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Twin Formation by a Compressive Stress on the Transition of CsCl

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Crystals of CsCl expand uniaxially in the transition from the CsCl-type to the NaCl-type structure under stress-free condition. When the expansion is mechanically inhibited, spinel twinning appears in the produced crystals. Two common symmetry axes of the produced twinned crystals of the NaCl-type structure, $[11\bar{1}]$ and [011], are kept parallel to [010] and [001], respectively, of the original CsCl-type structure. Although this relation is different from that in the stress-free case, the transition mechanism is explained as a modification of that in the latter case.

Introduction

Cesium chloride undergoes a transition between the CsCl- and NaCl-type structures. Ammonium halides containing Cl, Br, and I also have similar structural changes.

Orientation relations were observed for the down-temperature transitions in CsCl (*1*) and in NH_4Br (*2*). Those in the up-temperature transition are reported for the above ammonium halides (*3*), and at the same time the data on shape deformation were shown using photographs for NH_4Br also. Fraser and Kennedy (*4*) claimed to agree well with shape deformations calculated from martensite theory with the lattice correspondence proposed by Shoji (*5*).

On the other hand, the shape change of CsCl crystals, uniaxial expansion along one of ⟨110⟩ (CsCl), in the transition has been observed under stress-free conditions by Watanabe *et al.* (*6*). Its transformation has been explained by them in terms of systematic movements of ions consisting of intralayer rearrangement and interlayer translational movement.

If the uniaxial expansion in the transition is inhibited by the surroundings of the crystals, the grain of the high-temperature form cannot be a single crystal but becomes polycrystalline. Under appropriate conditions, however, twinned crystals which have a definite orientation relative to the low-temperature form develop. In this paper, the formation of twinning under a compressive stress condition is described and the interface structure is discussed.

Experimental

CsCl crystals of 99.9% purity were obtained from Nakarai Chemicals Co. They are granular single crystals between 200 and 400 μm in size. Single crystals of about 200 μm were first annealed at 300°C for 10 days to eliminate existing strains.

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The single crystals were placed in quartz glass capillaries as illustrated in Fig. 1. One of ⟨110⟩ was chosen parallel to the capillaries. The crystals expand by about 2.6% in a linear dimension from room temperature to 450°C. Because thermal expansion is negligible for quartz glass, a mechanical interaction takes place between the specimen, capillary, and glass rods. In order to decrease the interaction, the specimen was coated with polystyrene film by dipping it in a cyclohexanone solution of polystyrene. The film was decomposed by heating, resulting in narrow interstices between the specimen and the glass rods.

The largest thermal gradient, 25°C/mm, was kept nearly parallel to the direction of the capillary. The temperature of the specimens was increased with steps of 20°C between room temperature and 430°C, 2.5°C between 430 and 440°C, and 1.0°C above 440°C. It took a few days to raise the temperature from room temperature to 430°C. Above 430°C, the specimens were held for 30 min at every step.

Precession photographs were taken by MoK_α radiation with an exposure time of 7 min and a μ angle of 10°, using a super-high-power X-ray generator (60 kV–500 mA). The specimens were held at the temperature where the phase change was first detected until the transition was completed. The crystals were kept for 1 day at the temperature where the high-temperature form was stable, and then the temperature was decreased.

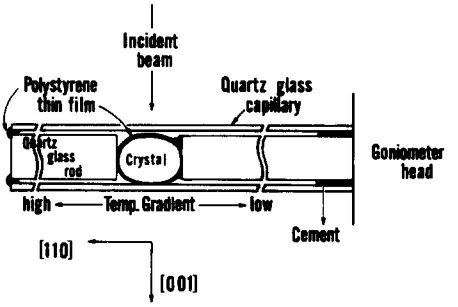

FIG. 1. Crystal mounting in the heating experiments. The single crystal of CsCl coated with polystyrene thin film is enclosed in a silica glass capillary and supported by silica glass rods. The largest thermal gradient is parallel to the direction of the capillary. The stress takes place along [110].

Results

When the film thickness is inadequate for expansion of the crystal, the single crystal becomes polycrystalline without keeping any orientation relation between the starting and final crystals. The results reported by Menary *et al.* (*7*) are considered to have been obtained by paying no attention to the stress due to the expansion in the transition.

When the crystals were subjected to a moderate stress owing to a proper thickness of the film, they transformed to the high-temperature form in twin relation. The transition took place at 450 ± 1.0°C, a slightly higher temperature than in the case with no stress described in the previous work (*6*), and the transition continued for as long as 40 min until completion. The transition to the low-temperature form (H → L) took place at 445 ± 1.0°C and was much more rapid than that of the high-temperature form (L → H). The transition was completed, at the latest, within 7 min.

The precession photographs (Fig. 2) were taken during the transition process under a moderate stress. Figure 2a shows the diffraction pattern of the low-temperature form. The reflections from both low- and high-temperature forms are observed together in Fig. 2b. The twin relation in Fig. 2c was observed at the first detection of the transition, and the reflection intensities from both twin individuals were roughly equal to each other. They hold in common one threefold and one twofold axis in and normal to the photograph, respectively. The twinning plane is one of {112} of the NaCl-type lattice. Figure 2d shows the low-temperature form reproduced from the high-temperature one in Fig. 2c.

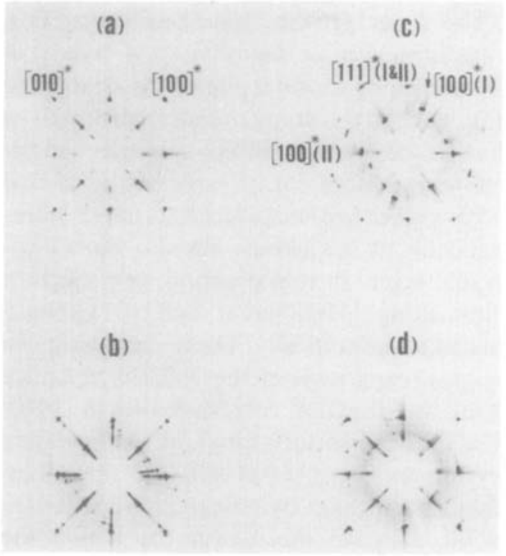

FIG. 2. Precession photographs. (a) The 0-th layer normal to [001]* of the low-temperature form taken at 449 ± 1.0°C. (b) At 450 ± 1.0°C, where the new spots of the high-temperature form appear together with those of the low-temperature form. (c) At 450 ± 1.0°C and after about 1 hr from b, only the high-temperature form is observed to form a twin. The individuals share $[11\bar{1}]$ and [011] in and normal to the photograph, respectively. (d) At 445 ± 1.0°C in cooling from c.

The high-temperature form has a definite orientation relative to the low-temperature one. The common twofold axis of the NaCl type corresponds to the fourfold axis normal to the thermal gradient of the CsCl type, and the common threefold axis, to one of the other fourfold axes. These relations are expressed by $[010](CsCl)//[11\bar{1}](NaCl)$ and [001](CsCl)//[011](NaCl). However, discrepancies of about 4° were generally observed in these correspondences. The idealized orientation relation is illustrated by the stereographic projection in Fig. 3 as $a \rightarrow b+c$. The same relation was commonly observed with twinning for ammonium halides (*3*).

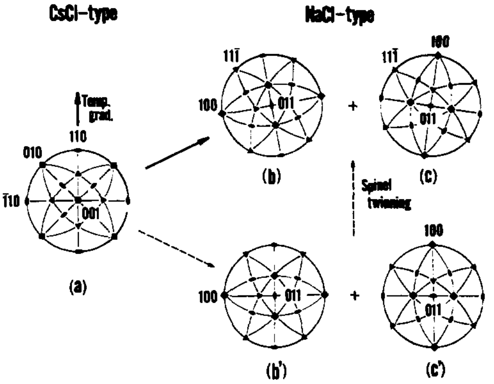

FIG. 3. Stereographic projections of the orientation relations. (a) Changes b + c in the transition from the low- to the high-temperature forms. These high-temperature lattices share $[11\bar{1}]$ and [011], and form the spinel twin. It is expected from the transition mechanism (*6*) that, at the early stages of the transition, the nuclei with orientation b' or c' correspond to the orientation relation between the low-and the high-temperature forms under stress-free conditions (*6*).

Discussion

Under stress-free conditions, a (100)-(NaCl) plane is made from a (110)(CsCl) plane by intralayer rearrangement and uniaxial expansion of the interval (Fig. 4a). In the present case, the (100)(NaCl) plane is made from a vicinal plane, consisting of narrow bands of (110)(CsCl), which is approximately parallel to (750)(CsCl) (Fig. 4b).

Because the vicinal planes have a higher surface energy than the planes with low

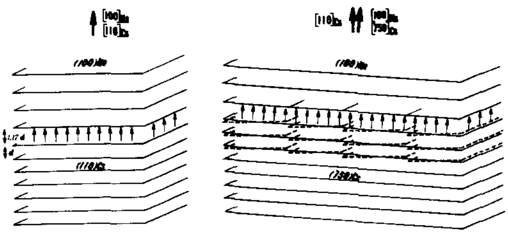

FIG. 4. Schematic illustrations of the formation of (100)(NaCl) layers. (a) Under stress-free conditions, a (110)(CsCl) layer changes into a (100)(NaCl) layer and the direction of expansion is normal to these planes (*6*). (b) Under compressive stress conditions, a vicinal plane consisting of narrow bands of (110)(CsCl) changes into a (100)(NaCl) plane. The vicinal plane is indexed approximately by (750)(CsCl). The narrow bands are shown by broken lines, and the expansion direction between adjacent layers by small arrows.

rational indices, a transition process involving vicinal planes is possible only when uniaxial expansion is inhibited and the transition temperature becomes higher by a few degrees than that for the free uniaxial expansion. At the very early stages of the transition, the nuclei of the high-temperature form seem to have the usual orientation relative to that of the low-temperature form, a → c′ in Fig. 3 (*6*). The direction of the expansion is parallel to the thermal gradient along the axis of the capillary. Near the contact area of the crystal with the glass rods, a compressive stress appears. As the stress reaches an appropriate magnitude, the uniaxial expansion in this direction is disturbed and another expansion occurs along one of the other crystallographically equivalent directions perpendicular to the stress. These nuclei have the orientation relative to that of the mother crystal, a → b′ in Fig. 3. The orientation relation between these two nuclei, b′ and c′, cannot be described by any simple crystallographic relation at this stage. However, if they rotate about 10° to each other around the common twofold axis, they are combined by the spinel twin law (Figs. 3b and c). A pair of nuclei joined to each other in this orientation is expected to persist because both individuals have a common plane of high density which can be used as an interface of the twin boundary.

The growth of the twinned seed seems to start from nucleation at an active center on an edge of the twin boundary. The nucleation center is subject to a compressive stress because of a large volume increment in the phase change, resulting in difficulty in the following nucleations. However, a layer growth of (100)(NaCl) after the nucleation seems to relax the compressive stress. Therefore, the nucleation and the layer growth processes are considered to occur alternately until completion of the transition of the whole specimen.

The layer growth described above is a transformation of many narrow bands of (110) forming a vicinal plane into a flat plane (Fig. 4b). As this transformation proceeds at the boundary area between the high- and the low-temperature forms, ions of the vicinal (750) planes are considered to move systematically to the closest sites in the (100)-(NaCl) layer. In this situation, two kinds of slips along [100](NaCl) and $[01\bar{1}]$(NaCl) take place periodically. These slips result in a uniaxial expansion of the NaCl-type lattice along the direction corresponding to [110]-[CsCl) for one individual of the twinned crystals and to $[1\bar{1}0]$(CsCl) for the other. Thus, the present twinning can be regarded as an effective mechanism by which the crystals can divide the volume changes in the transition between two directions normal to each other and reduce the effect of stress.

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