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CRYSTALLOGRAPHIC STUDY OF THE TRANSFORMATION MECHANISM IN CAESIUM CHLORIDE

BY

MAMORU WATANABE

1974

Acknowledgments

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Contents

Abstract

Caesium Chloride has been found to retain a particular orientation relation in transition between the CsCl- and the NaCl-type structures by the x-ray diffraction method. The relation is $[110]_{\mathrm{Cs}} /\!/ [100]$ and $[001]_{\mathrm{Cs}} /\!/ [011]_{\mathrm{Na}}$. A uniaxial expansion (or shrinkage) parallel to one of the two-fold axes in the CsCl-type structure has been observed during the transformation by optical microscopy. The amount of uniaxial expansion was about 15 percent in ratio to the size of the low form. This means that the volume change in transition was attained approximately by the uniaxial expansion only.

The orientation relation and the shape deformation in this transition have been reasonably explained by systematic movements of ions. The closest net planes of both structures, which retain and have the approximately equal density of ions at the transition temperature, play an important role for the change of the structures.

The correspondence of lattice points in the structures before and after the transition can be expressed by the following relations:

$$L'' = L' + M'$$

$$N'' = N' - M' + \left[\frac{L'' + 1}{2}\right] - 2\left[\frac{N' + M' - [L''/2]}{X}\right]$$

$$M'' = N' + M' - \left[\frac{L''}{2}\right] + 2\left[\frac{M' - N' - [(L'' + 1)/2]}{Y}\right]$$

where $(X, Y) = (10, 14)$.

I. Introduction

Caesium Chloride has been known to appear as two polymorphs of the CsCl-type and the NaCl-type forms under one atmospheric pressure. The former is stable below about 445°C and the latter between about 445°C and the melting point (1961). Both lattices are the simplest basic ones introduced always in the fields where crystal structures are necessary. This structural transformation is a typical example where not only the first coordination number but also the large amount of volume changes. The first coordination changes in number from eight to six, or inversely. The volume change is about 17 percent of the low-temperature form at the transformation.

Buerger proposed without any experimental data a mechanism of this kind of structural transformation in his works on crystallographic classification of phase transitions (1951). His mechanism will be briefly given in Chap.IV § 1. This transition has been also experimentally studied from the crystallographic view point. Menary observed by means of the x-ray diffraction method that a CsCl single crystal was divided into several grains without orientation relations to each other and to the original structure after the transition from the low to the high form (1951). However, Chatterji observed this transition by an electron microscope and reported that the transition was topotactic only when the high form changed to the low form (1971). The same kind of transition has been reported to take place in NH_4X (X=Cl, Br and I), RbCl, and RbX (X=Cl, Br and I) under high pressure (B, 1921; W, 1936; J, 1938). The transitions of NH_4Br and $RbNO_3$ were observed by Fraser (1972) and Iversen (1973), respectively. The reports of Chatterji, Fraser and Iversen have shown the description of experimental results without structural consideration of the transition mechanism.

In the present study, the transition of CsCl is observed by means of the x-ray diffraction method and by optical microscopy. The atomistic mechanism of this transition is obtained from the crystallographic consideration on experimental results by the x-ray diffraction on the basis of the systematic movement of all constituent ions.

Optical observation was also employed to detect various macroscopic phenomena in the transition process and play a role for appreciation of the present mechanism.

The analysis of lattice viblations is necessary to consider the stability of both structures and to understand the energetics of transition. Although these analyses have been done by the measurements of heat capacity and elastic constants, and more directly by the measurements of inelastic scattering of neutrons by many investigators, this study is restricted only to the geometrical aspects of the transition.

For the simplicity of description, the transition from the low to high form and from the high to low form are represented as transition ($\underline{L} \rightarrow \underline{H}$) and transition ($\underline{H} \rightarrow \underline{L}$). If we concerned with both types of the transition, transition ($\underline{L} \rightleftarrows \underline{H}$) is used all through this paper.

II. Experimental

1. Synthesis of CsCl crystals

The CsCl crystals obtained from Nakarai chemicals Co., contain 5 ppm of Na and K, 0.011 ppm of Pb, Cu, Zn, Fe, Al and Mn, 0.005 ppm of Co and Ni. The crystals are anealed at 300°C under vacuum for 10 days. They are single crystals of 200∿400μ in size with no special faces.

Attempts were made to grow single crystals of CsCl with good faces by recrystallization from the aqueous solution of

CsCl. Slow recrystallization was made at various temperatures by covering the beaker containing aqueous solution with a sheet of vynil of a few small holes with no success. Chemical transportation was also attempted as follows.

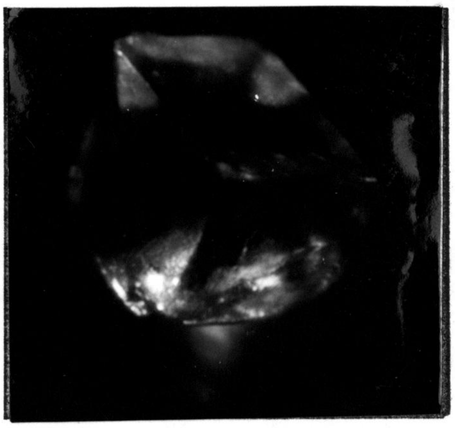


Plate 1. A CsCl crystal with three good faces of {110}, obtained by a chemical transportation method. (×80)

About 50 mg CsCl was enclosed in a evacuated quartz glass tube of 120 mm length and 12 mm diameter and the tube was kept in a furnace specially designed with nearly uniform temperature gradient. One end of the tube is kept at 570°C. This temperature is in the stable field of the high form and lower than the melting point by 30°C. The other end was kept at 300°C where the low form is stable. The pressure in the tube is considered to be about 1 mmHg. The tube was kept for one and a half months and opened. The crystals obtained are about 300∿600μ in size with clear $\{110\}$. However, they have only one to four of $\{110\}$ clear planes.

Although the conditions for best growth have not been studied thoroughly, it is evident that crystals with good faces were made as mentioned above. One of the crystals obtained by this method is shown in Plate 1.

2. The x-ray diffraction study of single crystals of CsCl at various temperatures

A micro-furnace for a precession camera. A micro-furnace attached to the precession camera in this investigation is shown in Plate 2. The cross and front sections are also illustrated (Fig.1(a) and (b)). The mixture of alumina-cement, water glass and water was used to build the furnace. The coil of Pt (0.6 mm in dia.) was used to heat directly single crystals of CsCl. In order to prevent temperature fluctuation of specimens, the furnace was designed as follows.

(a) To avoid temperature fluctuation of specimen, the appropriate size of cavity was experimentally decided.

(b) The windows for the passage of the x-rays and for the insertion of specimens are minimized.

The windows for the passage of the x-rays are covered with thin films of pyrex glass to prevent temperature disturbance caused by the motion of camera.

The temperature of the furnace is controlled by the P.I.D. system. The chromel-almel thermocouple was used for control and measurements of temperature. The fluctuation is ±0.7°C at 500±2 °C. The pyrex films attached at the windows remarkably reduced temperature fluctuation.

Preparation and mounting of specimens. Preparation and mounting of specimens are very important and difficult part of this kind of experiments. The following methods were used.

(i) Mounting with binding agents.

Inorganic binding agents had to be used in spite of possible contamination of CsCl, because organic agents do not work above 300°C because of combustion. The dental cement of fine powder was used as illustrated in Fig.2(a). Care was made to reduce the joining part between the specimen and glass rod in order to decrease stress and contamination. In this method, specimens moved from the original position by breaking of the joining part during or after the transition process ($\underline{L} \rightarrow \underline{H}$). Therefore, the reverse transition process was not observed.

(ii) Mechanical mounting by capillary

The mechanical mounting used in the study is illustrated in Fig.2(b). The specimen was dipped in liquid polymer and dried. The specimen covered by thin film of polymer is softly supported by contact with two ends of thin capillary in a capillary of quartz glass. The polymer was burnt down by heating, resulting in very narrow interstices between the specimen and the ends of capillary. Crystals of CsCl expand by about 2.6% in linear dimension by heating from room temperature to the transition point (Solid-Solid). Owing to existence of the interstices, mechanical interaction between the crystal and the ends of capillary was negligible. Furthermore, this method resulted in little contamination except for that from polymer and carbon.

However, it was difficult to avoid the stress from the wall on the specimens by the expansion of the specimens in transition. This resulted in occasional formation of twin or breaking of specimens during the transition. All experiments on the transition process ($\underline{H} \rightarrow \underline{L}$) were carried out by this mounting.

Use of a super-high power x-ray generator. Rapid measurements were necessary to obtain more data during the transition process. For this purpose a super-high power x-ray generator was employed. The maximum output (60kV-500mA) of the generator is about 40 times greater than that of the ordinary one (40kV-20 mA). A target of molybdenum was selected because the cell dimensions of the concerned material were small and the decrease of x-rays by passing the pyrex thin films placed at the windows of furnace was not negligible.

Only 5∿10 minutes were neccessary to take a precession photograph by this super-high power generator.

Measurements. The average size of the specimens of CsCl used in this investigation was about 200μ in diameter. The temperature of the specimens was stepwisely increased with the step of 20°C between room temperature and 430°C, and of 0.25°C or 0.5°C above 430°C. It took a few days to raise the temperature of specimens from room temperature to 430°C. The precession photographs were taken above 430°C with exposure time of about 7 minutes and with the μ-angle of 10° to 15°. Phase change was detected by observing reduction of the old diffraction intensities or appearance of new spots. The temperature of specimen was kept at the temperature where phase change was first detected until the transition completed.

3. The measurements of the cell dimensions

The cell dimensions of CsCl were measured at several intermediate temperatures between room temperature and the transition point (Solid-Solid), and at just above the transition point by a Rigaku four-circle automatic diffractometer.

A micro-furnace for a four-circle diffractometer.

A special micro-furnace was made for a four-circle diffractometer. The furnace is shown in Plate 3. The cross and horizontal sections of the furnace are shown in Fig.3(a) and 3(b), respectively. Special care was made to avoid the scattering of the x-rays by the furnace. The goniometer head can move from -87° till 95° along the χ-circle. The intensities can be measured within $2\theta \leqq 109°$. The temperature of the furnace is controlled by the P.I.D. control system. Fluctuation of temperature is ±1°C between room temperature and 300°C and ±2°C between 300°C and 500°C. The temperature is measured by the chromel-almel thermocouple.

Measurements. A CsCl single crystal used for the measurement of the cell dimensions was ellipsoidal in form and 300μ in maximum diameter. The specimen was mounted mechanically or by a capillary, as mentioned above. The CuKα radiation was used with the graphite monochromator. The collimator and the receiving slit used were 0.5 mm and 1.5 mm in diameter, respectively. The resolution between the $K\alpha_1$ and $K\alpha_2$ was satisfactorily even by the above slit.

Assuming that 400, 040 and 004 reflections were equivalent, the refinement of the positions of reflections was completed when the three spots were same in θ-value. The θ-values of 222 and 033 reflections with strong intensities were precisely determined, starting from the position estimated by the primary three spots. In the process of the above refinements, the crossed half slit was used. The difference between the count of each half and the averaged count of four halfs was reduced within about 2 percent. Each θ-value is checked up through the examination of the peak profiles obtained by θ and 2θ-θ step scans with 2/100° in width.

4. Optical observations

The crystal of CsCl was observed by an optical microscope during the transition process.

The magnification less than 40 was appropriate in order to obtain a view of whole crystal of about 400μ. To obtain this magnification, the distance between the objective lens and a specimen is only 40 mm. A special micro-furnace prepared for this purpose was 15mm×25mm×15mm in dimensions. Two coils of nichrome which have the same turns are joined togther in a line with the interval of 5 mm in the body of the furnace. The temperature of furnace is controlled by the P.I.D. system and the fluctuation of temperature is ±2.5°C at about 500°C.

Transparent crystals of CsCl were put on a small seat of graphite to enhance the contrast of crystals relative to the back.

About 30 CsCl crystals with the size of 200 to 400μ in diameter were optically examined. The temperature of the specimens was increased or decreased stepwise with the intervals of 2.5° or 25°C in most cases. Three specimens were set in a line at a time on the graphite seat. They underwent the transition in turn because of the temperature gradient in the furnace. The transformations between low and high forms were repeated and observed with all specimens.

<ins>The direction of expansion.</ins> Attempts were made to observe the anisotropic expansion along $\langle 110 \rangle$, of crystals of the CsCl-type structure. Temperature gradient seemed to play an important role for determining one direction among eqivalent ones. The furnace designed for this experiment had the main temperature gradients along proper directions. The heater of the furnace consists of two coils of 3 mm diameter and 1.5 mm length which are joined in a line with the intervals of 2 mm. The turns of one coil are twice more than the

other. When the coils are set horizontally, two main directions of gradient appear in the furnace. One is parallel to the axis of coils and the other vertical to the axis. Both main gradients are about 20°C/mm at 500°C.

[110] and [$1\bar{1}0$] of the low form crystals were oriented parallel to the axis of coils and vertical to the axis, respectively. The temperature of specimens was controlled by the P.I.D. system and was stepwise increased or decreased with the interval of 2.5°C. Observations were carried out about three specimens. The furnace was set vertically for one of the three in an attempt to obtain only one main direction of gradient.

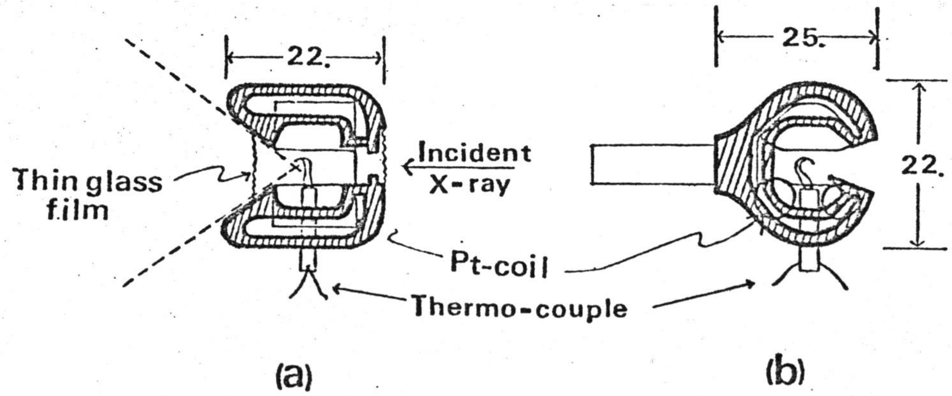


Fig.1. The cross (a) and front (b) sections of the micro-furnace for a precession camera.

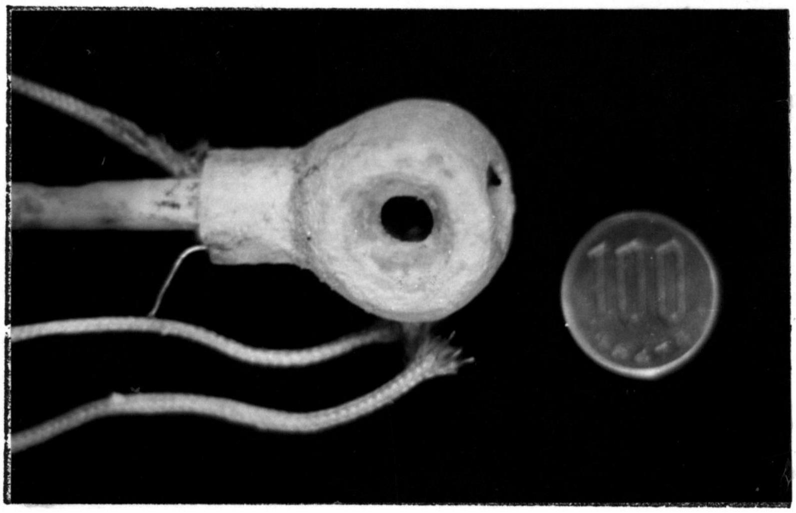
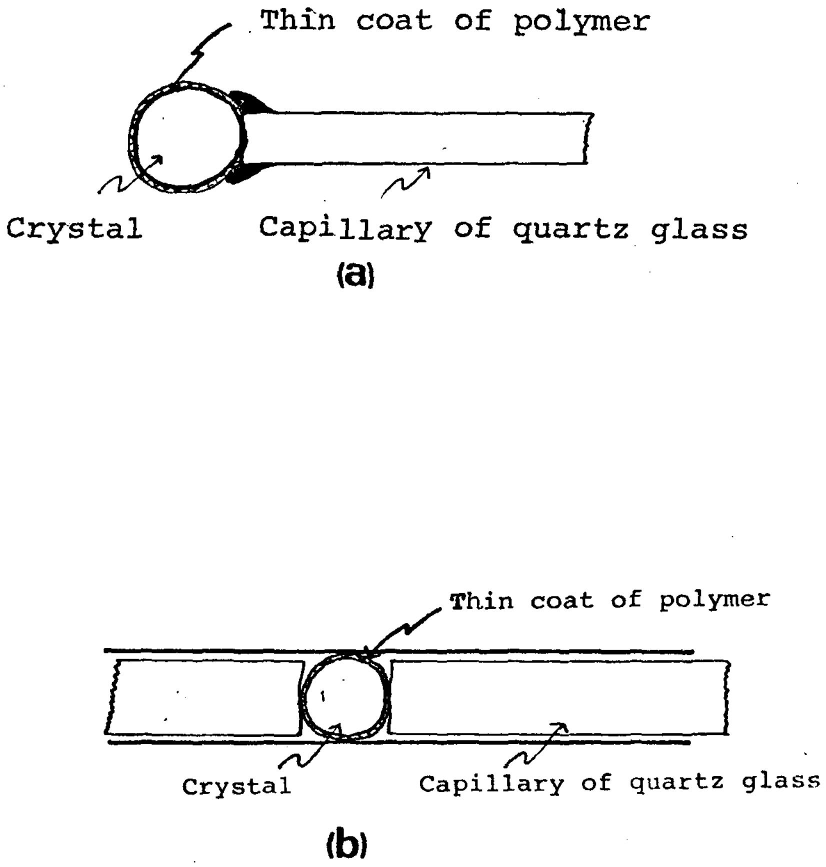


Plate 2. Photograph of the micro-furnace for a precession camera (front view).

Fig.2. Mounting methods by binding agents (a) and by capillary (b).



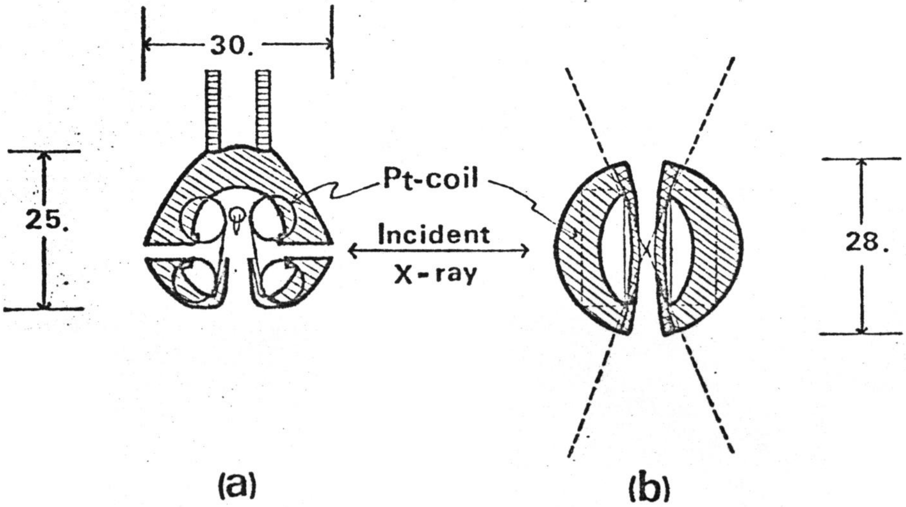


Fig.3. The cross (a) and horizontal (b) sections of the micro-furnace for a four-circle diffractometer.

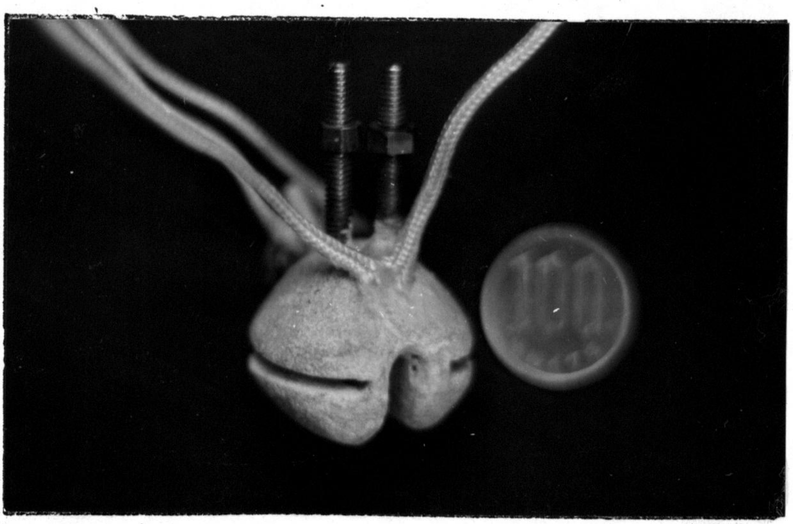


Plate 3. Photograph of the micro-furnace for a four-circle diffractometer (side view).

III. Experimental results

1. The orientation relations between the two polymorphs.

One or two precession photographs could be taken usually while the transition was in progress. No spots indicating existence of any intermediate state were detected on the photographs taken just before and during the transition. No distinct thermal diffuse scatterings were observed on the photographs. In most cases, the single crystal patterns of the high form was observed with weak powder lines after the transition.

The unique orientation relations between the CsCl-type and NaCl-type lattices were obtained experimentally. The different relations were observed according to the two different experimental conditions.

(a) The first orientation relation was observed when crystals were mounted by binding agents. The experiments were succeeded only when the low form transformed to the high form. In this transformation, the following relations were always found:

$$[001]_{Cs} /\!/ [011]_{Na} \text{ and } [100]_{Cs} /\!/ [100]_{Na}$$

These relations were not strict, but only approximate with 3°∿5° diffence in general as shown by the stereographic projection in Fig.4(a).

Same relations were reported by Chatterji (1971). However, his experiment was quite a different procedure from the present one, in that CsCl crystals of the NaCl-type structure were precipitated from saturated aqueous solution of CsCl by adding a large excess of alcohol to the solution. The precipitate of the NaCl-type structure was unstable at room temperature and merely a small part of the total precipitates. The unstable form was converted to the stable one by electron beam heating. The orientation relations of the two forms were examined by the electron diffraction before and after the transition. He also reported that no orientation relation was observed from the low to high form.

(b) The second orientation relations were obtained when the specimens were mounted mechanically in capillary tubes of quartz glass. Two specimens were used in this experiment.

For the first specimen, polycrystallization of the specimen took place during the transition (L→H) and no orientation relation was observed. This is the situation reported by Menary (1951).

For the second specimen, the low form transformed to the high form with twin relation. The orientation relation for each twin individual (I and II) is shown by stereographic projection in Fig.4(b). The orientations of the twin individual I are described as a form of $hk\ell^{I}$ and those of II $hk\ell^{II}$. The orientation of the twin individual II is indexed with the left handed system to exphasize correspondence between the twin individuals. Twinning plane $(2\bar{1}1)$ includes directions of $[11\bar{1}]_{Na}^{I\text{ and }II}$ and $[011]_{Na}^{I\text{ and }II}$. In Fig.4(b), the relation of $[110]_{Cs}$ to $[100]_{Na}^{I}$ is equivalent to that of $[\bar{1}10]_{Cs}$ to $[100]_{Na}^{II}$. Thus, the orientation relation between I and the parent correspond with that between II and the parent.

In the transformation (H→L), the twins coalesced into a single crystal. The orientation of the low form reproduced is shown by the mark (▲) in Fig.4(b), which is in good correspondence with the initial orientation. This fact strongly suggests that the transition of CsCl takes place reversibly.

The discrepancy of orientation relation has been quantitatively estimated as follows.

a. transition from the low to high form (I and II)

$[110]_{Cs}\wedge[100]^{I}_{Na}$ $\sim 8°$

$[\bar{1}10]_{Cs}\wedge[100]^{II}_{Na}$ $\sim 12°$

$[010]_{Cs}\wedge[11\bar{1}]^{I\text{ and }II}_{Na}$ $\sim 4°$

b. transition from the high (I and II) to low form

$[100]^{I}_{Na}\wedge[110]_{Cs}$ $\sim 11°$

$[100]^{II}_{Na}\wedge[\bar{1}10]_{Cs}$ $\sim 9°$

$[11\bar{1}]^{I\text{ and }II}_{Na}\wedge[010]_{Cs}$ $\sim 4°$

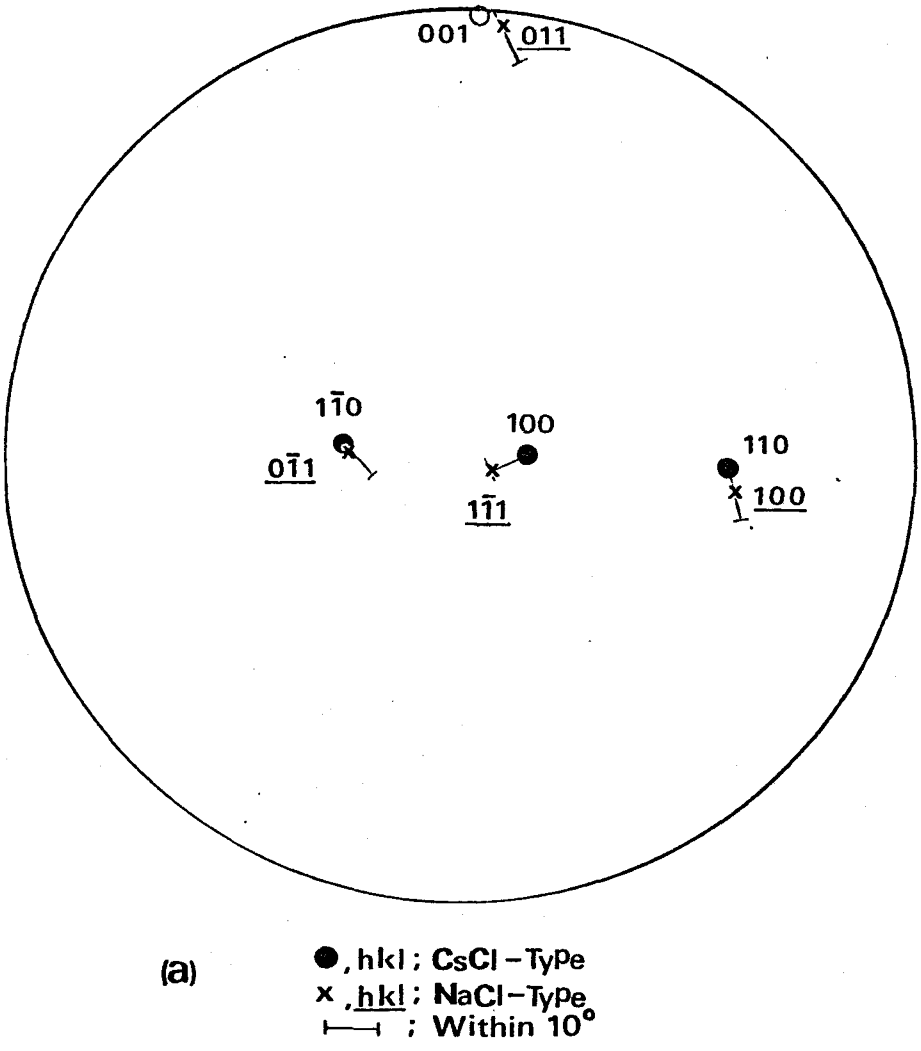
2. The comparison of the orientation relations in two cases

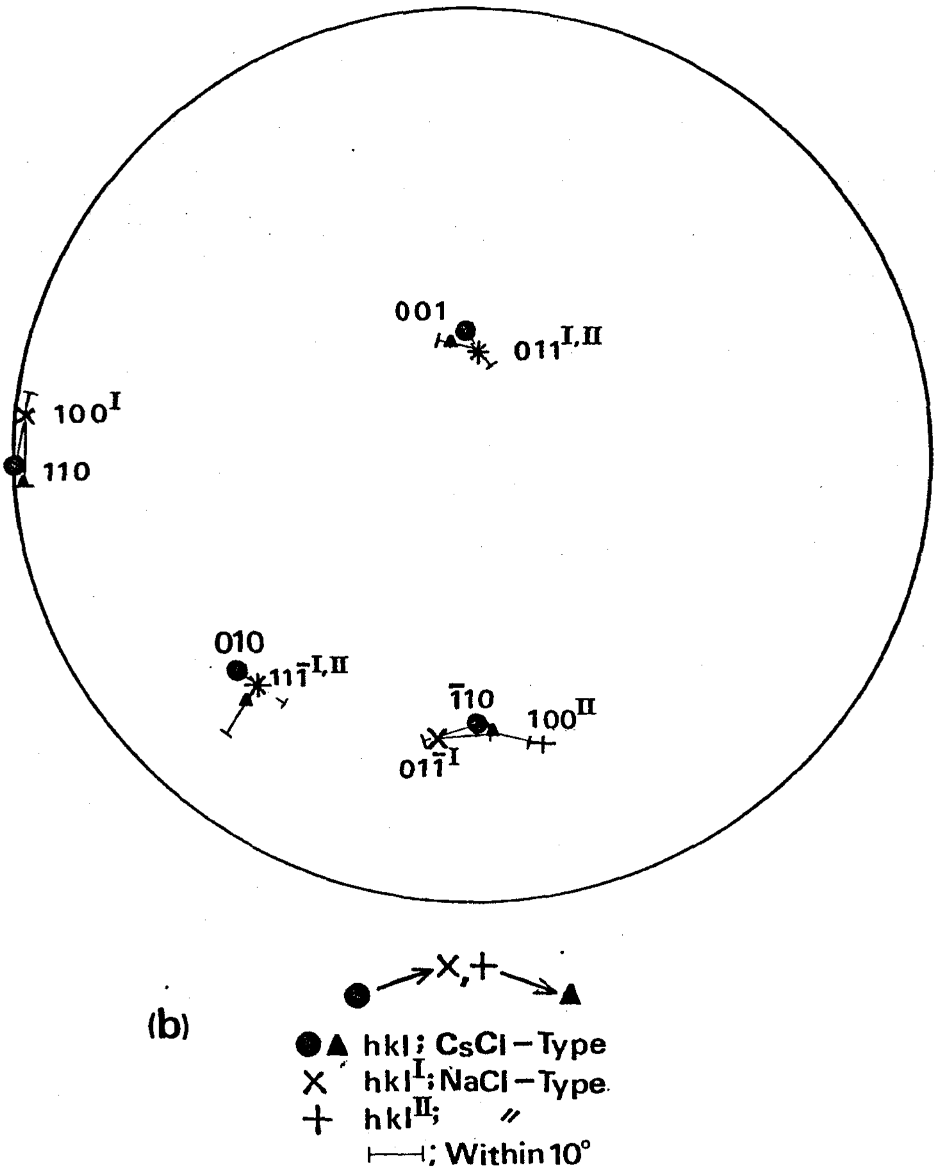
The displacement from $[110]_{Cs}$ to $[100]^{I}_{Na}$ and from $[\bar{1}10]_{Cs}$ to $[100]^{II}_{Na}$ in the second case (Fig.4(b)) is larger than that from $[\bar{1}10]_{Cs}$ to $[100]_{Na}$ in the first case (Fig.4(a)), while the displacement from $[010]_{Cs}$ to $[11\bar{1}]^{I\text{ and }II}_{Na}$ is smaller than that from $[100]_{Cs}$ to $[1\bar{1}1]_{Na}$. This may be explained by difference in the experimental conditions between the first and second cases. Because this transition takes place with a large volume change, the transition in the second case led

Fig.4. Stereographic projections of the orientation relations between the CsCl-type and the NaCl-type lattices.

(a) Relation obtained by the mounting method using binding agents.

(b) Relations of twins obtained by the mechanical mounting.




001
011^I,II
100^I
110
010
111̄^I,II
1̄10
100^II
011̄^I
● → ×,+ → ▲
●▲ hkl; CsCl−Type
× hkl^I; NaCl−Type
+ hkl^II; 〃
⊢—⊣; Within 10°

(b)

to the twinning or aggregates of the high form crystals. Because the expansion at the transition is anisotropic, crystals must be affected by the anisotropic stress along the direction of expansion in the second case. To reduce the anisotropic stress,the crystals is likely to expand along other equivalent directions different from the direction discussed above. Because twinning seems to play an important role in reducing the strain, the discrepancy between the first and second cases can be explained. A more detail explanation of the twinning will be given later (in Chap. V §3) after the explanation of the transition mechanism and the macroscopic observation of the transition.

2. Cell dimensions

The cell dimensions of the low form were determined at eight different temperatures: 18, 98, 173, 262, 332, 433, 435 and 446°C. The cell dimensions of the high form were determined at the temperature only just above the transition point. At the temperatures close to the transition point of 446°c, the peak height and the integrated intensity of each diffraction spots became about one sixth of the original ones at room temperature. At the higher temperatures than 430°C, the peak positions of reflections 222 and 033 were not precisely determined because of a large fluctuation of counts. A strong reflection 222 was precisely measured in place of 222 and 033, though it is smaller in 2θ than 222 and 033. For CsCl of the NaCl-type structure, the θ-values of the equivalent reflections of 400, 040 and 004 were independently refined and the mean θ-value was used to obtain the cell dimensions.

The cell dimensions are shown at various temperatures (Table 1). The estimated errors of the cell dimensions represent the maximum deviation from the mean value.

CsCl–Type

t/°C	cell (a/A) dimensions	t/°C	cell (a/A) dimensions
18±1	4.119±0.002	332±2	4.197±0.001
98 1	4.142 0	433 2	4.223 1
173 1	4.160 0	435 2	4.224 4
262 1	4.179 1	446 2	4.227 4

NaCl–Type

t/°C	cell (a/A) dimensions
446 2	7.077 3

Table 1. Temperature dependence of the cell dimensions of the CsCl-type lattice and those of the NaCl-type lattice just above the transition point.

3. The deformation of crystal form through transition

<u>General observations.</u> The crystals of the CsCl-type structure underwent transition with drastic and anisotropic expansion. The beginning of the transition could be detected by appearance of an optically different part in the initial crystal. This new part had a tendency to form a plate of visible thickness in many specimens. This plate-like part in considered to be the region where the transition is just in progress. It took one to two seconds for the front part to traverse from one end to the other of a crystal of about 300μ in size. The expansion of the crystals took place in the direction of movement of the plate. The amount of linear expansion was 12 to 15 % in the ratio to the size of low form along the direction. No visible change of crystal size took place along the direction normal to the expansion. These values were measured on photomicrographs or V:T.R. or through the scale on a lens. Some specimens lost transparency after the transition. However, most of them regained transparency by anealing at slightly higher temperature or at lower temperature than the transition. The transition ($\underline{H}\rightarrow\underline{L}$) takes place very rapidly. The transition temperature ($\underline{H}\rightarrow\underline{L}$) is always lower than the temperature ($\underline{L}\rightarrow\underline{H}$) by 15∿25°C. When the

temperature is decreased slower, the transition temperature (*H*→*L*) becomes lower. Most of the specimens contracted to the original shape. The transition between the low and high form were repeated. After two or more repetation of the transition, the expansion direction was parallel to or normal to the initial one. The temperatures of the transition (*L*→*H*) were nearly constant independent from the number of repetition. But the temperature of the transition (*H*→*L*) were apt to lower with the increase of the number of repetition.

Unless sufficient anealing was made after the transition, the transparency of crystals was rapidly lost with increase in number of the transition. And the transition temperature and the deformation of shapes, especially for the transition (*H*→*L*), become unclear.

Due to the hysteresis of this transition, only the transition (*L*→*H*) was intermittently proceeded by using the waving fluctuation of temperature with control. The photomicrographs (Plate 4(a)∿(d)) were taken under such conditions.

The direction of expansion. Two directions, normal to each other and equivalent to $[110]_{Cs}$, were oriented parallel to the two main temperature gradients of the furnace, which were parallel and normal to the axis of coil.

when the coil of the furnace was horizontal, the crystal expanded approximately parallel to ⟨110⟩, or normal to the axis of coil. The direction of expansion was constant at all cycles attempted.

When the coil was vertical, expansion of the crystal was approximately parallel to ⟨110⟩, or parallel to the axis at the first two cycles, but along ⟨110⟩, or normal to the axis at the third cycle.

In both cases, the maximum expansion occured approximately parallel to the direction equivalent to $[110]_{Cs}$.

From the optical observation of the transition of single crystals of CsCl, the following conclusions were obtained.

(a) The expansion and contraction of crystals in transition were anisotropic and reversible.

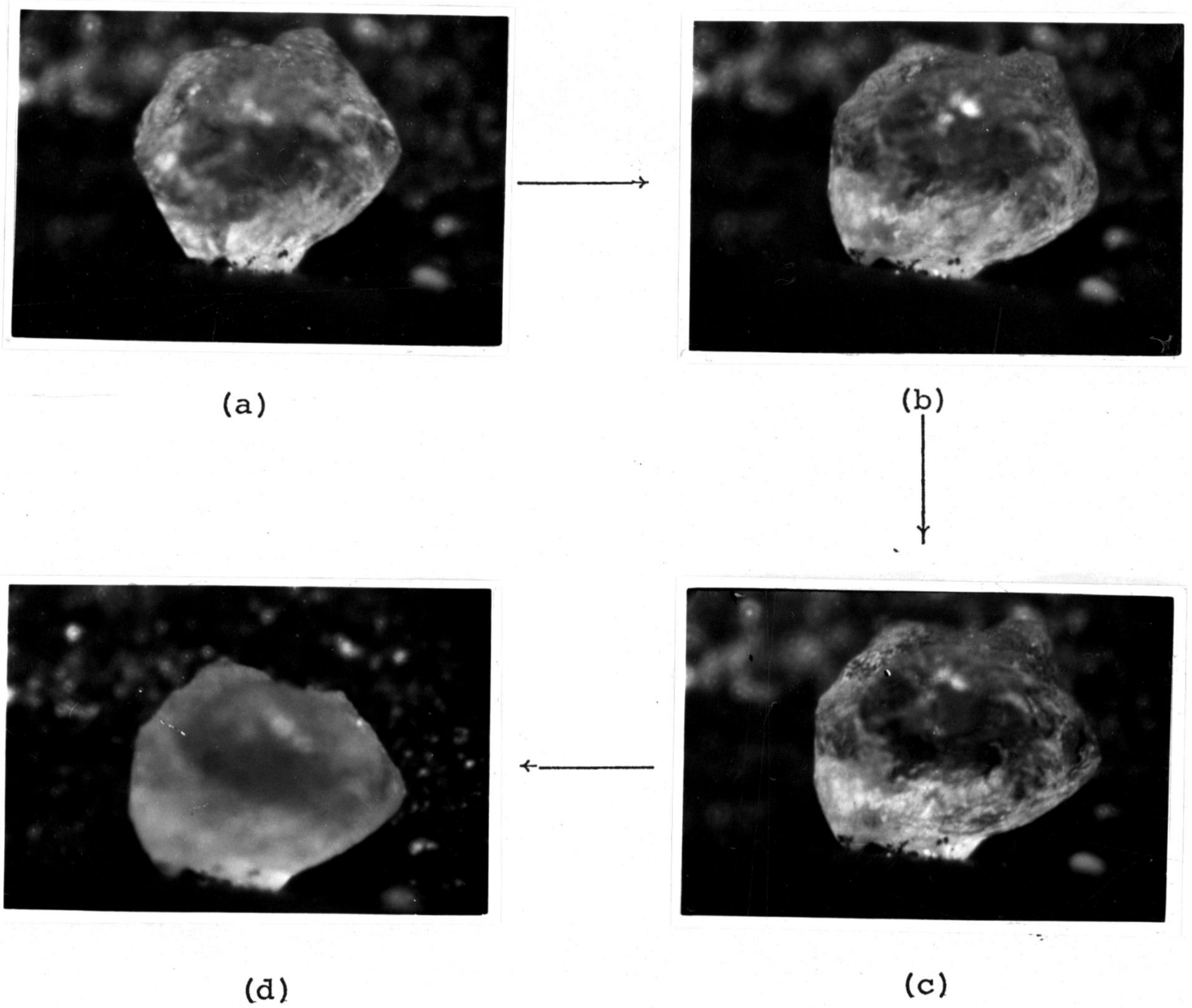
(b) The amount of the change in volume is about 15 percent of the original size of the low form, but no detectable change was observed perpendicularly to the direction.

(c) The direction of expansion and contraction is approximately parallel to [110] of the low form.

(d) Two phases can coexist only for a short period of the order of a second.

Plate 4. Microphotographs showing one cycle of transition between the CsCl-type and the NaCl-type structures.

(a) Before starting the transition.
(b) During the transition.
(c) After the transition to the high form
(d) After retruning to the low form



IV.Interpretation of the experimental results

Based on the unique orientation relations of the low and high form mentioned in the previous chapters, the structural mechanism of the transition has been presented in this chapter. The front of transformation traverses in the crystal changing the parent structure into the new one. On the movement of the transformation front, ions make strongly cooperative behavious together and conserve the orientation relations between the initial and final products.

1. The Buerger's model for the transformation

In his crystallographic classification of the phase transition (1951), Buerger classified the transformation of CsCl as a typical one caused by differential dilatation. This transformation consists of a uniaxial dilatation and a homogeneous constraction on the plane normal to the axis of dilatation, where the number of first coordination can vary.

According to his explanation, dilatation occurs along one of four three-fold axes and contraction occurs on the plane normal to the three-fold axis in the CsCl crystal structure. The three-fold axis conserves its symmetry through the transition. This transformation is equivalent to a deformation of the primitive cube of the low form to a rhombohedral cell with three two-fold axes which make 60° to each other. Based on the Buerger's idea the "ion correspondence" between both structures is shown (Fig.5). In addition, Fig.5 clearly indicates that B_7 and B_8 on the unique axis move out of the coordination of the central ion A due to dilatation. His mechanism is apparently reasonable from the view point of symmetry, though simple computation reveals that the unit cell of CsCl-type structure makes 45 percent dilatation and 10 percent homogenious contraction along the plane normal to the dilatation axis.

As described by Verma and Krishma (1966), the deformation of the crystal shape should appear in the transition as a result of Buerger's mechanism. The present results of x-ray diffraction and the optical microscope mentioned above for single crystals do not support Buerger's mechanism in the transition.

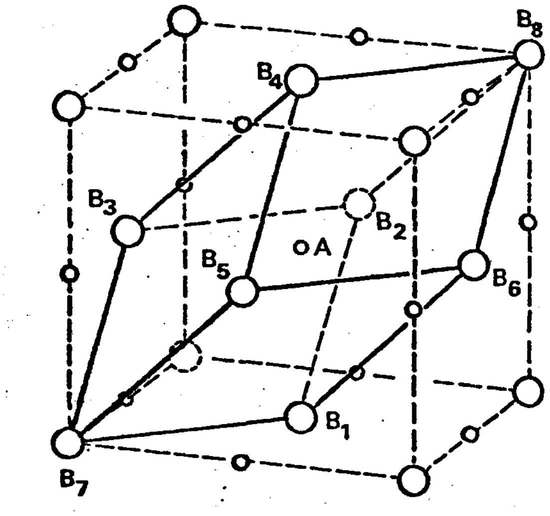
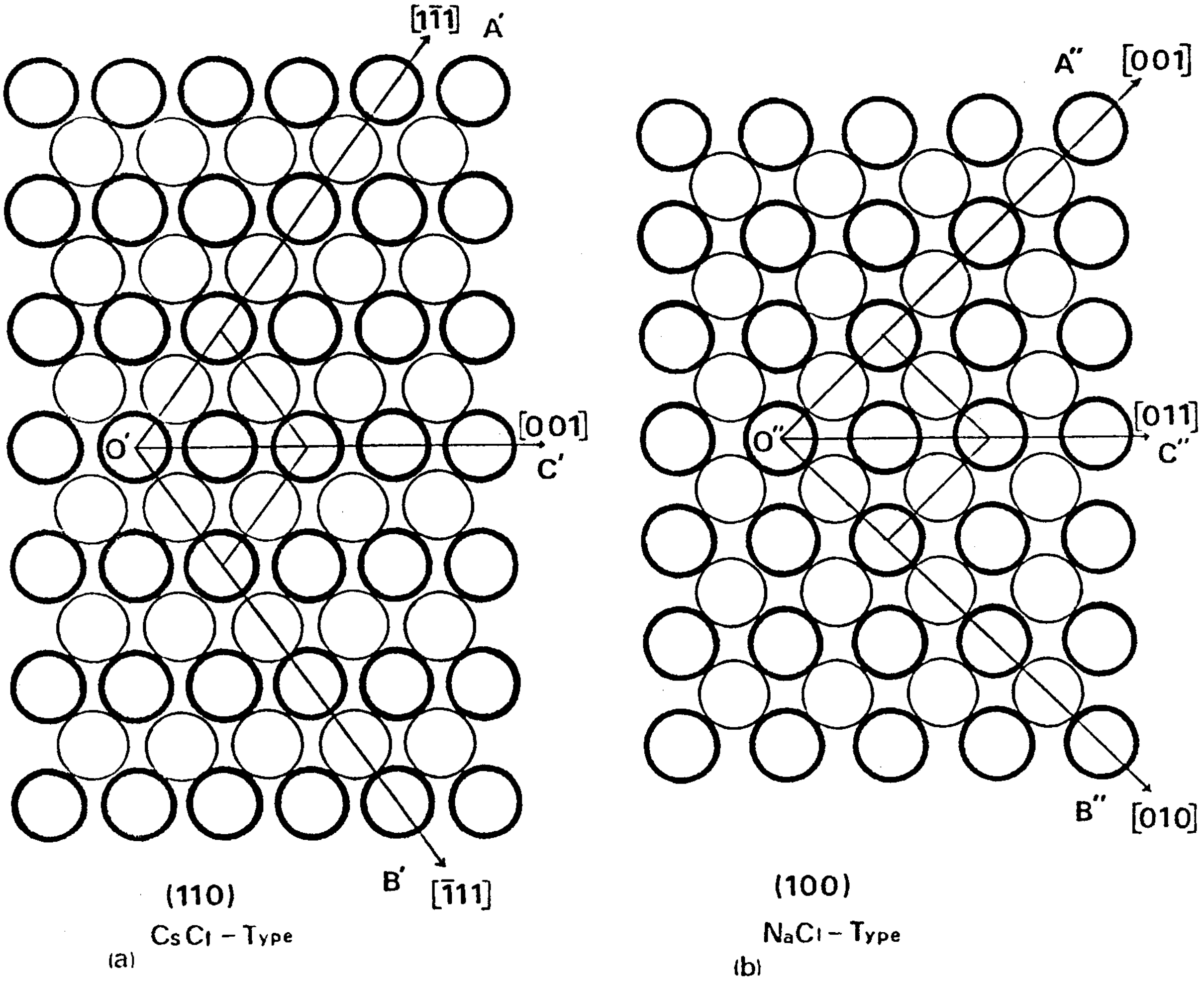


Fig.5. Structural relation between the CsCl-type and NaCl-type lattices according to Buerger.

2. The orientation relations of both structures

The CsCl-type and NaCl-type structures have a primitive and a face-centered cubic lattices, respectively. In the former, each ion is at the center of a cube of eight different ions and is most nearest to the ions of different sign on all the three-fold axes. It is obvious that the density of ions in (110) planes are greatest because they have the largest d-spacing in the structure. Two kinds of ion are found on (110) planes with 1:1 ratio. In the latter, each ion is coordinated by six different ions at the corners of a octahedron. All the nearest neighbors are on the four-fold axes and have the



(110)
CsCl - Type
(a)

(100)
NaCl - Type
(b)

Fig.6. The arrangements of ions, (a) in (110) layer of the CsCl-type structure and (b) in (100) layer of the NaCl-type structure.

opposite charge. The closest net plane in this structure is (100) plane, where positive and negative ions alternate.

The results obtained by x-ray diffraction indicate the relation of $[110]_{Cs} /\!/ [100]_{Na}$, that is, $(110)_{Cs} /\!/ (100)_{Na}$, in the transition. This relation indicates that the closest net plane are considered through the transition. To make clear the characteristics of the closest planes in both structures, structural layers parallel to $(110)_{Cs}$ and $(100)_{Na}$ are illustrated in Fig. 6(a) and 6(b), respectively. The directions of $[1\bar{1}1]_{Cs}$, $[\bar{1}11]_{Cs}$, and $[001]_{Cs}$ in Fig.6(a), and $[001]_{Na}$, $[010]_{Na}$ and $[001]_{Na}$ in Fig.6(b) are designated $\overrightarrow{O'A'}$, $\overrightarrow{O'B'}$, $\overrightarrow{O'C'}$, $\overrightarrow{O''A''}$, $\overrightarrow{O''B''}$ and $\overrightarrow{O''C''}$, respectively. In each layer, there are two characteristic directions along which ions are closest. In the $(110)_{Cs}$ layer, they are $\overrightarrow{O'A'}$ and $\overrightarrow{O'B'}$ with tetrahedral angle between them, while they are $\overrightarrow{O''A''}$ and $\overrightarrow{O''B''}$ in the $(100)_{Na}$ layer and are normal to each other. Furthermore, both layers are similar in arrangement of ion. However, they are different in the following properties; the distance between the nearest ions, the angle between the two closest directions, that is, $\angle A'O'B'$ and $\angle A''O''B''$, and the area per one lattice point or one chemical formula.

3. Cell dimensions and structural properties

The lattice constants of the low form of CsCl is 4.119 A at 18°C under one atmospheric pressure. The crystal of the low form linearly expands with temperature increasing untill the transition point (Solid-Solid). At this point, the cell dimensions of CsCl is 4.227 A. Just above the transition point, the cell dimensions of the high form of CsCl is 7.077 A. Therefore, the volume change in transition is about 17 percent of the volume of the low form. This amount of change is very large and comparable only to those of ammonium halides, rubidium nitrate in analogous transition and tin.

α is defined as the ratio of the cell dimension of the high form at the transition point to that of the low form at t°C, that is, $\alpha=7.077/a_{Cs}(t)$. The ratio, S of the area per one lattice point in a given plane to that in (100) plane of the low form can be calculated by using α. The ratio were obtained for (100), (110) and (112) in the low form and for (100), (110) and (111) in the high form. The closest three planes in each structure were selected. The values of S are described in following table for the different planes.

	CsCl-Type	NaCl-Type
	S	
(100)	1	$\alpha^2/4$
(110)	$\sqrt{2}/2$	$\sqrt{2}\alpha^2/4$
(111)	——	$\sqrt{3}\alpha^2/4$
(112)	$\sqrt{6}/2$	——

Table 2. S-values (explained in the text) of the closest three planes in the CsCl- and NaCl-type structures.

In this table, the S-values increase in the order of (110) < (100) < (112) for the CsCl-type and of (100) < (110) < (111) for the NaCl-type. The density per unit area, therefore, decreases with the above order.

It is understood from Table 2 that both $(001)_{Cs}$ and $(011)_{Na}$ planes are the second smallest in the order of S-values. Thus, in the present transition, the closest and the second closest planes in one structure changes into the corresponding planes in the other structure, respectively.

Since the cell dimension of the low form varies from 4.119 A at room temperature to 4.227 A at the transition point. The S-value of $(110)_{Cs}$ becomes 5.3 percent larger during the period. At the transition point, therefore, the S-value of

$(110)_{Cs}$, is only 0.9 percent larger than that of $(100)_{Na}$. Furthermore the S-value of $(00\bar{1})_{Cs}$ is approximately equal to that of $(011)_{Na}$, because $S(110)_{Cs}/S(100)_{Na}$ is equal to $S(011)_{Cs}/S(011)_{Na}$. As for the 110 plane of the low form, the change of the area per one lattice point with temperature is shown in Fig.7 from 18°C to 446°C. In conclusion, the closest planes which can be conserved in the transition have approximately equal S-values at the transition temperatures.

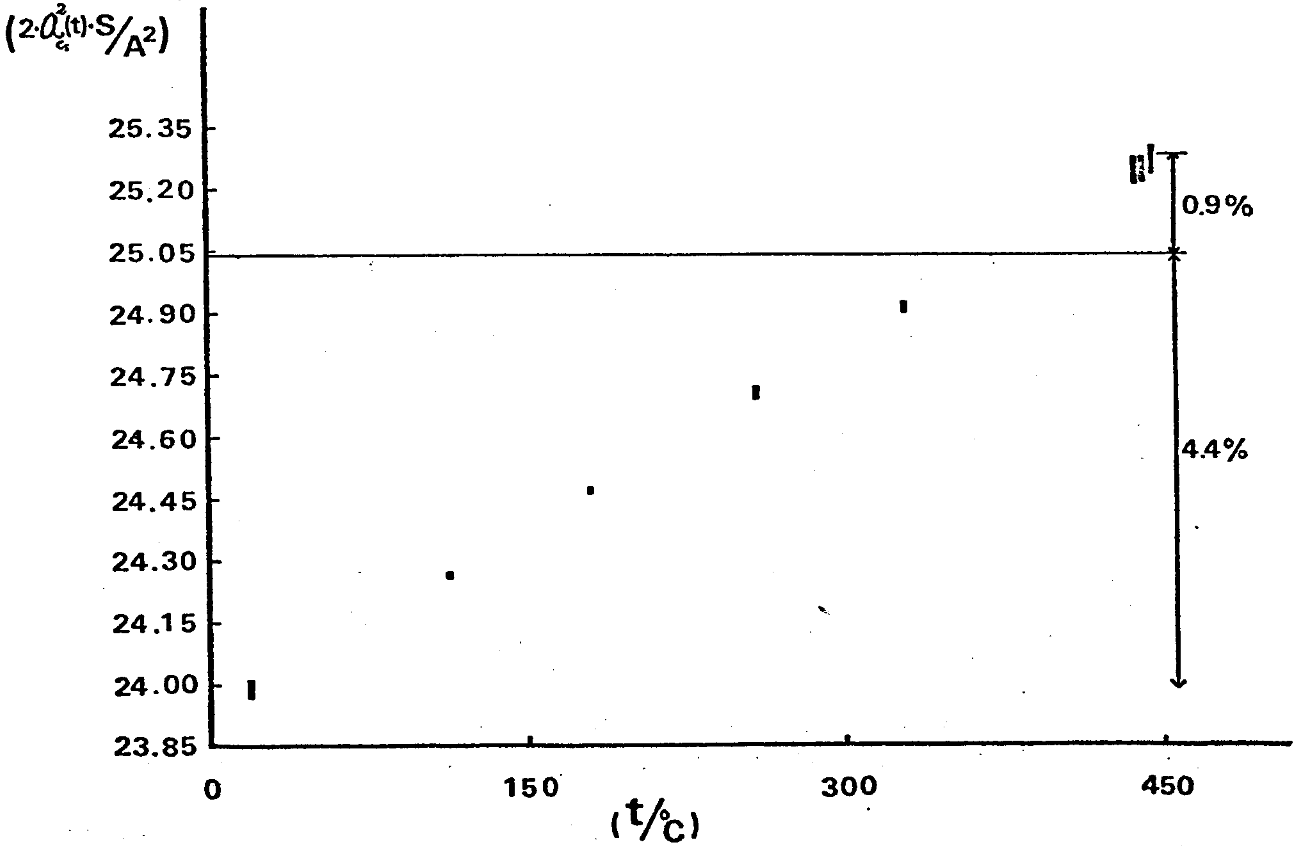


Fig.7. Change of the area per one lattice point of {110} of the low form, between 18°C and 446°C.

V. Possible transition mechanism

Based on the preceding considerations, one layer parallel to $(110)_{Cs}$ appears to become into one layer parallel to $(100)_{Na}$ in the transition by a systematic rearrangement of the constituent ions in the layer. Therefore, the transition mechanism is divided into the following elementary two processes :

(a) One layer parallel to $(110)_{Cs}$ changes to that parallel to $(100)_{Na}$.

(b) Formation of $(100)_{Na}$-type propagates in the parent along the directions perpendicular to the layer.

1. Two-dimensional movements of ions in transition

The arrangement of ions of $(110)_{Cs}$ layer changes into that of $(100)_{Na}$ by the movement of ions, resulting in $\angle A'O'B'$ (Fig.6(a)) of 90° from tetrahedral angle. This can be done as follows. A circle is drawn on a lattice plane of $(110)_{Cs}$ (Fig.8(a)). Suppose that the row lines, O'B' and O'B', rotate in this circle symmetrically with O'C' till ∠A'O'B' becomes 90°. Then O'A' and O'B' in Fig.8(a) move to O"A" and O"B" in Fig.8(b), respectively. This operation results in four-fold symmetry instead of two-fold symmetry, and a circle changes to an ellipse. Therefore, the crystal of CsCl dilatates 18 percent along $\overrightarrow{O'C'}$ and shrinks 16 percent normal to $\overrightarrow{O'C'}$ in $(110)_{Cs}$ layer. However, such a deformation is conflict with the experimental results and reasonable explanation must be given.

(i) Mechanism of non-linear transformation.

In the above section, only a linear transformation has been considered. Each square of the ellipse must glide along the small arrows in Fig.8(b) to build the circle shown by the dushed line starting from the ellipse. This means that the initial bold straight lines, O"A" and O"B", in Fig.8(b) must be transformed to the bold broken lines, O"A" and O"B", in Fig.8(c). All row lines parallel to the bold line O"A" and O"B" in Fig.8 (b), must be arranged as those parallel to the broken lines, O"A" or O"B", in Fig.8(c). No deformation of lattice plane takes place through this non-linear transformation.

(ii) The formula describing the transformation of one layer.

The movement of each ion in this transition is considered in more detail here. In this discussion, we shall consider

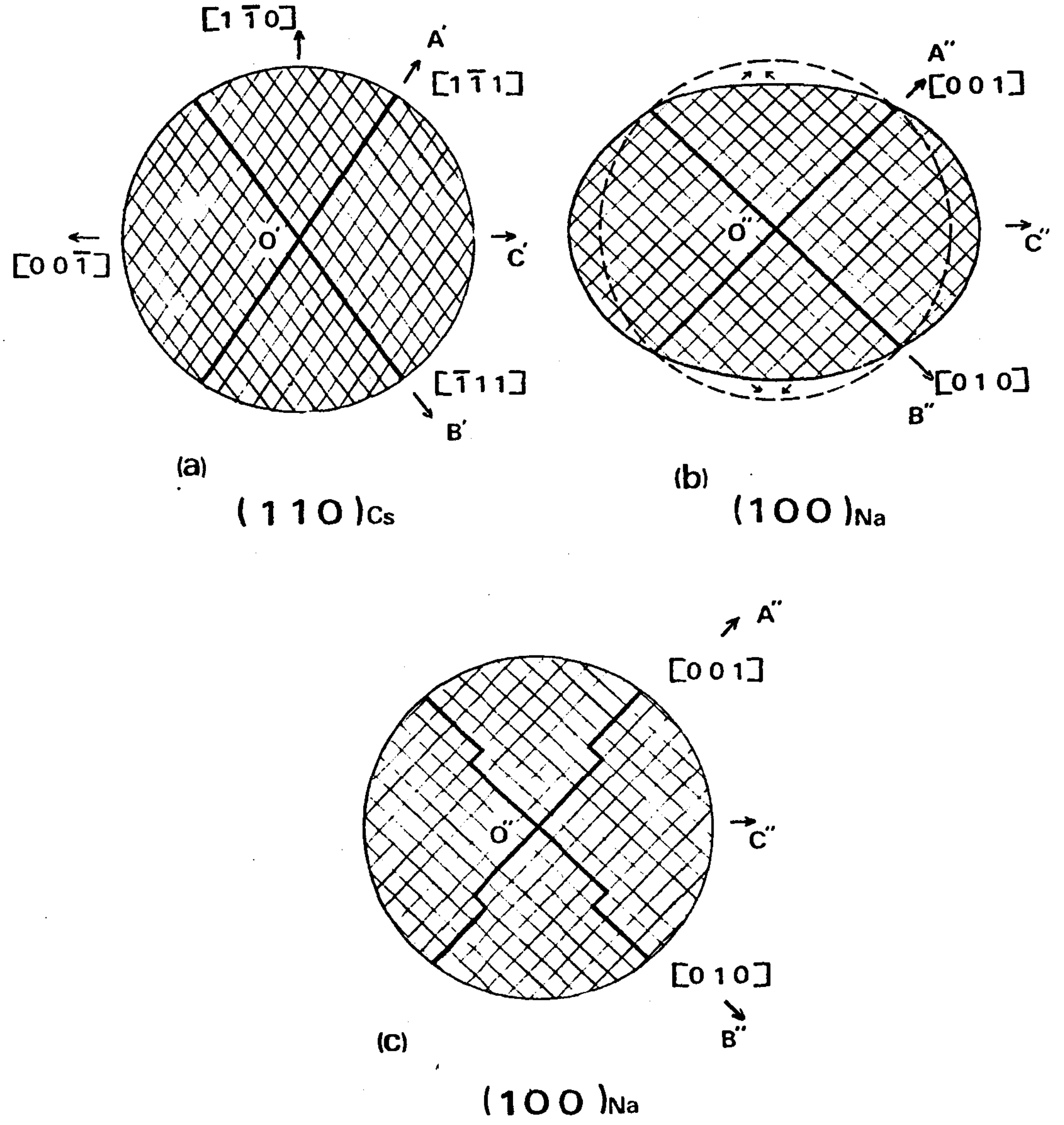


Fig.8. (a) A circle of the lattice net plane with two-fold symmetry.
(b) A ellipse of the lattice plane with four-fold symmetry, after linear-transformation of the circle lattice plane in (a).
(c) Lattice plane with square symmetry after gliding in the lattice of (b).

only the transformation (L→H). All the movements of ions are treated by two components parallel to O'A' and O'B' in the low form (Fig.6(a)). Let's consider first the ions on a straight row line O'A'. Suppose that the Nth ion from the O' moves just $\sqrt{3}a_{Cs}$ from the initial position along O'B' in the transition (L→H), where a_{Cs} is the cell edge of the low form. The ion reaches a position where the same kind of ion exists. This indicates that the movement of the Nth ion is not necessary for the transformation of ion. The movement of the nth ion, required for changing the initial line to a broken line, is $(\sqrt{3}/N)a_{Cs}(n-[n/N])$ in amount, where [n/N] represents the integer part of n/N. The x and y axes in $(110)_{Cs}$ layer are refered to O'B' and O'A', respectively. The Xth ion on x and Yth ion on y are assumed to move just $\sqrt{3}a_{Cs}$ from the initial position along the y and x axes, respectively. After the movement, the ion corresponding to the Xth or Yth is on one of the row lines parallel to O'B' or O'A'. In each layer of ions, the movement of ions with least deformation results in the following correspondence between the lattice points of the low form and those of the high form, which can be described by the following equations :

$$N'' = N' - M' - 2\left[\frac{N' + M'}{X}\right]$$

$$M'' = N' + M' + 2\left[\frac{M' - N'}{Y}\right] , \qquad (1)$$

where N' and M' are the addresses of the lattice points of the low form and, N" and M" are those of the lattice points of the high form. Three principal axes for each lattice are referred to the four-fold ones. N' and N" are the addresses along [001] and, M' and M" along [010]. When dealing with the transformation in the single layer, the above equations are simplified by the condition, L"=L'+M'=0. L' and L" are the addresses along [100].

(iii) Possible pair of (X, Y).

A rhombus with a circle of 7.077/2 A radii, shown in Fig. 9, represents a cell with the all edges parallel to the three-fold axes of $[\bar{1}11]$ and $[1\bar{1}1]$ in $(110)_{Cs}$ layer in the low form. Directions of $[1\bar{1}1]_{Cs}$, $[\bar{1}11]_{Cs}$ and $[001]_{Cs}$ are designated as the vectors, $\overrightarrow{O'A'}$, $\overrightarrow{O'B'}$ and $\overrightarrow{O'C'}$, respectively. The distance between ions is 7.321/2 A on row lines parallel to O'A', while 7.077/2 A along four-fold axis in the NaCl-type structure, at the transition point.

The values of integers X and Y in equation(1) were obtained by finding movements of ions to reduce the difference between 7.321/2 and 7.077/2.

Ions are initially at the positions of O', A' and B'. When an ion at O' is fixed and that at A' moves to D' (the intersection of the cell edges and the circle), the ion moved to D' is just 7.077/2 A far from O'. To change the initial angle ∠A'O'B' into the angle ∠D'O'F' of the right angle, the ion at B' must move into F'. The ion on F' is required to shift 0.9 percent out side along $\overrightarrow{O'F'}$ in order to make the distance between this ion and O', 7.077/2 A. The same geometry is held when an ion at A' moves to E' with 0.9 percent shifts along $\overrightarrow{O'E'}$ and an ion on B' into G' because of mirror symmetry. Simple computation shows that the total of absolute values of shifts along the two directions, for example, $\overrightarrow{O'F'}$ and $\overrightarrow{O'E'}$, is minimized when ions at A' and B' move into segments D'E' and F'G', respectively. Deformation of layers also becomes less. If a possible pair (X, Y) is one of (7, 17), (8, 16), (9, 16), (9, 15), (10, 14), (11, 13) and (12, 12), the ions at A' and B' are in the range of the segments D'E' and F'G'. The angles between the two intersected row lines at O' are 89°39', 90°30', 89°13', 89°59', 90°22' and 90°36' in turn with the seven pairs. As a result, the pair (10, 14) with 89°59' can be regarded as the most preferable choice. If this pair is kept in whole crystal, $[001]_{Cs}$ and $[011]_{Na}$ show a misfit of about two degrees,which is also observed in the experiments.

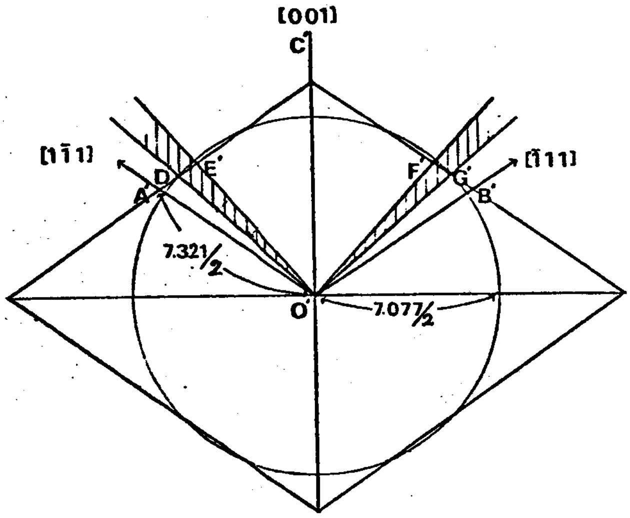


Fig.9. A rhombus representing a cell in (110) layer in the low form. Acircle with a radii of 7.077/2A is drawen in the rhombus for the explanation of the movement of ions in the transition (see text). In this form similar ions are at the apices and center of the rhombus and another at the middle points of the edges.

2. The structural change in transition

Uniaxial expansion in transition. The structural change in the uniaxial expansion is schematically in Fig. 10. The atomic configurations of the CsCl-type of the bottom half are joined with those of the NaCl-type structures of the upper half in the figure, representing coexistence of the two forms. The top half shows (001) layer of the high form. In the low form, every other row line of ions on $[\bar{1}11]$ in the plane parallel to the (001) of the high form makes a zig-zag broken layer consisting of parts of (101) and $(0\bar{1}1)$. The uniaxial expansion can take place by a transformation in which the broken layer of the low form changes to the flat layer of (001) with only slight displacements of ions. In the transition (L→H), $(110)_{Cs}$ plane of the low form transforms to $(100)_{Na}$ plane of the high form with constant area as explained above. Therefore, all the volume change of 17 percent should appear along the direction normal to $(110)_{Cs}$ plane.

The two dimensional general formula representing the correspondence between the lattice points of the low and high forms has been derived in the previous section on the assumption that ions move the shortest distances in the transformation. The correspondence between the lattice points of both lattices can be represented as follows from Fig.10.

$$\begin{aligned} L'' &= L' + M' \\ N'' &= N' - M' + \left[\frac{L''+1}{2}\right] - 2\left[\frac{N' + M' - [L'/2]}{X}\right] \\ M'' &= N' + M' - \left[\frac{L''}{2}\right] + 2\left[\frac{M' - N' - [(L''+1)/2]}{Y}\right] \end{aligned} \tag{2}$$

where (X, Y)=(10, 14).

<u>The change of coordination number.</u> The reduction of coordination number in transformation can be explained as follows based on the structure change described above. Several polyhedrons of both structures are shown in Fig.11. The plane, passing through O_3, O_4, O_7, O_8 and a central ion, is parallel to (110) in the low form and to (100) in the high

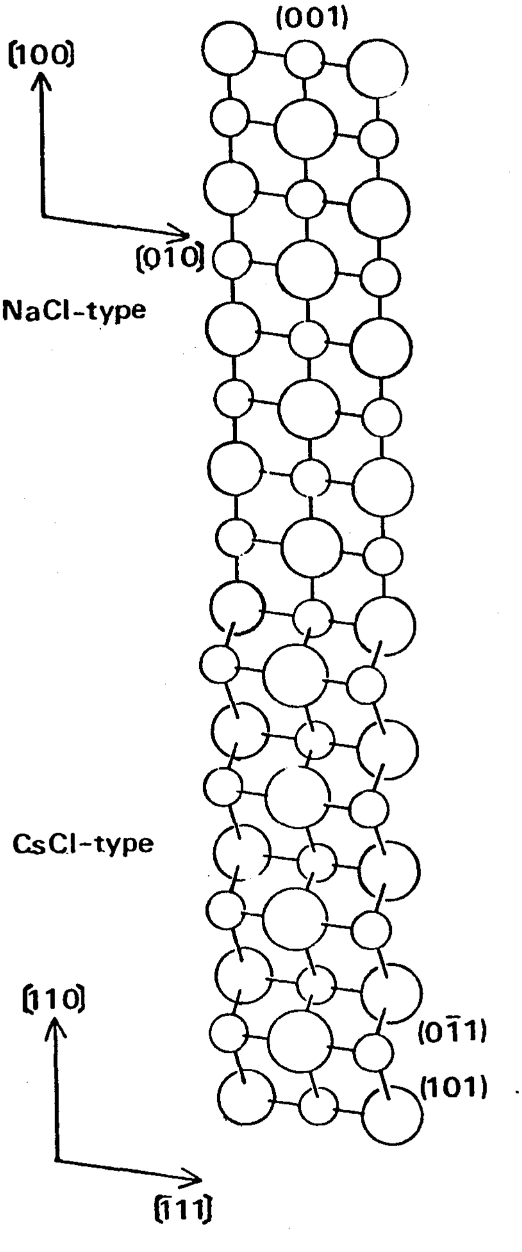


Fig.10. Change of the zig-zag plane consisting of (101) and (01̄1) to the flat plane of (001) causing the uniaxial expansion in the transition.

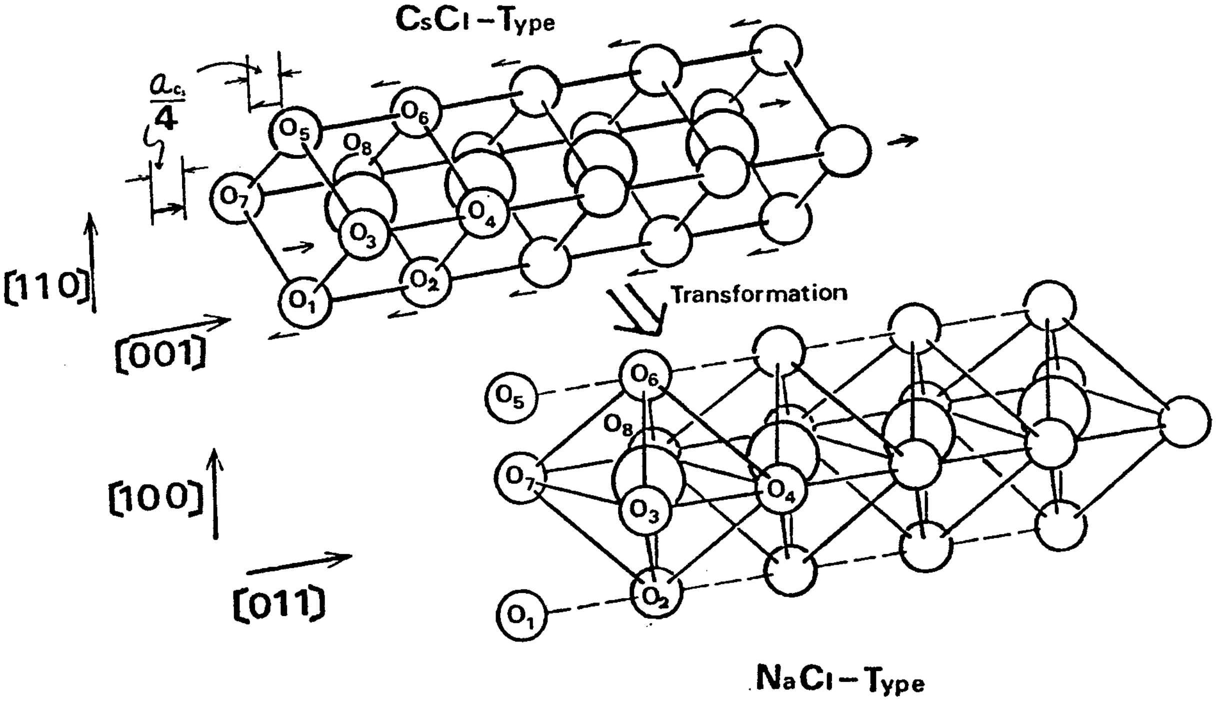


Fig.11. The change of the first coordination in transition, from cube to octahedron or vice versa.

form. If O_1, O_2, O_5 and O_6 translate by $a_{Cs}/4$ toward left and O_3, O_4, O_7, O_8 and a central ion by $a_{Cs}/4$ toward right, the coordination around the central ions decreases from eight to six. O_1 and O_5 move out of the coordination of the central ion. The rectangle $O_3O_4O_8O_7$ is deformed to a square with same area. The distance between O_3 and O_4 elongates 18 percent and that between O_3 and O_7 shortens 16 percent compared with the original distances.

3. The anisotropic expansion and twinning

When the crystals are mounted mechanically, they undergo twinning. The twinning must be explained by the fact that the crystal makes anisotropical expansion along $[110]_{Cs}$ of the low form. Because each specimen is mounted in different direction by the mechanical mounting, a moderate stress works on a crystal along the direction which it is obliged to expand, and the crystal behaves to avoid the effect of the stress. This stimulates twinning or breaking of crystals. In case of the twinning, another expansion may be expected to occur along the direction equivalent to [110] and normal to the stress, i.e., with no component of the stress. The orientation relation in twinning has been shown by stereographic projection in Fig.4(b). The orientations of the twin individuals are represented by x and +, and that of the parent crystal by •. $[110]_{Cs}$ changes to $[100]^{I}_{Na}$ of one of the twin individuals, and $[\bar{1}10]_{Cs}$ to $[100]^{II}_{Na}$ of the other individual. These changes of the two-fold axis to the four-fold one indicate that the uniaxial expansion has occured along each of two directions of $[110]_{Cs}$ and $[\bar{1}10]_{Cs}$. It is important that the direction of $[110]_{Cs}$ is normal to $[\bar{1}10]_{Cs}$. Therefore, the present twinning can be regarded as an effective mechanism by which the crystal can divide the uniaxial expansion between two directions normal to each other and to reduce the effect of stress. This explanation well explains the conservation of the orientation relation, $[110]_{Cs}/\!/[100]_{Na}$ and $[001]_{Cs}/\!/[011]_{Na}$, in the transition.

4. The observed and estimated values of expansion

The value of the uniaxial expansion is estimated to be 18 percent of the original size of the low form based on the structure change. The observed values were 12 to 15 percent and always smaller than the estimated value. The amount of expansion (or shrinkage) becomes less and the transparency of specimens becomes worse by the repetition of the transition process. This situation may imply that increase of polycrystallization or strain in parts of a specimen with repetition. Polycrystallization or strain possibly takes place because of the present unskilled technique of heating and cooling.

According to the recent observations on V.T.R., the shrinkage is often not sufficient in crystals and completes only after prolonged cooling and anealing. The incomplete shrinkage is considered to have caused the discrepancy between the estimated and observed values.

5. Consideration on other transition mechanisms

The transition between simple lattices, as shown in CsCl, has been observed in many metals and alloys, for example, Fe, Co, Ti, Zr and alloys of these metals (1951, 1971). The transition of these materials has been studied usually in the process from the high to low form or rapid cooling from temperatures above eutectoid. This kind of transition is called martensite transition, which is regarded to be diffus-

ionless and to make cooperative movements of atoms. In the martensite transition, the structure of *fcc* changes to that of *bcc*, *bct* or *hcp* and the structure of *bcc* to that of *hcp*, where the orientation relations are kept between the parent and the martensite lattices. And the habit plane between both structures is observed. Martensite transitions show pronounced hysteresis and show deformation. Surface upheaval are also produced. The volume changes in martensite transitions are about 5 percent even in maximum of Fe alloys (1973).
The observations on CsCl described previously are not sufficient to regard the transition of CsCl to be martensitic. However, the transition of CsCl shows a few properties common to the martensite one , especially the reservation of lattice orientation relation and the deformation caused by a systematic movement of ions.

Lattice orientation relations found in martensite transitions are $(111)_{fcc}//(110)_{bcc\ \text{or}\ bct}$, $(111)_{fcc}//(0001)_{hcp}$ and $(110)_{bcc}//(0001)_{hcp}$ for the transitions from *fcc* to *bcc* or *bct*, from *fcc* to *hcp* and from *bcc* to *hcp*, respectively. These relations are equivalent to convert the closest net plane of one structure to that of the other one. CsCl also shows this kind of convertibility as described above. These observations mean that in transitions between at least, simple structures with ionic and metalic bonds, the closest net planes play an important role for the structural change. The equality of the densities in the closest planes is expected to take place in the martensite transitions, though most of lattice constants of both phases have not been reported.

Buerger has interpreted the phase transitions from the structural view point. His interpretation seems reasonable in order to understand the discontinuity or continuity of internal energy at a transition structurally and the rapidity with which a transition takes place, etc. He also describes that the transition in which the number of the first coordination changes is sluggish because the primary bonds must be broken in this transition. However, he introduced a mechanism of differential dilatation in order to explain that the transition of CsCl and a few metals is rapid in spite of the change of the first coordination number. The present work on the transition of CsCl indicates that the closest net plane plays an important role in the transition and must be examined carefully for most transitions of metals and alloys. Because of this result, Buerger's mechanism of differential dilatation is considered not appropriate as a mechanism for changing the first coodination number with rapid rate for this kind of transition.

Because of large sublimation, the transition ($\underline{L}\rightarrow\underline{H}$) of NH_4Br was not fully studied, but was found to be topotactic by the x-ray diffraction method. The orientation relation observed was similar to that in CsCl, indicating that NH_4Br transforms by the same process as in CsCl. The above orientation relation was found to be reversible by Fraser (1972).

Conclusions

Caesium Chloride has shown an anisotropic expansion of about 15 percent parallel to [110] of the CsCl-type structure in the transition from the CsCl-type to the NaCl-type structure. The orientation relations, $[110]_{Cs} // [100]_{Na}$ and $[001]_{Cs} // [011]_{Na}$, are held between both type lattices in transition, that is, the closest and the second closest planes in one structure are converted into the corresponding ones in the other one. It has been found by the comparison of the cell dimensions that the densities of the convertible planes of both type structures are approximately equal at the transition point.

Based on the movement of ions that can explain the anisotropic expansion(or shrinkage) and the orientation relations, general formulae representing the correspondence between the lattice points of both structures have been obtained as equations(2) in Chap. V § 2. This mechanism of transition does not need further deformation of crystal shape in the uniaxial expansion.

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