R^3}\left(\frac{4c_{11}-4c_{12}+13c_{44}}{K_3} + \frac{5}{3c_{11}+2c_{12}+4c_{44}}\right),$$

$$E_{[110]} = -\frac{1}{2}\left(E_{[001]}\right) + \frac{P_{2s}^H P_s^{Rb}}{\sqrt{2}\ 8\ R^3} \qquad (4\cdot4\cdot2)$$

$$\left(\frac{13c_{11}-13c_{12}+37c_{44}}{3K_5} + \frac{5}{3c_{11}+2c_{12}+4c_{44}}\right),$$

where c_{11}, c_{12} and c_{44} are elastic constants, R is the distance between two centers. The constants, K_3 and K_5 are abbreviations of following functions of elastic constants;

$$K_3=\frac{1}{25}[(47c_{11}+16c_{12}+74c_{44})(3c_{11}-c_{12}+c_{44}) -\frac{18}{7}(3c_{11}+4c_{12}+c_{44})^2],$$

$$K_5=\frac{1}{75}[(137c_{11}+52c_{12}+230c_{44})(c_{11}+c_{12}+5c_{44}) -\frac{6}{7}(8c_{11}+13c_{12}+5c_{44})^2].$$

The problem now concerns the value of double force tensor of a Rb^+ ion in KBr. It has been shown that the lattice constant changes linearly as a function of the concenteration in K - Rb system.[14] Therefore, the change in lattice constant due to 1 mol of Rb^+ ions in KBr, $\Delta a/a$, is given by

$$\frac{\Delta a}{a} = 4.5 \times 10^{-2}. \qquad (4\cdot4\cdot3)$$

Since P_s of the Rb^+ and $\Delta a/a$ are combined with following relation;

$$\frac{\Delta a}{a} = \left(\frac{a}{2}\right)^{-3}\frac{P_s}{2G}\frac{1-2\nu}{1-\nu}, \qquad (4\cdot4\cdot4)$$

where G and ν are shear modulus and Poisson ratio of the bulk crystal,[15] P_s can be calculated to be

$$P_s = 2.44 \times 10^{-13} \text{ erg}. \qquad (4\cdot4\cdot5)$$

Three types of orientations of the line of the centers can be resolved in the case of interaction between the H center and a Rb^+ ion, as seen in Fig.4.4.6. Substituting values of P_s^{Rb}, P_0^H, and P_{2s}^H into eq.(4·4·2), one can obtain following interaction energies for paticular directions;

$$\begin{aligned} E_{\langle 001\rangle} &= -\,0.022 / r^3 \text{ eV},\\ E_{\langle 110\rangle} &= +\,0.0082 / r^3 \text{ eV},\\ E_{\langle 1\bar{1}0\rangle} &= +\,0.014 / r^3 \text{ eV}, \end{aligned} \qquad (4\cdot4\cdot6)$$

where $r = R/(a/2)$.

These results indicate that the interaction of the H center with a Rb^+ ion along [110] direction is repulsive, and that along [001] is fairly attractive.

Based on the results of anisotropic property of the

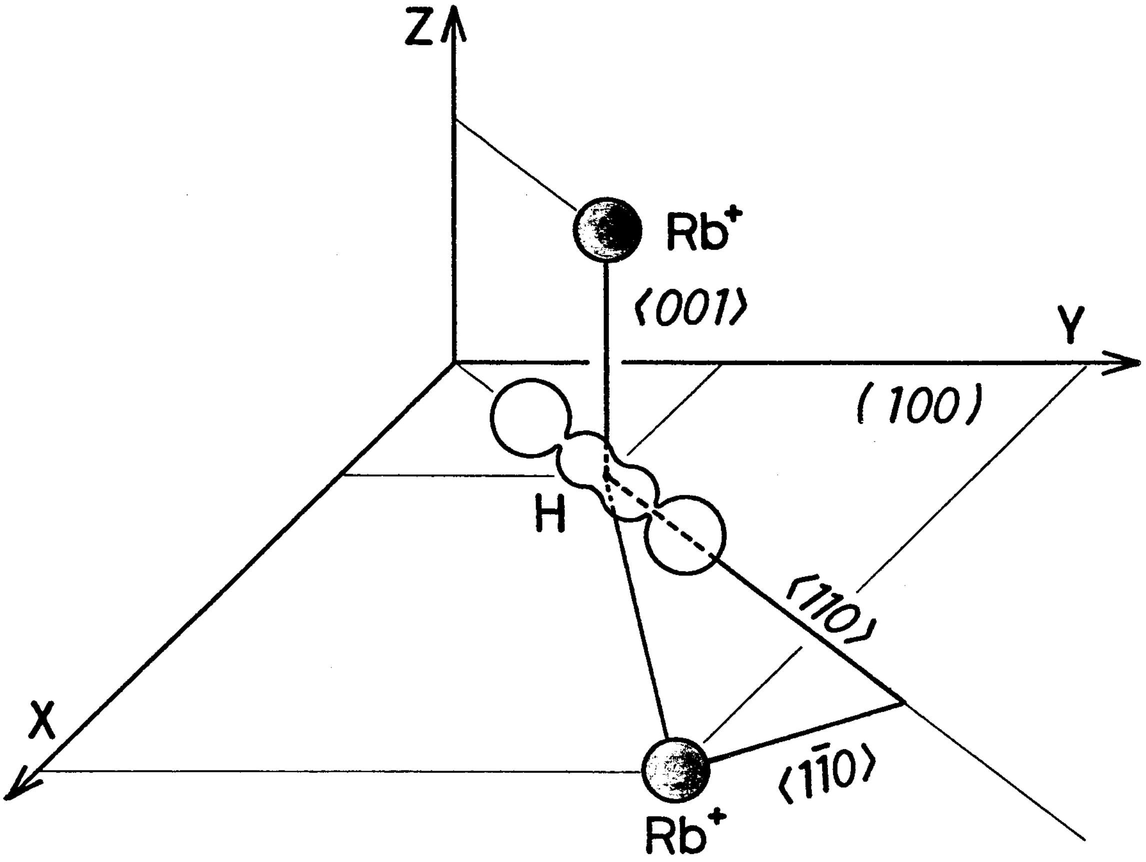

Fig.4.4.6. Schematic representation of the interaction between the H center and a Rb$^+$ ion. Three different orientations in the interaction, <110>-, <1$\bar{1}$0>-, and <001> - modes, are possible.

interaction, the experimental results that the $H_A(Rb^+)$ center is formed only in the thermal migration process of the H center can be explained as follows.

In the interaction of the interstitial bromine atom in the form of replacement sequence with a Rb^+ ion, the main mode of interactions should take place along a given $\langle 110 \rangle$ direction, since the motion of the interstitial atom is considered to be restricted to one dimentional along the $\langle 110 \rangle$ direction. In such a case, the interaction is always repulsive. Therefore, approach of the crowdion toward a Rb^+ ion may be interrupted by the repulsive force, and it cannot arrive at a Rb^+-ion site to form the $H_A(Rb^+)$ center. On the other hand, the thermal migration of the H center is considered to be sequence of random walk. In this mode of motion, the interaction along $\langle 001 \rangle$ direction may become also aveilable. Since the $\langle 001 \rangle$ mode of the interaction is fairly attractive as shown before, the $H_A(Rb^+)$ center could be formed during the thermal migration of the H center.

Thus, one can conclude that the anisotropic property in the elastic interaction between the H center and a Rb^+ ion plays the essential role in the formation of the $H_A(Rb^+)$ center in KBr.

(3·2) The association energy of the H center with a Rb^+ ion and the configuration of the $H_A(Rb^+)$ center in KBr

Here the thermal stability of the $H_A(Rb^+)$ center, or the association energy of the H center with a Rb^+ ion is discussed.

The isochronal annealing curve of the F center shown in Fig.4.4.2 makes it possible to determine the activation energy for the disappearance of the interstitial centers, assuming a simple rate equation;

$$- \left(\frac{dn}{dT} \right) = n^x \left(\frac{s}{\beta} \right) \exp(- E/kT), \qquad (4\cdot4\cdot7)$$

where n is the concentration of the interstitial centers,

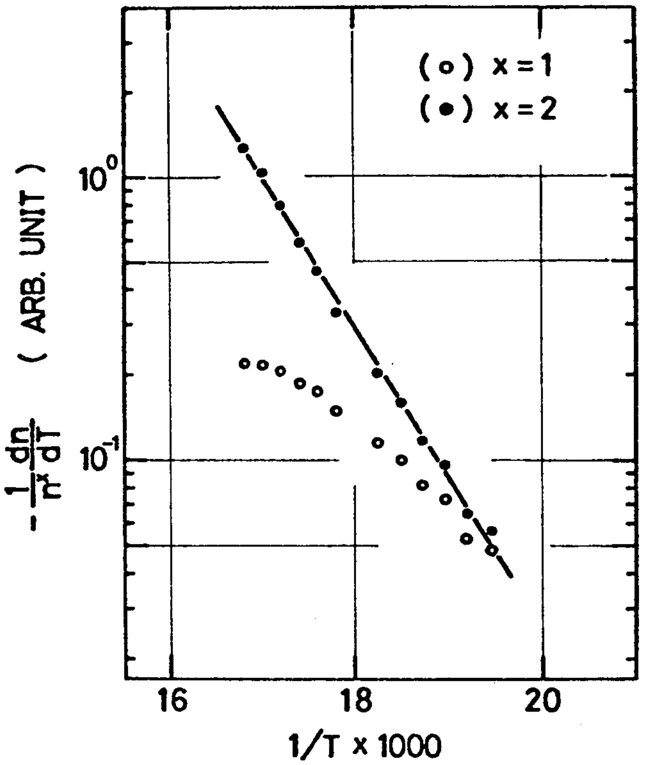

Fig.4.4.7. Plot of (-dn/dT)/n^x vs. 1/T of third annealing stage of the F center in KBr:Rb(1.0 mol%). The straight line in the figure gives the value of 0.102 eV for the activation energy.

x the order of reaction, s the frequency factor, β the heating rate, and T the temperature, respectively. The energies for the first and second annealing stages in pure KBr have been obtained by Saidoh and Itoh to be 0.06 and 0.12 eV, respectively.[16)] They have attributed these energies to the energy for recombination between correlated F - H pair and to the thermal-migration energy of the H center, respectively.

The similar analysis was made for the stages in pure KBr, based on the present data. It was confirmed that the order of reaction for the first stage or the second stage is first or second order, as concluded by Saidoh and Itoh. The values of activation energies are, however, 0.042 and 0.085 ± 0.005 eV for the first and second stages, respectively. These are somewhat less than those obtained by Saidoh and Itoh. The value for the second stage is, however, the same as that of migration energy of the H center obtained by Ueta,[17)] within the experimental error.

Fig.4.4.7 shows the plot of $(-dn/dT)/n^x$ v.s. $1/T$, for the third stage of a KBr:Rb(1.0 mol%). One can see that the third stage corresponds to the second order reaction, similarly as the second stage of pure KBr. The activation energy obtained from the result is 0.102 eV.

The difference between activation energies for second stage and for third stage, 0.017 eV, may give the association energy of the H center with a Rb^+ ion.

The interaction energy between the H center and a Rb^+ ion can be calculated by the elastic theory described above. The most favorable configuration in the one where the connection line between the defects is along $\langle 001 \rangle$ and where the molecular axis of the H center is parallel to $\langle 110 \rangle$, and a Rb^+ ion is situated at the nearest neighbor site of Br_2^- of the H center. In this case, since $R = a/2$, the interaction energy becomes 0.022 eV, which is roughly equal to that obtained experimentally.

It should be noted that this configuration of the $H_A(Rb^+)$ center, which is most favorable, is the same as that of H_A center associated with a Na^+ ion in LiF which has been found by Dakss and Mieher.9) shown in Fig.4.1.4.

From above results and discussions, one can conclude that the alkali impurity ion which has larger ionic radius than that of host cation can stabilize the H center, and ions with smaller ionic radius do, though the configurations of the complex centers are considered to be different from each other.

(3·3) Suppression of colorability by Rb^+ ions at 6 K

As seen in Fig.4.4.1, the formation yield of the F center as well as the H center is suppressed by Rb^+ impurity ions. The mechanism of the suppression in this case may be different from that in KBr containing alkali impurity with smaller ionic radius(or higher first ionization potential) than that of the host cation. In the latter, the selective interaction of the impurity ion with the exciton of the state responsible for the F - H pair formation to form ($V_K e$ $)_A$ is the main origin of the suppression of colorability, as discussed elsewhere.18)

However, as mentioned above, no supplementary emission bands were observed in KBr:Rb crystals upon the x-ray excitation at 6 K, which may indicate that the exciton trapped by a Rb^+ ion is not formable.

Possible mechanism of the suppression of colorability by Rb^+ ion is the interruption of the ion to the replacement collision sequence, which has been considered in KCl:Rb and in KBr:I systems.8,19)

Still and Pooley have attributed the decrease in F center formation efficiency in KBr:Rb at 5 K to the kinetic energy loss of replacement collision sequence of interstitial halogen ions owing to the deflection of the direction at the ' K - Rb lens '. It has now been cleared that the collision sequence of atom is important in KBr and KCl crystals.20) Therefore, some reconsideration may be needed for the availability of their model at present.

Here another mechanism is proposed; it is based on the repulsive elastic interaction between the dynamic crowdion and a Rb^+ ion discussed above.

In KBr:Rb crystals, it appears that a force is acting on the H center to prevent it from separating from the initial position where an F center is formed. In Fig.4.4.2, one can see that the first annealing stage of the F center begins relatively lower temperature in KBr:Rb crystals than in pure KBr. This stage is considered to be due to the recombination between correlated F - H pairs, whose configurations may be the one where the connection line between F and H centers is along ⟨110⟩ and where the molecular axis of the H center is parallel to ⟨110⟩.* The fact that the recombination of such pairs takes place at relatively low temperature in KBr:Rb crystals may indicate that a force is active on the H center to reflect it back more easily to its initial position. It may not be unplausibe to think that the force is originated from the repulsive elastic interaction of the H cneter with a Rb^+ ion along ⟨110⟩ direction.

When the repulsive potential is effective, the replacement collision sequence starting from its original vacancy cannot separate enough to form stable F - H pair, which results in the decrease in the formation yield of the F center after x-ray irradiation at 6 K.

We can obtain experimentally the interaction volume within which a Rb^+ ion reflect back the replacement collision sequence to annihilate the created F - H pair. In the process of dynamical motion of the H center along a given ⟨110⟩ direction, the probability that the interstitial bromine atom will travel a distance, L, without "collision" with Rb^+ ions, is considered to be given by $\exp(-L\sigma C_{Rb})$, where σ is the effective cross-section of Rb^+ ion to

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*) Though this configuration is repulsive in elastic interaction, another interactions, such as electric one, may make it somewhat attractive.13)

reflect the interstitials back. This exponential term may, therefore, represent the formation efficiency of F and H centers in KBr:Rb crystals.

Since the product of L and σ, which is the present interaction volume, is considered to be small, the exponential term can be expanded into $(1 - L\sigma C_{Rb})$. The result shown in Fig.4.4.1 indicates that such a relation is the case, and gives the value of $L\sigma$ of 15 v_o.

Saidoh and Itoh have concluded that the L is about $7 \times \sqrt{2}a/2$ along a $\langle 110 \rangle$ direction.[21)] Then σ is about $(\sqrt{3}a/2)^2$. This value of σ can be interpreted as follows: The replacement collision sequence could be reflected back when a Rb^+ ion is situated at nearest neighbor cation sites enclosing the $\langle 110 \rangle$ halogen lines where the collision sequence take place. It is sure that the component of repulsive potential of elastic interaction, $E_{\langle 110 \rangle}$ is most effective in such cases.

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5

DEFECT ANNIHILATION AND INTRINSIC TERMOLUMINESCENCE

[5·1]

INTRODUCTION

Patterns of stored-energy release are briefly discussed. Main attention is focused on the present problem of thermoluminescence mechanism in pure crystals. The term " intrinsic thermoluminescence "is newly defined, which appropriately describes the luminescenct phenomena concerned. An overall plan of the contents in this part is briefly sketched.

§1 Release of stored energy

Defects produced by irradiation store a part of radiation energy in the form of lattice energy in the crystals. Radiation-induced defects in pure crystals are essentially Frenkel defects of a variety of configurations. The energy a given type of Frenkel pair possesses, the formation energy, should be different each other, depending on the configurations. It is also sure that the thermal stability of a pair of particular formis not the same as that of a pair of different configuration. Thus the release of stored energy due to the annihilation of defects takes place, in general, at steps, when irradiated crystals are warmed to temperatures greater than the radiation temperature.

In the case of solids having a band gap, the annihilation of defects due to recombination results in the release of stored energy in the forms of light and of heat, corresponding to the radiative and non-radiative transitions which originate from the recombination events.

Figures 5.1.1 and 5.1.2 show typical examples of the release of stored energy in alkali halide crystals. The former is the results of measurement of "stored energy"(in a narrow sense) by a differential-heat-flux calorimeter for KCl after reactor irradiation.1) Figure 5.1.2 (Top)

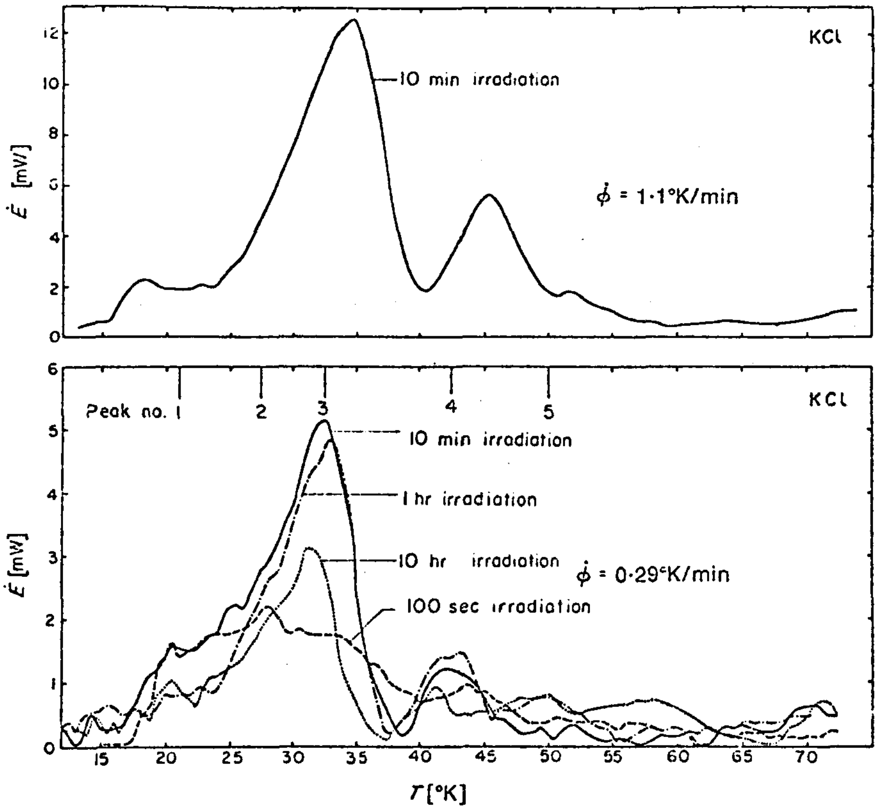

Fig.5.1.1. Time rate of release of stored energy, $\dot{E}$, of KCl as a function of temperature during a linear rise of temperature after reactor irradiation at 4.6 K. (from ref.1).

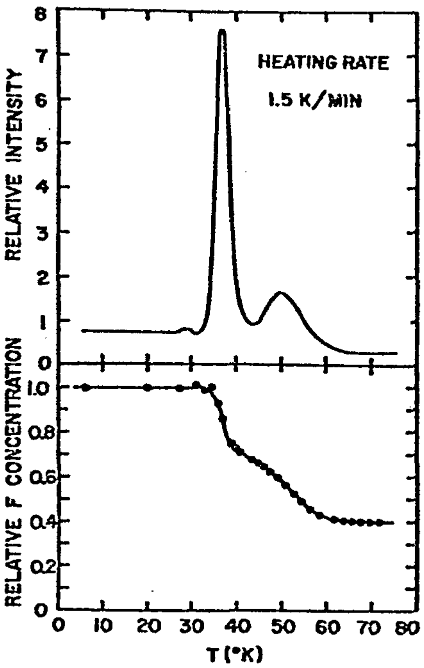

Fig.5.1.2. Thermoluminescence glow curve (Top) and relative F-center concentration (Bottom) of KCl after x-irradiation at 7 K. Heating rate is 1.5 deg/min. (from ref.2).

shows the thermoluminescence glow curve of x-ray irradiated KCl crystals.[2)]

One can see the similar behaviour for two forms in energy release, which is considered to be originated from the defect annihilation shown in the bottom of Fig.5.1.2.

Radiolysis in alkali halides is a process of energy conversion from electronic-excitation energy to the lattice energy. Then special interest here concerns the thermoluminescence, or the release of stored energy in the form of luminescence, since this phenomenon involves the reverse property to radiolysis, and is the process of energy conversion from lattice energy into the electronic-excitation energy which results in the radiation.

§2 Intrinsic thermoluminescence

Thermoluminescence in alkali halides has been studied by many workers for a long time, partly to gather information about the reactions of the radiation-produced defects,[3,4)] and partly to develop a dosimeter.[5)] But few works has been performed under the aim to make the intrinsic mechanism of thermoluminescence clear in pure materials.

Mattern et al.[6)] have studied the thermoluminescence in KCl:Tl phospher using their excellent method. Figure 5.1.3 shows a three dimensional plot of the thermoluminescence, which was obtained by simultaneous intensity and spectral distribution measurements. It can be seen that the most fraction of the emission band is a broad band which peaks at about 3050 Å.

This emission band, as they have shown in terms of classical configuration-coordinate diagram (Fig.5.1.4), corresponds to the well known emission of Tl^+ ion substituted at cation site in KCl.

The mechanism of thermoluminescence in " activated " alkali halides is, therefore, rather simple, since the main radiation effect is essentially the electronic process and

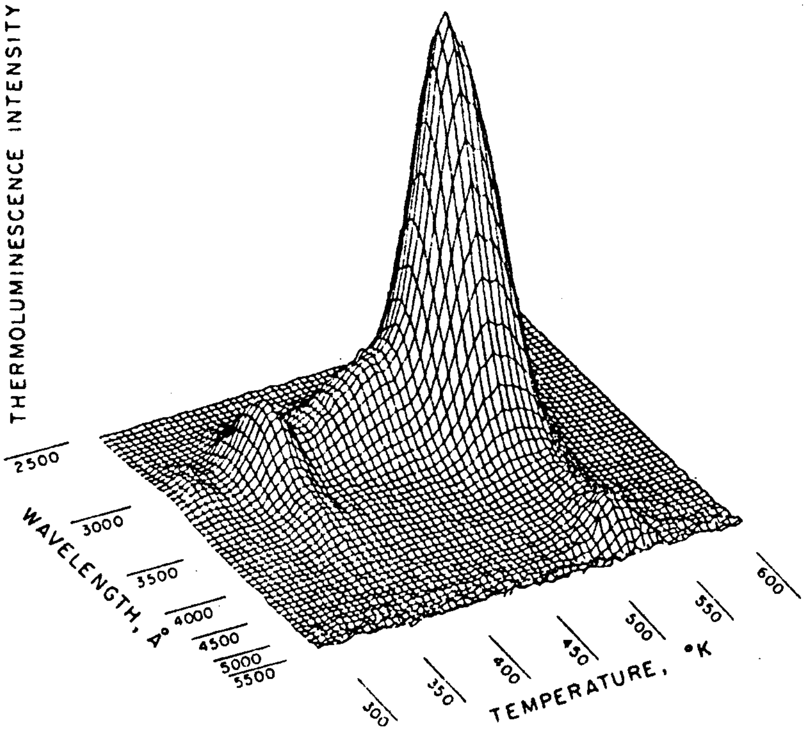

Fig.5.1.3. A three dimensional plot of the thermoluminescence from a KCl:Tl(100 ppm). Heating rate is approximately 10 deg/min. (from ref.5).

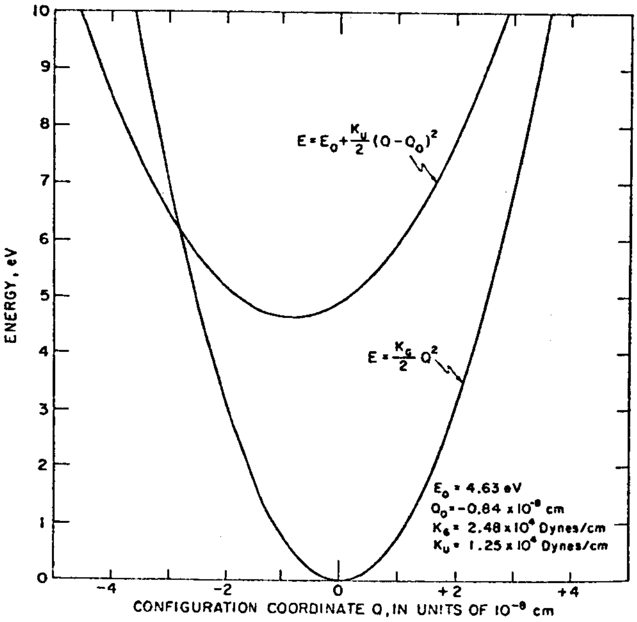

Fig.5.1.4. A classical one-dimensional configuration-coordinate diagram describing the absorption and emission of substitutional Tl^+ ions in KCl. (from. ref.5).

the properties of thermo-luminescence center have been well established.

On the other hand, there is no extrinsic luminescence center such as impurity in the case of pure materials. The thermo-luminescence center in such a crystal, therefore, must be formed through the intrinsic reactions which should take place during thermal annealing of irradiated crystal.

Thus the term " intrinsic thermoluminescence " is considered to appropriately describe the luminescent phenomena concerned.

So far, details of the intrinsic-thermoluminescence mechanism have not been known at all, though many works have been done on the luminescenct phenomena in irradiated pure crystals. This is considered to be mainly due to following two reasons:

1) Intrinsic TL has relatively weak intensity comparing other luminescent phenomena, such as x-ray excited luminescence etc. and is essentially the irreversible reaction. These facts may prevent one from experimentally studying the mechanism in detail.

2) And, the main aim of the studies on thermoluminescence in pure crystals which were performed before concerned not the mechanism of intrinsic TL itself, but the understanding of reactions of radiation-produced defects which can be obtained from analysis of glow curves.

Probably owing to these reasons, the important findings we will obtain here had not been established, though similar phenomena as those in this study were investigated by several authors before.4,7,8)

The aim of the study in this part of the present work is to make the intrinsic TL mechanism clear. An overall plan of the studies under the aim is briefly sketched in the next section.

§3 Outline of the work in this chapter

In order to understand the intrinsic-TL mechanism, we begin with the clarification of responsible reactions for thermoluminescent emissions. Detailed analysis of correlation between glow peaks and the reactions of freed halogen interstitial and trapped-hole centers is made for KBr crystals.

Three different types of recombination reactions are established as the origins of glow peaks at temperature region from 80 to 273 K. The most important reaction is the recombination between a neutral Frenkel pair. It is also shown that the recombination between charged Frenkel pairs is an non-radiative process.

Having established the radiative-recombination reactions, thermoluminescence below 80 K is studied, where radiation-induced defects are the most simple forms. It is shown that the intrinsic thermo-luminescent center at low temperature is the relaxed exciton. It is also demonstrated that the recombination between F - H pair creates only $(V_K e)_\pi$.

Based on these results, defect annihilation process is discussed.

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[5·2]

THERMOLUMINESCENCE AND REACTIONS OF FREED INTERSTITIAL AND TRAPPED-HOLE CENTERS IN KBr CRYSTALS BELOW 300 K

Thermoluminescence mechanism has been studied in connection with reactions of thermally freed interstitial and trapped-hole centers in KBr crystals at temperature region from 80 to 300 K. Annealing behaviours of these centers are studied by means of optical absorption and EPR measurements. Glow peaks appear at temperatures where the F center annihilates. The shape of several glow peaks are the same as the first derivative of annealing curve of the F center. Na^+-concentration and γ-ray dose dependences of glow curves are also analysed. Three different types of recombination reactions, Br_i° + F, Br_2^- + F, and Br_i^- + Br_2^-, are established as origins of glow peaks. It is shown that the recombination between a charged Frenkel pair is an non-radiative process.

§1 Introductory Remarks

In the study of TL mechanism, it is first nescessary to make clear what kinds of reactions are responsible for TL emission. Even such fundamental understandings have not been clearly obtained, especially in the case of intrinsic thermoluminescence, though some suggestions have been done.[1,2]

We begin with the experimental study to establish the responsible reactions of created defects for TL in KBr crystals.

Since TL is release of stored energy in the form of luminescence, fundamental reactions are considered to be defect annihilation during thermal annealing. It is generally accepted that the mobile entities are mainly interstitial and trapped hole centers below room temperature. Thus, for understanding the origin of a glow peak, it is supposed to be significant to establish correlations between a given glow peak and reactions of thermally freed centers which take place at the temperature where the glow peak appears.

Here such correlations are studied in KBr crystals at temperature region from 80 to 300 K. In order to observe the reactions of freed halogen interstitials at wider temperature region, we kave made use of the different thermal stability of interstitials trapped by alkali impurity ions, such as Na^+ and Li^+.

§2 Results and Discussions

(2·1) Glow peaks in KBr crystals below room temperature

Figure 5.2.1 shows the change in optical density at 610 nm and glow curves measured at 500 nm during warming irradiated samples up with a heating rate of 3.8 deg/min.

The change in otical density does not exactly represent the change in concentration of the F center, since the peak position and the halfwidth of the F absorption band depend on temperature of the crystal.3) Qualitatively, however, it shows annealing behaviour of the F center.

Annealing curves for two samples are clearly different: The largest annealing stage occurs around 100 K in KBr:Na, whereas the stage around 210 K is main in KBr:Li.

Glow curves depend on the kind of impurity, too: Glow peaks below 130 K seen in KBr:Na are negligibly weak in KBr:Li, whereas the strongest glow peak at 215 K in KBr:Li is not clearly separable in a KBr:Na.

Although the correlation between the intensity of a given glow peak and the amount of annealed F centers at the corresponding stage is poor, we can see from the figure that annihilation of the F center accompanies a glow peak.

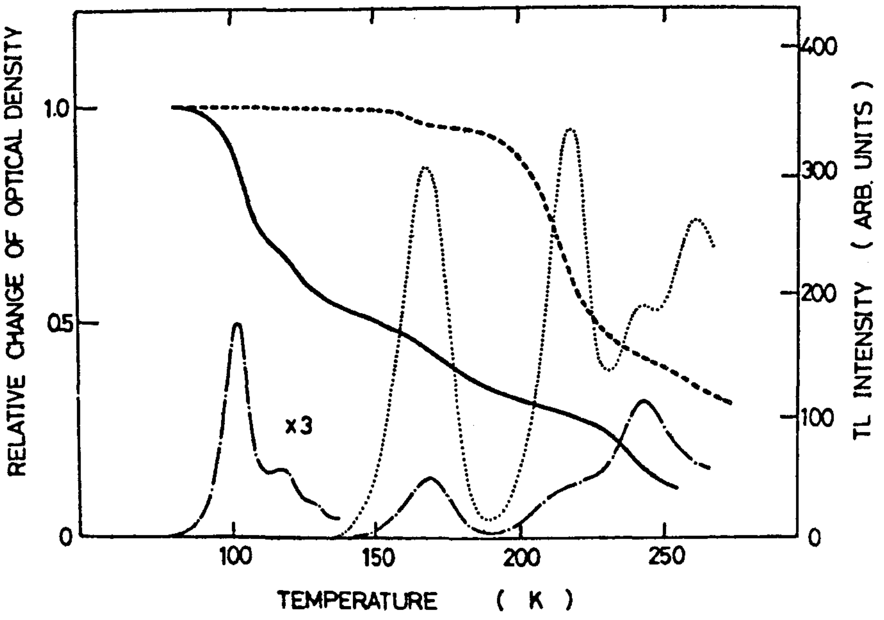

Fig.5.2.1. Changes in optical density at 610 nm and glow curves during isochronal annealing of irradiated KBr crystals. Solid and broken curves are the change in optical density at the F-band region in KBr:Na(0.10 mol%) and in KBr:Li(0.07 mol%), and the chain and dotted lines represent glow curves of KBr:Na and KBr:Li, respectively. Initial F-center concentrations are about 2.6 X 10^{17} and 1.8 X 10^{17} cm^{-1} in KBr:Na and in KBr:Li, respectively.

The result, therefore, suggests that the origin of a glow peak is closely related to such a reaction that results in annihilation of the F center.*

The V_K center has the electron affinity which is several orders of magnitude larger than that of interstitial centers.[5] Then in order to separate the contribution of reactions of the V_K center on glow curves, measurements were made on the changes in glow curves by the F light($\lambda>570$ nm) illumination after γ-ray irradiation at 80 K.

Figure 5.2.2 shows an example of such measurements. The solid curve and the broken one in the upper part of the figure indicate the glow curves of an as-irradiated sample and of sample illuminated with F light after γ-irradiation, respectively. The changes in glow curves, or difference between two curves, are shown in the bottom of the figure.

One can see that optical illumination at 80 K removes peaks situated at 115 and 165 K. These peaks are, hereafter, abbreviated as P(115) and P(165), respectively. It was observed for all KBr:Na crystals used in this study that the two glow peaks, P(115) and P(165), are always affected, though the relative ratio between intensities of reduced peaks changes depending on Na^+ concentration(C_{Na}).

The result shown in Fig.5.2.2 suggests that the V_K center plays an important role for these glow peaks, and that other peaks have their origin in the reactions of interstitial centers.

Figure 5.2.3 shows the glow curves of several KBr crystals with different C_{Na}. Glow curves depend strongly

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*) It is known that the F^- center is formed by low temperature irradiation. In the present study, however, F^- absorption bands are scarcely observed. The decay of the center, release of an electron, results in the growth of the F center.[4] Such a growth was not observed in annealing curves of the F center, which involve isochronal pulse annealing one. These results may indicate that F^- centers are hardly formed in the present samples.

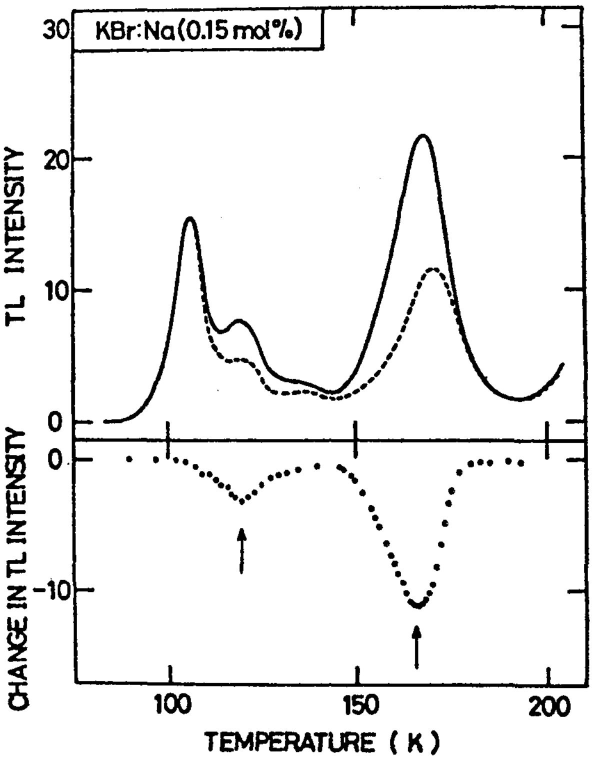

Fig.5.2.2. Top; Thermoluminescence glow curves of γ-ray irradiated KBr:Na(solid line) and of the sample illuminated with F-light at 80 K after γ irradiation(broken line), respectively. Bottom; The difference between these two glow curves. Arrows indicate the peak positions of optically removed glow peaks.

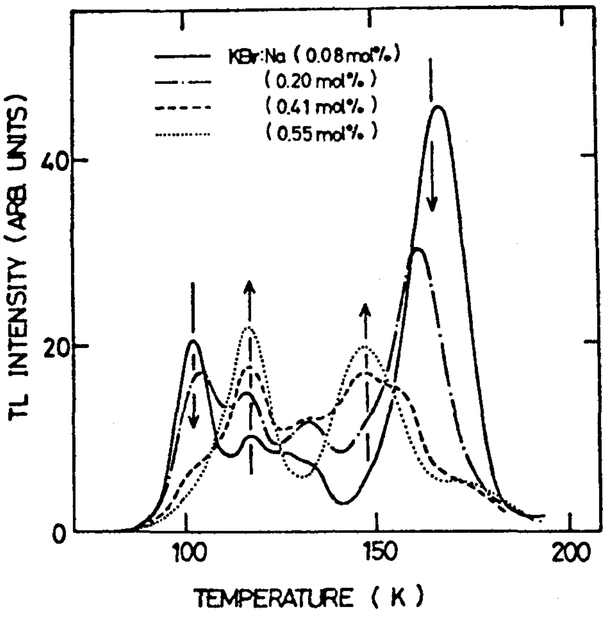

Fig.5.2.3. Na^+-concentration dependence of glow curves in KBr:Na crystals. Samples were irradiated by γ ray at 77 K. Dose of γ ray is about 2×10^6 r, for each sample.

on the impurity concentration. Main changes with increasing C_{Na} are followings;

1) The intensity of the glow peak at 102 K, P(102), which increases up to 0.15 mol% of C_{Na}, gradually decreases for higher concentration.

2) The intensity of the glow peak at 145 K, P(145), increases monotonically.

3) The intensity of P(115) increases, whereas that of P(165) decreases.

The P(115) and P(165), both of which are very sensitive to the F light illumination at 80 K as shown in Fig.5.2.2, appear to compete each other.

The results in Fig.5.2.3 indicate that Na^+ ions give significant effects on the reactions of interstitial and trapped hole centers responsible for TL.

(2·2) Annealing behaviours of interstitial and trapped hole centers

Since the TL emission has close correlation with the annihilation of the F center as shown in Fig.5.2.1, it is essentially important to analyse reactions which occur at a given annealing stage of the F center. In order to see such reactions, pulse annealing experiments were carried out.

In Fig.5.2.4 are shown the results of a KBr:Na(0.09 mol%) and of a KBr:Na(0.50 mol%).

The I_A center decays at 110 K for both samples, and there are no differences in annealing patterns. However, the annealing behaviours of the V_1 band depend on the Na^+ concentration. In a sample containing 0.09 mol% of Na^+, the V_1 band decays with three stages at 100 K(stage 1), 130 K(stage 2), and at 170 K(stage 3), respectively. The main stage of this sample is the stage 1 where about 70% of fractions decay thermally, accompanying the simultaneous decrease of about 40 % of the initial-Fcenter concentration. The V_1 band in KBr:Na(0.50 mol%) also has three annealing stages, though temperatures which give the maximum decay rate of annealing

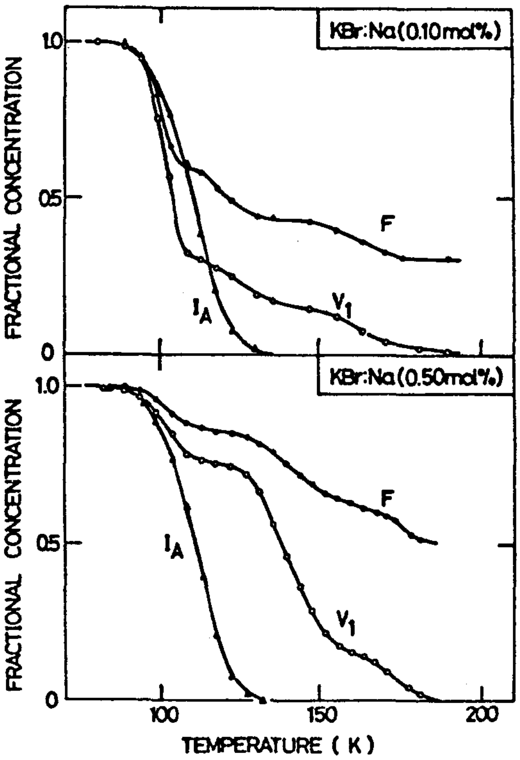

Fig.5.2.4. Isochronal pulse annealing curves of F, I_A and V_1 bands in KBr:Na crystals. Samples were γ-rayed at 77 K. Measurements were made at 80 K.

stages are not always the same as those in a KBr:Na(0.09 mol%). The three stages are situated at 100 K, 140 K and 175 K, respectively. The largest decrement of the V_1 band (about 60%) in this sample occurs in the stage at 140 K, where about 25% of the initial-F center concnetration decreases.

These results shown in Fig.5.2.4 clearly show that the annihilation of the F center below 200 K in KBr:Na crystals is mainly due to the thermal decay and subsequent recombination of the centers responsible for the V_1 band, and that annealing behaviours of the V_1 bands depend on the Na^+ concentration.

Isochronal pulse annealing experiments were made also on the pure KBr and KBr:Li crystals.

In pure KBr crystals, the V_4 center decayed at 235 K accompanying the simultaneous decrease of the F center-concnetration and a glow peak.

For KBr:Li crystals, it was confirmed that the $H_A(Li^+)$ center and the F center decay thermally at 215 K, where the strongest glow peak appears. Results on annealing of V_4 and $H_A(Li^+)$ centers are respective similar as previously reported results.6,7)

These results that simultaneous decrease between an interstitial center and the F center takes place at temperature where glow peaks appear suggest that the recombination between neutral Frenkel pairs is an origin of TL emission. Clear confirmation of this suggestion will be done later.

The V_K center in KBr has an broad absorption band at 3.22 eV. However, overlap of other absorption band in this energy region makes it difficult, not possible, to study the annealing behaviour of the V_K center by means of optical absorption study. To know annealing behaviour of the V_K center, therefore, EPR measurements were made on this center.

In Fig.5.2.5 are shown the results of isochronal pulse annealing experiments, by means of EPR measurements, of V_K centers in KBr crystlas.

One can see in Fig.5.2.5 that three annealing stages

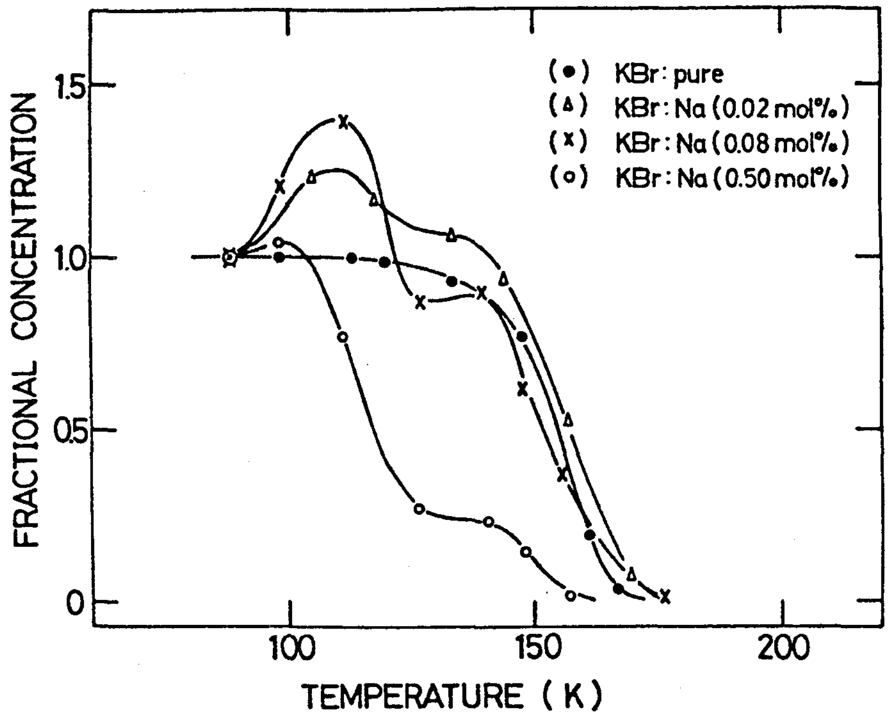

Fig.5.2.5. Annealing curves of the V_K center in KBr crystals, measured by EPR at 80K. Samples were irradiated with γ ray at 77 K. The initial concentration of the center in as irradiated each crystal is normalized to unity.

of the V_K center are distinguishable in KBr:Na crystals: the center grows from 80 to 105 K, and annihilates at two stages at 115 and at 160 K, respectively. The increment and the decrement at given stages depend on the impurity concentration.

The V_K center in pure KBr, on the other hand, decays thermally only at 160 K. The center in KBr:Li showed similar annealing behaviour as that in pure KBr.

It is evident, therefore, that changes in concentration of the created V_K center below 140 K are characteristic to Na^+ impurity ion in KBr. Origins of the changes in V_K-center concentration are disscussed in the later paragraph.

(2·3) Origin of the glow peaks in KBr crystals

Here responsible reactions for a glow peak in KBr crystals are assigned. Main attention is paid on four glow peaks, P(102), P(115), P(145), and P(165), which show characteristic C_{Na} dependence, as seen in Fig.5.2.3. Both P(115) and P(165) are very sensitive to F-light illumanition after irradiation, whereas P(102) and P(145) are resistive, as shown in Fig.5.2.2. Then we can devide four peaks into two groups, based on the response for F-light illumination. First, origins of the glow peaks of P(102) and P(145) are discussed.

(a) Responsible reactions for P(102) and P(145)

Following characteristics have been cleared in preceding paragraphs;

1) These glow peaks are optical-resistive, which suggests that these are originated from reactions of interstitials.

2) In fact, the V_1 band which is mainly due to interstitial bromine atom, Br_i°, decays thermally at temperatures where these peaks appear, as seen in Fig.5.2.4.

3) Intensities of these glow peaks depend on the C_{Na}. These characteristics may indicate that glow peaks are closely correlated with interstitial-Na^+ complex centers responsible

for the V_1 band.

The V_1 band in KBr:Na crystals has been investigated in Chap.[4·3]. It has been cleared that at least two interstitial-atom centers associated with Na^+ ions, probably with different configurations, are responsible for the V_1 band, though the lattice configurations of the centers have not been established. These centers have been called tentatively as H_{A1} and H_{A2} centers, respectively.

Following properties of these centers have been revealed.

1) The H_{A1} center has double absorption bands at 423 and 380 nm, and decays thermally at 100 K with an activation energy of 0.23 eV.

2) The H_{A2} center has an absorption at 406 nm, and decays at 140 K.

3) Formation yields of H_{A1} and H_{A2} centers depend, in different way, on C_{Na}; the yield of the H_{A1} center increases rapidly up to 0.15 mol% and decreases above 0.15 mol% gradually with increasing C_{Na}, and the yield of the H_{A2} center increases monotonically with increasing C_{Na}.8)

Based on these results for the H_{A1} and H_{A2} centers, we can ascribe the first annealing stage of the V_1 band to the thermal decay of the H_{A1} center, and the stage at 140 K in KBr:Na(0.5 mil%) to the decay of the H_{A2} center, respectively.

As seen in Fig.5.2.3, P(102) is dominant in the crystals having relatively low Na^+ concentration, and the intensity decrease with increasing C_{Na}, similarly as the formation yield of the H_{A1} center.

Thermal decay of the H_{A1} center is accompanied with simultaneous decrease of the F center concentration, as shown in Fig.5.2.4, and appears to be accompanied with the glow peak of P(102). Such correlations suggest that the origin of this glow peak is the recombination of the interstitial atom with the F center, the former of which is freed from the H_{A1} center.

If the suggestion is the case, following relation;9)

$$I(T) \propto -(dF/dT) = -(dV/dT), \qquad (5.2.1)$$

should be satisfied, where I is TL intensity of a glow peak and (dF/dT) and (dV/dT) are the first derivative of isochronal annealing curves of the F and a given Br_i°-type center in terms of temperature, respectively.

In order to check the suggested model for the origin of P(102), we examined applicability of eq.(5.2.1) to the case of P(102). To obtain the relation between annealing curve of the F center and the glow peak with least ambiguity, we carried out following experiment where both the isochronal annealing curve of the F center and the glow curve were simultaneously measured for the same sample. An irradiated crystal was illuminated with F light before heating, in order to prevent P(115) from overlapping with P(102).

Figure 5.2.6 shows the result of KBr:Na(0.10 mol%). The solid line in the figure is the constant-wavelength(500 nm) glow curve, and closed circles indicate slope of annealing curve of the F center (broken line in the figure) obtained by numerical differentiation.

Good agreement between both quantities is evident, which confirms the assignment of the origin of P(102) that it originates from the recombination between a neutral Frenkel pair.

Similar relations have also been obtained for the V_4 center in pure KBr and for the $H_A(Li^+)$ center in KBr:Li.

P(145) is the main peak in the glow curve of KBr:Na(0.50 mol%), though several components are superposed at this temperature region, as seen in Fig.5.2.3. One can see in Fig.5.2.5 that the H_{A2} center decays at the temperature region accompanying simultaneous decrease of the F center. It appears that the P(145) is due to the same mechanism as that for P(102), though Br_i° is freed from the H_{A2} center in this case.

In order to establish the origin of the 140 K glow peak, we obtain the correlation between the maximum intensity of the glow peak vs. absorption coefficient of the H_{A2} band of the crystals with the same C_{Na}, instead of obtaining the relation of eq.(5.2.1). The absorption coefficient of the H_{A2} center, or the concentration of the H_{A2} center, was con-

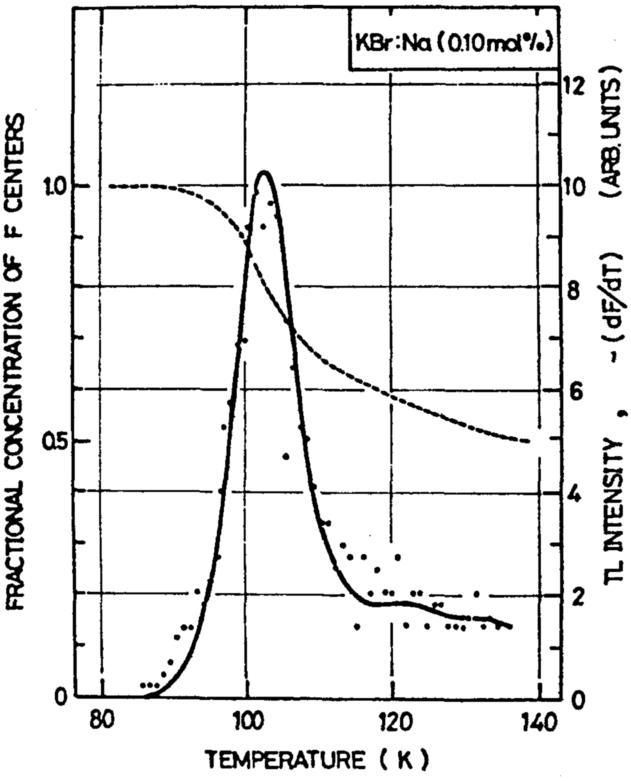

Fig.5.2.6. Simultaneously measured annealing curve of the F band(610 nm), broken line, and glow curve of a constant wavelength(500 nm), solid line, respectively. Slope of the annealing curve at a temperature, obtained by numerical differentation, is also shown by solid circles, and is compared with the shape of the glow peak.

trolled by changing irradiation dose of γ ray.

The result is shown in Fig.5.2.7. It is seen that the intensity of P(145) is in proportion to the concentration of the H_{A2} center in wider range.

This result strongly supports the assignment that the P(145) is due to the thermal decay of the H_{A2} center, which results in the recombination between neutral Frenkel pairs.

Based on the results obtained in this paragraph, one can safely conclude that recombination of interstitial atoms with F centers is an origin of thermoluminescence.

(b) Responsible reactions of P(115) and P(165)

Then origins of glow peaks of P(115) and P(165) are discussed.

As shown in Fig.5.2.2, these glow peaks are very sensitive to F-light illumination at 80 K. Such a characteristic suggests that these are closely related with the V_K center. In fact, the V_K center annihilates at temperatures region where these two glow peaks appear.

It has been reported by Schoemaker$^{10)}$ that the decay temperature of the V_K center in KBr is 160 K, which is very close to the temperature that gives maximum decay rate of the third annealing stage of the V_K center in Fig.5.2.5. It can be, therefore, concluded that annihilation of the V_K center at 160 K is due to thermal migration and successive recombination of the V_K center.

Thus P(165) may be attributed to such a reaction of the V_K center in KBr.

The results in Fig.5.2.5 indicate that the substantial amount of the V_K center annihilates around 110 K before its thermal migration. This annihilation process is considered to be responsible for P(115). It is, therefore, important to make clear the mechanism of the annihilation of the V_K center at the second stage.

It is not reasonable to attribute the annihilation to thermal decay of the F^- center, since it is hardly formed in the present specimens, and the formation yield of the

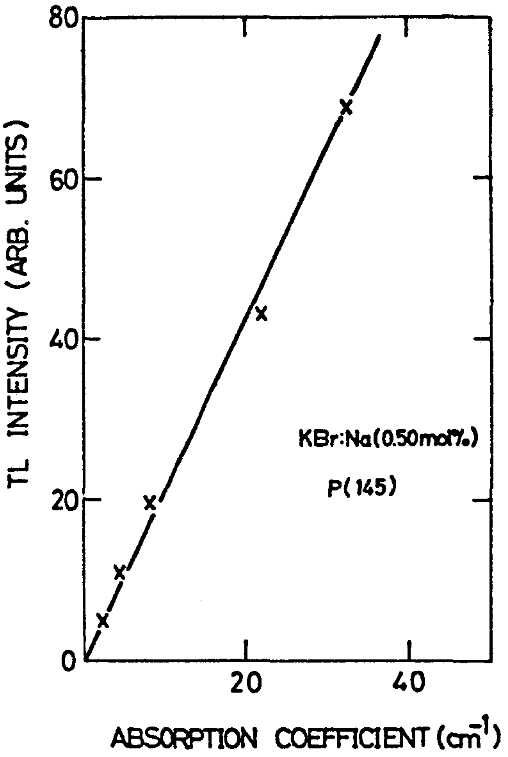

Fig.5.2.7. Relation between the maximum TL intensity of P(145) and the absorption coefficient of the H_{A2} band in KBr:Na(0.50 mol%), induced by γ irradiation at 77 K.

F^- center may depend neither on the kind nor on the concentration of alkali impurities. The decrement of the V_K center at the second stage depends on the concentration of Na^+ impurity: it increases with increasing C_{Na}.

In Fig.5.2.4, it can be seen that the decay temperature of the H_{A1} or of the I_A center is respectively close to the temperature of the first or the second annealing stage of the V_K center.

The increment at the first stage increases first and then decreases, with increasing C_{Na}. Such a dependence on C_{Na} is very similar as that of formation yield of the H_{A1} center described above.

One can, therefore, conclude that the increase of the concentration of the V_K center at temperatures from 90 K to 110 K is due to the reaction of Br_i° freed from the H_{A1} center. Schoemaker have shown that the recombination between interstitial atoms and F^+ centers forms V_K centers.11) Therefore, such a reaction may be responsible for the growth of the V_K center at the first annealing stage.

Hays and Hodby12) have shown from their EPR experiments for irradiated KCl crystals that an interstitial ion converts into an interstitial atom through its recombination with a V_K center about 32 K. Behr at al.13) have also suggested the similar reaction from their optical absorption study in KCl.

Considering such a reaction, together with the result that the I_A center decays thermally at the temperature where V_K center annihilates, it may be acceptable that the recombination between V_K centers and Br_i^-, which is freed through thermal decay of the I_A center, is responsible for the second stage of annihilation of the V_K center.

Thus it is apparent that P(115) has correlation with both V_K and I_A centers.

Thermal decay of the I_A center is considered to result in the free migration of interstitial bromine ion, Br_i^-. Br_i^- may have following reactions; 1) the recombination with F^+ center to restore the perfect lattice, 2) the recombination with V_K centers mentioned above, and 3) recombinations

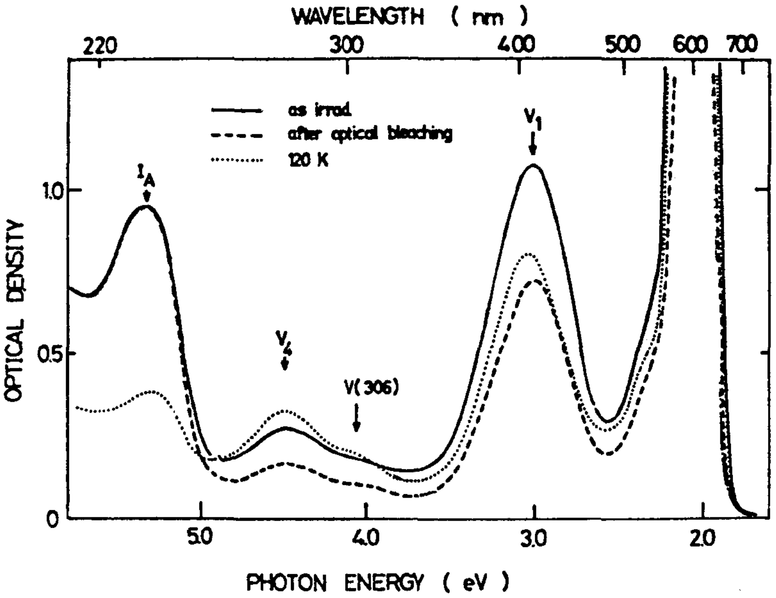

Fig.5.2.8. Optical absorption spectrum of γ-irradiated KBr:Na(0.50 mol%) ant its change due to warming up to 120 K or to F-light illumination. Measurements were made at 80 K.

with another imperfections (which is not known yet).

In order to know the responsible reaction for P(115), following experiments were made. In Fig.5.2.8, changes in optical absorption spectrum by the F-light illumination and by thermal treatments for irradiated KBr:Na(0.5 mol%) are shown.

One can see that I_A as well as F^+ band are hardly bleached by the optical illumination at 80 K, though the illumination removes P(115) almost completely, as seen in Fig.5.2.2. The I_A band disappears with simultaneous decrease of the F^+ band, when the sample is warmed up to 120 K.

These results is supposed to indicate followings:

1) Recombination between chraged Frenkel pairs contributes little to TL emission, which means that the recombination is an non-radiative process.

2) Presence of the V_K center is essential for P(115), which indicates that the responsible reaction for P(115) is the recombination between a Br_i^- and the V_K center.

(2·3) Discussions

Results and discussions made in the preceding paragraphs revealed that recombination between neutral Frenkel pairs involves radiative process before reestablishing perfect lattices. The recombination is intrinsic and is the typical reaction which takes place when an irradiated crystal at low temperature is warmed.

It can be concluded,therefore,that such a radiative recombination is main source of thermoluminescence in non-activated alkali halides, or intrinsic thermoluminescence.

On the other hand, the recombination between a charged Frenkel pair is confirmed to be non-radiative. This conclusion is consistent with the result obtained by Fuchs and Taylor for I center in KBr.[14)]

It has clearly shown that the interstitial bromine ion contribute to TL emission only when it recombines with the V_K center. The recombination may result in the formation of Br_i° which is unstable at the temperature around 110 K. Therefore, the recombination between $Br_i^- + V_K$ may be followed by reactions of Br_i°. It is not clear either the recombination of Br_i^- with a V_K center or the reactions of created Br_i° is responsible for the emission of P(115).

Another type of reactions has also been established as an origin of TL emission, which concerns the thermal migration of the V_K center taking place at around 160 K.

The glow peak due to unknown reaction of migrating V_K center, P(165), is observed for both KBr:Na and KBr:Li, as shown in Fig.5.2.1. One can see in Fig.5.2.1, especially for the curve of KBr:Li, that the glow peak accompanies the annihilation of the F center.

Ueta[15)] has shown from his pulse experiments that the V_K center recombine with F center to reduce the concentration of the F center. It is, therefore, reasonable to conclude that the responsible reaction of P(165) is the recombination of the V_K center with an F center.

Such a recombination reaction may result in the formation of an anion vacancy, whereas the recombination between a neutral Frenkel pair restores the perfect lattice.

Further detailed study, based mainly on the measurement of emission spectrum of glow peaks, may be nescessary for understanding the nature of luminescence center formed through these recombination reactions.

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[5·3]

INTRINSIC THERMOLUMINESCENCE AND THE RELAXED EXCITON FORMATION THROUGH THE H CENTER RECOMBINATION WITH THE F CENTER

Intrinsic thermoluminescence has been studied in KBr, NaCl, and KI by means of emission-spectrum measurements of glow peaks as well as the analysis of correlation between thermal decay of H and F centers and a glow peak. The thermo-luminescence center at the temperature region from 10 to 110 K is the relaxed exciton. The recombination between F and H centers can create only the exciton state of ($V_K e$)$_\pi$. The formation energy of the neutral Frenkel pair is estimated to be about 5.5 eV in KBr. Based on these results, the mechanism of defect annihilation is discussed using a proposed schematical two-dimensional configuration coordinate diagram.

§1 Introductory Remarks

The study in the previous chapter (Chap.[5·2]) has revealed that the recombination between a neutral Frenkel pair releases its formation energy in terms of luminescence. This result clearly indicates that the lattice energy stored in the form of lattice defects is converted into the electronic-excitation energy which is responsible for the thermoluminescence (TL). The mechanism which takes place in such an energy-conversion process is a reverse reaction to the radiolysis where the electronic-excitation energy is converted into the lattice energy.

Thus the study on the mechanism of intrinsic TL is very interesting and important in the field of radiation-damage research in alkali halides.

It is supposed to be natural and advantageous to study the energy-conversion mechanism for the most ideal case where the form of Frenkel pairs and thermally induced reactions of them are as simple as possible. Thus we study here the intrinsic TL mainly below liquid nitrogen temperature where most of neutral Frenkel pairs consist of H and F centers, and mobile entity is essentially the primary interstitials.1)

It may be of great importance to know the properties of thermo-luminescence centers which are formed through the recombination events, for the clarification of the mechanism concerned. The emission-spectrum measurements of glow peaks are, therefore, carried out here, which had never been performed for low-temperature glow peaks in pure alkali halide crystals. The detailed analysis is also made as to correlations between glow peaks and reactions of defects at temperature concerned.

Followings are the important results obtained here:

1) The thermo-luminescence center at low temperature is the relaxed exciton which is responsible for the intrinsic luminescence in alkali halides, and

2) the recombination between an F - H pair can create only the state of ($V_K e$)$_\pi$.

The mechanism of defect annihilation, or of intrinsic TL is finally discussed based on these important findings.

§2 Experimental Results

Figure 5.3.1 shows the glow curve measured at 230 nm (the Top) and the relative change in the F-center concentration (Bottom) during isochronal annealing of a NaCl crystal irradiated by x ray at 6 K. The change in the F-center concentration was determined by means of measuring the change in intensity of transmitting light of 450 nm during annealing. The peak position and the halfwidth of the F band hardly depend on temperature at least from 10 K to 60 K. Therefore, the change in optical density at the peak of the F band can represent that in F-center concent-

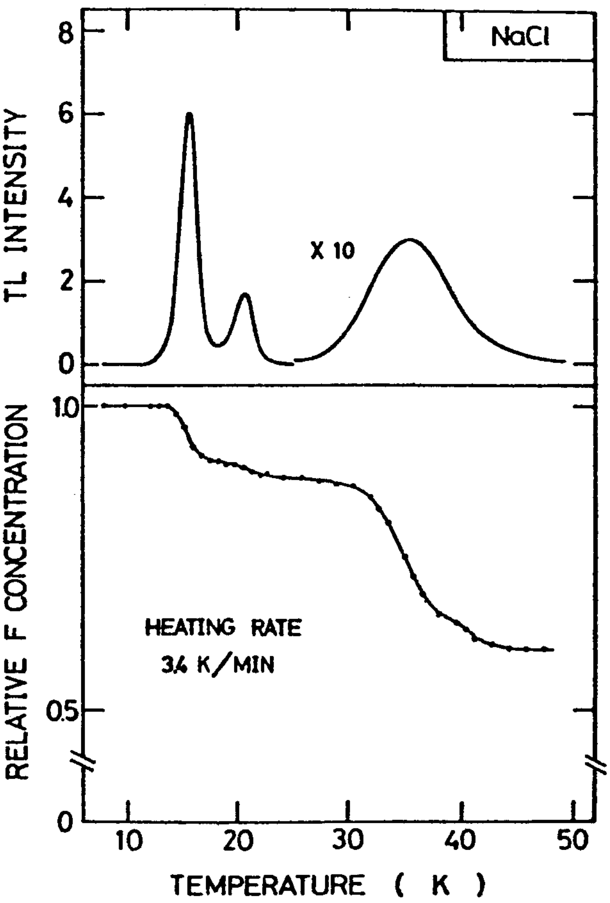

Fig.5.3.1. Simultaneously measured thermoluminescence glow curve and the annealing curve of the F center in NaCl x-rayed at 6 K. Top: A constant-wavelength glow curve measured at 230 nm. Bottom: Relative F-center concentration change during isochronal annealing, determined by the continuous recording of optical density at 450 nm

ration. The glow curve and optical-density change were measured for the same sample simultaneously, in order to obtain correlations between these quantities with least ambiguity.

Glow peaks appears at 16, 21, and 37 K where the F center has annealing stages, respectively.

The similar results of a KBr crystal are shown in Fig.5.3.2: The glow curve measured at 280 nm is shown in the upper part, and the relative concentration changes of F and H centers in the bottom in the figure, respectively.

A strong glow peak has its maximum at 29.5 K and the peaks with TL intensities of about two orders of magnitude weaker appear in the temperature region from 35 to 50 K.

At the temperature where glow peaks occur, F as well as H centers decay thermally, similarly as NaCl shown in Fig.5.3.1.

No thermoluminescent glow were observed below 22 K, where most charged pairs consisting of F^+ and I centers disappear.

Glow curve of an irradiated KI crystal was also measured, though the changes in F center concentration could not be obtained, since this salt colors very poorly at 6 K. It was found that the main glow peak appears at 76 K and peaks with very weak intensities at 22, 30, 40, and 55 K, respectively.

The emission spectra of typical glow peaks of NaCl, KBr, and KI crystals are shown in Fig.5.3.3. Solid, broken, and chain lines of the figure represent the spectra of a glow peak at 16 K in NaCl, of that at 29.5 K in KBr, and of the strongest peak at 76 K in KI, respectively.

Scanning the wavelength range 200 - 700 nm was done within 20 sec, so that a full emission spectrum could be obtained while the sample warmed about 1 deg. By simultaneous monitoring of the glow curve through another window of the cryostat, the spectra were measured at the maximum of respective glow peaks where the change in TL intensities within scanning time was small (less than 4% for most serious

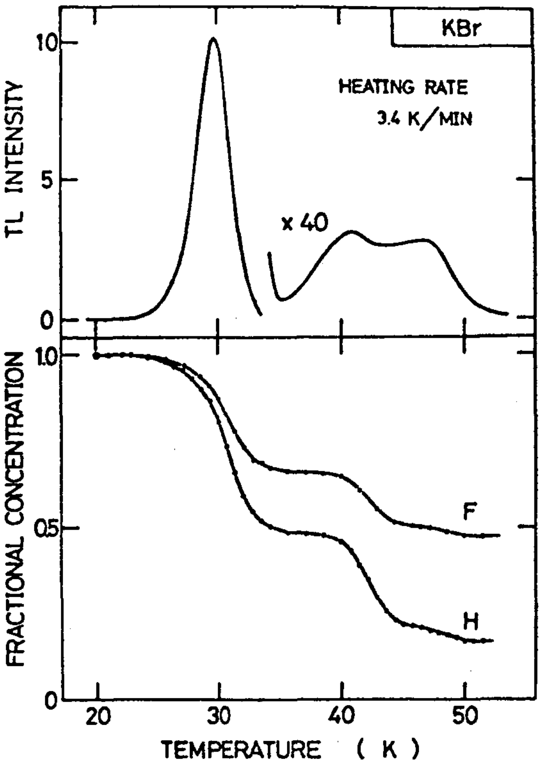

Fig.5.3.2. Simultaneously measured thermoluminescence glow curve and the annealing curves of the F and H centers in KBr x-rayed at 6 K. Top: A constant-wavelength glow curve measured at 280 nm. Dottom: Relative F- and H- center concentration changes during isochronal anneaing, determined by the continuous recording of optical densities at 600 nm and 380 nm, respectively.

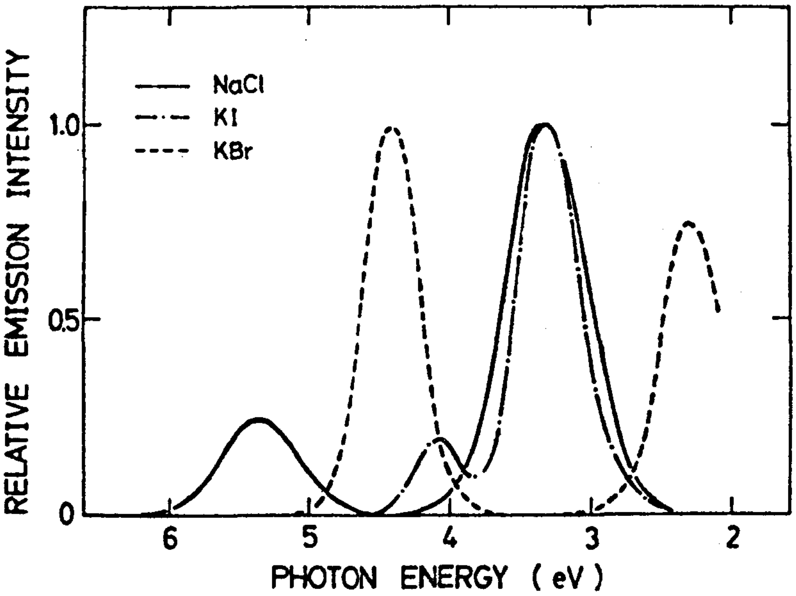

Fig.5.3.3. Emission spectra of glow peaks at 16 K in NaCl, at 29.5 K in KBr, and at 76 K in KI, respectively.

case of KBr). It was confirmed that another glow peaks in these salts have essentially the same emission spectrum as those shown in Fig.5.3.3.

It is evident that the emission spectrum of a glow peak is the same as that of intrinsic luminescence in respective salt, though the relative ratio between σ- and π- emission intensities is not all the same as that due to x-ray excitation.

This result clearly indicates that the thermo-luminescence center of the intrinsic TL is the relaxed exciton which results in the so-called intrinsic luminescence.

In order to obtain the more quantitative correlations between the emission intensity of a glow peak and the concentration of annihilated F and H centers, detailed measurements were made on KBr.

First, the correlation was obtained between the decrements of F and H centers in the stage around 30 K and TL intensities of σ and π emissions of the glow peak at 29.5 K. The decrements of F and H centers were controlled by changing the dose of x ray. Results are shown in Fig.5.3.4.

The linear relation between the decrements of F and H centers is evident, which confirms that the annihilation of the F center around 30 K is due to the recombination with the H center.2) The emission intensity of σ emission increases rapidly and then becomes constant for higher decrements of the H center. On the other hand, the intensity of π emission continues to increase for higher decrements where the intensity of σ emission is saturated. The different behaviour between σ and π emission indicates that formation of each state of exciton has its origin in different reaction in the case of TL.

If one assume that the increase in emission intensity of π luminescence involves one saturation component similar as that of σ luminescence, and that the ratio of saturated values of σ and π luminescences is the same as that of x-ray excited emission spectrum, then the increase of π-emission intensity as a function of the decrement of the H center can be re-

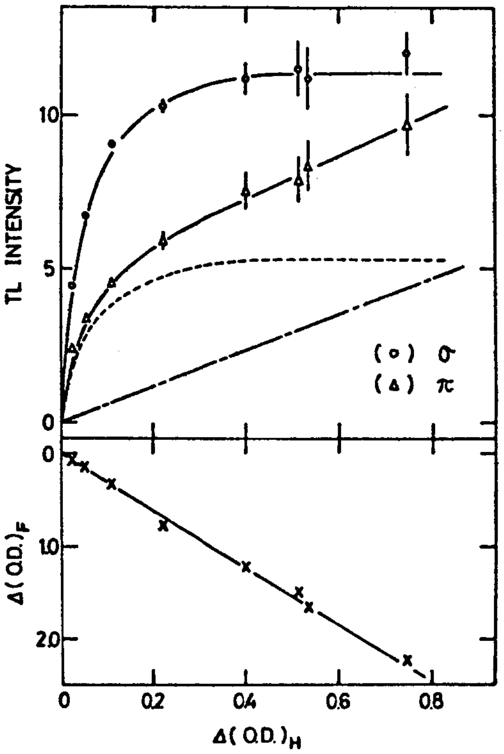

Fig.5.3.4. Maximum TL intensities of σ- and π-emission components of the glow peak at 29.5 K, and the decrement of the F center at the first annealing stage as functions of the decrement of the H center at the annealing stage in KBr. Four quantities were measured simultaneously for the same sample. The decrement of the H center at the stage was controlled by changing irradiation time of x-ray. TL intensities are corrected for self-absorptions due to color centers. Broken and chain lines represent resolved two components of the increase in TL intensity of π-emission component of the glow peak. Heating rate is 3.4 deg/min for all measurements.

solved into two components; one is the saturating component (broken line in Fig.5.3.4), and the other is a linear one (chain line) as shown in the figure.

This suggests that π component of the emission has supplementary origin through which the formation yield of ($V_K e$)$_\pi$ increases propotionately to the decrement of the H center at the annealing stage.

In order to make the presence of two origins for the π-emission component of the glow peak clear, measurements were made on the changes in glow curves due to optical illumination after x-ray irradiation.

Figure 5.3.5 shows the σ-emission intensity of the glow peak as functions of the decrement of the H center at the annealing stage of about 30 K. Data points of closed circles are similar ones as results shown in Fig.5.3.4. On the other hand, for points of open circles, the decrement was controlled by changing the time of F-light illumination after x-irradiation with a fixed dose.

It is clear that the σ-emission intensity, or the saturating component, is very sensitive to the F light. The result that the intensity of σ-emission component is not uniquely determined for a fixed value of the decrement of the H center suggests that the origin of this component is not the thermal decay of the H center.

Fig.5.3.6 shows the glow peaks of the π component of the as-irradiated crystal with low x-ray dose and of the sample illuminated F light after x-ray irradiation of considerable high dose. The former sample involves mainly the saturating component of the π emission, whereas the latter hardly possesses such a component because of the strong sensitivity of the saturating component to the F light illumination shown in Fig.5.3.5.

It is evident that glow peaks in such samples have distinctly different shapes and peak positions. The glow peak in the optically illuminated sample, which has considerable resistivity to the F light, peaks at 30.5 K.

It was confirmed that the intensity of optically resis-

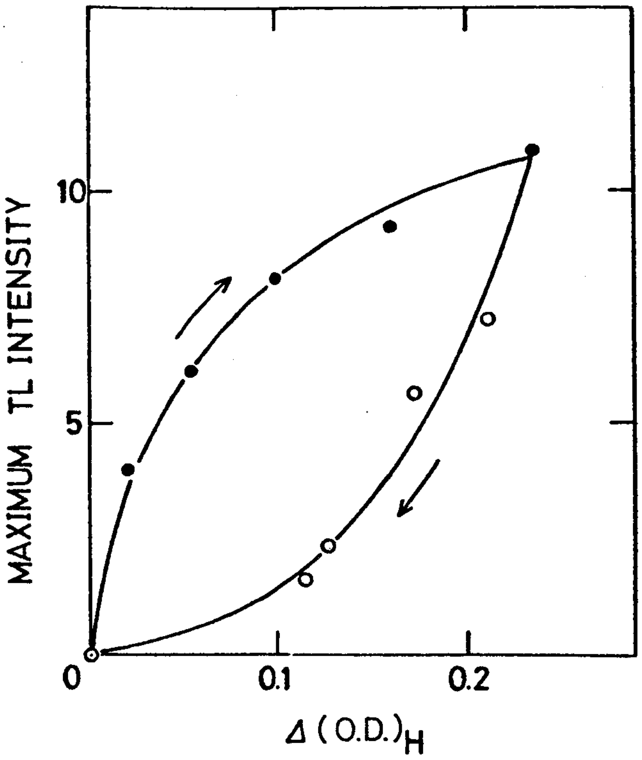

Fig.5.3.5. Maximum TL intensity of the σ-emission component of the glow peak at 29.5 K as a function of the decrement of the H center at the first annealing stage in KBr. Solid circles represent the intensities of as-irradiated samples with different x-ray dose, and open circles show the intensities of samples illuminated by F light with different intervals after x-irradiation with the same dose at 6 K.

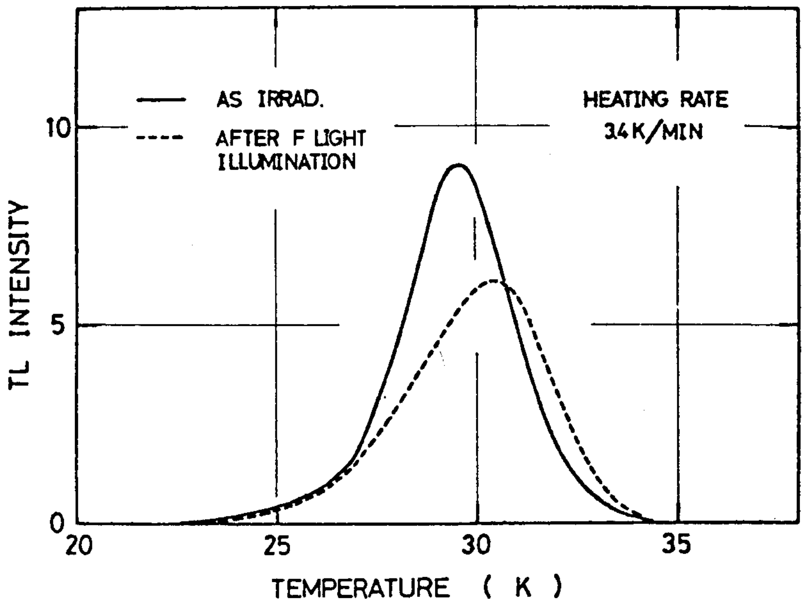

Fig.5.3.6. Glow peaks of π-emission component in KBr: Solid curve is the glow peak of an as-irradiated sample with low x-ray dose, and broken one shows the glow peak of a sample illuminated with F light after x-irradiation with considerably high dose. Relative intensities of the two peaks are arbitrary.

tive component of the glow peak (broken curves in Fig.5.3.6) is in proportion to the decrement of the H center as well as the F center.

Thus it can be concluded that the different two types of reactions of defects are responsible for the π emission of TL, whereas only one, saturating component, is for the σ emission in KBr.

Figure 5.3.7 shows the emission spectrum of the glow peak due to thermal decay of the $H_{A1}(Na^+)$ center in KBr:Na (0.09 mol%). The origin of the glow peak at 102 K in such a sample, P(102), has been discussed in preceding chapter, and has been identified to be the recombination between a freed H center from a Na^+ ion and an F center, or the neutral Frenkel pair.

The spectrum consists of a single band which is essentially the same as π-emission band in KBr. No emission bands having higher energy were not observed in this glow peak. The intensity of this π-emission component was confirmed to increase proportionately to the decrement of the H_{A1} and F centers.

§3 Discussions

The results obtained in the preceding section indicate that two different types of reactions are responsible for the relaxed exciton formation in thermoluminescence. One has a saturating nature, which results in the formation of both (V_Ke) and (V_Ke) , and the other which can be relevant only to (V_Ke $)_\pi$ results in the linear increase of the formation with increasing the decrement of the H center. First, origins of these two types of reactions are discussed.

(3·1) Origin of the saturating component

The low-temperature glow peaks in KBr have been studied by Cape and Jacobs,2) and by Fuchs and Taylor.3) On the

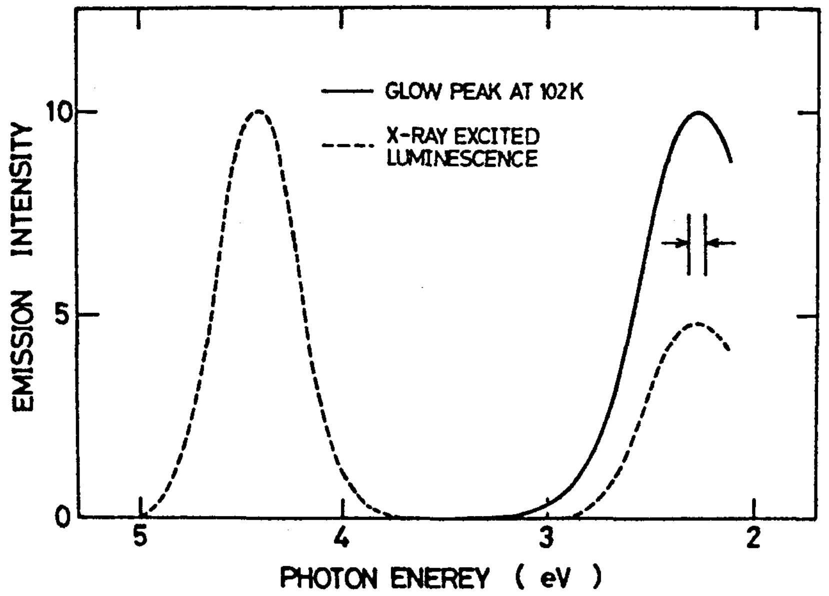

Fig.5.3.7. Emission spectrum of the glow peak appearing at 102 K due to the recombination of thermally freed interstitial bromine atoms from the H_{A1} centers with the F centers in KBr:Na(0.09 mol%). The x-ray excited emission spectrum of KBr at 6 K is also shown for comparison.

basis of the fact that the H center decays thermally at the temperature region where the glow peak (whose peak position is at about 30 K) appear, Cape and Jacobs have assigned the origin of the glow peak to the thermal decomposition of the H center. Fucks and Taylor have also deduced the same conclusion.

The decay of the H center in the first annealing stage at about 30 K in all literatures has been assigned to be due to the recombination of correlated pair of the F and H centers.2) It has also been demonstrated that the decay of the H center at the annealing stage obeys the first order rate equation.2)

From present results of annealing curves of F and H centers shown in Fig.5.3.2, it was confirmed that the first stage is described by the first order kinetics, though the values of activation energy are not the same as that obtained by Saidoh and Itoh.2)

Fig.5.3.8 shows the least-square fit of a first-order reaction equation to the first stage of isochronal annealingcurves of F and H centers. The solid curve is obtained from the calculation with values of $2.8 \times 10^{5} \mathrm{sec}^{-1}$ and 0.042 eV for frequency factor and for activation energy, respectively. Good agreement between experimental data and the calculated curve is evident.

If the glow peak at 29.5 K orriginates from the decay of the H center, the TL intensity, I(T), of the glow peak and the concentration of the H center, n[H], should satisfy following relation;5)

$$\begin{aligned} I(T) &\propto -dn[H]/dT \\ &= n[H](s/\beta)\exp(-E/kT) \end{aligned} \tag{5.3.1}$$

where E, s, and β are activation energy, the frequency factor, and the heating rate, respectively.

The equation involves that the shape of the glow peak is essentially the same as the first derivative of the annealing curve of the H center in terms of temperature, and that the maximum TL intensity is in proportion to the decre-

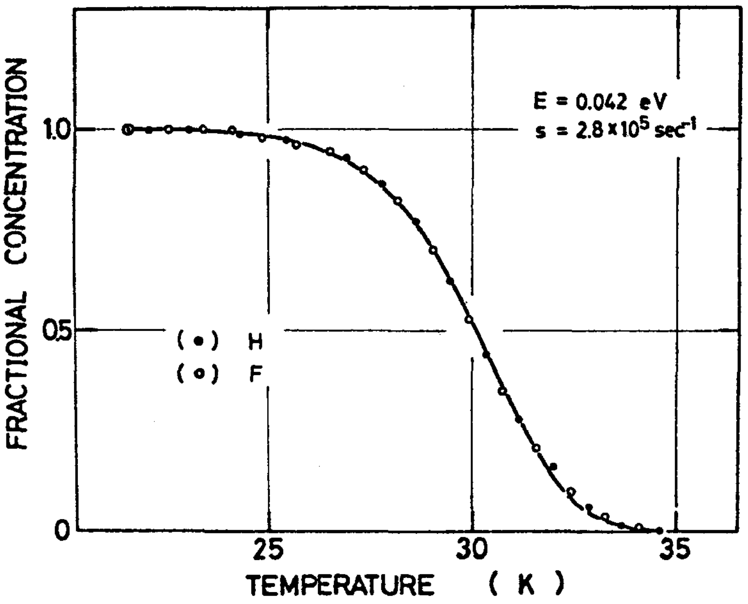

Fig.5.3.8. The least-square fit of a first-order reaction equation to the first annealing stage of the F and H centers in KBr. The solid curve represents the calculated result of the first-order rate equation using values of parameters indicated in the figure.

ment of the H center at the annealing stage, since the maximum intensity is proportional to the integration of I(T) over the corresponding temperature region.

From results shown in Fig.5.3.4, it is evident that the maximum TL intensity of σ emission as well as π emission of the glow peak at 29.5 K, is not in proportion to the decrement of the H center.*

Furthermore, one can confirm that the first derivative of the annealing curve of the H center does not describe the shape of the glow peak: The temperature which is expected to give the maximum TL intensity from the first derivative of the annealing curve is 30.7 K, whereas the glow peak of σ component is situated at 29.5 K.

Thus these results rules out the possibility that the glow peak at 29.5 K in KBr is only due to the thermal decay of the H center. Another mechanism of glow peak having saturating property should be taken into account.

Fuchs and Taylor4) as well as Cape and Jacobs3) have shown that the current burst due to conduction electrons occurs at the same temperaure region where luminescent glow appears.

Since the luminescence center of the glow peak is the relaxed exciton, of (V_Ke), most probable reactions responsible for the glow peak at 29.5 K is considered to be the

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*) Fuchs and Taylor3) have shown that the emission intensity of the 27 K glow peak, which is considered to be the same as the present glow peak at 29.5 K, increases linearly with increasing γ-ray dose. However, the concenrations of the F and H centers in their study is about two orders of magnitude smaller than those of the present study. For such low concentrations of defects, the emission intensity of the glow peak appears to increase linearly with increasing irradiation dose, as seen in Fig.5.3.4.

However, it is clear that the TL intensity of the glow peak does saturate for the higher concenration of defects.

trapping of such conduction electrons by the V_K center created by x-ray irradiation at 6 K.

It may not be unreasonable to think that the formation of the V_K center in pure crystals has saturating property, since the concentration of electron trapping centers such as impurities, which is essential for the V_K-center formation, may be limited in such specimens. Therefore, this may be a possibility explaining the saturation of TL intensity of the glow peak.

Another possibility may also be available, which concerns the saturation of thermally stimulated conductivity. Fuchs and Taylor have shown that the conductivity which takes place at the temperature where the TL peak appears shows signs of saturation for relatively low dose of γ-ray. Therefore, the limitation of the number of conduction electrons could be a reason of saturation of TL intensity.

The mechanism of excitation of conduction electron during thermal annealing of irradiated crystals is far from being well understood. Various reactions could be considered for the origin of the conductivity.3,6)

Cape and Jacobs have concluded that the recombination energy between F and H centers ionizes the F-center electron, leaving the V_K center at or near the site of original F center. However, their conclusion involves that the number of created electron hole pair should be in proportion to that of annihilated F - H pairs. Therefore, their explanation is contradict to the experimental result obtained by Fuchs and Taylor, and probably also to the results obtained here.

Hayes and Hodby6) have proposed that the conduction electron is created by the recombination between I centers and F centers during annealing. However, current burst takes place at the temperature where H centers recombine with F centers in KBr crystal.3,4)

Though the details of the electron-excitation mechanism are not clear, it may be sure that the recombination energy between a Frenkel pair plays an important role in this process.

(3·2) Origin of the linearly increasing π component of the glow peak

As shown in previous section, π luminescence of the glow peak involves linearly increasing component with increasing the decrement of the H center and also the F center at the annealing stage at about 30 K. It has also been shown that this component is more resistive to the F-light illumination, than the saturating component.

The linear correlation between the maximum intensity and the decrement of the H center as well as of the F center suggests that the component originates from the recombination between neutral Frenkel pairs, since one consequence of eq.(5.3.1) is satisfied. Then another consequence is checked here.

Since the luminescence efficiency of the π emission from (V_Ke)$_\pi$ decreases above 25 K,$^{7)}$ the shape of glow peak must be modified in terms of the efficiency, for the accurate representation of the concentration of (V_Ke)$_\pi$ at each temperature.

Thus modified shape of the glow peak of the linearly increasing π component (the chain line in Fig.5.3.6) is compared with the first derivative of the annealing curve of the F or H center in Fig.5.3.9. The solid curve in the figure represent the calculated first derivative of the rate equation decsribing the annealing curve of F and H centers, determined in Fig.5.3.8, using the same values of parameters. One can see good agreement between both quantities.

Thus linearly increasing π component of the glow peak satisfies the expected relations from eq.(5.3.1).

Above results lead us to conclude that the component is due to the recombination between the H center and the F center in KBr.

The experimental result that the glow peak at about 30 K does not include such a linearly increasing component of σ luminescence indicates that the recombination between neutral Frenkel pairs can not result in the formation of (V_Ke)$_\sigma$.

The conclusion that the pair of F and H center produces

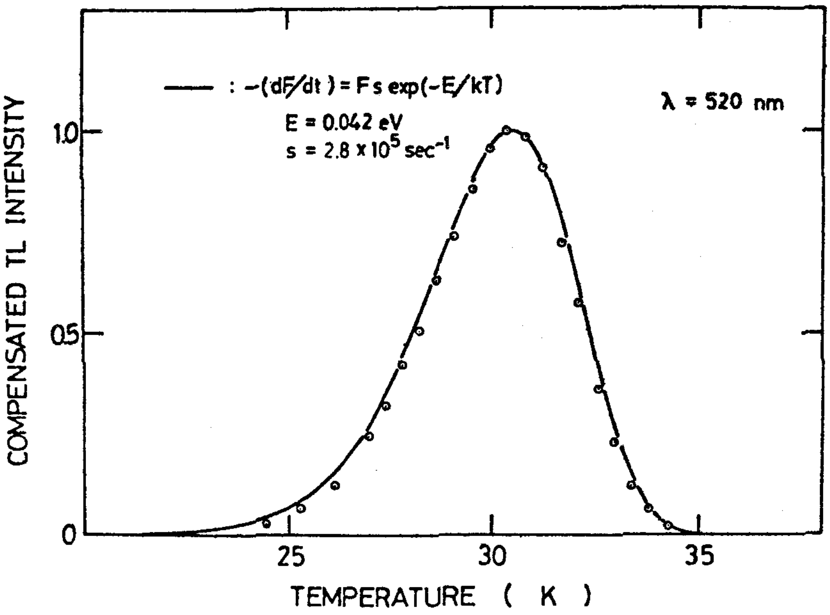

Fig.5.3.9. The shape of the glow peak of the linearly increasing π-emission component corrected for the temperature-dependent change in luminescence efficiency of (V_Ke)$_\pi$. Luminescence efficiency at a given temperature was obtained from the result of Karasawa and Hirai (ref.7). The solid curve shows the calculated result of eq.(5.3.1), using the same values of E and s for the annealing curve of the F or the H center shown in Fig.5.3.8.

only ($V_K e$)$_\pi$ is confirmed by another experimental result; the emission spectrum of the glow peak due to the recombination between an F center and an H center, the latter of which is freed from the H_{A1} center at 102 K, consists of only the π-emission band, as shown in Fig.5.3.7.

These results and discussions may indicate that the state of a pair of F and H centers is energetically higher than ($V_K e$)$_\pi$ and lower than ($V_K e$)$_\sigma$.

It should be stressed here that the quantum efficiency of creation of ($V_K e$)$_\pi$ through the recombination between F and H centers is considerably smaller than unity.

As mentioned before, it is generally believed that only a small number of V_K centers are produced by the irradiation of pure KBr and KCl at low temperature near liquid helium temperature. Kanzig and Woodruff8) have measured by EPR the ratio of the V_K-center concentration to the H-center concentration in pure KCl crystals after x-irradiation at 4.2 K, and found to be 0.46. Srinivasan and Compton9) have obtained the similar value from their optical absorption measurements. There have been no clear data of the ratio for KBr crystals, and the V_K band was not clearly observable in the present optical absorption measurements. However, it may not be unreasonable to estimate that the ratio in KBr is the order of 10^{-1}— 10^{-2}.

As shown in Fig.5.3.4, the π-emission intensity due to the F - H recombination becomes equal to the intensity of saturating component at the highest decrement of the H center (about 2.0×10^{17} cm^{-3}). It may be estimated that the quantum efficiency of the formation of ($V_K e$)$_\pi$ through the F - H recombination is about two orders of magnitude smaller than that through the recombination between V_K centers and electrons which is considered to be responsible for the saturating component.

It was also found that the quantum efficiency is about the same order for the case of thermal decay of the H_{A1} center, which takes place at 102 K. Therefore, it appears that the formation of ($V_K e$)$_\pi$ from the recombined state of F and

H centers is not connected with thermally activated mechanism.

(3·3) Mechanism of defect annihilation in KBr

Above results and discussions may indicate followings;

1) The state of the pair of F and H centers in KBr is energetically higher than (V_Ke)$_\pi$, but lower than (V_Ke)$_\sigma$.

2) The quantum efficiency of the formation of (V_Ke)$_\pi$ through the recombination between F and H centers is considerably small.

One of the important conclusion which we can deduce from these important findings concerns the formation energy, E_F, of an F-H pair. This quantity is very significant in defect formation mechanism in alkali halides; (V_Ke)$_F$ is a state whose level is energetically higher than, at least, the formation energy, and the energy imparted into interstitial halogen for replacement sequence is essentially the difference between the total energy (V_Ke)$_F$ possesses and E_F.

Below, we discuss the correlation between an exciton and the state of a pair consisting F and H centerd in defect annihilation process.

Fig.5.3.10 shows the schematical energy diagram for defect annihilation process. The ordinate of the figure represent approximately the energy, E, of the electron - hole pair state, involving the form of F-H pair. The coordiante, Q, is associated with the internuclear distance of Br_2^- in (V_Ke) state, and coordinate, Z, represents approximatery the location of the center of the Br_2^- as it translates parallel to its axis along <110> .[10)]

Since the Br_2^- in the H center has a smaller internucler distance than that in (V_Ke) system, the intersection of (E - Z) plane with (E - Q) plane should take palce at the larger value of Q than that which gives the minimum points of the states of radiative STE's.

The formation energy of the F - H pair in KBr, which was produced from the higher excite state of an exciton,

(V_Ke)$_F$, could be roughly estimated to be 5.5 eV, based on the following considerations:

1) From the results obtained in this study, it may be evident that an F - H pair state possesses the formation energy higher than the energy level of (V_Ke)$_\pi$ and lower than that of (V_Ke)$_\sigma$ at their minimum points.

2) Ikezawa and Kojima[11] have shown that the optical creation of (V_Ke)$_\sigma$ needs the energy higher than the threshold energy of 7.28 eV. The transition energy of the σ emission is 4.42 eV.[12] Assuming roughly that energy spent by non-radiative relaxation are equal for both the initial and final states, the energy corresponding to the minimum point of (V_Ke)$_\sigma$ is thus obtained to be about 6 eV. Under a similar assumption, the corresponding energy for (V_Ke)$_\pi$ is about 4.5 eV.

Thus the formation energy of a F - H pair of 5.5 eV may not be unplausible.

Kabler has pointed out, using a Born - Harber cycle with appopriate theoretical energies, that the energy to form an F - H pair is probably 2 - 3 eV greater than that to form an isolated I - F^+ pair.[10] Schultze and Hardy[13] have calculated the formation energy of I - F^+ pair. According to their result, the energy for KBr is 4.173 eV. The author

Thus the estimated formation energy of an F - H pair is roughly consistent with the Kabler's estimation.

The formation energy of an I - F^+ pair of about 4.0 eV is lower than the minimum-point energy of (V_Ke)$_\pi$ discussed above, which is consistent with the experimental result that the recombination between a charged Frenkel pair can not contribute to TL emission in KBr.

In order to explain the small quantum efficiency of the formation of (V_Ke)$_\pi$ through the recombined state of F and H centers, it should be nescessary to put a potential barrier between two states. The barrier is considered to be high enough for the thermal activation not to be active in the range between 10 K and 110 K, as mentioned above. Thus only a small fraction of F - H pairs could form (V_Ke)$_\pi$,

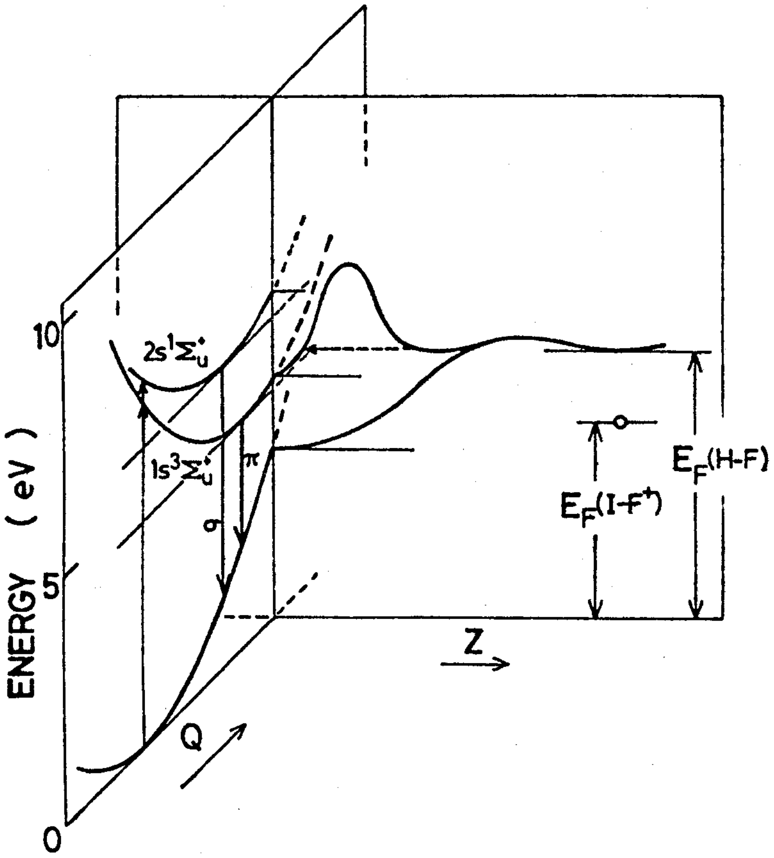

Fig.5.3.10. Schematic configuration coordinates curves for the defect annihilation in KBr. Along the coordinate Q, the exciton is relaxed into $2s^1\Sigma_u^+$ and $1s^3\Sigma_u^+$. The coordinate Z represents approximately the location of the center of the X_2^- as it translates parallel to its axis along a <110> direction. The F-H pair, with the formation energy of about 5.5 eV recombines into exciton levels of the lowest excited state and the ground state, through the intersection between two planes.

possibly owing to tunneling.

The origin of such a potential barrier is not very clear. One possibility is the repulsive potential between Br_2^- and nearest neighboring cations.

In the color-center formation, such a potential exists, which results in the drastical reduction of the F center formation yield at low temperature below 4.2 K.[15] However, in such a case, the potential is very low and the value of a few meV.

Itoh and Saidoh[16] have pointed out that the repulsive potential depends significantly on the electronic configuration of X_2^-: The potential for the X_2^- having a Σ_u^- configuration is larger by factors of 5 than that for the X_2^- with a Π_g (or Π_u) configuration.

It is clear that in the annihilation process of the H center, the configuration of Br_2^- is evidently Σ_u. Therefore, it might be possible that the repulsive potential is considerably high in the case of defect annihilation.

By such a potential, the most part of the formation energy may be released,without forming (V_Ke)$_\pi$,non-radiatively. Thus the stored energy (energy release in the form of heat) measurement is considered to be of importance for the more quantitative understanding of the defect annihilation process.

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6

MECHANISM OF LOW TEMPERATURE RADIATION HARDENING

[6·1]

INTRODUCTION

Present problems in radiation-hardening study are clarified. First, characteristic features of radiation hardening phenomenon are discussed, in order to make clear the correlations with other areas of research on mechanical property of alkali halides. Next, important concepts of solution hardening are summalized. Then crucial questions in radiation-hardening study are proposed. Finally, an overall plane of the contents in this chapter is sketched.

§1 Radiation Hardening as a Property in the radiation-Induced Excited State of Alkali Halides.

Effects of radiation-induced defects on bulk properties of crystals have been an active and important field in the research of radiation damages in alkali halides. The main interest of such studies concerns the interaction of radiation-induced defects with other species the host crystal involves.

Several works in this line of researches have been performed so far, e.g. on thermal conductivity,1) volume expantion,2-4) mechanical properties,5-7) and so on. Radiation hardening has been a typical and interesting problem of such fields of radiation-damage study, where the fundamental problem lies in the interaction between radiation induced defects and the dislocations in a crystal.

In the following part of this section, we briefly discuss the characteristic features of radiation hardening, in order to make clear the correlations with other areas of research in mechanical properties of alkali halides.

There are several methods to determine the hardness, which is a typical mechanical properties of materials, e.g.

a tensile test, a compression test, an indentation test, and so on. Compression tests are usually applied for alkali halides, because of their fragility and easier analysis of the test. Here we restrict the hardness to the elastic limit, or the flow stress, which is the stress at the transfering point from the elastic deformation to the plastic one in the stress-strain curve.

Most of the present understanding of the mechanism of deformation of alkali halides is based on the extensive and definitive studies of Gilman and Johnston.8-9) They have shown that the elastic limit is mainly determined by the resistance for the moving dislocations.

Principal resistances for the dislocation movement in solids are considered to originate from Peierls stress, the interaction with impurity and other point defects, the interaction with other dislocations, etc. In the covalent crystals, Peierls stress strongly contribute to its hardness, whereas its contribution is small and the interaction with other imperfections becomes dominant in f.c.c. crystals. The b.c.c. crystals and ionic crystals are considered to be situated in the middle of them.10)

Radiation hardening, that is, the hardening phenomenon of crystals induced by radiation has been accounted as a ploblem which concerns the interaction between radiation-induced defects and dislocations, the former of which, in most cases, can be treated as point defects in solids. Thus, in this sense, we should pay our attention to the similarlity between radiation hardening and solution hardening. In fact, most work on radiation hardening has based on the concepts which have been developed in the research of solution hardening. Then, we summalize the important features of solution-hardening concepts concerned.

§2 Solid Slution Hardening

Solid solution hardening is the hardening effects due to the atomic size defects dispersed in the crystal, where a substitutional solute or a impulity atom, an atomic vacancy, interstitial atoms, and their complexes are considered to be the defects.

When the defects are uniformly distributed throughout the crystal with the concentration of C, the stress necessary for a dislocation move at 0 K, τ_o, can be deduced as follows: Assume that F_{max} represents the maximum force exerted by the defect on a dislocation attempting to move pass it, and let L be the spacing between defects on a given slip plane. The force per unit length of dislocation is then F_{max}/L, and the increase in stress nescessary to move the dislocation is thus

$$\tau_o = F_{max}/bL \tag{6.1.1}$$

where b is the Burgers vector.[11)]

Uniform defect distribution gives the correlation of $L \propto C^{-1/2}$. Then the crucial problem concerns the estimation of F_{max}.

It is natural first to describe the atomic size defect-dislocation interaction in terms of the elastic interaction. Fleisher[12)] evaluated the value of F_{max} with the similar way to Cochhardt et al.[13)] did. He has dealt with the interaction of the stress field of the dislocation with the strain field of the point imperfections, and pointed out that the effect upon flow stress is much greater for defect with tetragonal strain field than for those with isotropic ones. Fleisher has calculated the flow stress at 0 K in the hardened crystals by tetragonal defects to deduce following descriptions;

$$\tau_o = \frac{G\ \Delta\varepsilon\ C^{1/2}}{3.3} \quad ;\ \text{for screw dislocation} \tag{6.1.2}$$

$$\tau_o = \frac{G\ \Delta\varepsilon\ C^{1/2}}{3.3(1-\nu)} \quad ;\ \text{for edge dislocation} \tag{6.1.3}$$

where G is the shear modulas, $\Delta\varepsilon = |\varepsilon_1 - \varepsilon_2|$ is a measure of tetragonality of the strain in terms of the elastic strain ε_1 and ε_2 of the defect in two perpendicular directions.

Fleisher's model on solid solution hardening shown above can explain some experimental results,[14)] and seems to be useful, even now, for the elementary understanding of solid solution hardening.

But, many studies for solid solution hardening done after Fleisher have brought forward several criticisms on his theoretical treatments.[15-18)] Instead of decussing these critisisms, we here point out following further problems, which involve close correlation with radiation hardening in alkali halides, one should take account of in the analysis of dislocation - point defect interaction:

1) Fleisher assumed that the flow stress is mainly dominated by the resistance force against a screw dislocation. The force against an edge dislocation should be, however, employed, from following reasons; a) the resistance force against the latter dislocation is usually larger than that for the former, and b) the flow stress is dominated by the resistance force against the dislocation with lower speed.

2) Pratt et al.[19)] and Chang and Graham[20)] have suggested that the dislocation-strain field causes the reorientation of some types of defects such as divalent cation-vacancy pair. The effects due to such motions of defects should be taken into account in the evaluation of the stress magnitude of hardening phenomena.

3) Sibley[21)] has recently suggested that the electrostatic interaction between dislocations and charged defects can not be neglected, and may play a significant role, under certain conditions. We should, therefore, pay our attention also to such a type of interaction in the hardening phenomena especially in ionic crystals.

3 Present Problems in Radiatiom-Hardening Study

Principal inquries concerning radiation hardening have been following two: 1) what kinds of defect introduced by irradiation mainly contribute to hardening ? and 2) How such defects interact with moving dislocations ?

For the clarification of these problems, it should, therefore, be fruitful to study the hardening mechanism in detail in a system containing the defects whose configurations are simple, and properties are well known, since a detailed analysis should be easier for such a system.

Now it is evident that the radiolysis products are Frenkel pairs, as described in Chap.[1.2]. Several works performed before14,18) have suggested that complementary defects to anion vacancies, or the interstitials, play an important role in the radiation hardening; nevertheless, no clear works have been done on the role of interstitials in radiation hardening. This is supposed to be mainly due to the fact that radiation induced simple interstitials, the H and the I center, can exist only at a low temperature, which then leads us to the more difficulty in performing mechanical test because of the fact that the sample becomes too brittle in such low temperatures. This situation may result in another disadvantage in experiments: Since these primary interstitials are stable only at low temperature, for example the I center below 20 K and the H center below 40 K in KBr, respectively,21,22) measurements on temperature dependent mechanical property should be restlicted to the very narrow temperature regions, which may make the full analysis of temperature dependent behaviour difficult.

At present, it has been clearly shown that these primary interstitials are stabilized by alkali impurities such as Na^+ and Li^+ in KBr and KCl crystals, which are thermally stable above 80 K.23-25) This gives a strong possiblity of analyzing the radiation hardening by simple interstitial type defects with nearly primary forms.

Thus we study here the mechanism of low temperature radiation hardening to solve the crucial questions, making use of the stabilization of interstitials by alkali impurity in KBr crystals.

§4 Outline of the contents

First, we solve in Chap[6.2] the first question; what kinds of defects mainly contribute to hardening at low temperature. γ-irradiation at liquid nitrogen temperature is performed throughout the present study, for the uniform coloration which is essential in the quantitative analysis of the interaction between dislocation and radiation-induced defects.

Detailed analysis is made on the correlation between thermal recovery of induced flow stress,$\Delta\tau$, and thermally induced defect reactions at the stages. The results, together with the ones of optical bleaching effects on the recovery of $\Delta\tau$ and color centers, reveal that the I_A center is mainly responsible for the radiation hardening. Then, calculations are carried out on the interaction energy between the dislocation and primary interstitials in terms of the linear elasticity theory. Results again indicate that the interstitial-ion center is more effective than the atom as the hardening agent. A few discussions on the obtained results are made.

In Chap.[6.3], we attempt to solve the second question; How the defect interacts with dislocations? There thermally activated mechanism is applied to the interaction of dislocations with the I_A center in KBr:Li system. Wide range of temperature dependences as well as annealing patterns are measured on the induced flow stress and the activation volume. Description of these results in terms of thermal activation mechanism is good.

Through such an analysis, we finally determine values of several important parameters in the hardening mechanism.

Thus the mechanism of low temperature radiation hardening is clearly solved in this work.

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[6·2]

HALOGEN INTERSTITIALS AS THE HARDENING AGENT IN KBr CRYSTALS AT LOW TEMPERATURE

Mechanism of low-temperature radiation hardening in KBr crystals has been studied from the view-point that what defects induced by irradiation are mainly responsible for hardening. Detailed analysis is carried out on the thermal recovery stages of induced flow stress, $\Delta\tau$, accompanied by thermally induced reactions of color centers. Four and three annealing stages can be distinguished in KBr:Na and KBr:Li, respectively. The I_A and/or H_A centers contribute considerably to the radiation-induced flow stress increment in both systems. Optical bleaching effects on the recovery of $\Delta\tau$ and color centers reveal that the I_A center is mainly responsible for the hardening at the stage concerned. The result of calculation on the interaction energy between the dislocation and primary interstitials also shows that the interstitial halogen ion is more effective than the atom as the hardening agent. Some discussions are made on the conclusion obtained here.

§1 Introductory Remarks

As a general principle to the radiation hardening study, it is very important to clarify two big problems by taking following steps: 1) What defects induced by irradiation contribute to the hardening ? 2) How such defects interact with moving dislocations ? For the clarification of these problems, it should therefore be fruitful to study the hardening mechanism in detail in a system containing the defects whose lattice configurations are as simple as possible, since a detailed analysis should be easier for such a system.

In this chapter, the first problem in mechanism of low-temperature radiation hardening is solved, based on the experimental results and the calculation in terms of the linear elasticity theory.

First, detailed analysis is made on the thermal recovery of radiation-induced flow stress and on the annealing behaviour of produced color centers. Optical bleaching effects on the mechanical property and on the color centers will give the clear identification that the interstitial halogen ion is the main hardening agent at the low temperature. This conclusion is confirmed by the results of calculations on the interaction energy between dislocations and primary interstitials. Thus the first problem of radiation hardening research will be solved clearly in this chapter.

§2 Experimental Results

Figure 6.2.1. shows the changes of induced flow stress in KBr crystals accompanied by γ-ray dose. It is seen that the change is rapid below 1.0×10^7 r, and is slow above the dose. The hardening rate in the doped samples with alkali impurities is observed to be higher than that in pure crystal in the region corresponding to early stage of coloration.

Formation of various types of color centers has the similar tendency on dose, so that it is difficult to analyze the contribution of a given center to the increase in $\Delta\tau$ in this result.

One of the easy methods to make clear the contributions of various defects to the radiation-induced hardening, is to analyze the correlation between the thermal recovery of and themal decay of these defects. Then isochronal pulse annealing experiments were carried out as to the recovery of $\Delta\tau$ as well as color centers.

Thermal-recovery curve of $\Delta\tau$ in KBr:Na is shown in Fig.6.6.2, together with annealing curves of typical color centers. Recovery of $\Delta\tau$ in this system can be divided into following four stages.

Stage I(77 K - 150 K): About 27% of $\Delta\tau$ recover in

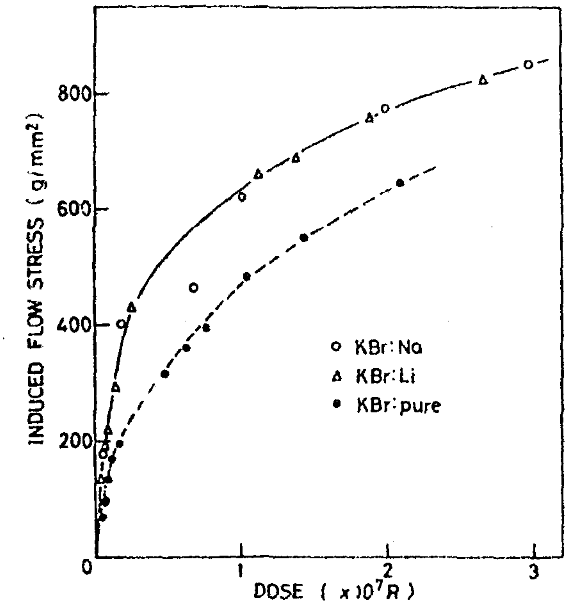

Fig.6.2.1. Dose dependence of induced flow stress in KBr:Na(○), KBr:Li(Δ), and KBr:pure(●), respectively. Measurements were made for as-irradiated specimens at 77 K.

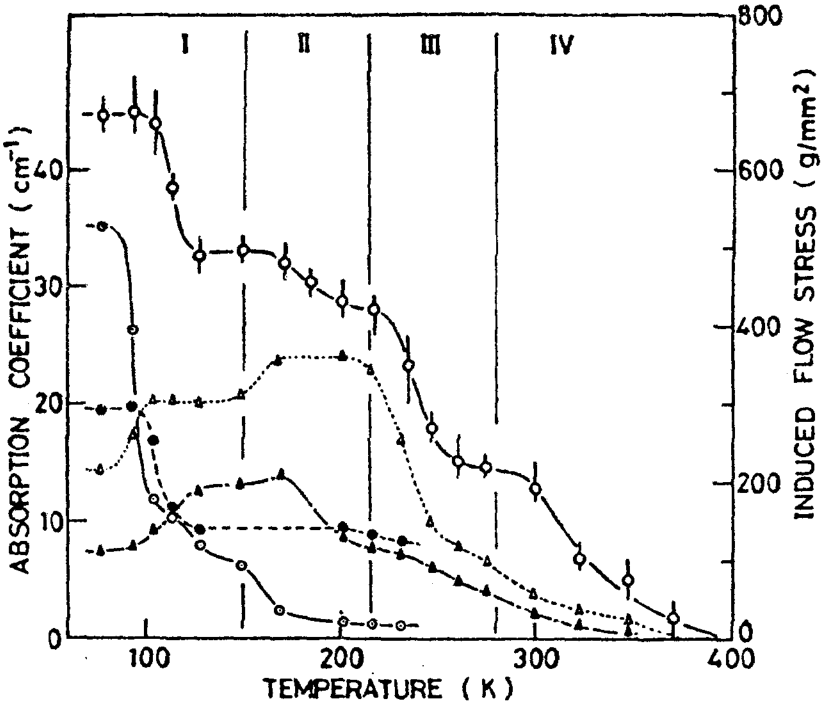

Fig.6.2.2. Results of isochronal pulse annealing experiments for induced flow stress(o), the V_1 band(⊙), the I_A band(●), the V_4 band(Δ), and the V(306) band(▲) in KBr:Na, respectively. Samples were warmed for 10 min at a constant temperature. All measurements were made at 77 K.

this stage. Most of the V_1 band decrease, owing to the thermal decay of the H_{A1} and H_{A2} centers, which has been discussed in Chaps.[4·3] and [5·2]. Simultaneously, the I_A band decays almost completely. On the other hand, the V_4 and V(306) bands grow corresponding to the annealing stages of the V_1 band. About 50% of initial F center concentration decrease in this stage.

Stage II(150 - 215 K): About 9% of $\Delta\tau$ recover in this temperature region. In the absorption spectrum, main changes are the decreases of the V(410) band and V(306) band, the former of which is a component of the V_1 band. The F-band height decreases by 13%.

Stage III(215 - 280 K): Induced flow stress has about 30% of recovery here. Corresponding change in optical absorption spectrum is the decay of the V_4 band. The decrement of the F band is 25% in this stage.

Stage IV(280 - 400 K): The rest of $\Delta\tau$(about 30%) completely recover and the value of flow stree returns to that before irradiation. Decreases of broad absorption bands are observed in uv region of the absorption spectrum. The F band height decreases by about 13% in tis temperature region.

Similar results for KBr:Li system are shown in Fig.6.2.3. It is possible to divide annealing behaviours of $\Delta\tau$ and color centers into following three stages.

Stage I(77 - 180 K): Induced flow stress remains almost unchanged, though two small sub-stages are observable around 95 K and 160 K. The fractional recovery of $\Delta\tau$ is about 9%, which is small compared with those in later stages. Change in optical absorption due to color centers can be also disregarded.

Stage II(180 - 260 K): About 31% of the fraction of $\Delta\tau$ recover in this stage. Corresponding changes of color centers are thermal decays of the $H_A(Li^+)$ bands and the $I_A(Li^+)$ band. On the other hand, the V(306) band grows considerably owing to the conversion of the $H_A(Li^+)$ centers. The H-band height decreases by about 46% in this stage.

Stage III(260 - 410 K): The rest of $\Delta\tau$ recovers com-

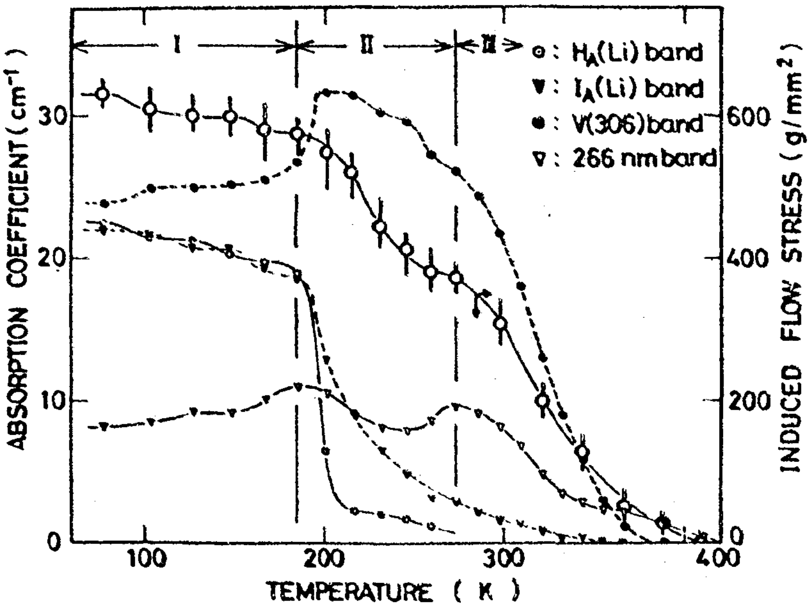

Fig.6.2.3. Results of isochronal pulse annealing experiments for induced flow stress(o), the H_A(Li) band(⊙), the I_A(Li) band(▼), the V(306) band(•), and the V(266) band (▽), in KBr:Li, respectively. Samples were warmed for 10 min at a constant temepature. All measurements were made at 77 K.

pletely in this temperature region, and the value of flow stress becomes essentially the same as that before irradiation. In this stage, various V-type bands, situated in uv region, for example the V(306) band and the band peaking at 266 nm, decay with similar patterns, accompanied by the decrease of the F-band hight.

In most annealing stages distinguished above, more than two types of interstitial centers decay thermally. This situation is especially the case for the last stages in both samples.

Our main interest here concerns the nature of the center consisting of the single halogen interstitial atom and ion as the hardening agent. Then focus our attention on the annealing stages due to thermal decay of such centers.

An interstitial atom and ion can exist, respectively, as H_A and I_A centers in the present samples. These two types of centers decay thermally almost the same temperature region, i.e. in Stage I for KBr:Na and in Stage II for KBr:Li, respectively, where considerable amount of recovery in $\Delta\tau$ takes place. Therefore, it is clear that these single interstitial-type centers act as the effective obstacle for the dislocation movement.

It can be seen that for both samples the decay of the H_A center precedes that of the I_A center and the recovery of $\Delta\tau$. This result suggests that the I_A center is mainly responsible for the recovery of $\Delta\tau$ in respective stages. In order to make clearer the contribution of the two types of interstitial centers to flow stress increment, we examined the recovery of $\Delta\tau$ in samples which contains I_A centers and little H_A centers. Such specimens were prepared by means of optical bleaching after γ-irradiation.

Figures 6.2.4 and 5 show the changes in optical absorption spectra due to illumination of visible light ($\lambda > 390$ nm) to the irradiated KBr:Na and KBr:Li, respectively. In KBr:Na, the H_A centers were almost completely bleached out, whereas the I_A center was hardly affected by such a treatment. On the other hand, the $I_A(Li^+)$ center grows, corresponding to

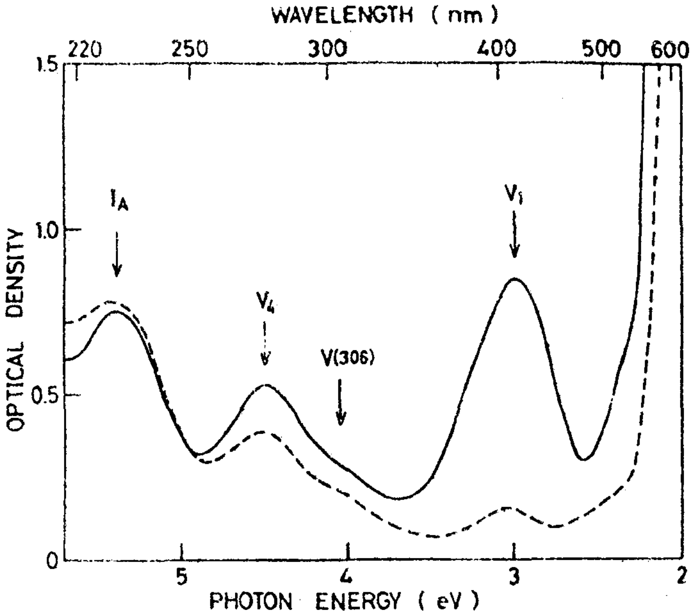

Fig.6.2.4. The optical absorption spectra of KBr:Na irradiated by γ ray at 77 K(solid line) and of the sample illuminated with visible light for 220 min after irradiation (broken line), respectively. Measurements were made at 77 K.

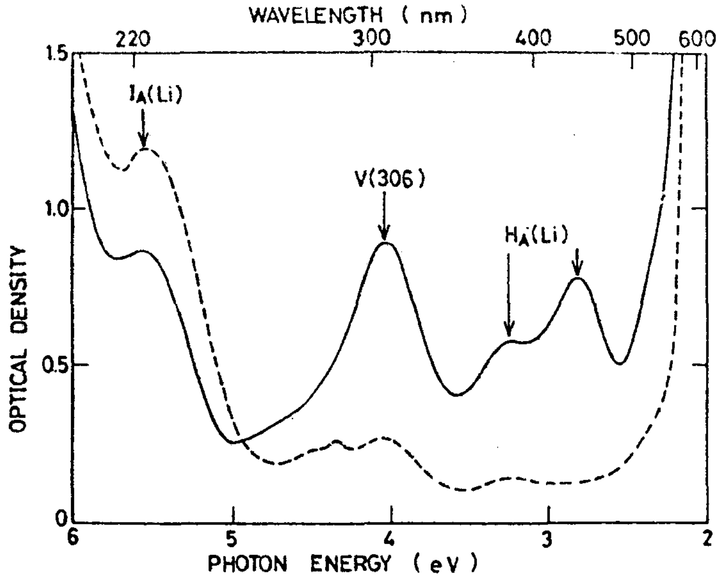

Fig.6.2.5. The optical absorption spectra of KBr:Li irradiated by γ ray at 77 K(solid line) and of the sample illuminated with visible light for 670 min after irradiation (broken line), respectively. Measurements were made at 77 K.

the decreases of the $H_A(Li^+)$ center and of other halogen-atom type centers.[1)] Thus, such samples are considered to be the best one to separately analyze the responsibility of the H_A or the I_A center for the flow-stress increment.

Figure 6.2.6 shows the thermal-recovery curves of $\Delta\tau$ in the samples which were illuminated with light before thermal treatment. Results of as-irradiated samples are also shown for comparison.

One can see that recovered amount of $\Delta\tau$ in KBr:Na does not change by the optical bleaching. On the other hand, it increases in KBr:Li, probably due to the increase in concentration of the $I_A(Li^+)$ center by the optical conversion.

The result shown in Fig.6.2.6 strongly indicates that the main hardening agent in the stage is not the H_A center but the I_A center.

§3 Discussions

Results obtained in the preceding section indicate that the color center consisting of a single halogen interstitial significantly contributes to the radiation-induced flow stress increment at low temperature. Furthermore, experimental results of optical bleaching effect clearly show that the interstitial ion-type center, the I_A center, is the main hardening agent in the present case.

In this section, we will first represent the results of calculations for the elastic interaction between dislocations and halogen interstitials. Then based on the results, together with the present experimental results, the nature of the interstitials as the hardening agent is discussed.

(3·1) Calculation of elastic interaction force between dislocations and primary halogen interstitials in KBr

The technique used for obtaining the interaction energy and the force between a defect and a dislocation is based

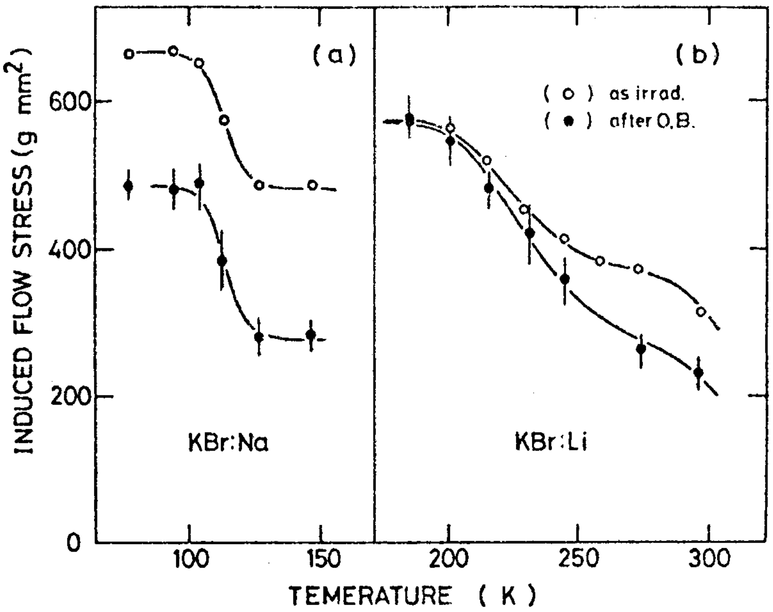

Fig.6.2.6. Thermal recovery curves of induced flow stress of optically bleached KBr:Na;(a), and KBr:Li; (b), respectively. KBr:Na and KBr:Li crystals were illuminated with visible light for 220 min and for 670 min at 77 K, respectively. Samples were warmed for 10 min at a constant temperature. Measurements were made at 77 K. The recovery curves of as irradiated samples are also shown for comparison

on the work of Cochardt et al.[2] who have used essentially Eshelby's method for the transformation strain problem for a misfitting sphere.[3]

We consider the tetragonal defect induced in the solid within a small sperical volume, V, to undergo a following pure strain;

$$\varepsilon_{ij} = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix} \qquad (6.2.1)$$

written for a coordinate system aligned with the principal distortion axis of the defect.

Then, following Eshelby, the total interaction energy between the defect and a dislocation is given by

$$E_{int} = - \sigma_{ij}\varepsilon_{ij} V \qquad (6.2.2)$$

where the repeated subscripts imply summations and σ_{ij} is the (ij) component of the dislocation stress field in a coordinate system aligned with the principal axes of the tetragonal defect. When a dislocation glides on the slip place, the interaction force on the dislocation is given by

$$F = \frac{\partial E_{int}}{\partial x} \qquad (6.2.3)$$

where x stands for the distance between a dislocation and a defect.

Strain tensors of the primary interstitials, the H center and the I center can be obtained, by the transformation, from the double force tensors of them.[3,4] The double force tensor for the H center in KBr obtained by Bachmann and Peisl has been given by eq.(4.4.1) in Chap.[4·4]. The tensor for the I center has been obtained from diffuse x-ray scattering by Lohstoter et al.[5] They obtained following two possible values of the tensor;

$$P_I = \begin{pmatrix} 11.05 & 0 & 0 \\ 0 & 11.05 & 0 \\ 0 & 0 & 26.11 \end{pmatrix} \text{ X } 10^{-12}\text{erg} \qquad (6.2.4)$$

and

$$P_I^* = \begin{pmatrix} 20.99 & 0 & 0 \\ 0 & 20.99 & 0 \\ 0 & 0 & 6.09 \end{pmatrix} \times 10^{-12}\,\mathrm{erg} \qquad (6.2.5)$$

in the crystal coordinates.

Here it should be pointed out that the H center has the [110] symmetry, and the I center [100] symmetry, respectively. There are six possibe orientations of the defect for the moving dislocation in the former case, whereas three possible ones in the latter.

When we assume that a dislocation glide on a plane aparted from the defect by one atomic plane, the force-distance relations for above possible cases are given by following equations(Details of the calculation are given in Appendix in this chapter):

1) For the I center with P_I and a screw dislocation;

$$F_{s1} = 0$$

$$F_{s2} = F_0 \ (-1.443)\ \frac{-\xi^2+1}{(\xi^2+1)^2} \qquad (6.2.6)$$

$$F_{s3} = F_0 \ (1.443)\ \frac{-\xi^2+1}{(\xi^2+1)^2}$$

2) For the I center with P_I and an edge dislocation;

$$F_{e1} = F_0 \frac{4.178(\xi^3+\xi)}{(1-\nu)(\xi^2+1)^3}$$

$$F_{e2} = F_0 \frac{1.443\xi^4+5.476\xi^3-8.658\xi^2+5.476\xi+1.443}{(1-\nu)(\xi^2+1)^3} \qquad (6.2.7)$$

$$F_{e3} = F_0 \frac{-1.443\xi^4+5.476\xi^3+8.658\xi^2+5.476\xi-1.443}{(1-\nu)(\xi^2+1)^3}$$

3) For the I center with P_I^* and a screw dislocation;

$$F^*_{s1} = 0$$

$$F^*_{s2} = F_o \ (1.484) \ \frac{- \xi^2 + 1}{(\xi^2 + 1)^2} \tag{6.2.8}$$

$$F^*_{s3} = F_o \ (-1.484) \ \frac{- \xi^2 + 1}{(\xi^2 + 1)^2}$$

4) For the I center with P_I^* and an edge dislocation;

$$F^*_{e1} = F_o \ \frac{6.176(\xi^3+\xi)}{(1-\nu)(\xi^2+1)^3}$$

$$F^*_{e2} = F_o \ \frac{-1.484\xi^4+7.520\xi^3+8.904\xi^2+7.520\xi-1.484}{(1-\nu)(\xi^2+1)^3} \tag{6.2.9}$$

$$F^*_{e3} = F_o \ \frac{1.484\xi^4+7.520\xi^3-8.904\xi^2+7.520\xi+1.484}{(1-\nu)(\xi^2+1)^3}$$

5) For the H center and an screw dislocation;

$$F_{s1} = F_{s2} = 0$$

$$F_{s3} = F_o \ \frac{- 0.435\xi^2+0.780\xi+0.435}{(\xi^2+1)^2}$$

$$F_{s4} = F_o \ \frac{0.435\xi^2-0.780\xi -0.435}{(\xi^2+1)^2} \tag{6.2.10}$$

$$F_{s5} = F_o \ \frac{- 0.435\xi^2-0.780\xi+0.435}{(\xi^2+1)^2}$$

$$F_{s6} = F_o \ \frac{0.435\xi^2+0.780\xi-0.435}{(\xi^2+1)^2}$$

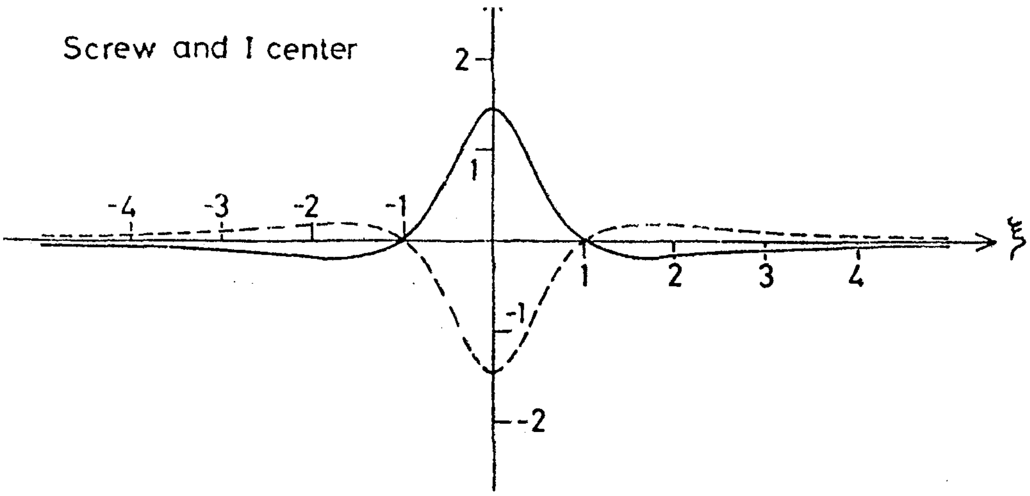

Fig.6.2.7. Force-distance relation in the interaction between the screw dislocation and the I center. The solid line shows the results of F_{s3} in eq.(6.2.6) and of F^*_{s2} in eq.(6.2.9), and the broken line that of F_{s2} in eq.(6.2.6) and of F^*_{s3} in eq.(6.2.9), respectively.

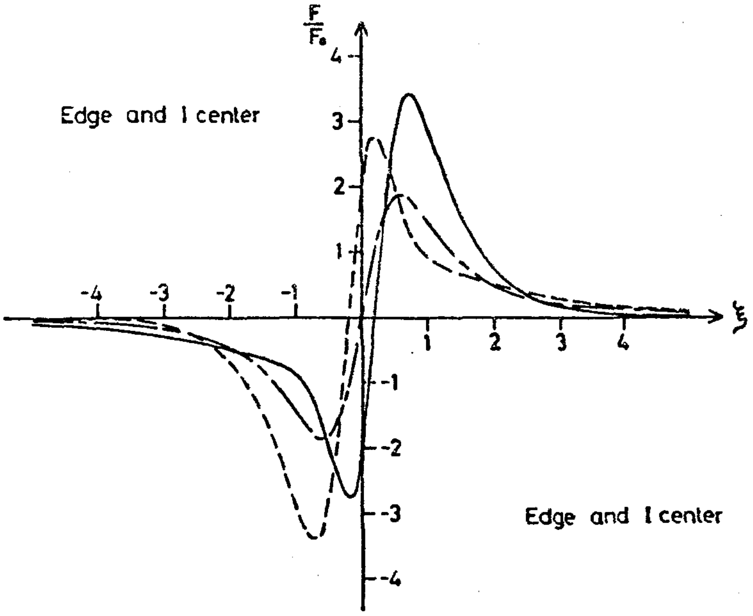

Fig.6.2.8. Force-distance relation in the interaction between the edge dislocation and the I center with P_I. Solid, broken, and chain lines indicate results of F_{e3}, F_{e2}, and F_{e1} in eq.(6.2.7), respectively.

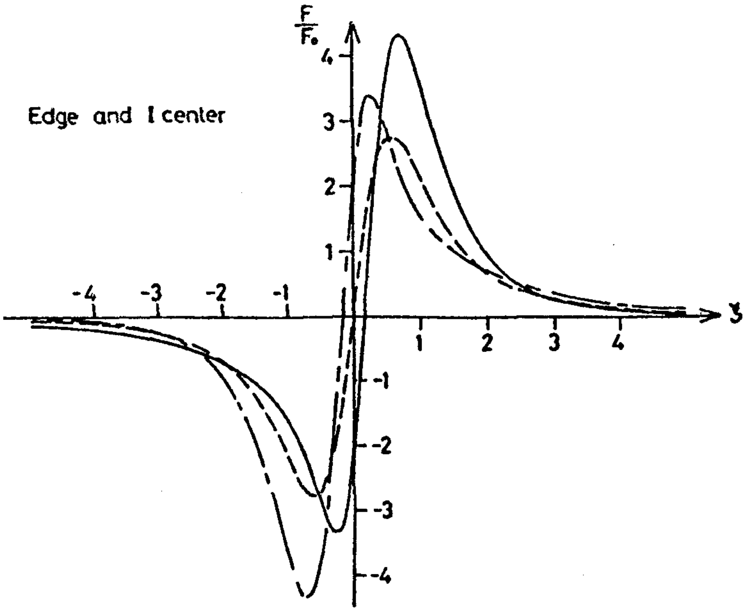

Fig.6.2.9. Force-disance relation in the edge dislocation and the I center with P_I^*. Solid, broken, and chain lines show results of F^*_{e3}, F^*_{e2}, and F^*_{e1} in eq.(6.2.9), respectively.

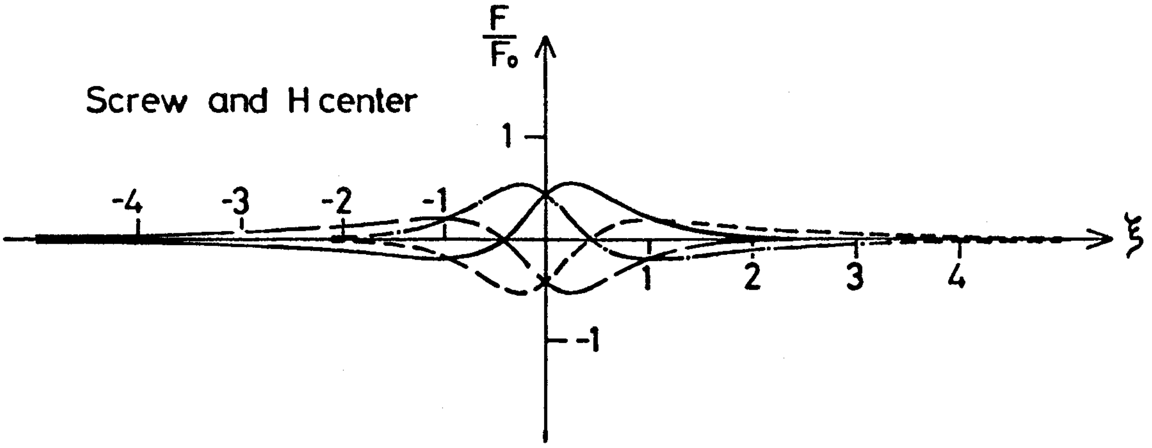

Fig.6.2.10. Force-distance relation in the interaction between the screw dislocation and the H center. Solid, large broken, chain, and small broken curves show results of F_{s3}, F_{s4}, F_{s5}, and F_{s6} of eq.(6.2.10), respectively.

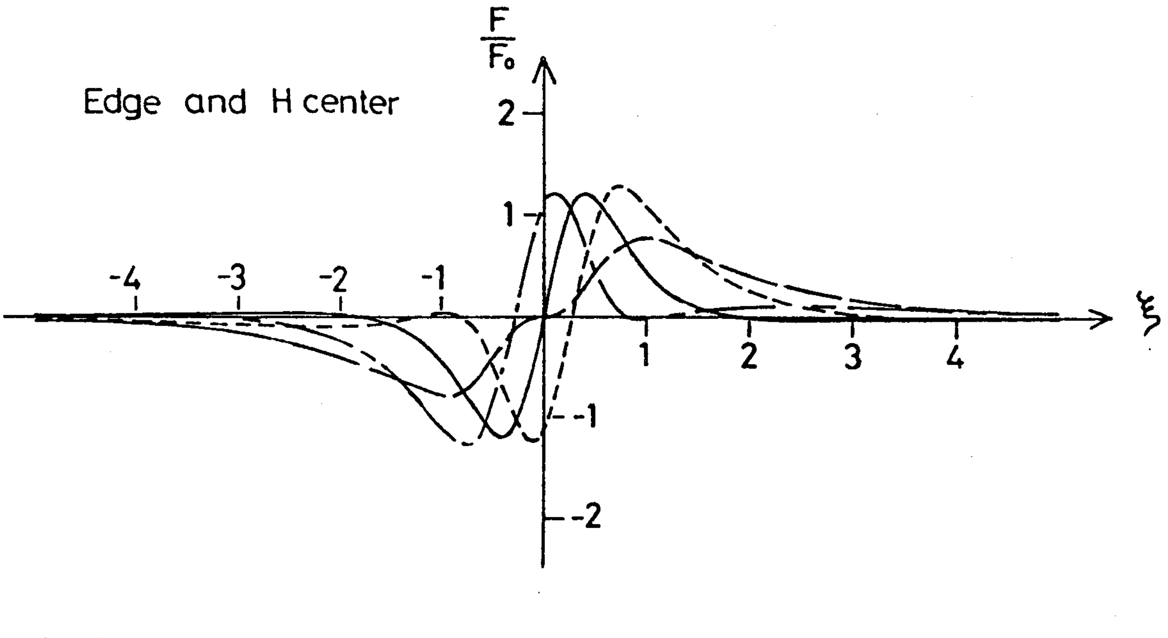

Fig.6.2.11. Force-distance relation in the interaction between the edge dislocation and the H center. Small broken, chain, large broken, and solid curves indicate results of $F_{e1}(F_{e2})$, $F_{e3}(F_{e4})$, F_{e5}, and F_{e6} in eq.(6.2.11), respectively.

6) For the H center and an edge dislocation;

$$F_{e1} = F_{e2} = F_o \frac{-0.819\xi^4+1.559\xi^3+4.913\xi^2+1.559\xi-0.819}{(1-\nu)(\xi^2+1)^3}$$

$$F_{e3} = F_{e4} = F_o \frac{0.819\xi^4+1.559\xi^3-4.913\xi^2+1.559\xi+0.819}{(1-\nu)(\xi^2+1)^3}$$

$$F_{e5} = F_o \frac{-0.861\xi^3+3.482\xi}{(1-\nu)(\xi^2+1)^3} \qquad (6.2.11)$$

$$F_{e6} = F_o \frac{4.503\xi^3+0.088\xi}{(1-\nu)(\xi^2+1)^3}$$

In these equations, F_o is defined as;

$$F_o = \frac{G\ V}{2\ \pi\ b} \qquad (6.2.12)$$

where G and b are shear modulus and the Burgers vector, respectively, and ξ stands for x/b. ν is the Poisson ratio.

Calculated force - distance curves using above obtained equations are shown in Figs.6.2.7 to 11.

One can see in these figures that the maximum force exerted by the I center on a dislocation, F_{max}, is always larger than that by the H center, irrespective of the different values of the double force tensor for screw and edge dislocations. This result strongly indicates that the I center is more than three or four times effective as the hardening agent than the H center, since F_{max} is correlated with flow stress in the form of eq.(4.1.1).

(3·2) Nature of the halogen interstitials as the hardening agent

Caluculations performed in the preceding paragraph indicate that the interaction force of dislocation for the I cen-center is stronger by factors of 3 or 4 than for the H center in KBr. This result agrees qualitatively with the present experimental result that the I_A center is the main hardening agent in KBr crystals containing alkali impurity.

The I_A center is, of course, is not "pure" interstitial ion, but associated with a nearest neighboring cation inputity. The strain caused by such an I_A center is not exactly the same as that of intrinsic halogen ion center. For qualitative discussion, however, the difference due to association with alkali impurities is not supposed to be essential.

Thus we can safely conclude that the interstitial halogen ions play the most important role in the change of mechanical property of irradiated alkali halides at low temperature.

It should be pointed out here that there may be following additional circumstances that make the contribution of the interstitial ions enhance and that of the atoms lower to the obstruction of dislocation movement.

1) It has been shown 6) that the H_A center in KCl exhibits the rotational motion, i.e. disorientation, above 16.8K though there is no loss in the number of the center due to the motion. Such a property of the H_A center may allow it to orientate in the direction with least interaction energy between the center and a dislocation, when the latter approaches the former. Present measurement made at 77 K, therefore, might involve such an effect of the H_A center. The more accurate experimental determination of the effectiveness of the H center as a hardening agent should be done at the temperature below the disorientation temperature.

2) Since the dislocation should be charged in alkali halides, not only elastic but also electrostatic interaction may be important in the interaction of dislocations with other defects in this material.7) The I and F^+ center constitute a charged Frenkel pair, whereas the H and F centers a neutral pair. Therefore, it may be expected that the interaction of the interstitial ion with a dislocation is more effective than that of the interstitial atom, when the electrostatic interaction is active and is repulsive. The fact that the interstitial ion is the main hardening agent in alkali halides might come from also in this electrostatic interaction. However, such a feature of the interaction of dislocation in alkali

halides is far from being well understood, and must be clarified in future.

Appendix

Here the formulas describing the force - distance relation between the screw dislocation and the defect with [100] symmetry are deduced. The equations for other cases can be obtained with same procedure.

The stress components of the screw dislocation are expressed in terms of dislocation coordinates by [8)]

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma_{xy} = \sigma_{yx} = 0$$

$$\sigma_{xz} = \sigma_{zx} = -\frac{Gb}{2\pi}\,\frac{y}{x^2+y^2} \qquad (A.1)$$

$$\sigma_{yz} = \sigma_{zy} = \frac{Gb}{2\pi}\,\frac{x}{x^2+y^2}$$

where G is the shear modulas, b the Burgers vector, and x-axis stands for the moving direction of a dislocation. These components are converted in crystal coordinates as follows:

$$\sigma_{XX} = \frac{Gb}{2\pi}\,\frac{x}{x^2+y^2}$$

$$\sigma_{YY} = -\frac{Gb}{2\pi}\,\frac{x}{x^2+y^2} \qquad (A.2)$$

$$\sigma_{ZZ} = 0$$

For possible three orientations of the defect for the moving dislocations, the interaction energy between them are expressed by following set of equations, from eq.(6.2.2);

$$E_{s1} = \frac{G\ b}{2\ \pi} \frac{x}{x^2 + y^2} (\varepsilon_1 - \varepsilon_2) V$$

$$E_{s2} = \frac{G\ b}{2\ \pi} \frac{x}{x^2 + y^2} (\varepsilon_2 - \varepsilon_3) V \tag{A.3}$$

$$E_{s3} = \frac{G\ b}{2\ \pi} \frac{x}{x^2 + y^2} (\varepsilon_3 - \varepsilon_1) V$$

where ε_i (i=1,2,3) is the strain component of the defect described by eq.(6.2.1). The interaction force as a function of distance between them can be obtained from the derivative of these interaction energy with respect to the distance on the slip plane as shown by eq.(6.2.3). Assumption that a dislocation glides on a plane aparted from the defect by one stomic plane means y = b. Then the interaction force is expressed by the following set of equations;

$$F_{s1} = \frac{\partial Es1}{\partial x} = \frac{G\ V(\varepsilon_1-\varepsilon_2)}{2\ \pi\ \ b} \frac{-\ \xi^2+ 1}{(\ \xi^2+ 1)^2}$$

$$F_{s2} = \frac{\partial Es1}{\partial x} = \frac{G\ V(\varepsilon_2-\varepsilon_3)}{2\ \pi\ \ b} \frac{-\ \xi^2+ 1}{(\ \xi^2+ 1)^2} \tag{A.4}$$

$$F_{s3} = \frac{\partial Es3}{\partial x} = \frac{G\ V(\varepsilon_3-\varepsilon_1)}{2\ \pi\ \ b} \frac{-\ \xi^2+ 1}{(\ \xi^2+ 1)^2}$$

where = x/b.

On the other hand, the double force tensor for the I center, for example P_I of eq.(6.2.4), can be transformed in following strain tensor; $^{4)}$

$$\varepsilon_{ij} = \begin{pmatrix} 0.508 & 0 & 0 \\ 0 & 0.508 & 0 \\ 0 & 0 & 1.951 \end{pmatrix} \tag{A·5}$$

Substututing the strain components into eq.(A·4), we obtain the equation describing the force-distance relation between the I center and the screw dislocation.

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[6·3]

THERMAL ACTIVATION MECHANISM OF THE INTERACTION BETWEEN THE DISLOCATION AND HALOGEN INTERSTITIALS IN KBr CRYSTALS

The interaction between dislocations and interstitial halogens in KBr crystals has been studied from the viewpoint of thermal activation mechanism based on the thermodynamical consideration for dislocation movements. The activation volume as well as flow stress during irradiation and thermal annealing has been obtained experimentally. Temperature dependence of these quantities has also been examined at wide range from 4.2 K to 200 K for irradiated KBr:Li. Analysis of the behaviours of them has been carried out in terms of thermal activation mechanism of dislocation dynamics. Description of the interaction as a thermally activated process is good for such a system. Total activation enthalpy and F_{max} for the interaction between dislocations and the I_A(Li) center are evaluated through these thermodynamical analysis.

§1 Introductory Remarks

In the preceding chapter, it has been clearly shown that the halogen interstitial ions are the dominant hardening agents in irradiated KBr crystals at low temperature. Here, we will solve the second crucial question in radiation hardening; How the defect interacts with dislocations ?

As an approach to this problem, we attempt to apply the thermal activation mechanism into the interaction between dislocations and the I_A center in KBr:Li. We then summalize the concept of dislocation dynamics as a thermally activated process in the following part of this section.

When a dislocation moves through a crystal lattice at low temperature, a force is exerted on it by obstacles present in the lattice. The features are schematically sketched in Fig.6.3.1.

Then, the resistive force against the moving dislocation can be separated into two components as follows;

$$\tau_o = \frac{F^* + Fg}{L\ b} = \tau^* + \tau_g \qquad (6.3.1)$$

where L is the average length of dislocation available to each obstacle, b the Burgers vector, τ^* and τ_g are thermal and athermal components of the stress due to obstacle, respectively.$^{1)}$

At any finite temperature, atomic fluctuations can assist the applied stress in moving a dislocation past obstacle. Thus, the stress to overcome a short-range obstacle depends sensitively on temperature, whereas that to surmount a fixed long-range one does only through the temperature dependence of the shear modulus.

When a linear segment of dislocation of length L moves reversively and isothermally from its equilibrium position to the saddle point of an obstacle, the minimum Gibbs free energy, ΔG, whixh has to be supplied, is given by$^{2,3)}$

$$\Delta G = \Delta g - \tau^* Lb\Delta R \qquad (6.3.2)$$

where Δg represents the change in free energy associated with the localized atomic displacement during activation events and is equivalent to a Helmholtz free energy, and ΔR is the so-called activation distance.

Then the rate of deformation $\dot{\gamma}$ is usually expressed as

$$\dot{\gamma} = \dot{\gamma}_o \exp(- \Delta G/kT) \qquad (6.3.3)$$

a) Activation volume

Activation volume is obtained by differentiating eq.(6.3.2) with respect to the effective stress;

$$V^* = -\left(\frac{\partial \Delta G}{\partial \tau^*}\right)_T = Lb\Delta R \qquad (6.3.4)$$

Utilizing eq.(6.3.3), activation volume can be rewritten as

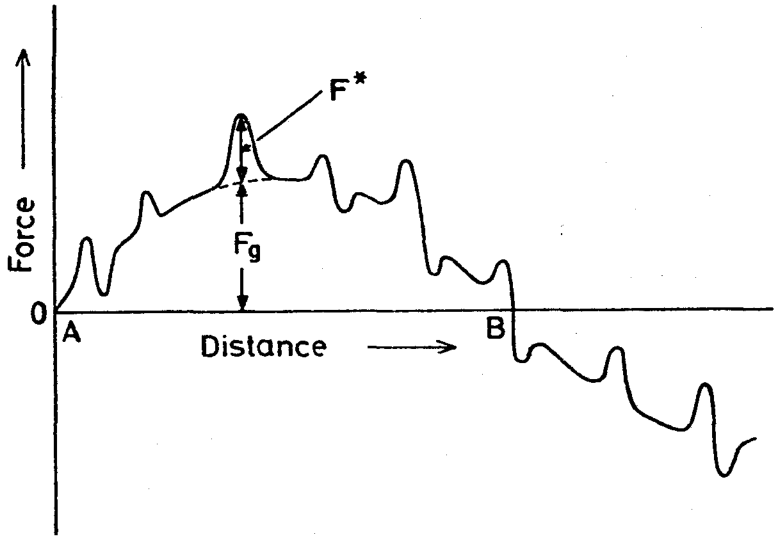

Fig.6.3.1. Schematic description of the force - distance relation in the interaction of dislocation with short- and long-range obstacles.

$$V^* = kT\left(\frac{\partial \ln \dot{\gamma}}{\partial \tau}\right)_T . \tag{6.3.5}$$

b) Activation enthalpy

Differentiating eq.(6.3.3) with respect to temperature, and putting as

$$\left(\frac{\partial \Delta G}{\partial T}\right)_\tau = -\Delta S , \tag{6.3.6}$$

$$\Delta H = \Delta G + T\Delta S , \tag{6.3.7}$$

activation enthalpy, ΔH, is represented as

$$\Delta H = kT^2\left(\frac{\partial \ln \dot{\gamma}}{\partial T}\right)_\tau . \tag{6.3.8}$$

This is easily modified as

$$\Delta H = \left(\frac{\partial \tau}{\partial T}\right)_{\dot{\gamma}} V^* \ T. \tag{6.3.9}$$

Therefore, both activation volume and activation enthalpy can be determined experimentally from differential constant strain-rate test.

§2 Experimental Results

(2·1) Changes of activation volume and induced flow stress during irradiation and thermal annealing

Figure 6.3.2 shows the γ-ray dose dependence of the activation volume and induced flow stress in KBr:Na and KBr:Li at 77 K. A similar tendency is observed in the change of the activation volume as well as flow stress for both system. In the lower dose region less than 1.0×10^7r, which corresponds to the early stage of coloration, an abrupt drop of the activation volume is evident, which is accompaned with a rapid increase in Δτ. On the other hand, the higher dose region, the activation volume remains almost unchanged, and induced flow stress increases gradually.

It appears, from the result in Fig.6.3.2, that irradiation induced change in activation volume mainly originates

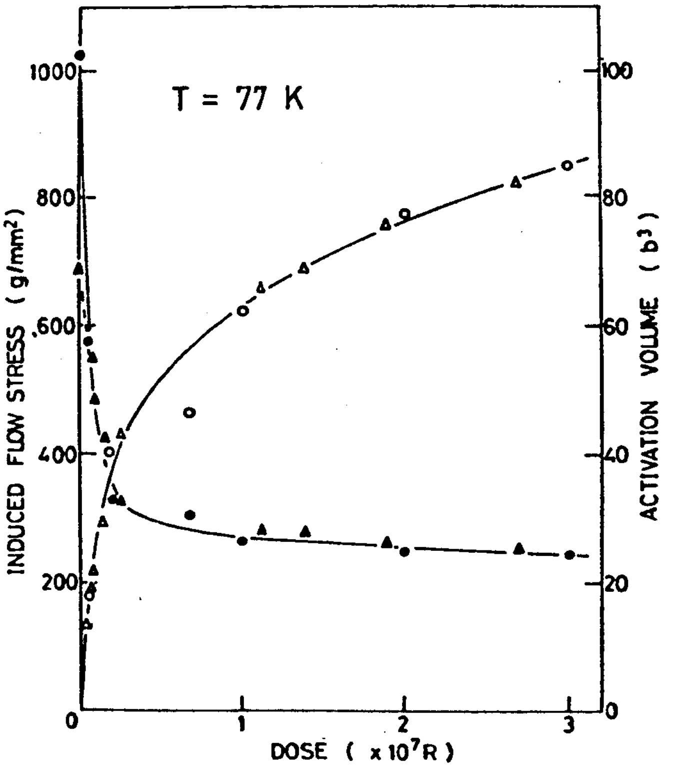

Fig.6.3.2. γ-ray dose dependence of the activation volume(●,▲) and induced flow stress (o,Δ) in KBr crystals. Circles and triangles indicate results in KBr:Na and KBr:Li, respectively.

mainly from the radiation-induced defects at the early stage coloration, or the trapped interstitials by alkali impurity, similarly as induced flow stress.

Figure 6.3.3 show the change of the activation volume in the thermal recovery process of $\Delta\tau$ in KBr:Na. The volume increases at the recovery stages I, II, and III, defined in the preceding chapter. It has been shown that these stages are due to the decay of the $I_A(Na^+)$, V(306), and V_4 centers, respectively.

Anti-correlation between $\Delta\tau$ and V* in these stages is clear. In contrast with such a correlation, the activation volume is maintained almost constant irrespective of the decrease of $\Delta\tau$, in stage IV where various kinds of higher aggregate interstitials annihilate.

From such results, one can distinguish two different types of recovery stages of $\Delta\tau$; one accompanies the change in V*, and the other does not.

Such a distinction is more typical in KBr:Li system, as seen in Fig.6.3.4 where the change of V* is shown in the thermal recovery process of $\Delta\tau$. Both $\Delta\tau$ and V* scarcely shange in stage I of KBr:Li. In stage II, where $I_A(Li^+)$ centers are mainly responsible for the recovery of $\Delta\tau$, the activation volume, together with the decrease of $\Delta\tau$, increases to recocer the value of un-irradiated samples. In stage III, however, the activation volume does not change in spite of the larger recovery of $\Delta\tau$.

On the basis of above experimental results, it is reasonable to suppose that there exist some differencies in the interaction of dislocations with responsible defects for above-defined two different types of recovery stages of $\Delta\tau$. Thus, let us hereafter distinguish following two types of samples; one involves the I_A center (Sample A), and the other does not have the I_A center, though it does other higher aggregate interstitials(Sample B).* Furthermore, we rest-

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*) These samples in KBr:Li were prepared by warming irradiated ones up to 180 K and to 260 K, respectively. Un-irradiated samples is hereafter abbreviated as Sample C.

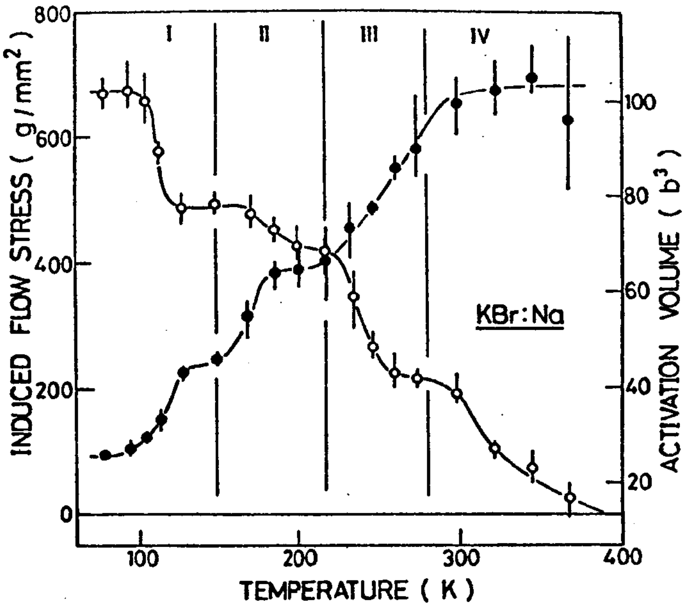

Fig.6.3.3. Changes in the activation volume(●) and induced flow stress(o) during thermal annealing of γ-irradiated KBr:Na.

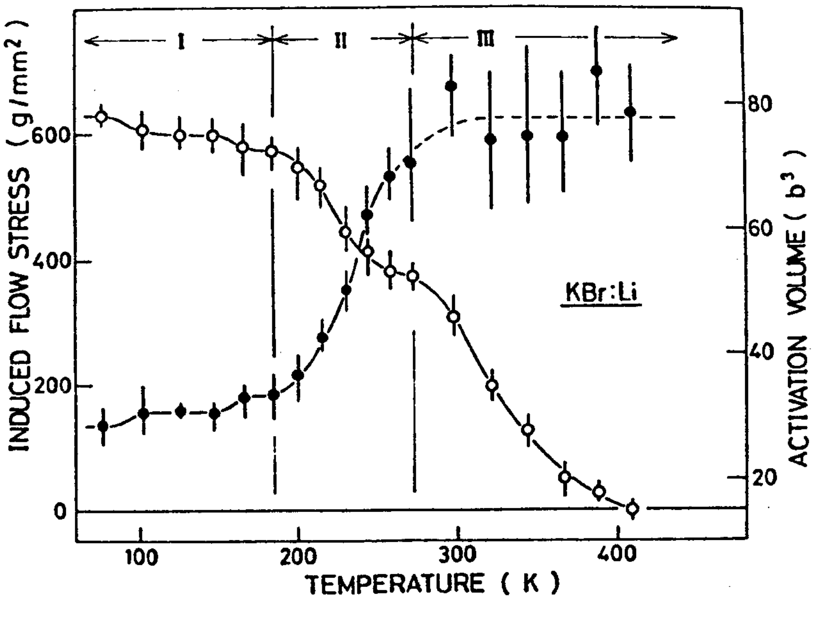

Fig.6.3.4. Changes in the activation volume(●) and induced flow stress(o) during thermal annealing of γ-irradiated KBr:Li.

rict our attention to the KBr:Li system, since this typically shows two different types of hardening phenomena.

(2·2) Temperature dependence of flow stress and activation volume

Figure 6.3.5 shows the temperature dependence of flow stress in Samples A, B, and C of KBr:Li. The differences in flow stress of Samples A and B from Sample C are shown by solid and broken curves in the inset of the figure, respectively.

The temperature dependence of flow stress in Sample B resembles that in Sample C, and the difference in flow stress between them is almost constant against temperature, as shown in the inset. On the other hand, flow stress of Sample A exhibits a different pattern of temperature dependence from those of Samples B and C: a remarkable increase in flow stress is evident with decreasing temperature, though exact data could not be obtained for Sample A near by 4.2 K because of the sample brittleness.

Figure 6.3.6 indicates the relation between the activation volume and the deformation temperature. It is clear that the activation volume of all three types of samples increases with increasing temperature. It should be pointed out that considerable increase is seen, especially for the samples where the I_A centers are absent(Samples B and C). This behaviour is clearly distinguishable from that of Sample A.

Thus we can see the different temperature dependences of flow stress and activation volue in Sample A from those in Samples B ans C.

§3 Discussions

(3·1) Radiation hardening mechanism as a thermally activated process

First, we examine the validity of the application of

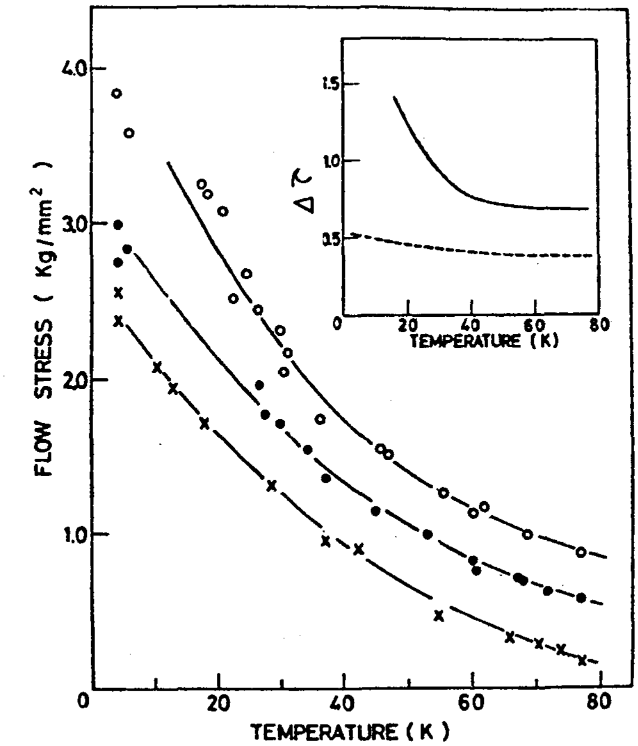

Fig.6.3.5. Temperature dependence of flow stress in KBr:Li. Open circles, closed ones, and crosses show the results of Samples A, B, and C, respectively. In the inset, solid and broken curves represent the differences in flow stress of Samples A and B from that of Sample C, respectively.

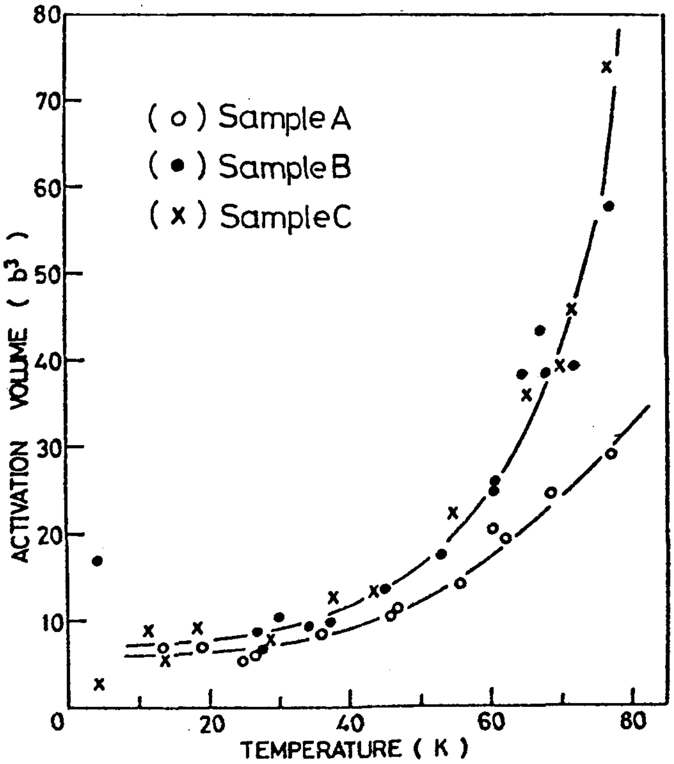

Fig.6.3.6. The relation between the activation volume and the deformation temperature in KBr:Li crystals

thermal activation mechanism to the present radiation hardening mechanism. For this purpose, we focus our attention to the temperature dependence of Gibbs free energy, ΔG.

As a consequence of thermodynamical description for dislocation dynamics, ΔG should be proportional to the temperature, when measurements are made for the system with the same structure. From eq.(6.3.3), ΔG is rewritten as;

$$\Delta G = kT \ln(\frac{\dot{\gamma}_o}{\dot{\gamma}}) = \alpha kT. \tag{6.3.10}$$

The value of α can be evaluated from the usual definition of $\dot{\gamma}_o$;[4)]

$$\dot{\gamma}_o = b\rho\nu L \tag{6.3.11}$$

where ρ is the dislocation density, L the average length of the dislocation segment and ν is the attempt frequency, which can be evaluated as $\nu_D(b/L)$, with Debye frequency, ν_D.

Using generally acceptable values;

$$\rho = 10^7 \text{ cm}^{-2}$$
$$\nu_D = 2.3 \times 10^{13} \text{ sec}^{-1}$$

and the present rate of deformation; $\dot{\gamma} = 1.4 \times 10^{-4} \text{ sec}^{-1}$, the value of α in this case is

$$\alpha = 22.$$

Now we will analyze the Gibbs free energy in the present experiment to compare the above theoretical consequence.

The activation enthalpy, ΔH, can be calculated using eq.(6.3.9) from the results of temperature dependence of frow stress and activation volume shown in Figs.6.3.5 and 6. Thus calculated values of ΔH are plotted against temperature in Fig.6.3.7. The characterized differences among three types of samples are hardly observable at low temperatures, whereas at higher temperature region above 60 K, ΔH of Samples B and C appears to show a super-linear dependence on temperature in contrast with Sample A.

Except high temperature region, a overall dependence of ΔH on temperature is linear, which involves lenear relation

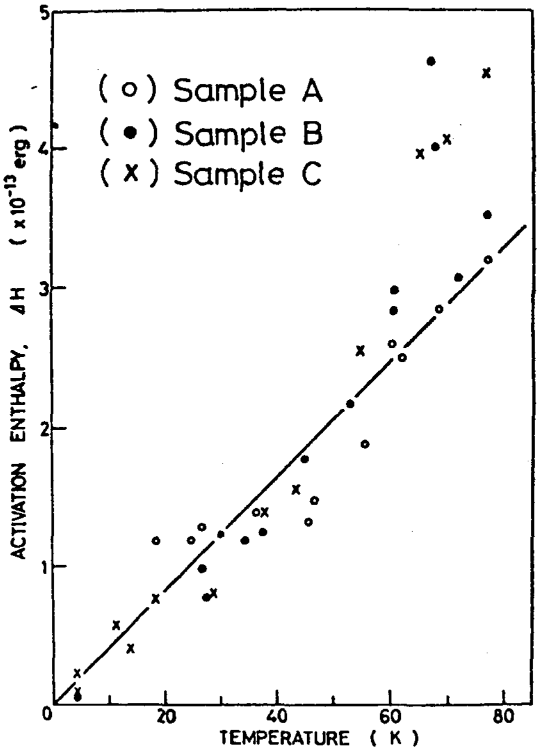

Fig.6.3.7. The relation between the activation enthalpy and the themperature in KBr:Li crystals.

between ΔG and T, since $\Delta H = \Delta G + T\Delta S$.

Since the contribution of the entropy term to ΔH is considered to be small at low temperature,[4] we can estimate the value of α in the present experiments from the results in Fig.6.3.7.

Estimated value is 28 which is very close to the theoretical value of 22. This result is supposed to prove the validity of our attempt of applying the thermal activation mechanism to the present experiment.

(3·2) The I_A center as an origin of thermal component of flow stress

As shown in Fig.6.3.5, flow stress of Sample A exhibits a remarkable increase at low temperature. On the other hand, Sample B shows the similar temperature dependence of flow stress to that of un-irradiated samples. The resemblance of the dependence in latter two means that the same defects are acting as the barrier exerting a short range force, or thermal component of flow stress in these samples. This fact clearly indicates that the defects induced by radiation which exists in Sample B, probably higher aggregates of interstitials, acts on dislocations as a long-range obstacles. On the other hand, additional thermal component in Sample A where the I_A center is the main hardening agent, may originate from the I_A center.

Thus, the I_A center interacts with dislocations in short range, whereas higher aggregate interstitials in long range, respectively.

(3·3) Total activation enthalpy for the interaction between the I_A center and disloations

An important parameter for the identification of activation mechanism is the total activation enthalpy, H_o, which is given by

$$\Delta H_o = \Delta H + \int_0^{\tau} V d\tau + T(\Delta S_o - \Delta S) \qquad (6.3.12)$$

where the second term represents the mechanical energy requir-

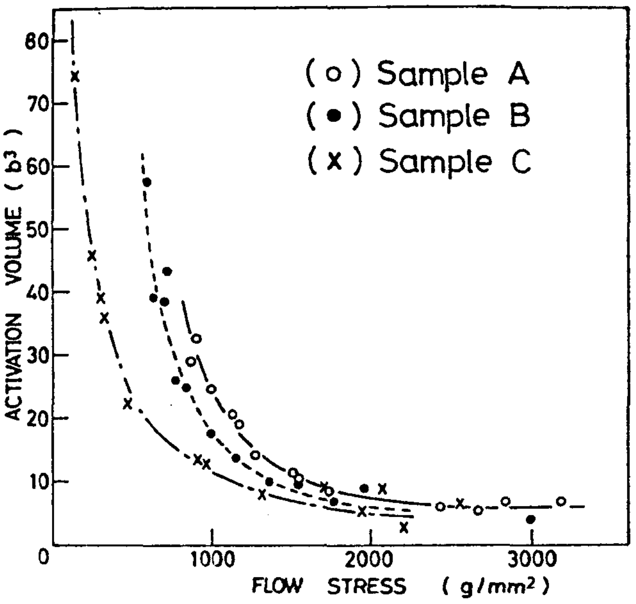

Fig.6.3.8. The relation between the activation volume and flow stress in KBr:Li.

ed to overcome the barier of obstacle, ΔS_o the activation entropy at zero effective stress and ΔS that at finite temperature, respectively.[1)] When ΔS varies only slowly with stress (temperature), eq.(6.3.12) is, in approximate form, expresses as follws;

$$\Delta H_o = \Delta H + \int_0^{\tau} V d\tau \ . \qquad (6.3.13)$$

If the same obstacle is concerned throughout the temperature range where interaction takes place, ΔH_o must be independent on temperature. Thus, evaluation of ΔH_o provides valuable informations about the dislocation - defects interaction where thermally activated process is active.

Here we obtain the value of ΔH_o for the case of the I_A center.

To evaluate this value, according to eq.(6.3.13), it is nescessary to draw an activation volume vs. flow stress curve. The obtained relation, from the results shown in Figs.6.3.5 and 6, is shown in Fig.6.3.8.

The mechanical energy, or the second term in eq.(6.3.13), can be evaluated by graphical integration of the curve in Fig.6.3.8. at each temperature. By using the activation enthalpy vs. temperature curve in Fig.6.3.7, together with the result of graphical integration, values of ΔH_o for Samples A and C are obtained to be 0.66 and 0.3 eV, respectively. These values are supposed to determine the heights of the potential barrier before moving dislocations interact with the obstacles.

(3·4) The maximum interaction force of the I_A center with dislocations

Finally, we discuss here the maximum force in the interaction between dislocations and the I_A center.

Above results and discussions have confirmed that the thermal activation mechanism is also available for this case. This means that the most important quantity in the interaction of dislocations with defects, F_{max}, can not be obtained from the flow stress measurement at the temperature where thermally activated process is active. Thus it should be nescessary to determine the value of F_{max} based on the low temperature data of flow stress. Let us, then focus our attention on the results of low-temperature flow stress shown in Fig.6.3.5.

For Sample A where the main thermal component of flow stress comes from the I_A center, one can obtain the value of 4.0 kg/mm^2 as the flow stress at 0 K, from the reasonable extrapolation of the data points.

It is apparent that the thermally activated process is active at 77 K for the hardening events due to the I_A center, since the activation volume is mainly determined by the center in Sample A at 77 K. Therefore, the value of flow stress at 77 K in Sample A may involve a fraction of thermal component. We adopt, as the athermal component, the value of flow stress in Sample B at 77 K; that is about 0.7 kg/mm^2.

Then, τ_o in the interaction between the I_A center and dislocations is about 3.3 kg/mm^2.

From eq.(6.1.1), F_{max} is

$$F_{max} = \tau_o \, b \, L \, . \tag{6.3.14}$$

The concentration of the I_A center in Sample A can be obtained from the optical absorption measurement. Evaluated value of the concentration, using Smakula's equation, is about $2.4 \times 10^{17} cm^{-3}$. From this result, we can determine the value of L in eq.(6.3.14).

Inserting thus obtained values of τ_o, L and b into the above equation, we obtain

$$F_{max} = 1.2 \times 10^{-5} \text{ dyne} = 0.3 \, F_o \, .$$

The total activation enthalpy for the interaction of the I_A center with dislocations has been obtained to be 0.66 eV. This value, together with the value of F_{max} give the average interaction distance of 2.7×10^{-8} cm, which is comparable with a/2 in KBr, where a is the lattice constant. This consequence is consistent with our assignment that the I_A center acts as an obstacle which results in the temperature-sensitive resistive force for the dislocation movement, i.e. thermal component of the flow stress.

Here we compare the value of F_{max} with the result of theoretical calculation performed in Chap.[6.2]. In Figs.-6.2.8 and 9, the maximum interaction force between the I center and edge dislocations is about $3F_0$, though it varies from $2F_0$ to $4F_0$, depending on the orientation between them. This value is about one order of magnitude larger than that of the I_A center with dislocations.

Qualitatively, the smaller value of F_{max} for the I_A center is quite reasonable, since the Li^+ ion in the I_A center is supposed to relax considerably the strain field due to the interstitial ions. Taking into this situation, we may say that the I_A center - dislocation interaction could be attributed mainly to the elastic interaction between them.

Decisive work on the radiation hardening due to intrinsic I centers will answer the question; electrostatic interaction is important or not in the interaction between dislocation and point defects in alkali halides.

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7

CONCLUSIONS

[7·1] Summary

Ionizing radiation damages in alkali halide crystals have been studied, mainly by means of internal perturbation method, in order to make clear the mechanism of storage and release of ionizing radiation-induced energy.

Based on the view-point that radiation damage corresponds to the radiation-induced change in energy the crystal possesses, overall process concerned has been divided into four regions; ionization damage process, transient phenomena, an "excited state", and defect-annihilation process.

The first part of this work concerns the relaxation and dissociation of an exciton which is the primary process of defect formation, i.e. the radiation-energy storage. Achievements of this part of the study can be summalized as Fig.7.1.1.

The hot exciton relaxes into particular states with the fixed ratio of relaxation probabilities. The primary origin of the energy-storage is the formation of $(V_K e)_F$ with probability, d, which depends strongly on the kind of alkali halides. This precursor of the Frenkel pair is the higher excited state of the triplet exciton. In KBr crystal, about 80% of the triplet exciton relaxes into $(V_K e)_F$ at 6 K, whereas most of that into $(V_K e)_\pi$ in NaCl.

The $(V_K e)_F$ forms another excitonic product, $(V_K e)_A$, through its selective interaction with alkali impurities, when the crystal includes the latter. This selective reaction involves an adiavatic motion of $(V_K e)_F$, which is characterized by μ^* of V^*.

Thus formed (V_Ke)$_A$ has similar electronic structure and properties as those of (V_Ke)$_\pi$, though the perturbationof nearby impurity ion makes the state de-excite more radiatively. Then, the formation of (V_Ke)$_A$ in some alkali halides results in the suppression of defect formation rate.

Another channel of the formation of (V_Ke)$_A$ can take place in other crystal(such as NaCl), which originates from the hopping motion of (V_Ke)$_\pi$.

Next part of the present work concerns the motion and reactions of primary halogen interstitials created from the (V_Ke)$_F$.

Two different modes of motion of the X_i^o have been clearly resolved. Dynamic motion of X_i^o along a particule <110> direction results in the formation of the (H_A)$_d$ center through the attractive interaction with a Na^+ ion, but is reflected back through the repulsive interaction with a Rb^+ ion to reduce the colorability in this secondary process of defect formation in KBr.

On the other hand, thermally induced migration of the H center forms the (H_A)$_t$ center and the $H_A(Rb^+)$ center in the interaction with a Na^+ and a Rb^+ ion, respectively.

The dependence of the interaction of the interstitial halogen atom with other imperfections on the mode of motion of the former originates from the anisotropic elastic interaction of the H center.

Then, defect annihilation process has been studied. Most important establishment in this part of the study can be represented by Fig.4.3.10. Primary product of radiolysis, the pair of F and H centers, possesses the formation energy of about 5.5 eV in KBr, and can recombine into (V_Ke)$_\pi$ during their annihilation process.

Another mechanism to convert the stored energy into the electronic-excitation energy creates (V_Ke)$_\sigma$ as well as (V_Ke)$_\pi$ during thermal annealing of irradiated KBr, NaCl, and KI crystals. Thus the intrinsic thermoluminescence is the same as intrinsic luminescence, in the sense that the luminescence center is the relaxed exciton for each phenomenon.

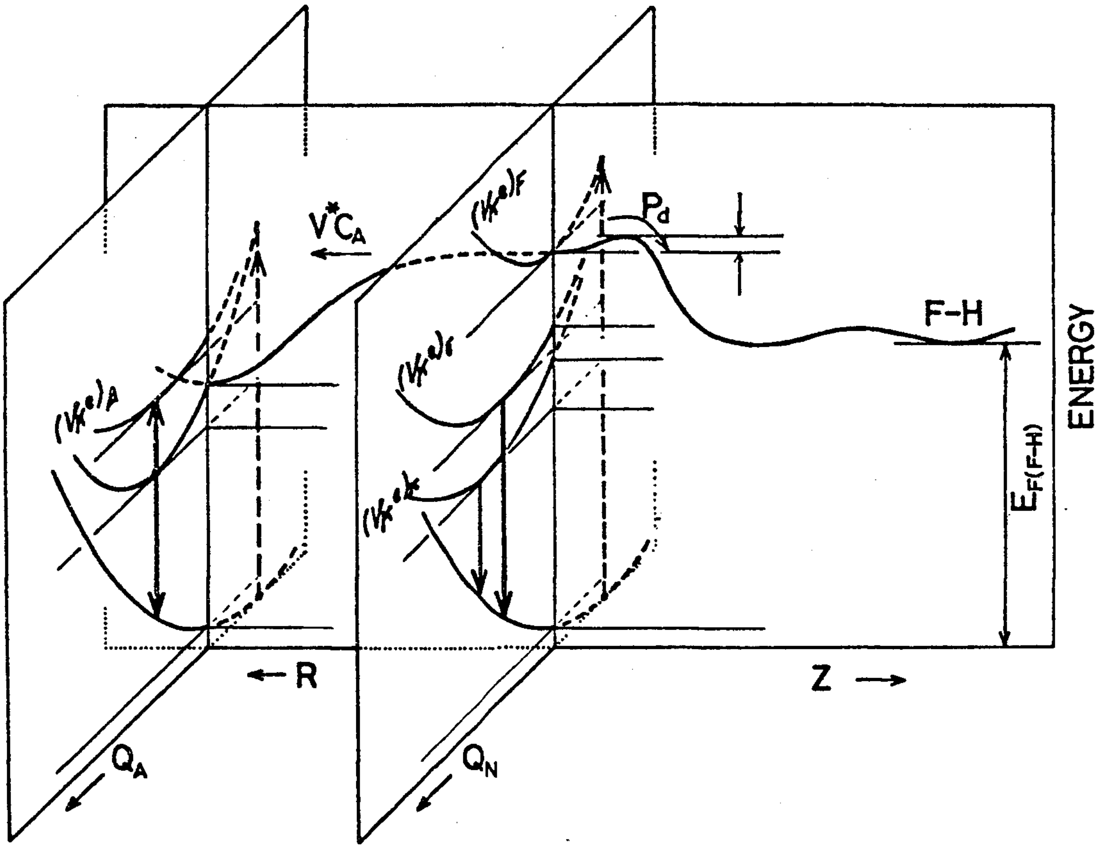

Fig.7.1.1. Schematic configuration coordinates curves for the relaxation of an exciton in a KBr:Na-type system. Coordinates Q_N and Q_A are associated with the internuclear distances of X_2^- in ($V_K e$) and ($V_K e$)$_A$ states. Z is the same as that with the same notation in Fig.5.3.10. R represents the shift of ($V_K e$)$_F$ from the position where it is initially formed. P_d is the dissociation probability of ($V_K e$)$_F$ into the F - H pair. V^*C_A indicates the formation probability of ($V_K e$)$_A$ in a crystal containing the alkali impurity.

Finally, as one of the research on the properties of an radiation-induced " excited " state, mechanism of radiation hardening has been studied, which is the typical problem of radiation damages in the narrow sense.

Interstitial halogen ions are the main hardening agent at low temperature, and act as the short-range obstacle for the dislocation movement. Dynamics of the dislocation - the defect interaction can be described in terms of thermal activation mechanism.

Through this work, significant insight has been given in the relaxation and dissociation of an exciton, and clear answers have been presented to the problems which had remained unsolved in other fields concerned.

[7·2] Future Ploblems

The most important and interesting problems we must solve hereafter in radiation damages in this material is supposed to concern the relaxation and dissociation of an exciton. Additional efforts of the study on other categories of color center physics, which have been studied extensively in this work, might not give us further new and important findings in physics. Thus, color center physics in alkali halides should be re-termed the exciton physics in this insulator.

Various excited states of STE have been established so far. And several important properties of ($V_K e$ $)_F$ have been revealed. In spite of these recent knowledge, the clear identification of the initial state of color center formation has not been done yet. Furthermore, detailed mechanism of energy conversion of electronic-excitation energy into the kinetic energy with momentum is far from being well understood.

On the other hand, other interesting problems have remained unsolved in the relaxation dynamics of the exciton; mechanism of the absence of the π emission in some alkali halides, the origins of the third exciton-like emission and of the edge emission seen especially in Iodides, etc.

Through the study on these problems, we must clarify the role of higher electronic-excited states on the ionizing radiation damages, or radiolysis, in this insulators.

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(Jan., 1977)

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at
International Conference on Color Centers in Ionic Crystals

(Sendai, Sept.1974)

1) Thermoluminescence through Interstitial Recombination in Alkali Halides, Abstract No.D40.

2) Br_i^o Interaction with Na^+ Impurity Ion During Defect Formation at LNT in KBr:Na, Abstract No.87.

3) Halogen Interstitial Centers and Their Interaction with Dislocations, Abstract N.68.

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