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## Internal Stark Effect Caused by Inhomogeneous Distribution of Ionized Impurities in Highly Compensated Semiconductors

by

Yoshiyuki Harada

(1995)

#### DISSERTATION IN PHYSICS



# THE OSAKA UNIVERSITY GRADUATE SCHOOL OF SCIENCE TOYONAKA, OSAKA

Internal Stark Effect Caused by Inhomogeneous Distribution of Ionized Impurities in Highly Compensated Semiconductors

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#### Abstract

Stark broadening of Zeeman absorption line caused by imhomogeneous electric fields in highly compensated semiconductors has been studied by means of far-infrared (FIR) magneto-optical absorption measurement. Various compensated InSb and Ge samples were employed in this work. Moreover, transmutation-doped Ge samples with systematic variation of the compensation ratio were also used.

In InSb sample, time-resolved absorption spectrum for an acceptor Zeeman absorption line under an intrinsic photopulse excitation has been studied. It is observed that the full width at half maximum (FWHM) of the absorption line increases as the lapse of delay time after photopulse excitation increases. In Ge samples, FWHM of absorption line for Ga acceptor has been investigated as a function of the intensity of excitation light with the above-band gap energy. The FWHM of the absorption line increases as the intensity of the photopulse excitation decreases. The absorption lines observed in InSb and Ge are due to transition from ground state to excited state in neutral impurities.

These line-broadening phenomena originate in the Stark effect due to inhomogeneous electric fields caused by the random distribution of ionized impurities. Since the electric fields induced by ionized impurities vary from one neutral impurity center to another one, this effect results in the inhomogeneous distribution of the strength of the Stark effect. Stoneham calculated the Stark broadening analytically. His theory gives qualitative explanation of experimental results in this study.

In order to understand the mechanism for the Stark-broadening intensively, a numerical approach based on Monte Carlo simulations has been also done. In this calculation, it is found that the inhomogeneity of the field-distribution becomes larger with increasing density of ionized impurities. The calculation based on a perfectly random distribution for an initial impurity arrangement gives fairly good agreement with both the theory of Stoneham and the present experimental results. The relation between the linewidth of an absorption spectrum and the distribution of impurities in a semiconductor will be discussed from the experimental and theoretical aspects in detail.

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#### **§1** Introduction

There has been considerable attention given to studies of highly compensated semiconductors. These semiconductors are interesting for the electronic properties of impurities because of the existence of the induced internal electric field, mainly due to the Stark effect by ionized impurities. In equilibrium at low temperature, a highly compensated *p*-type semiconductor has  $N_A$ - $N_D$  of neutral impurities, where  $N_A$  and  $N_D$  are concentrations of acceptors and donors, respectively. Only the neutral acceptors and donors can show Zeeman absorption in the far-infrared region.

Photoexcited electron-hole pairs are immediately captured by ionized impurities. A dominant relaxation process subsequent to the impurity-neutralization is a Donor-Acceptor (D-A) recombination. The luminescence spectra for this recombination in GaP crystals have been studied by Thomas *et al*<sup>1</sup>. The recombination probability is closely related to the distance between a donor and an acceptor, and for samples with low impurity concentrations this distance is considerably large. Therefore the relaxation time may be several seconds for samples with low impurity concentrations.

As a result of the recombination, impurities are ionized and inhomogeneous electric fields are induced by them. The resultant inhomogeneous electric fields give rise to Stark shifts of energy levels in each neutral impurity. An electron bound to a neutral impurity experiences the sum of Coulomb potentials from all other ionized impurities around the neutral impurity. The internal electric fields affect a position and a width of a Zeeman absorption line.

Absorption spectra of shallow impurities in semiconductors have been extensively investigated by several authors.<sup>24)</sup> The FWHM of various lines of the spectra contain important information. The line-broadening is caused by the following mechanisms:

(a) Phonon Broadening,

(b) Concentration Broadening,

(c) Strain Broadening,

and

(d) Stark Broadening.

(a) Phonon broadening

Phonon broadening is due to the interaction between bound carriers and phonons. Lax and Burstein<sup>5)</sup> proposed that the line-broadening is caused by the interaction between bound carriers on the impurity and acoustic phonons. The line-broadening is caused by the broadening of the 1*s*-ground state by the acoustic phonon. Kane<sup>6)</sup> has pointed out that the line-broadening arises from a lifetime effect due to a transition to a lower state with the emission of a phonon. Later, Barrie and Nishikawa<sup>7.8)</sup> have evolved detailed theoretical studies of the line-broadening mechanisms. They confirmed that weak electron-phonon interactions play an important role. The width of the excited state is affected by coupling of the state with all other excited states. Navarro *et al.*<sup>9)</sup> have measured the photo-

thermal conductivity generated by the far-infrared laser radiation on a stressinsensitive hydrogen and oxygen donor complex in Ge present at concentration of  $10^{11}$  cm<sup>-3</sup>. They observed the FWHM in the fundamental 1*s-np* (*n*=2, 3, 4, 5, 6) transitions of the donor in the ultrapure Ge. The FWHM is dominated by the lifetime of excited state due to the interaction between the bound electron on the donor and the acoustic phonon. They found that the excited state lifetimes experimentally deduced from the FWHM are in agreement with the values calculated from the Barrie and Nishikawa theory.<sup>78)</sup>

#### (b) Concentration Broadening

With increasing concentration of impurities, the wavefunction of the groundand excited-states overlap each other. Concentration broadening is caused by the overlap of the wavefunctions of bound carriers. Baltensperger<sup>10</sup> has calculated the 1s, 2s, and 2p bands for hydrogenic shallow impurities as a function of the distance between the interacting impurities. He used the Wigner-Seitz method based on the assumption that impurities build up a regular closed-packed lattice. This broadening of absorption line in the hydrogenic impurity shows a rapid rate of increase in the following condition :

$$r_S \le 6na_0, \tag{1-1}$$

where *n* is the principal quantum number of the level,  $a_0$  the effective Bohr radius of the carrier bound on the impurity and the notation  $r_s$  is an average distance and defined by

$$\frac{1}{N} = \frac{4}{3}\pi r_S^3.$$
 (1-2)

Here N is the impurity concentration. Newman<sup>11)</sup> experimentally demonstrated the concentration broadening effect on an absorption line of holes bound to acceptors in Si, and showed that the lines begin to broaden when the acceptor concentration is about  $10^{16}$  cm<sup>-3</sup>.

#### (c) Strain broadening

Strain broadening is caused by the presence of imperfections, which are both electrically active and inactive<sup>12</sup> impurities and dislocations in crystal. For example, in CZ-Si, oxygen and carbon, which are electrically inactive, are typically important with concentrations between  $10^{15}$  cm<sup>-3</sup> and  $5 \times 10^{16}$  cm<sup>-3</sup>. This broadening is mainly caused by two mechanisms; One is the random strain due to the presence of the electrically inactive impurities resulting in a line-broadening. The order of the broadening width  $\Delta$  is estimated to be,

$$\Delta \approx e^2 a'^2 N_{EII}, \qquad (1-3)$$

where e is an elementary charge, a', the lattice constant and  $N_{EII}$  the concentration of the electrically inactive impurities.

The other is the local potential of the electrically inactive impurities which perturbs the state of impurities.

#### (d) Stark Broadening

Stark broadening has its origin in internal electric fields induced by ionized impurities. Historically, for this problem, Colbow<sup>13)</sup> has investigated the temperature dependence of an infrared absorption in boron-doped Si. In this case, a line-broadening of absorption with increasing temperature is attributed to phonon broadening as well as another contribution containing the Stark broadening by thermally ionized impurities.

White<sup>14-15)</sup> has carried out detailed experiments to investigate external and internal electric fields on the boron-doped Si. He pointed out that the observed Stark broadening is attributed to an unresolved partial removal of acceptor excitedstate degeneracy. In uncompensated boron-doped Si at higher temperature than 50K, neutral boron absorption lines are affected by the screened coulomb fields of thermally ionized impurities. In compensated boron- and phosphorus-doped Si, the compensation effects at low temperature are attributed to the unscreened Coulomb fields of ionized impurities.

Moreover the width of a impurity resonance line in InSb has been discussed by Kal'fa *et al*<sup>16</sup>, under the condition that the width was dominated by the electric field induced by randomly distributed ionized impurities.

Theoretically, Larsen<sup>17-20)</sup> has dealt with these problems and compared calculations with the experimental results obtained in GaAs. The inhomogeneous broadening of Zeeman absorption lines of shallow donors in a magnetic field was discussed intensively. Lineshapes of absorption spectra were calculated and

compared with observed lineshapes in GaAs.

In the study of internal Stark effect in a highly compensated Ge by Ohyama<sup>21)</sup>, the width of impurity absorption line was investigated through controlling the number of ionized impurities by changing the intensity of a photoexcitation. It was found that the observed line-broadening of an In acceptor line is attributed to unresolved splitting due to perturbations of Coulomb fields of ionized impurities.

The broadening in the energy levels of an hydrogen atom caused by an external electric field of strength E is called the Stark effect in quantum mechanical theory. When the energy levels are degenerate, as 2s and 2p states, the first-order Stark effect which is in proportion to E removes them. If there is no degeneracy in states, the second-order Stark effect mainly contributes to the energy shifts. The quantity of the energy shift is in proportion to  $E^2$ . Effects of internal electric fields on a hydrogenic impurity state can be considered with the same analogy as this hydrogen model.

The relation between the linewidth and concentration of ionized impurities with random distribution is well known.<sup>22-23)</sup> In the first-order Stark effect and second-order Stark effect, the line-broadening  $\Delta$  is in proportion to  $N_i^{2/3}$ ,  $N_i^{4/3}$ , respectively, where  $N_i$  is the ionized impurity concentration.

Moreover at low concentrations, a field-gradient effect plays an important role in the broadening of a spectrum. This effect is due to the interaction between an electric quadrupole moment in a neutral impurity and the field-gradient induced by ionized impurities. In this case, the line-broadening is in proportion to  $N_i$  In all cases, it is supposed that the distribution of impurities in a semiconductor is completely random.

In the present work, we have studied far-infrared magneto-optical absorption in highly compensated Ge and InSb under bandgap photoexcitation. With use of this method, it is possible to observe properties of electrons bound to impurities in a semiconductor. In addition, transmutation-doped Ge samples which have systematic variations of compensation ratio are also employed.

The concentration of ionized impurities depends on the lapse of delay time after photopulse excitation and the intensity of excitation light. The linewidth of Zeeman absorption increases with increasing concentration of the ionized impurities. For transmutation-doped Ge, it is found that the line-broadening depends on the ionized impurity concentrations, as  $N_i^{4/3}$ , and is mainly related to the second-order Stark effect.

In addition we have carried out the Monte Carlo simulation to investigate this broadening mechanism theoretically, and compared it with the experimental results obtained in highly compensated semiconductors.

The results of the simulation indicate that the broadening of linewidth is related to the density of ionized impurities analogous to the case of the compensated  $Ge^{21}$  and increases with the inhomogeneous electric fields induced by the ionized impurities. The relation between a linewidth of an absorption line and the distribution of impurities has been discussed. Detailed investigations of the line-broadening allow us to classify the initial distribution of impurities in

semiconductor.

#### §2 Theoretical background

#### 2-1 Stark effect in a hydrogen atom

Energy levels of the hydrogen atom change by electric field of strength E. This is called Stark effect<sup>27)</sup>. When uniform electric field is applied parallel to z-axis, the Hamiltonian H of the hydrogenic atom is expressed by

$$H = H_0 + H' \,. \tag{2-1}$$

Here an unperturbed Hamiltonian  $H_0$  is

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r^2},$$
(2-2)

while a perturbed Hamiltonian H is

$$H' = -eEz = -eEr\cos\theta, \qquad (2-3)$$

*e* is elementary charge,  $\hbar$  Planck constant over  $2\pi$ , *m* mass of the electron,  $\varepsilon_0$  the static dielectric constant in vacuum, *r* position of the electron and  $\theta$  is angle between vector  $\vec{r}$  and direction of electric field.

The electric field along the z-axis has odd parity. The expectation value of H' is zero for states which have definite parities. Since there is no degeneracy in 1s state of a hydrogen except for spin state, the energy shift due to the first-order Stark effect vanishes.

The first excited states of hydrogen(n=2) are degenerate fourfold. A set of

quantum number is described by

$$(n, l, m) = (2, 0, 0),$$
  
=  $(2, 1, 0),$   
=  $(2, 1, 1),$   
=  $(2, 1, -1),$  (2-4)

where n is the principal quantum number, l the azimuthal quantum number and m the magnetic quantum number.

There is accidental degeneracy in which energy level between l=0 and l=1 states of the hydrogen occurs. In the case of the existence of the degeneracy, the secular equation between the four states (n=2) of the hydrogen atom is

The matrix elements of H' are

$$\langle \varphi_{200} | H' | \varphi_{210} \rangle = \langle \varphi_{210} | H' | \varphi_{200} \rangle$$
  
=  $-eE \int \varphi_{210} r \cos \theta \varphi_{200} d^3 r = -3eEa_0$ (2-6)

where  $\varphi_{200}$  and  $\varphi_{210}$  are unperturbed wavefunctions of the (2, 0, 0) and (2, 1, 0) states, respectively, and the notation  $a_0$  denotes a Bohr radius of the hydrogen atom. These states mix each other, and the mixed wavefunctions are

$$\varphi_{+} = \frac{1}{\sqrt{2}} (\varphi_{200} + \varphi_{210}), \tag{2-7}$$

and

$$\varphi_{-} = \frac{1}{\sqrt{2}} (\varphi_{200} - \varphi_{210}),$$

respectively. Each energy level is 0, 0,  $+3eEa_0$ , and  $-3eEa_0$ , respectively, as shown in Fig. 2.1.

In the second-order Stark effect, for example, the energy shift of (2, 1, 1) state is expressed by

$$E_{211} = \sum_{i \neq (211)} \frac{\left\langle \varphi_{211} \middle| H' \middle| \varphi_i \right\rangle \left\langle \varphi_i \middle| H' \middle| \varphi_{211} \right\rangle}{E_i - E_{211}}$$
$$= -78 (4\pi\varepsilon_0) a_B^{-3} E^2, \qquad (2-8)$$

where the special *i*-states are summed up except for (2, 1, 1) state.

Moreover, the 1s state shifts toward the lower energy as  $-(9/4)(4\pi\varepsilon_0)a_0^3E^2$ . The first excited states also shift toward lower energy as shown Fig.2.1. It is important that energy shift is proportion to  $E^2$  in the second-order Stark effect. 2-2 Stark effect due to internal electric fields induced by ionized impurities

The effective Hamiltonian H of a neutral impurity perturbed by the electric fields induced by all ionized impurities is expressed as

$$H = H_0 - eV_{ext}(r), \qquad (2-9)$$

where  $H_0$  is written by

$$H_o = -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\varepsilon_o \varepsilon r^2}, \qquad (2-10)$$

and  $V_{ext}$  is the electrostatic potential due to the surrounding ionized donors and acceptors and  $m^*$  effective mass of a carrier and  $\varepsilon$  relative dielectric constant. Defining the charge and the position of the *j*-th ionized impurity by  $e_j$  and  $R_j$ , respectively, the potential energy evaluated at the position *r* near a neutral impurity center can be written

$$V_{ext}(r) = \sum_{j} \frac{e_{j}}{4\pi\varepsilon_{0}\varepsilon|\vec{R}_{j} - \vec{r}|}$$
  
$$= \frac{1}{2} \sum_{j} \frac{e_{j}}{4\pi\varepsilon_{0}\varepsilon R_{j}} \sum_{k=0}^{\infty} \sum_{m=0}^{k} s_{m} \frac{(k-m)!}{(k+m)!}$$
  
$$\times P_{k}^{m}(\cos\theta_{0})P_{k}^{m}(\cos\theta_{j})\cos[m(\varphi_{j} - \varphi_{0})](r/R_{j})^{k}.$$
  
(2-11)

where  $s_m=2$  for m>0 exception  $s_0=1$ ,  $e_j$  is the charge of the *j*-th ionized impurity,  $R_i, \theta_j$  and  $\varphi_j$ , the spherical coordinates in the *j*-th ionized impurity, r,  $\theta_0$  and  $\varphi_0$  the spherical coordinates of r, k and m integer and  $P_n^m$  associated Legendre function.

The multiple expansion for  $V_{ex}$  about the neutral impurity center at r=0 is deduced in the following: The n=0 term is

$$V_R^{(0,0)}(r) = \frac{1}{4\pi\varepsilon_0\varepsilon} \sum_j e_j$$
$$= V_R(r).$$
(2-12)

This term shifts all the levels of a neutral impurity up or down by the same amount. Thus it leaves optical transition energies unchanged. The n=1 term shows as

$$V_R^{(1,0)}(r) = -E_z(0)z, \qquad (2-13)$$

$$V_R^{(1,1)}(r) = -[E_x(0)x + E_y(0)y], \qquad (2-14)$$

and

$$E_i = -\frac{1}{4\pi\varepsilon_0 \varepsilon R^3} X_i \sum_j e_j \tag{2-15}$$

where E(0) is the electric field associated with the electrostatic potential  $V_{ext}$ :  $E(r)=-grad_r V_{ext}$ . This term is physically important for producing the Stark effect on the neutral impurity levels and therefore causes shifts in the transition energies. Moreover the affection is classified by a first-order, second-order and higher-order Stark effect. Defining the *j*-th bound eigenstate of a impurity by  $|\varphi_j\rangle$ , the expectation value of  $V_{ext}$  gives the first-order Stark shift of the *j*-th impurity level:

$$\Delta E_i = \left\langle \varphi_i \left| - E(0) \cdot r \right| \varphi_i \right\rangle.$$
(2-16)

As the description in previous section, this expectation value is zero for the states which have definite parities. Since the 1s state in the impurity has even parity, the energy level does not change by the first-order Stark effect. The 2s and 2p states, which are degenerate each other, split as well as the case of the hydrogen problem.

The second-order energy shift induced by  $V_{ex}$  on the unperturbed eigenvalues of H can be written

$$\Delta E_i^{(2)} = e^2 \sum_k \frac{\left| \left\langle \varphi_k \left| V_{ext} \left| \varphi_i \right\rangle \right|^2}{E_i - E_k} \right|^2}{E_i - E_k}$$
$$= e^2 \sum_k \frac{\left| \left\langle \varphi_k \left| -E(0) \cdot r \left| \varphi_i \right\rangle \right|^2}{E_i - E_k} \right|^2}{E_i - E_k}.$$
(2-17)

The n=2 term is described by

$$V_{R}^{(2,0)}(r) = -\frac{1}{4}(3z^{2} - r^{2})\frac{\partial E_{z}(0)}{\partial z}, \qquad (2-18)$$

$$V_{R}^{(2,1)}(r) = -z(x\frac{\partial E_{z}(0)}{\partial x} + y\frac{\partial E_{z}(0)}{\partial y}), \qquad (2-19)$$

$$= -z(r \cdot \nabla_{r}E_{z}(0) - \frac{\partial E_{z}(0)}{\partial z}), \qquad (2-19)$$

$$V_{R}^{(2,2)}(r) = -\frac{1}{4}(x^{2} + y^{2})\left(\frac{\partial E_{x}(0)}{\partial x} - \frac{\partial E_{y}(0)}{\partial y}\right) -xy\frac{\partial E_{y}(0)}{\partial x}, \qquad (2-20)$$

and

$$\frac{\partial E_i(0)}{\partial j} = -\frac{1}{4\pi\varepsilon_0 \varepsilon R^5} (R^2 \delta_{ij} - 3X_i X_j) \sum_j e_j , \quad (2-21)$$

where  $\delta_{ij}$  is written by

$$\delta_{ij} = \begin{cases} 1 & (i=j) \\ 0 & (i\neq j) \end{cases}$$

$$(2-22)$$

For example, considering the term of  $V_R^{(2,0)}$ , the energy shift is given by the first-order perturbation theory. Physically, this expectation value is the energy of an electric quadrupole in a field gradient. Since the electric quadrupole moment associated with state  $|\varphi_j\rangle$  is expressed by

$$Q_i = e \langle \varphi_i | 3z^2 - r^2 | \varphi_i \rangle .$$
(2-23)

The energy shift of the first-order perturbation is given by

$$\Delta E_i^{(1)} = \frac{1}{4} Q_i \frac{\partial E_z(0)}{\partial z} . \qquad (2-24)$$

This shift is as important as the Stark shift induced by n=1 terms.

# 2-3 Inhomogeneous line-broadening theory by random distribution of ionized impurities

An extreme example of inhomogeneous line broadening is illustrated in Fig.2.2. Peak frequencies differ in each resonance centers. Each linewidth is usually similar, but a whole width is larger than each linewidth. For example, the line-broadening contains broadening due to inhomogeneous electric field, electric field gradient, and strain etc.

In general, lineshape  $A(\omega)$  is expressed by

$$A(\omega) \propto \int f_j(\omega) g(\omega_j) d\omega_j, \qquad (2-25)$$

where  $f_j(\omega)$  is a lineshape-function of frequency  $\omega$  and  $g(\omega_j)$  distribution function contributes to frequency  $\omega_j$ . When  $f_j(\omega)$  is nearly  $\delta(\omega)$  around at frequency  $\omega$ ,  $A(\omega)$  is approximately described by

$$A(\omega) \propto g(\omega).$$
 (2-26)

Accordingly, the stastitical distribution of resonance centers directly affects the whole resonance line. In this following, a statistical summation of electric fields due to a random distribution of ionized impurities is described.<sup>22-23, 28-29)</sup>

A point charge e at a position of r generates components of electric field  $E_x E_y$ , and  $E_z$  of

$$E_{x} = \frac{es}{4\pi\varepsilon_{0}\varepsilon r^{2}},$$
  

$$E_{y} = \frac{et}{4\pi\varepsilon_{0}\varepsilon r^{2}}$$
  

$$eu$$

and

$$E_z = \frac{eu}{4\pi\varepsilon_o \varepsilon r^2}, \qquad (2-27)$$

respectively, where s, t, u, are the direction cosines of  $\vec{r}$ . The frequency shift of the resonance line is given by

$$\omega = a_s E_x + b_s E_y + c_s E_z, \qquad (2-28)$$

where  $a_s, b_s, c_s$  are constants due to Stark effect. Here, by introducing  $\alpha_c, \beta_c, \gamma_c$  as

$$\alpha_{c} = \frac{ea_{s}}{4\pi\varepsilon_{o}\varepsilon},$$
$$\beta_{c} = \frac{eb_{s}}{4\pi\varepsilon_{o}\varepsilon}$$

and

$$\gamma_{C} = \frac{ec_{S}}{4\pi\varepsilon_{0}\varepsilon}, \qquad (2-29)$$

the frequency shifts are described in the form

$$\omega_i = \frac{(s_i \alpha_c + t_i \beta_c + u_i \gamma_c)}{r_i^2}.$$
 (2-30)

The frequency shifts due to N point charges at  $r_1$ ,  $r_2$ , ...  $r_N$  are described in the form

$$\omega = \sum_{i} \frac{(s_i \alpha_c + t_i \beta_c + u_i \gamma_c)}{r_i^2}.$$
 (2-31)

When the constrained condition is denoted by

$$\omega < \sum_{i} \frac{s_i \alpha_C + t_i \beta_C + u_i \gamma_C}{r_i^2} < \omega + d\omega, \quad (2-32)$$

the probability function of finding between  $\omega$  and  $\omega + d\omega$  is given by

$$P(\omega) = (1/V^{N}) \int d^{3}r_{1} \int d^{3}r_{2} \cdots \int d^{3}r_{N}$$
$$\times \delta \{ \omega - \sum_{i} (s_{i}\alpha_{C} + t_{i}\beta_{C} + u_{i}\gamma_{C})/r_{i}^{2} \}, \quad (2-33)$$

where  $d^3r$  is a volume element by the *i*-th charges, V the total volume and  $\delta$  delta function. By introducing a Fourier component of the  $\delta$  function,  $P(\omega)$  is given as

$$P(\omega) = \frac{1}{2\pi} (1/V^N) \int d^3 r_1 \int d^3 r_2 \cdots \int d^3 r_N \int_{-\infty}^{\infty} d\rho$$
  
$$\times \exp\{-i[\rho\omega - \rho \sum_i (s_i \alpha_C + t_i \beta_C + u_i \gamma_C)/r_i^2]\}. (2-34)$$

Moreover,  $P(\omega)$  is rewritten as

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\rho \exp(-i\rho\omega)$$

$$\times [(1/V) \int d^{3}r \exp\{i\rho(s\alpha_{C} + t\beta_{C} + u\gamma_{C})/r^{2}\}]_{,}^{N} \quad (2-35)$$

because the multiple integrals are independent for every N.

Here, the factor  $s\alpha_c + t\beta_c + u\gamma_c$  is the scalar product between  $\vec{r}$  vector and the unit vector which defines the direction of the electric field. Thus, the factor is

$$s\alpha_C + t\beta_C + u\gamma_C = k\cos\xi. \tag{2-36}$$

and

$$k = \sqrt{\alpha_{C}^{2} + \beta_{C}^{2} + \gamma_{C}^{2}}$$
(2-37)

where  $\xi$  is the angle between the two vectors. The bracket term in (2-35) is therefore

$$\frac{2\pi}{V}\int_0^R drr^2 \int_0^\pi d\xi \sin\xi \exp\frac{i\rho k\cos\xi}{r^2}.$$
 (2-38)

Here, new V' term introduces as

$$V' = 4\pi \int_0^\infty dr r^2 \int_0^{\pi/2} d\xi \sin \xi (1 - \exp \frac{i\rho k \cos \xi}{r^2}) \quad (2-39)$$

Moreover, V and N are extended to infinity ), while N/V = n is constant,

$$\lim_{N,V\to\infty} (1 - V'/V)^{N} = \exp(-nV'), \qquad (2-40)$$

where n is concentration of ionized impurities. Thus  $P(\omega)$  is rewritten by

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\rho \exp(-i\rho\omega - nV'). \qquad (2-41)$$

Integrating with respect to r, V' is given by

$$V' = 4\pi (\sqrt{\pi}/6) \int_0^{\pi/2} d\xi \sin \xi (\rho k \cos \xi)^{3/2}, \qquad (2-42)$$

and

$$V' = \frac{4}{15} (\pi \rho k)^{3/2}.$$
 (2-43)

As using this term,  $P(\omega)$  is finally described by

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\rho \exp(-i\rho\omega) \exp\{-\frac{4}{15}n(\pi\rho k)^{3/2}\}.$$
 (2-44)

The linewidth is characterized by parameter

$$\omega_0 = (4/15)^{2/3} n^{2/3} \pi k, \qquad (2-45)$$

and the lineshape is found by integrating

$$P(\omega) = \frac{1}{\pi\omega_0} \int_0^\infty d\rho' \cos(\rho'\omega/\omega_0) \exp(-{\rho'}^{3/2}). \quad (2-46)$$

The FWHM,  $\Delta$ , can be numerically calculated, and is  $2.88 \omega_0$ , i.e.,

$$\Delta = 2.88\omega_0$$
  
=  $7.5n^{2/3} \frac{e}{4\pi\varepsilon_0 \varepsilon} \sqrt{a_s^2 + b_s^2 + c_s^2}$   
 $\propto n^{2/3}$ . (2-47)

The calculation mentioned above is performed for the first-order Stark effect. In the case of the second-order Stark effect, the value of  $\Delta$  is

$$\Delta \propto n^{4/3}.$$
 (2-48)

Summary, the inhomogeneous line-broadening due to the random distribution of ionized impurities is in proportion to the  $n^{23}$  power for the first-order Stark effect, and the  $n^{4/3}$  power for the second-order Stark effect. Moreover, it is known that the line-broadening by the interaction between the electric quadrupole and the field gradient is linear to n:

$$\Delta \propto n \tag{2-49}$$

#### §3. Experimental procedure

#### 3-1 FIR laser and detector

Two types of FIR lasers were employed. One was a discharge type pulse laser by using H<sub>2</sub>O and D<sub>2</sub>O vapor at pressure between 1 and  $2x10^{-1}$  Torr. The four wavelengths, 119, 220, 84 and 172 $\mu$ m were employed. The repetition rate was 30Hz. The other was an optically pumped laser. The four wavelengths, 96.5, 119, 57 and 103 $\mu$ m, having CH<sub>3</sub>OH and CH<sub>3</sub>OD vapor were employed. FIR light was detected by a Putley type *n*-InSb detector ( $\lambda > 84\mu$ m) or Sb-doped Ge detector ( $\lambda < 84\mu$ m) depending on wavelength,  $\lambda$ . These detectors were biased at a constant current.

#### 3-2 Experimental setup

Figure 3.1 shows a block diagram of the experimental setup. The FIR laser light went through the guide tube, and arrived at a sample position. The light transmitted through the sample was detected. The detected signal was amplified, and was led to the two-channel Boxcar integrator with a logarithmic amplifier. An applied magnetic field up to 9T was produced by a vertical type superconducting solenoid. The absorption spectra were measured in Faraday configuration. The temperature was varied between 1.8K and 30K and monitored by a carbon glass resistance thermometer.

#### 3-3 Photo- and electric-field-excitation method

In optical excitation measurements, Xenon flash lamp and a tungsten incandescent lamp were employed. The repetition rate of the Xenon flash lamp was 15Hz and synchronized with every other turn of the FIR laser pulses. The intensity of excitation light was controlled by neutral density filters. Glass filters which cut energy larger than the bandgap energy were also employed. As I and  $I_o$  are intensities of transmitted FIR light with and without the photoexcitation, the quantity of absorbance is derived from

Absorbance = 
$$ln(I_0/I)$$
. (3-1)

Then, the absorbance is in proportion to the absorption coefficient,  $\alpha$  and the sample thickness, d. Accordingly,  $\alpha$  's given by

$$\alpha' = \frac{1}{d} ln(I_0 / I) \quad (3-2)$$

Instead of photoexcitation, electric field excitation method was also employed. This method was mainly used to investigate the effect of uniform electric fields on the line-broadening.

#### 3-4 Time-resolved signal measurement

A signal at any delay time after the photopulse excitation was selectively detected by means of a boxcar-integrator. The gate of the boxcar-integrator was opened at any delay time and the aperture time was kept open ~ $0.5\mu$ s for each pulse. For measurement of a time-resolved magneto-optical absorption, the variation of absorption intensities was obtained by sweeping the magnetic field at a fixed gate position.

#### 3-5 Samples

The specimens used in this study were compensated InSb and Ge. Their characteristics are listed in table I.

A highly compensated *p*-InSb was employed. To avoid the interference in an absorption measurement, the sample had a rectangular shape. The size of sample was  $4x4x1cm^3$ . The flat face normal to the <111> crystallographic axis was used. Both sides of the sample were ground with 3000 emery paper and polyester spheres and were etched with CP-4.

Six *p*-type Ge samples which were doped by transmutation method<sup>24-26</sup>) were employed. Donor and acceptor doped by this method are As and Ga, respectively.

The procedure of transmutation-doping is described as follows. A natural Ge sample contains such isotopes as Ge<sup>70</sup>, Ge<sup>72</sup>, Ge<sup>73</sup>, Ge<sup>74</sup> and Ge<sup>76</sup>. The respective abundances are 20.45, 27.41, 7.77, 36.58 and 7.79%. The neutron absorption cross sections are 3.4, 0.98, 14, 0.62 and  $0.36 \times 10^{-24} \text{ cm}^2$ , respectively. When thermal neutrons are irradiated on Ge, the relative absorption of neutrons is 30.4, 11.7, 47.2, 9.8 and 1.2%, respectively. The pertinent radioactive decay is given by,

$$Ge^{70}(n,\gamma)Ge^{71} \longrightarrow Ga^{71},$$
 (3-3)

$$Ge^{74}(n,\gamma)Ge^{76} \longrightarrow As^{75}$$
 (3-4)

and

where *n* indicates an absorption of neutron,  $\gamma$  emission of  $\gamma$ -ray. *K* and  $\beta$  are electron capture process and  $\beta$ -decay process, respectively. The acceptor Ga<sup>71</sup> slowly increases with a 12-days half-life. Conversely, the donor As<sup>75</sup> is rapidly produced with a 82-minute half-life. Since the produced Se<sup>77</sup> is relatively less than the Ga<sup>71</sup>, As<sup>75</sup>, one can ignore this impurity. By adjusting the quantities of isotopes, the various compensated Ge samples were prepared. The compensation ratio, *K*, defined by  $N_D/N_A$  was in the range from 0.082 to 0.76. The shape of sample is ellipse. The size is 7 x 5 x 1mm<sup>3</sup>. The flat face normal to the <100> crystallographic axis was used.

A *p*-Ge sample which was made by a FZ-grown method was also employed. The size of the sample which had a rectangular shape was  $4x4x1cm^3$ . The flat face normal to the <110> crystallographic axis was used.

#### §4 Experimental Results

#### 4-1 *p*-InSb

#### (a) Magnetic field dependence

Figure 4.1 shows the magneto-optical absorption spectrum in a photoexcited p-InSb at 4.2K for FIR laser line of 84 $\mu$ m. *C1* and *C2* denote cyclotron resonance of conduction electrons, and correspond to the transitions from  $0^+$  to  $1^+$  and from  $0^-$  to  $1^-$  Landau subband, where the number indicates the Landau quantum number and + and - indicate up- and down-spin states as shown in Fig.4.2. *ICR* denotes a transition of donor electrons from a ground state to an excited state, i.e., the so-called impurity-cyclotron resonance<sup>30</sup>. These donor states are associated with each Landau subband. An absorption peak observed at near 3T is a Zeeman-type absorption of acceptors and is denoted by  $\alpha$ . In the following discussion, I will take notice of this line.

Figure 4.3 shows the magnetic field dependence of transition energy for the line  $\alpha$  in InSb. Kaplan also observed the transition from a ground state to an excited state in InSb and identified transition as Cd<sup>+</sup> acceptor.<sup>31)</sup> Since the results obtained in this work are in good agreement with Kaplan's data, it can be concluded that the observed transition line  $\alpha$  is due to the Cd<sup>+</sup> acceptor.

#### (b) Donor-acceptor recombination

Figure 4.4 shows time variations of integrated intensity of the line  $\alpha$  after

photopulse excitation at 1.8K and 4.2K. The relaxation takes several milliseconds. Photoexcited electron-hole pairs are immediately captured by ionized impurities at low temperature. Accordingly, ionized impurities are neutralized by these photoexcited carriers under the strong photoexcitation. In the highly compensated semiconductor, a dominant relaxation process at low temperature is the donor-acceptor(D-A) recombination. If the distance between the interacting D-A pairs is large, the recombination rate is very small. The energy concerned with the D-A recombination, which is a function of the distance r for D-A pairs, is given by<sup>1)</sup>

$$E(r) = E_g - (E_D + E_A) + \frac{e^2}{4\pi\varepsilon_0\varepsilon r}, \qquad (4-1)$$

where  $E_g$  is the band gap energy,  $E_D$  and  $E_A$  the binding energy of the donor and the acceptor, respectively. The final term is the Coulomb energy between the ionized donor and the acceptor. The function E(r) thus changes with the distance r, and many luminescence lines arising from the D-A pairs with different r have been observed in GaP crystal<sup>32)</sup>.

Moreover it is found that the decay curve at 4.2K is faster than that at 1.8K due to the recombination process of electrons between the conduction band and the acceptor.

#### (c) Time variation and photoexcitation dependence

Figure 4.5 shows time dependence of the lineshape of the line  $\alpha$  at 4.2K.

Full width at half maximum of the line  $\alpha$  broadens as the lapse of time after photopulse excitation. Time variations of the FWHM at 1.8 K and at 4.2K are shown in Fig.4.6 and Fig.4.7. In the latter figure, time scale is extended. The change in the FWHM at 1.8K is gentler than that at 4.2K. It is clear that both curves gradually approach a same value with delay time. In general, the integrated intensity of the line  $\alpha$  is proportional to the number of neutral acceptor. Thus, neutral acceptors decrease as the lapse of time after photopulse excitation. Inversely, the reduction of the integrated intensity means the increment of ionized impurities.

The variations of the line  $\alpha$  for the intrinsic light intensity with 100, 50, and 5 % are shown in Fig.4.8. Maximum intrinsic light intensity is expressed by 100%. The signal obtained under no photoexcitation cannot be detected because of the high compensation rate. As decreasing of the intrinsic light intensity, the line  $\alpha$  becomes much broader. Accordingly it is concluded that the broadening of the FWHM is closely related to the increment of ionized impurity.

In order to explain the experimental results in the time-resolved measurements, a simple schematic picture is shown in Fig.4.9. Just after photoexcitation (a), there is a lot of neutralized impurities, where the notations  $A^{0}$  and  $D^{0}$  denote a neutral acceptor and donor, respectively. However, there is little ionized donors and acceptors denoted by  $A^{-}$  and  $D^{+}$ , respectively. As passing long time (b), impurities are ionized through a D-A recombination process, and induce inhomogeneous electric fields an neutral impuritiesas. Thus,
the inhomogeneous electric fields cause shift of energy states of neutral impurities by Stark effect. As the results of inhomogeneity of electric fields, it is explained that the FWHM of the line  $\alpha$  broadens.

### 4-2 *p*-Ge

(a) Magnetic field dependence

Figure 4.10 shows the FIR magneto-optical absorption spectrum in the sample *a* for the wavelength of 84 $\mu$ m. There is no change in the spectrum with and without photoexcitation. This sample contains only Ga acceptor impurities. The number of compensated donors is negligibly small. Various absorption lines appear in this spectrum which are identified to be due to Ga impurities. As shown in Fig. 4.11, an absorption spectrum for  $57\mu$ m line shows quite remarkable structure. There are a lot of sharp peaks. Two adjacent peaks of them seems to form a pair. Figure 4.12 shows inverse magnetic field dependence of labelled number of absorption peaks for two certain absorption peaks in Fig 4.11. Variations of the peak positions have two series.

The Kohn-Luttinger effective-mass approximation (EMA) has been used to describe the electronic structure of a impurity level in semiconductors.<sup>33-37)</sup> The states of group III acceptor in Ge and Si were studied in detail based on variational approach.<sup>35-37)</sup> In the EMA theory, it is known that the wavefunction of shallow acceptor states is expressed in the form

$$\psi(r) = \sum_{j} F_{j}(r)\varphi_{j}(r), \qquad (4-1)$$

where  $\varphi_j$  is the degenerate Bloch function at the top of valence band in a host crystal, and  $F_j(r)$  the so-called envelop function which satisfies the following effective mass equation:

$$\sum_{j} (D_{jj'}^{\alpha\beta} p_{\alpha} p_{\beta} + \frac{e}{4\pi\varepsilon_{0}\varepsilon r} \delta_{jj'}) F_{j'}(r) = EF_{j}(r) \quad (4-2)$$

where  $D_{jj'}^{\alpha\beta}$  is the inverse effective mass tensor,  $p_{\alpha}$  and  $p_{\beta}$  are the components of the momentum operator along  $\alpha$  and  $\beta$  directions, respectively. Since the acceptor states are made by Bloch wave functions near the top of the valence band, it is necessary to know some information about the structure of the valence band. However degenerate bands such as valence bands in Ge are more complicated than conduction bands.

The top of valence band in semiconductors is composed of a fourfold degenerate state (J=3/2) and a twofold degenerate state (J=1/2), which splits off by 0.29eV due to spin-orbit interactions shown in Fig.4.14. In  $k \neq 0$ , the upper band splits a set of a twofold degenerate heavy hole band (h.h.b), and light hole band (l.h.b). In Ge, it is enough for calculating the energy levels only to take into account of the upper fourfold degenerate states (J=3/2), because the binding energy of the acceptor (~11meV) is much smaller than the spin-orbit separation of 0.29eV. Thus, summation over j in the equation (4-1) and summation over j' in the equation (4-2) are performed for the four degenerate states, namely, the  $m_j$ =-3/2, -1/2, 1/2 and 3/2 states of the top of valence band. Mendelson and James<sup>35)</sup> employed trial functions of the form

$$F_{j}(r) = \sum_{l} \sum_{k} C_{lk} A_{j}^{lk}(\theta, \varphi) r^{l} f_{l}(r)$$
(4-3)

where  $A_j^{k}(\theta, \varphi)$  is linear combinations of spherical harmonics of the order 1. The coefficients  $C_k$  and the radial functions  $f_l(r)$  are obtained by means of a variational calculation method. This approximate calculation was in excellent agreement with experimental results by several authors.<sup>3, 38-39</sup>

The acceptor states in Ge under magnetic field based on EMA theory have been investigated in detail.<sup>40)</sup> In particular, these lines observed in Fig.4.12 have already been discussed by several authors.<sup>4, 41-45)</sup> Otsuka *et al.*<sup>41)</sup> have observed five Zeeman absorption lines labelled A through E in In-doped Ge. Especially, they pointed out that three strongest lines correspond to the transitions associated with the transition between Landau levels of N=0 and 1, where the notation Ndenotes the Landau quantum number.

In the uniform magnetic field *B*, the continuous states in the energy bands coalesces into discrete quantum states called Landau levels. These Landau levels form a ladder with equally spacing  $\hbar \omega_c$  defined by the cyclotron frequency  $\omega_c = eB/m^*, m^*$  being the effective mass of the charged carriers. Cyclotron resonance absorptions of the electrons and holes are induced electric-dipole transitions between these ladder states.

The Landau levels in the valence band of Ge calculated by Hensel and Suzuki.<sup>46-47)</sup> The Landau levels in the valence bands are very complicated due to degeneracy of them. The Hamiltonian describing the motion of a hole in magnetic field is given by Luttinger Hamiltonian<sup>48)</sup>:

$$D = (1/m)\{(\gamma_1 + \frac{5\gamma_2}{2})\frac{k^2}{2} - \gamma_2(k_x^2 J_x^2 + k_y^2 J_z^2 + k_z^2 J_z^2) -2\gamma_3(\{k_x k_y\}\{J_x J_y\} + \{k_y k_z\}\{J_y J_z\} + \{k_z k_x\}\{J_z J_x\}) + e\kappa J \cdot B + eq(J_x^3 B_x + J_y^3 B_y + J_z^3 B_z)$$

$$(4-4)$$

and

$$\{k_x k_y\} = \frac{1}{2} (k_x k_y + k_y k_x), \qquad (4-5)$$

where *m* is mass of an electron in vaccum,  $\gamma_1$ ,  $\gamma_2$  and  $\gamma_3$  dimensionless band parameters of valence bands,  $\kappa$  and *q* the spin splitting in magnetic field, the  $J_{\alpha}$ ( $\alpha = x, y, z$ ) the matrix representations of the total angular momentum operator for a state with J=3/2. The five parameters are determined by cyclotron resonance measurement.

For the values of these band parameters  $\gamma_1 = 13.38$ ,  $\gamma_2 = 4.24$ ,  $\gamma_3 = 5.69$ ,  $\kappa = 3.41$ and q = 0.06 at wavenumber,  $k_H = 0$  in Ge, the energy levels in a magnetic field are shown in Fig.4.15. The Landau levels are classified by  $(N_n, K^{\pi})^{46.47}$ , where *n* is a quantum number of harmonic oscillator function,  $K (=0, 1, \dots, v)$  is a quantum number in the *v*-fold rotational symmetry of the crystal about the direction of magnetic field and  $\pi$  the parity of the envelope function. The relation of among *N*, *n*, and *K* is represented by

$$N = M_j + \frac{3}{2} + n \tag{4-6}$$

and

$$K = N(mod v). \tag{4-7}$$

In simple case, as it is assumed that each distance of energy levels in light holes is approximately equal, the energy levels of an acceptor state associated with Landau levels is described by

$$N = (N + \frac{1}{2})\hbar\omega_{C} + E_{B} + \delta(N) \pm \frac{1}{2}g\mu_{B}B.$$
 (4-8)

This equation is resolved by about N:

$$N = \{E - E_b + \delta(N)\} \frac{m^*}{\hbar e} \frac{1}{B} \mp \frac{1}{2} \frac{g_h \mu_B m^*}{\hbar e}.$$
 (4-9)

Accordingly, it is expected that the number N is in proportion to the inverse magnetic field 1/B.

The effective masses estimated from the slope of the two lines in Fig.4.12 are 0.0459 and 0.0453. This results are in good agreement with the value of a light hole mass given by Hensel and Suzuki.<sup>46-47)</sup>

Thus, it is concluded that these acceptor levels are associated with the transition from  $2_0$  of the heavy hole Landau level to  $1_1$  of the light hole Landau level and the transition from  $0_0$  to  $1_1$  of the light hole Landau level as shown Fig.4.12. Here it is considered that weak peaks except main peaks in Fig.4.10 and Fig.4.11 are due to the transitions between heavy hole states.

Figure 4.17 shows the FIR magneto-optical absorption spectrum for the wavelength of  $119\mu$ m line. Various absorption-lines appear in the spectrum.

These lines may be due to the transitions between the complicated states composed from light hole and heavy hole bands.

### (b) Photoexcitation dependence

Figure 4.18 shows variation of Zeeman absorption spectra in the sample f as a function of the intrinsic light intensity with 100, 50, and 0 %(dark). The compensation ratio (K) of the sample is 0.76. As decreasing the intrinsic light intensity, all absorption lines become much broader. In dark signal, the intensities of all lines broaden extremely, and the absorption lines overlap each other.

Figure 4.19 shows the FIR magneto-optical absorption spectrum for sample b with K=0.40. Under photoexcitation, various absorption lines by Ga acceptors appear in the spectrum. However, the intensity of the absorption lines considerably decreases under the condition without photoexcitation, because almost all photoneutralized acceptors ionize in equilibrium state.

It is noticed that various absorption lines appear under the condition with photoexcitation, and especially a sharp absorption line appear near 2.3T. This line was previously identified as the Zeeman absorption of Ga acceptor associated with Landau levels. This Zeeman absorption line under the condition without photoexcitation is much broader and weaker than that under photoexcitation.

In order to study this peak in detail, the absorption lines with an blown up scale around this region in the sample c are shown in Fig.4.20. The compensation ratio of this sample is 0.49. The variations of the Zeeman absorption line for the

intrinsic light intensity with 100, 50, and 0 % are shown. As the intrinsic light intensity decreases, the absorption line becomes much broader. The result for the sample c is similar to that in the sample b. Here, the absorption observed at 1.95T is due to a transition of As donors. Figure 4.21 shows time variations of the integrated intensity of the absorption line with photopulse excitation. The relaxation time takes several milliseconds due to D-A recombination.

The difference in shape of these three lines is caused by the differences in the concentration of ionized impurities. Especially, it is expected that the FWHM is dominated by the distribution of ionized impurities.

The relation between the FWHM and the light intensity is shown in Fig.4.22. When the excitation light intensity increases above 50%, the FWHM decreases and saturates at a certain value. The saturated FWHM and a observed total FWHM are given by  $\Delta_{Sat}$  and  $\Delta_{Tot}$ , respectively. Hereafter, the difference between the total FWHM and the saturated FWHM will be discussed.

Figure 4.23 shows the dependence of the FWHM on the ionized impurity concentration. The ionized impurity concentration is estimated from the integrated intensity of the absorption-line. In subtracting the saturated FWHM from the total FWHM, only the contribution of the ionized impurities is picked up. This is expressed by  $\Delta_{tot}$ - $\Delta_{sat}$ . It is found that the line-broadening depends on  $N_i^{43}$  power law in the region where ionized impurity concentrations exceeds  $10^{15}$ cm<sup>-3</sup>. Here  $N_i$  denotes concentration of ionized impurity. Accordingly, the obtained result can be identified as the second-order Stark effect expected from the

inhomogeneous broadening theory.<sup>23,17-18)</sup> Figure 4.24 shows the dependence of the FWHM of the absorption line on various samples with compensation ratio of 0.082, 0.49, 0.61 and 0.76. Variation of line-broadening in the all samples almost shows the  $N_i^{4/3}$  power laws.

In order to give an explanation of the line-broadening of the FWHM under various photoexcitation condition, a simple schematic diagram is shown in Fig.4.25. Under strong photoexcitation (a), there is a lot of neutral impurities. However, without photoexcitation (b), impurities are almost ionized, and these induce inhomogeneous electric fields at each position of neutral impurity. Thus, the inhomogeneous electric fields make the FWHM of the absorption line broaden.

However, it is noticed that a large deviation from  $N_i^{4/3}$  power law is observed in above region of  $10^{15}$  cm<sup>-3</sup>, which seems to be due to the higher-order Stark effects or due to the ambiguous estimation of ionized impurities in higher concentration region.

Kogan *et al.*<sup>49)</sup> approximately calculated about the FWHM of an impurity absorption-line in GaAs. In this calculation, the random distribution of ionized impurity is assumed. They pointed out that the first- and second-order Stark effect is

$$\sim ea_0^4 E / a_B^3 \tag{4-10}$$

and

$$\sim \varepsilon a_B^{3} E^2, \qquad (4-11)$$

respectively, where  $a_0$  is a lattice constant. Since the effective Bohr radius  $a_B$  is much larger than  $a_0$ , the first-order Stark effect is extremely small.

The FWHM  $\Delta_2$  due to the second-order Stark effect is given by

$$\Delta_2 = 2.6 x 10^3 E_B (N_i a_B)^{4/3}, \qquad (4-12)$$

where  $E_B$  is binding energy of the impurity. In the Ga-doped Ge, the  $\Delta_2$  for  $N_i = 2.0 \times 10^{15} \text{ cm}^{-3}$  is estimated by

$$\Delta_2 \approx 0.3 meV.$$

Moreover, in the same concentration, the  $\Delta_{FG}$  due to the field-gradient broadening is estimated by

$$\Delta_{FG} = e^2 a_B^2 N_i / \varepsilon \qquad (4-13)$$

$$\approx 80 \,\mu eV,$$

while experimentally obtained  $\Delta_{obs}$  is

$$\Delta_{obs} \approx 0.27 \, meV.$$

Accordingly, the obtained result can be identified as the second-order Stark effect expected from theory by Kogan *et al.*<sup>49)</sup>

By the way, in the case of low concentration as  $1.0 \times 10^{14}$  cm<sup>-3</sup>, the broadening are estimated as

$$\Delta_2 \approx 4 \,\mu eV.$$

and

 $\Delta_{FG} \approx 3.4 \mu eV$ 

Each effect is comparable. It is found that the field-gradient broadening is very important in the lower density region such as  $10^{14}$  cm<sup>-3</sup>. However, this effect can be ignored in this study, because the samples employed in this work have concentration above  $10^{15}$  cm<sup>-3</sup>.

(c) Magnetic field, temperature and external electric field dependence

Figure 4.26 shows magnetic field dependence of the FWHM of the absorption line. Dependences of the FWHM of the absorption line on concentration of ionized impurities under magnetic field of 2.3 and 5.5T are plotted in this figure. The concentration dependence of the FWHM for 5.5T is smaller than that for 2.3T, but both data show the  $N_i^{4/3}$  power laws.

When the magnetic field is applied to a hydrogenic impurity, the wavefunction is compressed.<sup>50)</sup> Introducing the quantity of  $\gamma$  as denoted by

$$\gamma = \frac{\hbar\omega_c}{2R_y^*},\tag{4-14}$$

where  $R_{y}^{*}$  is the effective Rydberg energy. For 2.3 and 5.5T,  $\gamma$  are estimated to be 0.267 and 0.645, respectively. The shrinkage of the wavefunction means that the effective Bohr radius becomes smaller, and that the distance between the energy levels becomes wider. Thus, the Stark-broadening must decrease as magnetic field increases.

However, it is expected from the equation (4-12) that the dependence of the FWHM on the concentration of ionized impurities in magnetic field does not change except the absolute quantity of the line-broadening.<sup>49</sup>

Figure 4.27 shows the temperature dependence of the absorption line. With increasing temperature, the absorption line broadens. In order to see in detail, the temperature dependence of the FWHM of the absorption line is shown in Fig.4.28. Open circles denote the experimentally obtained FWHM of the absorption line. Triangles denote the contribution estimated by the Starkbroadening.

This line-broadening includes both contribution of the phonon-broadening and the Stark-broadening as temperature increases. The former is caused by lifetime effect due to the electron-phonon interaction. The latter is caused by increment of ionized impurities as temperature increases.

The contribution of the phonon-broadening is given by substrcting the Stark-broadening from the FWHM. Variation of the phonon-broadening, however, is not in agreement with Nishikawa and Barrie's formula.<sup>78)</sup> In this study, I do not touch upon the effect hereafter.

Figure 4.29 shows the external electric field dependence of the absorption line. The FWHM of the absorption line increases with increasing strength of the electric field. There is no contribution of the phonon-broadening because thermal effect can be ignored. Moreover, the external electric field is very smaller than the internal electric field. Accordingly, the line-broadening is only due to the internal Stark effect.

# §5. Application of Monte Carlo Simulation and Discussions

5-1 InSb

Just after photoexcitation, adjacent D-A pairs recombine immediately. If the distance between the interacting D-A pairs is large, the recombination rate is very small. The energy concerned with the D-A recombination, which is a function of the distance r for D-A pairs, is given by Equation (4-1).

The D-A recombination rate is governed by the overlap between a wavefunction of the donor and that of acceptor. Wavefunctions for 1s state of the donor and the acceptor are as follows<sup>32)</sup>

$$\psi_D(r) = C \exp(-r/a_B) \tag{5-1}$$

and

$$\psi_A(r) = C' exp(-|\vec{r} - \vec{R}|/a_B')$$
 (5-2)

respectively. Here C and C' are normalized factor,  $a_B$  and  $a_B'$  are a Bohr radius of the donor and acceptor, respectively, R distance between the donor and the acceptor. The recombination rate at position  $\vec{r}$  is expressed by

$$W(r) = C'' \int_{V} exp(-r/a_{B} - |\vec{r} - \vec{R}|/a_{B}') dV.$$
 (5-3)

The general form of W(r) is calculated exactly by Kamiya *et al*.<sup>51)</sup> However, in the case that a Bohr radius of the donor is much larger than that of the acceptor, the recombination rate is simply expressed by<sup>32)</sup>

$$W(r) = W_{max} \exp(-r/R_D)$$
(5-4)

where  $W_{\text{max}}$  is a constant related to the binding energy of the impurity, and  $R_{\text{D}}$  the half of the Bohr radius of the donor,  $a_{\text{B}}$ . Since the Bohr radius of donor is about ten times larger than that of an acceptor in InSb, the above situation is reasonable.

In order to analyze the time variation of the FWHM of the line  $\alpha$ , a Monte Carlo simulation<sup>52)</sup> carried out by using the function W(r). Procedure of the Monte Carlo simulation<sup>53)</sup> is shown in the following. Every labelled neutralized donors and acceptors of which total number are 583x2 were randomly distributed on the 3-dimensional box, which consists of  $(4000)^3$  lattice points. Every W(r) between one donor (or acceptor) and all acceptors (or donors) is calculated. Moreover, a numerically generated psudo random number  $\gamma$  between 0 and 1 was prepared. It is assumed that the following law as shown in the Ref.11 should be hold. All values of the  $W(r)/W_{max}$  are compared with  $\gamma$ , when that

$$W(r)/W_{max} \ge \gamma \tag{5-5}$$

all donor-acceptor pairs to which the above inequality is applicable, recombine immediately, and contrary to the above condition, for

$$W(r)/W_{max} < \gamma, \qquad (5-6)$$

the donor-acceptor pairs remain neutral.

Through the judgement based on these conditions, the probabilities of existence were repeatedly calculated for all sets of the impurities. The one process corresponds to 1 step on the calculation and the total calculation times reaches 583x583 times. After *T* steps, the distribution of electric fields induced by all ionized impurities which acted on remaining neutral impurities, and finally, standard deviation ( $\sigma$ ) of statistical distribution of internal electric field was obtained. In this calculation, it is assumed that there is no screening effect by free carriers on the electric field.

Thomas *et al.*<sup>32)</sup> numerically deduced time variation of the number of neutral impurities due to D-A recombination for completely compensated semiconductors. In our case density of the donor and acceptor is  $1.4 \times 10^{14}$  cm<sup>-3</sup> and  $a_{\rm B}$  is 500Å. The results obtained by Monte Carlo calculation (open circles) are comparable with curves by Thomas *et al.* (solid line) in Fig.5.1. The calculational values by two different methods show good agreement each other. This fact supports that the results of the Monte Carlo calculation are valid.

Actually, by comparing the decay curve obtained experimentally at 1.8K with the calculational data, the time scale per 1 step  $(T_{Istep})$  can be determined. With the properly adjusted time scale, both experimental and calculational data are superposed in Fig.5.2. It is found that 1 step approximately corresponds to  $2\mu$ s, because the  $W_{max}$  is given by  $T_{Istep}^{-1}$ . After all, it is evident that the value of  $W_{max}$  is 5.0x10<sup>5</sup>s<sup>-1</sup> for InSb at 1.8K. With use of the time scale obtained thus, the time variation of the distribution amplitude of electric fields on the every

position of neutral impurities is shown in Fig.5.3. It is clear that the distribution shifts towards higher electric field with the lapse of time after photoexcitation. As a result, it is expected that the FWHM of line  $\alpha$  broadens as the lapse of delay-time after photopulse excitation.

In order to analyze the FWHM of the line  $\alpha$ , time variation of the standard deviation ( $\sigma$ ) in the distribution of the electric field distribution is calculated and shown in Fig.5.4. As the delay-time increases, the standard deviation rapidly increases and saturates at a certain value. The result obtained by this simulation shows that the inhomogeneity of the electric field increases with increase of the ionized impurities. The experimentally obtained line-broadening shown in Fig.4.6 and 4.7 qualitatively agrees with the calculational result shown in Fig.5.4.

Here, the FWHM consists of two parts, namely the delay-time dependent part and independent one. The former reflects the contribution of the Stark broadening due to inhomogeneous distribution of electric field induced by ionized impurities. The time variation of the FWHM is explained in the above discussions. The latter, on the other hand, corresponds to the phonon broadening<sup>7-8)</sup> at a fixed temperature, and the residual width caused by uncertain imperfections.

The recombination rate W(r) contains two independent parameters,  $W_{max}$ and  $R_d$ . The quantity  $W_{max}$  was determined by the experimental decay curves. The half of the Bohr radius of the donor,  $R_d$ , was derived from the binding energy of the donor, assuming an isotropic wavefunction for donor in the magnetic field. The special correlation for the distribution between the donor and the acceptor is not considered in this calculation. As for more rigorous calculation, it is necessary to take into account the above-mentioned problems.

5-2 Ge

In order to analyze the dependence of the FWHM of absorption line on intrinsic light intensities, the Monte Carlo simulation method was employed as the discussion in the section 5-1. Especially, the relation between inhomogeneous internal electric fields and the distribution of ionized impurities is discussed.

As the first stage, the calculation was carried out in the case of completely random distribution of ionized impurities. The procedure<sup>54-55)</sup> is simply summarized in the following. Firstly, the initial configuration was decided.  $(3000)^3$  lattice points were employed as size of three dimensional system. Acceptors and donors which were the number of 1730 and 850, respectively ,were distributed in this space. Secondly, the electric fields at every position of neutral impurities were calculated. Thirdly, the distribution of the electric field were deduced. Finally, the standard deviation ( $\sigma$ ) of the distribution was obtained. Moreover, this calculational process for various density of ionized impurity was repeated.

Figure 5.5 shows  $\sigma$  in the distribution of the electric field for various system size, L, under the condition that  $N_i/V$  is a constant. The notation  $N_i$  and  $V(=L^3)$  denote the concentration of ionized impurities and volume of the system, respectively. It appears that  $\sigma$  saturates at a certain value. If the system size is small, neutral impurities located near the surface of the system are not negligible. With the large system size , the effect of the impurities near surface decreases. Since this figure shows a saturation, this surface effect can be ignored and the

system size is valid in the Monte Carlo calculation. The value denoted by an arrow is employed in this calculation.

Distribution amplitude of internal electric fields at neutral impurity positions for various concentration of ionized impurities is shown in Fig.5.6. The notation N denotes concentration of neutral impurities. When the density of ionized impurities to the total impurities is 30%, 70%, and 100%, the distributions of the electric fields at every position of neutral impurities are plotted in this figure. Each curve is obtained by smoothing a histogram with the deviation of 5%. With increasing ionized impurities, the distribution of the internal electric fields shifts toward higher field, and becomes much broader.

Figure 5.7 shows comparisons of the distribution amplitude of the strength of the electric fields due to randomly distributed ionized impurities by Monte Carlo calculation (open circles) with the same quantity calculated by a Holtzmark function(solid line).<sup>49, 56-58)</sup> In these cases, the concentrations of ionized impurities are  $8.34 \times 10^{14}$  cm<sup>-3</sup> and  $2.78 \times 10^{15}$  cm<sup>-3</sup>, respectively.

The Holtzmark function has been employed for various problems such as distribution of electric fields induced by charged particles in plasma<sup>22)</sup> and ionized impurities in semiconducters<sup>17-18, 56)</sup>. This function can be applied in the only case of random distribution of ionized impurities and expressed by<sup>57-58)</sup>

$$F(E) = \frac{2}{\pi E} \int_0^\infty x \sin x \exp[-(E_H/E)^{3/2} x^{3/2}] dx, \quad (5-7)$$

where characterized electric field  $E_{H}$  is defined by

$$E_H = 2.6 \frac{e}{4\pi\varepsilon_0 \varepsilon} N_i^{2/3}.$$
 (5-8)

The calculational values by two different methods are in good agreement with each other. This fact supports that the results of the Monte Carlo calculation is valid.

As described in section 4, the FWHM of the Zeeman absorption line is approximately in proportion to the inhomogeneous distribution of electric field. Thus, it is important to examine the concentration dependence of the distribution. Figure 5.8 shows the  $\sigma$  in the distribution of electric field squared for various density of ionized impurities in random configuration. The notation  $N_o$  denotes a normalized factor. It is found that  $\sigma$  is in proportion to the density of ionized impurities to the four-third power law. This results are in good agreement with the experimental results. Accordingly, it is considered that the second-order Stark effect strongly contributes to the observed line-broadening in transmutationdoped samples. Generally speaking, the distributions of ionized impurities in the transmutation-doped samples is nearly random. It is natural that the distributions are formed by completely random bombardment of neutrons.<sup>17</sup>

Finally, in order to applied to samples produced by usual way, for example, CZ-or FZ-grown methods, the relation between various configuration of ionized impurities and the line-broadening is discussed. In particular, density dependence of  $\sigma$  in the distribution of electric field for various configuration of ionized impurities is calculated in the following. Larsen<sup>17-18)</sup> pointed out the presence of

weak pairing between a donor and an acceptor. Actually, it is expected that the FWHM of a absorption-line obtained from experimental data in GaAs is smaller than that from his calculation assuming random distribution. However, the FWHM of the absorption line obtained experimentally by Stillman<sup>19</sup> is well explained by the correlated, i.e., weak pairing model.

The standard deviation in the distribution of electric field squared in three types of initial configuration which are random, dipole-like and lattice-like is shown in Fig.5.9.

As an extreme case, the distance between ionized donors and ionized acceptors was always about the effective Bohr radius(~50)Å of impurity. A pair of an ionized donor and ionized acceptor which have charge of plus and minus causes a dipole. The configuration of the pairs is assumed to be completely random. From Monte Carlo calculation, it is found that the variation of  $\sigma$  is in proportion to the  $N_i^2$  power law. This variation qualitatively explains by a simple nearest-neighbor approximation in the following.

## (a) Random configuration

At first, the random configuration of impurities is assumed. Mean distance between ionized impurities is

$$\bar{r} = \sqrt[3]{\frac{3}{4\pi N_i}} \propto N_i^{-\frac{1}{3}}.$$
(5-9)

Since the internal electric field by an ionized impurity is in proportion to the  $1/r^2$ , where r is the distance between a neutral impurity and an ionized

impurity, the mean electric field is expressed by

$$\overline{E} = \frac{1}{4\pi\varepsilon} \frac{e}{\overline{r}^2} \propto N_i^{-\frac{2}{3}}.$$
(5-10)

Here, because the line-broadening  $\Delta$  by the first-order Stark effect is in proportion to the  $\overline{E}$ , the  $\Delta$  is given by

$$\Delta \propto \overline{E} \propto N_i^{-\frac{2}{3}}.$$
(5-11)

while the line-broadening by the second-order Stark effect is

$$\Delta \propto \overline{E}^2 \propto N_i^{-\frac{4}{3}}.$$
 (5-12)

(b) Dipole-like configuration

About dipole-like configuration, since electric field by a dipole is in proportion to the  $1/r^3$ , the line-broadening by the first-order Stark effect is described by  $\Delta \propto \overline{E}' \propto N_i$  (5-13)

while the line-broadening by the second-order Stark effect is

$$\Delta \propto \overline{E}'^2 \propto n^2. \tag{5-14}$$

Thus, result in the Monte Carlo simulation is well explained by this approximation.

(c) Lattice-like configuration

In the case of the lattice-like configuration, the ionized donors and the ionized acceptors are with equal period in turn. It is found that  $\sigma$  is much smaller than the other cases. This effect is due to offset of the electric fields.

Moreover, the  $\sigma$  is in proportion to the  $N_i^{23}$  power law. The reason of the variation is well unknown.

**§6** Conclusion

The line-broadening due to the Zeeman absorption of acceptor impurity in highly compensated InSb and Ge has been observed. In highly compensated InSb, the FWHM for the line  $\alpha$  increases as the lapse of delay time after photopulse excitation increases. In highly compensated and transmutation-doped Ge, the FWHM of Zeeman absorption line for Ga acceptor increases as intensity of photopulse excitation decreases.

It is concluded that the line-broadening is caused by Stark effect due to the inhomogeneous electric field induced by the ionized impurities. Experimental results are qualitatively in agreement with the theory by Stoneham<sup>22-23)</sup> in randomly distributed ionized impurities and mainly dominated by the second-order Stark effect.

However, the distribution of impurities in semiconductors is not clear. The distribution of the electric field induced by ionized impurities in the presence of correlation between impurities cannot deduce analytically. In order to analyze the relation between the inhomogeneous electric field and the distribution of ionized impurities, the Monte Carlo simulation was carried out.

For InSb, the method of the Monte Carlo calculation with the function of D-A recombination probability W(r) was employed, and qualitatively explained the line-broadening. However, if the Bohr radius of donor is comparable with that of acceptor as the case in Ge, it is necessary to use the complete formula.

For Ge, the calculation assuming random configuration of ionized impurities is in good agreement with the experimental results. From this analysis, it is concluded that the distribution of ionized impurities in transmutation-doped Ge is almost random. Moreover, for the three examples of initial distribution of ionized impurities, as random, dipole-like and lattice-like configuration, the Monte Carlo simulation was attempted. Especially, the broadening of distribution in random configuration is in proportion to the density of ionized impurities to the four-third power law. On the other hand, in the case of system distributed dipoles-like D-A pairs, distribution of electric fields does not obey the density of ionized impurities to the four-third power law. It is found that broadening of the distribution is in proportion to the density of ionized squared. If non-transmutation doped sample is employed, aboveresult is supported.

Recently, inhomogeneous line-broadening of the impurity absorption in a quantum well has been analyzed theoretically.<sup>59-60)</sup> In such a low-dimensional system, it is expected that interesting phenomena concerning with the distribution of impurities will appeare.

Physically and engineeringly, study on the distribution of impurities is very important. The Monte Carlo method proposed in this study is useful to open the way to elucidate the distribution of impurities in semiconductors. In the future, line-broadening due to the internal Stark effect for various configurations of ionized impurities will be clarified in detail and investigated experimentally for various compensated semiconductors.

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# Appendix

Energy shift of  $2p_+$  state in a hydrogenic impurity due to the second-order Stark effect is expressed by

$$E_{2p_{+}} = -78(4\pi\varepsilon_{0}\varepsilon)a_{B}E^{2}.$$
 (A-1)

Accordingly, by considering the distribution of internal electric field squared that is caused by inhomogeneous distribution of ionized impurities, the shape of absorption line is given by

$$S(E_{2p_{+}}) = -78(4\pi\varepsilon_{0}\varepsilon)a_{B}W(E^{2}).$$
 (A-2)

The lineshape of Zeeman transition,  $1s-2p_+$  calculated by using (A-2) is shown in Fig.5.10. The notation  $B_0$  is resonance magnetic field without internal Stark effect. The distribution of the electric field squared,  $W(E^2)$  is calculated by the Monte Carlo simulation in section 5. In this calculation, concentration of ionized impurities is  $2.78 \times 10^{15}$  cm<sup>-3</sup>. Here, the lineshape contains another broadening (=0.12T) due to phonon broadening *etc*.

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## **Figure Captions**

- Fig.2.1 Variations in Energy levels of a hydrogen atom due to the first-order and the second-order Stark effect.
- Fig.2.2 Schematic diagram of inhomogeneous line-broadening. This linebroadening is caused by the difference of frequencies varying from one center to another.
- Fig.3.1 Block diagram of the experimental setup for the far-infrared magnetooptical absorption measurement.
- Fig.4.1 Typical magneto-optical absorption spectrum for  $84\mu$ m laser line with photoexcitation. *C1* and *C2* denote cyclotron resonance peaks of transitions from two lowest Landau subbands with opposite spin states, respectively. *ICR* and  $\alpha$  denotes a impurity-cyclotron resonance of donor electron and an absorption by the acceptor transition, respectively.
- Fig.4.2 Landau levels and donor levels in InSb under magnetic field. Each donor level is associated with every Landau levels. The *C1*, *C2* and *ICR* denote cyclotron resonances and impurity cyclotron resonance, respectively.
- Fig.4.3 Magnetic field dependence of the transition energy for the acceptor in InSb. Open circles and triangles denoted the data taken by Kaplan and by us, respectively.
- Fig.4.4 Time variations of the integrated intensity for the line  $\alpha$  at 1.8K (open

circles) and 4.2K (solid circles).

- Fig.4.5 Time-resolved spectra of the line  $\alpha$  due to acceptor in the highly compensated *p*-type InSb as a function of delay time.
- Fig.4.6 Time variations of the FWHM of the line  $\alpha$  at 1.8K (open circles) and 4.2K (solid circles).
- Fig.4.7 Time variations of the FWHM of the line  $\alpha$  at 1.8K (open circles) and 4.2K (solid circles) with the extended scale of time.
- Fig.4.8 The FWHM of the line  $\alpha$  for various intrinsic light intensities at 1.8K. With decreasing intrinsic light intensity, the FWHM increases.
- Fig.4.9 Schematic diagram in the creation of internal electric fields as passing time. The notations  $A^{0}$  and  $D^{0}$  denote a neutral acceptor and donor, respectively. The A and  $D^{+}$  denote an ionized acceptor and donor, respectively. Just after photoexcitation (a), there is little ionized impurities. However, passing long time after photoexcitation (b), ionized impurities are created through a donor-acceptor process, and induce inhomogeneous electric fields at each position of neutral impurities.
- Fig.4.10 Typical far-infrared magneto-optical absorption spectrum for  $84\mu m$  in Ga-doped Ge. Various absorption lines are identified to be due to Ga impurities.
- Fig.4.11 Far-infrared magneto-optical absorption spectrum for  $57\mu$ m in Ga-doped Ge. There are a lot of sharp peaks. Almost every adjacent two peaks seem to be coupled.

- Fig.4.12 Magnetic field dependence of the transition energy for Ga acceptor in Ge. The obtained data changes linearly .
- Fig.4.13 Inverse magnetic field dependence of labelled number of absorption peaks, which indicates quantum number of each state. The variation of the peak positions have two series.
- Fig.4.14 Energy band structure of the valence band in Ge. The upper set of bands is fourfold degenerate (J=3/2) at k=0 and the lower set is twofold degenerate (J=1/2). The lower bands called a spin-orbit split off band (s.o.s.b) separate from the upper set of bands with 0.29eV. In k=0, the upper band splits a set of a twofold degenerated heavy hole band (h.h.b), and light hole band (l.h.b), respectively.
- Fig.4.15 The Landau levels in the valence band calculated by Hensel and Suzuki. The value of the band parameters are  $\gamma_1 = 13.38$ ,  $\gamma_2 = 4.24$ ,  $\gamma_3 = 5.69$ ,  $\kappa = 3.41$ and q = 0.06. The Landau levels are classified by  $(N_{\mu}, K^{\pi})$ .
- Fig.4.16 Magnetic field dependence of the Zeeman transition energy for Ga in Ge as shown by closed circles. The  $E_c$  and  $E_I$  are transition energies of a free hole and an impurity, respectively. Dashed lines are due to the transition to the hole Landau levels. Solid lines are due to the transition between Landau levels added the binding energy for Ga impurity. This impurity levels of acceptor are associated with a light hole Landau level.
- Fig.4.17 Far-infrared magneto-optical absorption spectrum for the wavelength

of  $119\mu$ m in Ga-doped Ge. Various absorption lines complicatedly combined light hole states with heavy hole states appear in the spectrum.

- Fig.4.18 Far-infrared magneto-optical absorption spectrum for  $84\mu$ m in the sample f (K=0.76) under various photoexcitation. With decreasing the intrinsic light intensity, all absorption lines are broader and weaker than that under strong photoexcitation.
- Fig.4.19Far-infrared magneto-optical absorption spectrum for  $84\mu$ m in the sample b(K=0.40) with and without photoexcitation, respectively. A sharp line at near 2.3T without the photoexcitation is broader and weaker than that under strong photoexcitation.
- Fig.4.20 Time variation of the integrated intensity for the absorption line at 4.2K. An estimated relaxation time is about 1.5s. This effect of the long decay time is due to the donor-acceptor recombination.
- Fig.4.21 The absorption lines for three intrinsic light intensities as 0, 50, and 100%. With decreasing the intrinsic light intensity, the FWHM of the absorption line increases.
- Fig.4.22 The FWHM of the absorption line for various intrinsic light intensities. When the intensity increases above 50%, the FWHM decreases and saturates at a certain width.
- Fig.4.23 The dependence of the FWHM of the absorption line on concentration of the ionized impurity. The variation of line-broadening shows the  $n_I^{4/3}$ power laws which was predicted by Stoneham.
- Fig.4.24 The dependence of the FWHM of the absorption line on various compensation ratio samples which have 0.082, 0.49, 0.61 and 0.76, respectively. The variation of line-broadening in the all samples shows the  $n_1^{43}$  power laws.
- Fig 4.25 Schematic diagrams in the creation of internal electric fields by photoexcitation intensity in the compensated semiconductor. Under strong photoexcitation, there is a lot of neutral impurities. However, without photoexcitation, ionized impurities are created, and induce inhomogeneous electric fields at each position of neutral impurity.
- Fig.4.26 The temperature dependence of the absorption line for  $84\mu$ m. With increasing temperature, the FWHM of the absorption line increases.
- Fig.4.27 The temperature dependence of the FWHM of the absorption line. The open circles denote the experimentally obtained FWHM of the absorption-line. The triangles denote the contribution estimated by the Stark-broadening.
- Fig,4.28 The dependence of the FWHM of the absorption line on concentration of ionized impurities under magnetic field as 2.3T and 5.5T. The variation of the FWHM at 5.5T is smaller than that at 2.3T, but both data show the  $n_I^{43}$  power laws.
- Fig.4.29 External applied electric field dependence of the absorption-line. With increasing the strength of external electric field, the FWHM of the absorption-line increases.

- Fig.5.1 Time variations of the relative intensity for the absorption spectrum obtained by the Monte Carlo calculation (open circles) and that plotted by Thomas *et al.*'s formula (solid line)  $(N_{\rm D}=N_{\rm A}=1.0 \times 10^{14} {\rm cm}^{-3}, a_{\rm B}=500{\rm \AA})$
- Fig.5.2 The comparison for the time variation of the relative intensity of the experimental results(solid circles) with calculated results by Monte Carlo method (open circles).
- Fig.5.3 Time variation of the electric field distribution obtained by Monte Carlo calculation. With delay time, the distribution shifts towards the higher field and becomes broader.
- Fig.5.4 Time variation of the standard deviations ( $\sigma$ ) in the distribution of the electric field with  $W_{\text{max}}$ =5.0x10<sup>5</sup>s<sup>-1</sup>. As passing time,  $\sigma$  increases gradually.
- Fig.5.5 The standard deviation in the distribution of the electric field for various system sizes, L, under the condition that the  $N_i$  /V is a constant. The notation  $N_i$  and  $V (= L^3)$  denote the concentration of ionized impurities and volume of the system, respectively. The standard deviation is saturated a certain value. The value denoted by an arrow is employed in this calculation.
- Fig.5.6 Distribution amplitude of electric fields at every neutral impurities for various ionized impurities concentrations. The notation N denotes concentration as neutral impurities are all ionized. With increasing ionized impurities, the distribution shifts towards the higher field and

becomes broader.

- Fig.5.7 Comparisons of the distribution amplitude of the electric fields calculated by Monte Carlo method (open circles) with that calculated by a Holzmark function (solid line). In these cases, the concentrations of ionized impurities are  $8.34 \times 10^{14}$  cm<sup>-3</sup> and  $2.78 \times 10^{15}$  cm<sup>-3</sup>, respectively.
- Fig.5.8 The standard deviation in the distribution of electric field squared for the number of ionized impurities in random configuration. The notation  $N_0$  denotes a normalized factor. It is in proportional to  $N_i^{4/3}$ .
- Fig.5.9 The standard deviation in the distribution of electric field squared in three cases of initial configurations which are random, dipole-like and lattice-like. In each case, they are in proportion to  $N_i^{4/3}$ ,  $N_i^2$  and  $N_i^{2/3}$ , respectively.
- Fig.5.10 The lineshape of Zeeman transition,  $1s-2p_+$  calculated by using (A-2). The notation  $B_0$  is resonance magnetic field without internal Stark effect. In this calculation, concentration of ionized impurities is  $2.78 \times 10^{15}$  cm<sup>-3</sup>.

Energy levels of a Hydrogen

<without electric field>

1*s* 

<with electric field>



First-order Stark effect Second-order Stark effect



Frequency



































Valence band Landau levels in Ge at k<sub>H</sub>=0 Calculated by Hensel-Suzuki










































Distribution Amplitude (Arb.Units)









## Table I

## List of Samples

InSb

Sample	Туре	N <sub>D</sub> (cm <sup>-3</sup> )	N <sub>A</sub> (cm <sup>-3</sup> )	Compensation Ratio(K)

Ge (Transmutation-doped)

Sample	Туре	N <sub>D</sub> (cm <sup>-3</sup> ) As	N <sub>A</sub> (cm <sup>-3</sup> ) Ga	Compensation Ratio(K)
a	р	-	9.00x10 <sup>14</sup>	~ 0
b	р	6.00x10 <sup>14</sup>	7.30x10 <sup>15</sup>	0.082
c	р	$1.32 \times 10^{15}$	3.27x10 <sup>15</sup>	0.40
d	р	1.39x10 <sup>15</sup>	2.83x10 <sup>15</sup>	0.49
e	р	1.47x10 <sup>15</sup>	$2.42 \times 10^{15}$	0.61
f	р	1.54x10 <sup>15</sup>	2.02x10 <sup>15</sup>	0.76

Ge (Fz-grown)

Sample	Туре	N <sub>A</sub> (cm <sup>-3</sup> ) Ga	Compensatio Ratio(K)	
g	р	9.0x10 <sup>14</sup>	~ 0	

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