

## The Transition Mechanism between the CsCl-type and NaCl-type Structures in CsCl\*

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In the transition between the CsCl-type and NaCl-type structures, caesium chloride retains a definite orientation relation of  $[110]$  (CsCl)  $\parallel$   $[100]$  (NaCl) and  $[001]$  (CsCl)  $\parallel$   $[011]$  (NaCl). The closest-packing planes of both structures are retained in the transition and have an approximately equal density of ions at the transition temperature. A uniaxial expansion (or shrinkage) parallel to one of the twofold axes in the CsCl-type structure (or the fourfold axes in the NaCl-type structure) attending the transition was observed under the optical microscope. The amount of the uniaxial expansion is about 15% of the size of the low-temperature form, and the volume change of about 17% in the transition is mostly due to this uniaxial expansion. The transition mechanism is explained as being due to a combination of two systematic movements of ions: intralayer rearrangement and interlayer translation.

### Introduction

Caesium chloride occurs in two polymorphic forms at atmospheric pressure: the CsCl-type and NaCl-type. The former is stable below about 445°C and the latter between about 445°C and the melting point of 646°C (Landolt–Börnstein, 1961). In the transition from the CsCl-type to the NaCl-type, the first coordination changes from cube to octahedron and the volume increases by about 17%.

Shoji (1931) pointed out the possibility of a differential dilation which transforms the CsCl-type lattice to that of the NaCl-type by a relative expansion along one of the threefold axes, but did not consider this a realistic explanation.

However, this mechanism was illustrated by Zintle & Brauer (1935) and by Buerger (1951, 1961). Buerger inferred in his crystallographic classification of phase transitions that this transition takes place rapidly in spite of large changes in the first coordination, because no intermediate energy state exists between those of the two structures.

Menary, Ubbelohde & Woodward (1951) were the first to use single crystals to study the orientation relation in the transition of CsCl by means of an X-ray diffraction method. According to their study, the transition is not topotaxial because a single crystal of CsCl divided into several crystallites of the NaCl-type after the transition, without retaining any special orientation relations. Chatterji, Mackay & Jeffery (1971) studied CsCl crystallites of the NaCl-type produced from a saturated aqueous solution of CsCl. The crystallites were converted by electron-beam heating into the stable form of CsCl-type, retaining some orientation relations with the original NaCl-type.

These topotaxial relations were observed only in the transition from the high-temperature to the low-temperature form (hereafter H  $\rightarrow$  L), but did not correspond to those expected from the differential dilation suggested by Shoji (1931).

In the transition of  $\text{NH}_4\text{Br}$ , Fraser & Kennedy (1972) reported the orientation relations between the high-temperature and low-temperature forms and observed a change in crystal shape of the NaCl-type specimens which had been supercooled to room temperature. Based on the rapid propagation of the transition and deformations in shape, they suggested that the transition took place cooperatively. Kennedy, Patterson, Chaplin & Mackay (1974) determined the orientation relations in the transition of ammonium halides by X-ray diffraction and light microscopy. They explained the orientation relations in the transition of ammonium halides as well as in the transition (H  $\rightarrow$  L) of CsCl described by Chatterji *et al.* (1971), by multiplicity of the direction of pure strain due to the differential dilation.

Assuming that this transition is cooperative, Fraser & Kennedy (1974) applied the martensite transformation to the transition of CsCl as well as to ammonium halides and calculated the orientation relationship, the habit-plane indices and the shape deformation. According to them, the misfit in the transition was periodically moderated between the guest and host phases by a symmetry-equivalent deformation (twinning) and an additional displacement in one direction (slip). Many of their calculated results are apparently in accord with the experimental results, especially in the orientation relationship. However, their prediction of the shape deformation for CsCl does not agree with that observed in the present investigation with CsCl single crystals. Thus, the martensite theory does not seem adequate to explain the transition mechanism of CsCl, unless we extend the martensitic transformations to cover all dilational changes (Megaw, 1973).

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In this investigation, an atomistic mechanism of the transition between the CsCl-type and the NaCl-type structures of CsCl has been derived through studies of single crystals of CsCl by means of the X-ray single-crystal method and the optical microscope. The high-temperature and low-temperature forms are herein after called high and low forms respectively.

### Experiments and results

#### Materials

The CsCl crystals supplied by Nakarai Chemicals Co., contain 5 p.p.m. of Na and Ni. These crystals were annealed at 300°C under 1 mm Hg of air for 10 days. They are granular single crystals between 200 and 400  $\mu\text{m}$  in size, but well developed crystal faces are not observed. Small crystals were used for the X-ray diffraction experiments and large ones for the optical observations.

#### X-ray studies

(a) *Orientation relations.* The X-ray diffraction patterns of single crystals of CsCl were recorded at various temperatures with a precession camera using Mo  $K\alpha$  radiation. A super-high-power X-ray generator (60 kV–500 mA) was employed for rapid measurements during the transition process. A microfurnace was designed as an attachment to the camera and controlled by the P.I.D. system. A chromel–alumel thermocouple was used for control and measurement of the temperature. The temperature fluctuation was  $\pm 0.7^\circ\text{C}$  near 500°C.

The precession photographs were taken at room temperature at orientations where the fourfold or twofold rotation axes of the specimens were parallel to the incident X-rays. The photographs were taken at 20°C intervals up to 430°C, 2.5°C intervals up to 440°C and 1.0°C above 440°C. The specimens were exposed to the X-rays for 7 min and the temperature was kept constant within the limit given above during every exposure. Each film was developed soon after the exposure and compared with the preceding one. If any reduction of the intensity of the initial diffraction spots or the appearance of new spots was noticed, more photographs were taken at the same temperature until the transition was completed.

No spots indicating the existence of intermediate structures between the CsCl-type and the NaCl-type structures were detected on any photographs, including those taken just before and during the transition. No

distinct diffuse scattering was observed on the photographs.

In favourable cases, the single-crystal patterns of the high form were observed only with weak powder lines after the transition. The following orientation relations were always found between the CsCl-type and the NaCl-type lattices:  $[001](\text{CsCl}) \parallel [011](\text{NaCl})$  and  $[110](\text{CsCl}) \parallel [100](\text{NaCl})$ . Although the latter is obeyed strictly, the former generally deviates by  $\sim 3\text{--}5^\circ$  from being parallel.

The reverse transition (H  $\rightarrow$  L) was carried out consecutively. It took place at a somewhat lower temperature than that of the transition (L  $\rightarrow$  H), and the low-form lattice was reproduced with the same orientation relation as mentioned above.

(b) *Cell dimensions.* The cell dimensions of CsCl were measured at various temperatures up to just above the transition point by a four-circle automatic diffractometer utilizing a microfurnace for heating. Cu  $K\alpha$  radiation was used with a graphite monochromator.

The positions of several reflexions ( $\theta > 40^\circ$ ) were independently measured by using the crossed half slit. The angle of each reflexion was determined from the peak profile obtained by the  $\omega$  and  $2\theta - \omega$  step scans with  $2^\circ/100$  step width in the  $\omega$  value.

The cell dimensions at various temperatures are shown in Table 1. The crystal of the low form linearly expands with increasing temperature until the transition temperature of  $446 \pm 2^\circ\text{C}$  is reached. At the transition temperature the cell dimensions of the low form and high form are 4.227 and 7.077 Å, with the volumes for the chemical unit of 75.53 and 88.61 Å<sup>3</sup> respectively. The observed volume change in the transition is, therefore, 17.3% of the volume of the low form. However, the (110) (CsCl) plane is similar to (100) (NaCl) in ion arrangement (Fig. 2), and the area per chemical formula unit in (110) (CsCl) is only 0.9% larger than that in (100) (NaCl) at the transition temperature. Thus the density of the closest-packing plane is approximately equal in the low and high forms in spite of a big volume difference.

#### Optical observations

About 50 single crystals of CsCl were observed by means of an optical microscope and were recorded on photographs and videotapes during the (L  $\rightleftharpoons$  H) transition. Transparent crystals, placed on a small graphite seat in a microfurnace, were heated or cooled stepwise at intervals of 2.5°C.

Crystals of the CsCl-type structure underwent

Table 1. Cell dimensions of CsCl at various temperatures

	$t$ ( $^\circ\text{C}$ )	Cell dimensions $a$ (Å)	$t$ ( $^\circ\text{C}$ )	Cell dimensions $a$ (Å)
CsCl-type	$18 \pm 1$	$4.119 \pm 0.002$	$332 \pm 2$	$4.197 \pm 0.001$
	$98 \pm 1$	$4.142 \pm 0.000$	$433 \pm 2$	$4.223 \pm 0.001$
	$173 \pm 1$	$4.160 \pm 0.000$	$435 \pm 2$	$4.224 \pm 0.004$
	$262 \pm 1$	$4.179 \pm 0.001$	$446 \pm 2$	$4.227 \pm 0.004$
NaCl-type	$446 \pm 2$	$7.077 \pm 0.003$		

transition with an anisotropic expansion, as shown in Fig. 1(a) to (d), along one of the six  $\langle 110 \rangle$  directions. The temperature gradient of the furnace must have an important effect on the selection of a unique direction among the crystallographically equivalent ones.

At the beginning of the transition, a thin plate optically different from any other part appeared at one end of most of the crystals. This plate traversed in one or two seconds from one end to the other of crystals that were about  $300 \mu\text{m}$  in size. The expansion of the crystals took place in the direction of the movement of the front of the plate. The linear expansion was about 15% of the length of the low form along the expansion direction. No expansion was observed normal to the direction of the main expansion. The linear expansion of 15% compares with 18% as calculated from the ratio of  $\sqrt{2}a(\text{CsCl})$  and  $a(\text{NaCl})$  and is approximately equal to the volume change of 17%.

When the transition (L  $\rightarrow$  H) was completed, the reverse transition (H  $\rightarrow$  L) did not occur at the same temperature, but took place and progressed very rapidly at a temperature  $15\text{--}25^\circ\text{C}$  lower. When the low form partly remained in a crystal in the transition (L  $\rightarrow$  H) and the temperature of the specimen was lowered, the transition (H  $\rightarrow$  L) took place at the same temperature as the transition (L  $\rightarrow$  H). Many specimens reproduced their original shapes after reversal of the transition.

By repeating the transition (L  $\rightleftharpoons$  H) several times without annealing, we observed the following changes: the temperature of the transition (H  $\rightarrow$  L) had a tendency to become lower and less defined, the transparency of the crystals was gradually lost, and the external forms of the specimens became irregular.

### Discussion

According to the optical observation, the transition (H  $\rightleftharpoons$  L) proceeds by propagation of the front of a plate through the host crystal. The front constitutes a boundary between the two forms and is parallel to (110) (CsCl) and (100) (NaCl). These planes are both the closest-packing ones as shown in Fig. 2 and have almost the same atom density at the transition temperature as mentioned above. The uniaxial expansion or contraction is observed along the direction perpendicular to this boundary, although no deformation is observed in the direction of the boundary.

These experimental results suggest that the structure change takes place layer by layer parallel to (110) (CsCl) and (100) (NaCl) in the crystals. Thus the movements of ions in the structure change are composed of two kinds of cooperative motions: the intralayer rearrangement and the interlayer translational movement. They are described in more detail below.

#### The intralayer rearrangement of ions

In addition to a topological similarity between (110) (CsCl) (Fig. 2a) and (100) (NaCl) (Fig. 2b), a

fundamental rhomb  $OACB$  has equal area with a square  $O'A'C'B'$ . Thus the two-dimensional rearrangement, or the transformation between (110) (CsCl) and (100) (NaCl) starts at the lattice points which nearly coincide in both planes.

In order to find the lattice points at which the transformation starts, the concept of coincidence-site lattice (Brandon, 1966; Ranganathan, 1966) can be applied. The coincidence-site lattice common to both (110) (CsCl) and (100) (NaCl) can be easily found by super-

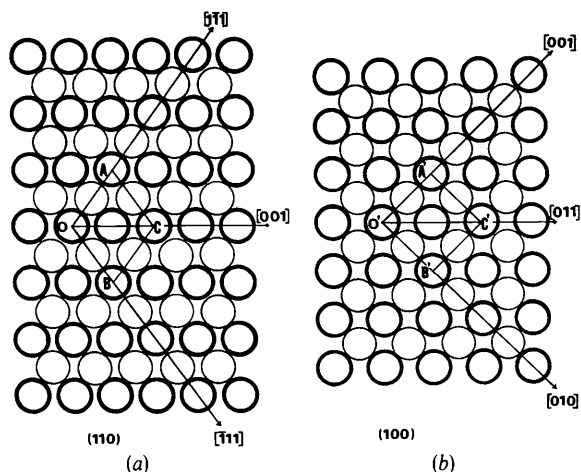


Fig. 2. The arrangements of the ions (a) in the (110) layer of the CsCl-type structure and (b) in the (100) layer of the NaCl-type structure. Thin-lined and thick-lined circles indicate different ions.

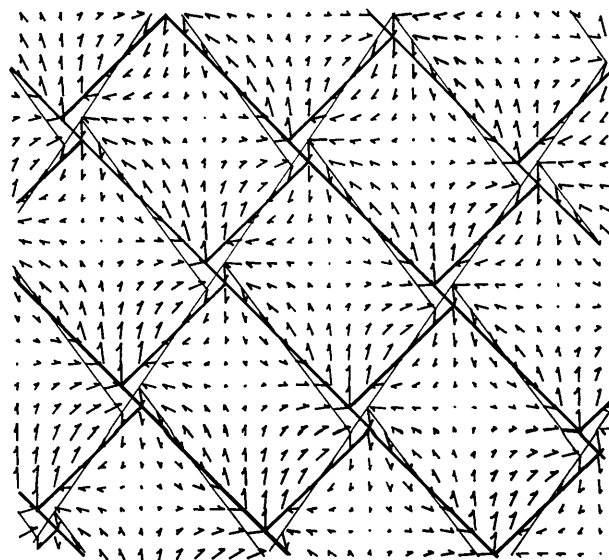


Fig. 3. The systematic movements of the lattice points in the rearrangement from the low to the high form. Arrows show the amounts and directions of the movements of lattice points. Thin and thick lines represent the domain boundaries in the low and high forms respectively. The parallelograms and rectangles corresponding to the domains are converted to each other by a homogeneous deformation.

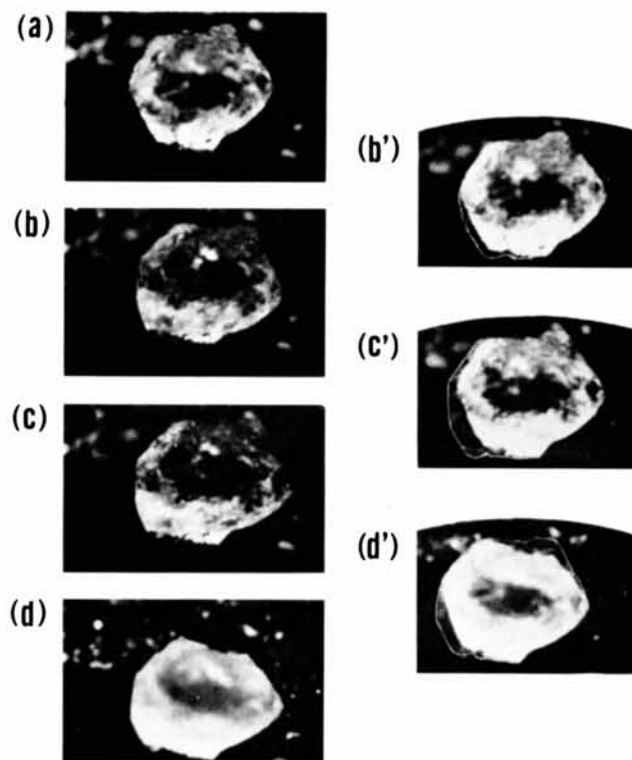


Fig. 1. Transition of CsCl. (a) A crystal of the CsCl-type structure on a graphite seat. (b) Slight uniaxial expansion due to a partial (L→H) transition at the lower left part of the crystal. This expansion can be clearly seen in the photograph (b'), which was taken by superposition of (a) onto (b). (c) Maximum expansion due to the complete (L→H) transition of the crystal. (c') is the superposed photograph of (a) and (c). (d) Contraction to the original crystal shape after the transition (H→L) by lowering the temperature by about 20° below the transition temperature. The crystal became cloudy. (d') is a superposition of (a) onto (d). This is a rare example in which the shrinkage occurred on the opposite side to the expansion.

imposing Fig. 2(a) on Fig. 2(b). Optimal fit between both lattices was obtained when  $5 \times \vec{OA}$  and  $\vec{OA} + 7 \times \vec{OB}$  in Fig. 2(a) correspond to  $5 \times \vec{O'A'} - \vec{O'B'}$  and  $7 \times \vec{O'B'}$  in Fig. 2(b), respectively, and the angle between  $\vec{OC}$  and  $\vec{O'C'}$  is  $1.6^\circ$ . Thus each domain around the optimal coincidence-site lattice has the size of  $5 \times 7$  with the lattice points of  $(5 \times 7) \times 2$  and forms a parallelogram in the low phase and a rectangle in the high phase.

In the transition, ions move systematically around the coincident lattice sites as shown by the arrows in Fig. 3 by homogeneous deformation and form domains of similar size in each layer. In order to avoid overlapping or cracking of the domains, their boundaries are confined in the direction of the pure shear in the deformation (Fig. 3).

#### Interlayer translational movement

The structural change in the interlayer translational movement is schematically shown in Fig. 4, in which the atomic configurations of the CsCl-type of the lower half are joined to those of the NaCl-type structure of the upper half where the row lines of ions on [010] make a flat plane of (001). In the lower half of the low form, however, every row line of ions in  $[\bar{1}11]$  is parallel to [010] of the high form and makes a zigzag layer consisting of (101) and  $(0\bar{1}1)$ .

The uniaxial expansion takes place by a transformation in which the zigzag layer of the low form changes

to the flat layer of (001) with only slight displacements of neighbouring ions. In the transition, the (110) plane of the low form transforms to the (100) plane of the high form with approximately constant area as explained above. Therefore, the volume change of 17% should appear along the direction normal to the (110) (CsCl) plane.

#### Transition process

In the above discussion, the transition mechanism has been treated separately as two cooperative motions of ions. They are correlated with each other because no layer undergoes rearrangement without expansion or contraction of about 17% of the space between the adjacent layers. In fact, these correlated motions take place simultaneously in a number of layers and this band sweeps the whole crystal.

Although only the optimal domain with the size of  $(5 \times 7)$  has been considered in the two-dimensional rearrangement, several coincidence-site lattices are found with different angles between  $\vec{OC}$  and  $\vec{O'C'}$  (Fig. 2). They have the domain sizes of  $(6 \times 6)$ ,  $(5.5 \times 6.5)$ ,  $(4.5 \times 7.5)$ ,  $(4 \times 8)$ , etc. In these cases, the angles between  $\vec{OC}$  and  $\vec{O'C'}$  are within about  $4^\circ$ . The observed discrepancies of  $3-5^\circ$  between [001] (CsCl) and [011] (NaCl) are attributed to the variation of angles for several approximately coincident lattices. Thus the two-dimensional rearrangement is considered to proceed by a mixture of optimal and approximately optimal domains.

Since the direction of expansion or contraction is selected among the equivalents as described above, it is possible, at least qualitatively, to impede expansion by adding stress to a crystal along the temperature gradient. We have often observed appearance of twinning and fracturing of specimens into polycrystals by the existence of stress in the direction of the temperature gradient.

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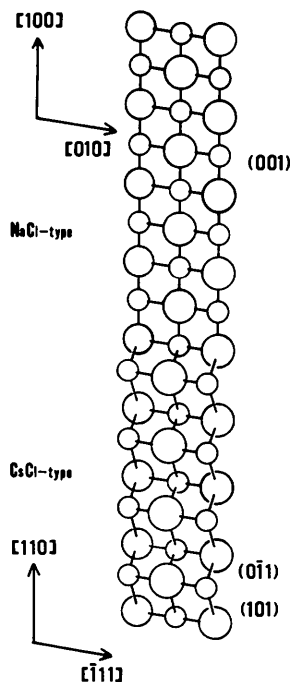


Fig. 4. Change of the zigzag plane consisting of (101) and  $(0\bar{1}1)$  of the CsCl-type structure to the flat plane of (001) of the NaCl-type structure resulting in the uniaxial expansion in the transition.

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## Probability Distribution of Anomalous Phase Angles in a Centrosymmetric Crystal

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Theoretical expressions for the complementary cumulative function of the anomalous phase angle  $\alpha_A$  are worked out for three cases: a centrosymmetric crystal containing 1, 2 and 4 anomalous scatterers in the unit cell besides a large number of similar normal scatterers. The results are used to study the influence of the number of anomalous scatterers on the distribution of  $\alpha_A$ . It is found that neglect of  $\alpha_A$  in the computation of the final difference map will lead to the largest spurious effects when the number of anomalous scatterers in the unit cell is least, namely, the  $P=1$  case (the other conditions such as  $k$  and  $\sigma_1^2$  being similar).

### 1. Introduction

The effect of the neglect of the anomalous phase angles  $\alpha_A$  (arising from the imaginary part of the atomic scattering factor) on the final difference map computed for the elucidation of finer details in the electron density distribution has been studied earlier (Parthasarathy, Sabesan & Venkatesan, 1970 – hereafter PSV, 1970). This study was substantiated by making use of the theoretical distribution of  $\alpha_A$  derived for the specific case of a centrosymmetric crystal containing a *large number* of anomalous scatterers in the unit cell besides a large number of normal scatterers of similar scattering power. Since in many actual cases the unit cell contains a *small* number of heavy atoms and since the distribution of  $\alpha_A$  is expected to be dependent on the number of anomalous scatterers in the unit cell, it is interesting to study how the number of anomalous scatterers influences the distribution of  $\alpha_A$ . In this paper we shall therefore work out such a distribution for three typical cases: a centrosymmetric crystal containing 1, 2 and 4 anomalous scatterers in the unit cell; we shall refer to these as the one, two and four-atom cases respectively. We follow the notation of the earlier paper (PSV, 1970).

### 2. Derivation of the probability distribution of $\alpha_A$

Consider a centrosymmetric crystal containing  $P$  anomalous scatterers of the same type and a large

number ( $Q$ ) of normal scatterers of similar scattering power in the unit cell. From PSV (1970) we obtain  $\alpha_A$  to be

$$\tan \alpha_A = |F'_P|/|F'_N| = k\sigma_1 y_P/y_N, \quad 0 \leq \alpha_A \leq \pi/2 \quad (1)$$

where

$$y_N = |F'_N|/\langle |F'_N|^2 \rangle^{1/2}, \quad y_P = |F'_P|/\langle |F'_P|^2 \rangle^{1/2} \\ \sigma_1^2 = \langle |F'_P|^2 \rangle / \langle |F'_N|^2 \rangle, \quad k = \Delta f'_P / (f'_P + \Delta f'_P). \quad (2)$$

By definition, the cumulative function of  $\alpha_A$  representing the probability that the value of the anomalous phase angle,  $\alpha_A$ , is less than or equal to a given value  $\alpha_A^0$ , say, is given by

$$N(\alpha_A^0) = P_r(\alpha_A \leq \alpha_A^0). \quad (3)$$

Since  $\tan \alpha_A$  is a monotonic function of  $\alpha_A$  in  $0 \leq \alpha_A \leq \pi/2$ , we can rewrite (3) by making use of (1) as

$$N(\alpha_A^0) = P_r(\tan \alpha_A \leq \tan \alpha_A^0) = P_r(k\sigma_1 y_P/y_N \leq \tan \alpha_A^0) \\ = P_r(y_N \geq c y_P) \quad (4)$$

where we have used the abbreviation

$$c = k\sigma_1 \cot \alpha_A^0. \quad (5)$$

For practical applications, it is more useful to obtain the fraction of reflexions for which  $\alpha_A \geq \alpha_A^0$  and this, referred to as the complementary cumulative function [and denoted by  $N_c(\alpha_A^0)$ ], is related to the cumulative function through the relation:

$$N_c(\alpha_A^0) = 1 - N(\alpha_A^0). \quad (6)$$

From (4) and (6) we obtain:

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