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Temperature Dependence of Domain Structure of Ammonium Rochelle Salt

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X-ray studies on ammonium Rochelle salt have been made mainly around the phase transition temperature by Weissenberg photographic method with an imaging-plate. We observed positions and intensities of Bragg reflections as a function of temperature. Spontaneous strain occurs below the phase transition temperature and the strain has no temperature dependence. Superlattice reflections occur at the phase transition temperature and its intensities gradually increase with decreasing temperature. The order parameter of the phase transition seems not to be the spontaneous strain but to be the change of the atomic arrangements in the unit cell.

I. INTRODUCTION

Ammonium Rochelle salt ($NaNH_4C_4H_4O_6{\cdot}4H_2O$, ARS) undergoes a first order phase transition from a non-polar orthorhombic phase to a polar monoclinic phase at $T_C = 109$K. ARS crystals are isomorphous with Rochelle salt ($NaKC_4H_4O_6{\cdot}\ 4H_2O$, RS), and the crystallographic space group of the non-polar phase is $P2_12_12$. The space group of the polar phase has been considered to be $P12_11$ since a study by Takagi and Makita, [1] and it has been confirmed by X-ray extinction rules obtained by Weissenberg photographs. [2]

The polar axis of ARS crystals is along the b axis and the monoclinic domain can be reversed only by mechanical stress. Although ARS crystals have interesting physical properties, few structural investigations using the single crystals in the polar phase have been accomplished until now.

Sawada and Takagi [3] first observed superlattice reflections along the a axis in X-ray oscillating crystal photographs at $(T_C - 10)$K. They found some Bragg reflections split into two parts. Later, neutron diffraction experiment of deuterated ARS crystals was carried out by Iizumi and Gesi. [4] So many reflections were detected between reciprocal lattice points (1 1 0) and (2 1 0) at 110K and down to 12K. They reported that these reflections were satellites of $(h \pm n\delta\ k\ l)$ or $(h + \frac{1}{2} \pm n\delta\ k\ l)$ type, and the parameter δ increases with decreasing temperature. Recently, a structural investigation of ARS crystals was carried out at 90K by Brożek and Stadnicka. [5] They reported the superlattice reflections and existence of one pair of satellite reflections around reciprocal lattice point (2 1 0). But correspondences among these experimental results are insufficient.

Domain structure of ARS crystals prevents from analyzing the crystal structure. Using powdered sample of ARS crystal, the Rietveld refinement determination was also carried out at 100K. [6] But the superlattice structure was not detected in the polar phase.

Preliminary studies like domain structure and superlattice structure in the polar phase are necessary to know the nature of the crystal before investigating precise crystal structure. In our previous X-ray measurements, [2] we observed superlattice reflections along the reciprocal a axis as found by Sawada and Takagi, and no incommensurate satellite reflection was detected. The domain structure turned out to be a twin structure and the twin plane is parallel to the b-c plane.

It is important to measure the temperature dependence of the fundamental structural properties to make clear the mechanism of the phase transition in ARS. We report here the temperature dependence of the domain structure and some intensities of Bragg reflections around T_C.

II. EXPERIMENTAL

Single crystals of ARS were grown from aqueous solution with equimolar ratio of $Na_2C_4H_4O_6$ and $(NH_4)_2C_4H_4O_6$ by slow evaporation at room temperature. A cylindrical specimen which is parallel to b-axis with dimensions $0.3\phi \times 1$ mm was prepared from the crystal. The specimen was coated with silicon oil to prevent dehydration and deliquescence and was placed in a glass capillary.

We devised a Weissenberg camera cassette for an imaging-plate. [7] The imaging-plate used here is Fuji Imaging Plate type BAS-III (size $20 \times 25\text{cm}^2$). Fuji BAS-2000 system was used for reading the X-ray scattering intensity distribution on the imaging-plate. Rigaku RU-200 X-ray generator with copper anode was used. A silicon (1 1 1) monochrometer was used to avoid $\lambda/2$ radiation. Reflection index of Bragg reflections are used of the non-polar orthorhombic phase throughout this paper.

Temperature of the sample was controlled by nitrogen cold gas flowing system. Stability of the temperature was ± 0.2K. The first order phase transition of ARS causes

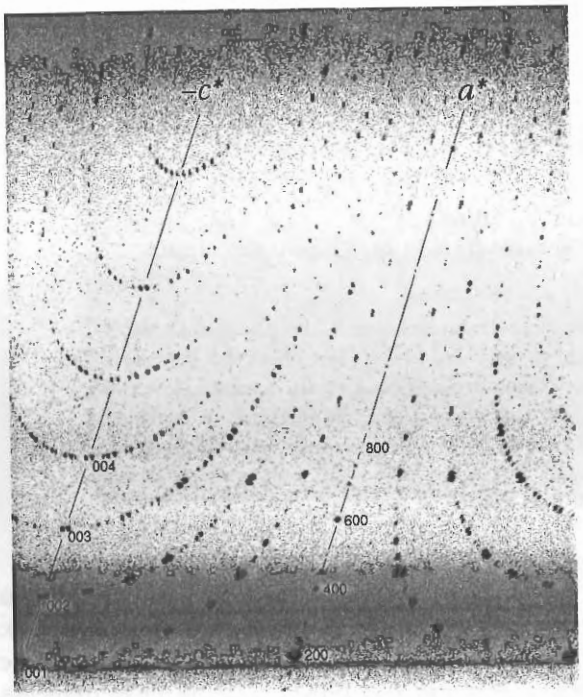

Fig. 1. The Weissenberg photograph of the b axis rotation of ARS at 97 K. A part below origin line of the reciprocal space is omitted. Depth of color of each pixels is not proportional to intensity.

sudden spontaneous strain below T_C. Therefore cooling speed around T_C was controlled within 1K/min to prevent the sample crystals from cracking.

Temperature of sample was measured by a thermocouple inserted into the glass capillary. Temperature of the phase transition of our ARS crystals was about 112K.

III. RESULTS AND DISCUSSION

Weissenberg photographs of the b axis rotation were taken from 293K down to 97K. Fig.1 is a part of the Weissenberg photograph of ARS crystal at 97K. There are three differences compared with photographs taken above T_C. (1) The superlattice reflections along the reciprocal a axis are observed, which indicates that the unit cell doubles in the a axis. (2) All Bragg reflections except reflections on the reciprocal a axis split into pairs of spots below T_C. This means that there are two orientations in ARS domain structure. (3) The odd (h 0 0) reflections on the reciprocal a axis are observed, which are inhibited in the non-polar orthorhombic phase. This shows that the space group of the polar monoclinic phase is $P12_11$. Other photographs taken below T_C have the same features.

Spontaneous strain x_5 is obtained by a distance of the splits of the Bragg reflections. The strain x_5 is related to the monoclinic angle β by

$$x_5 = \beta - \frac{\pi}{2}.$$

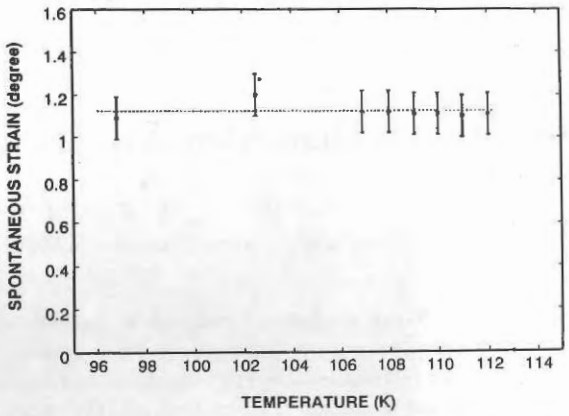

Fig. 2. The temperature dependence of the spontaneous strain x_5 derived from a split distance of Bragg reflection (0 0 1).

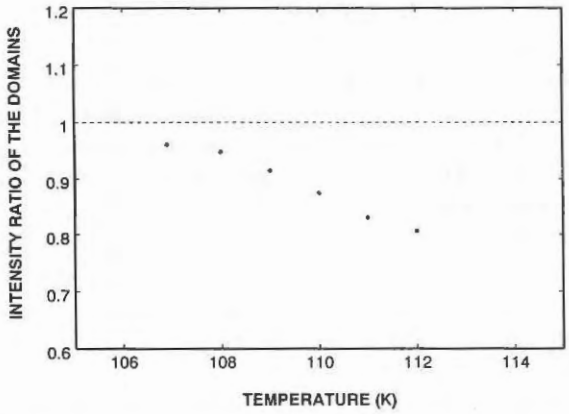

Fig. 3. The temperature dependence of the ratio of intensity of split Bragg reflection (0 0 1).

Note that the strain x_5 which we use here is the shear components of strain, and not equal to the strain tensor ϵ_{13} or ϵ_{31}. Temperature dependence of the spontaneous strain x_5 was measured from the Weissenberg photographs, where the rotation angle of the crystal is about 10 degree. We measured a distance of the splits of Bragg reflection (0 0 1) and derived the monoclinic angle from the distance. Temperature dependence of the spontaneous strain x_5 is shown in Fig.2. Each value has an error about 0.1 degree because of a resolution of the imaging-plate. The spontaneous strain occurs suddenly at T_C with decreasing temperature and the value x_5 is independent of temperature and is constant in the polar phase. This feature is the same as the observations of the temperature dependence of the angle between the extinction positions of the neighboring domains by a polarizing microscope. [1]

The ratio of volume of the two domains is derived by the ratio of intensity of the split Bragg reflections. The intensities were calculated by the least squares method fitting a one-dimensional intensity profile of the split Bragg reflection to two Gaussian distribution functions.

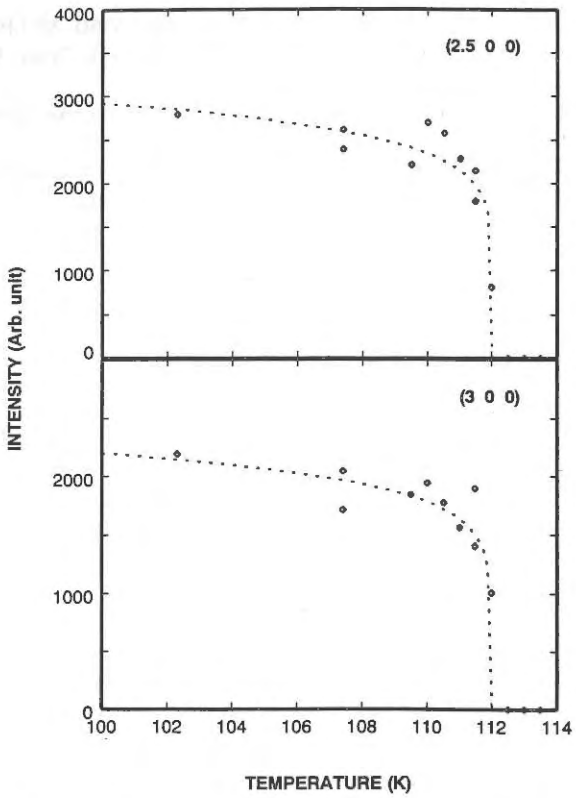

Fig. 4. The temperature dependence of intensities of the superlattice reflections (2.5 0 0) and (3 0 0). Broken line is a guide for eyes.

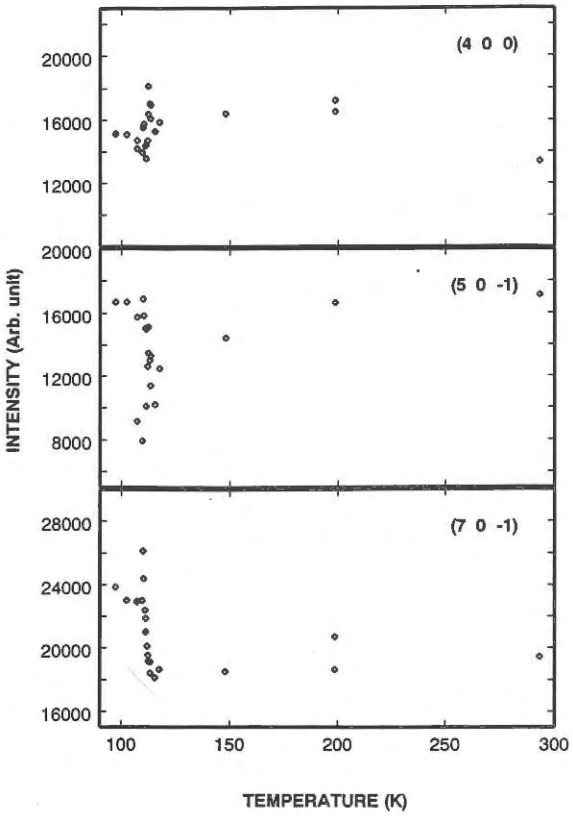

Fig. 5. The temperature dependence of intensities of the Bragg reflections (4 0 0), (5 0 -1) and (7 0 -1).

The one-dimensional intensity profile is obtained easily from two-dimensional intensity distribution of the Weissenberg photograph. Fig.3 shows the temperature dependence of the ratio of volume of the domains. The ratio "1" means that volumes of the two domains are equal each other. The ratio "0.9" means that the ratio of volume is 9:10. The ratio was derived from split Bragg reflection (0 0 1). The value of the ratio was not a certain constant value in every measurement, but we have obtained following feature. The volumes of two types of domains is not equal each other below T_C, and they seem to become equal with decreasing temperature.

The temperature dependence of intensities of superlattice reflection (2.5 0 0) and Bragg reflection (3 0 0) is shown in Fig.4. The intensities were estimated by the least squares method fitting a two-dimensional intensity profile of the superlattice reflection to a Gaussian distribution function. The superlattice reflection appears at T_C, and the intensity increases gradually with decreasing temperature. The feature of Bragg reflection (3 0 0) which are forbidden in the non-polar orthorhombic phase has the same temperature dependence as the superlattice reflections.

The temperature dependence of intensities of Bragg reflections (4 0 0), (5 0 -1) and (7 0 -1) is shown in Fig.5. Intensity of Bragg reflection (4 0 0) increases slightly above T_C with decreasing temperature, and drops slightly at T_C, and increases gradually. Intensity of Bragg reflection (5 0 -1) decreases slightly above T_C with decreasing temperature, and drops at T_C, and increases. Intensity of Bragg reflection (7 0 -1) increases slightly above T_C with decreasing temperature, and still increases gradually below T_C. The intensity is derived from the two-dimensional background peak background method. [8]

In this study, the temperature dependence of the deformation of ARS crystals around T_C is obtained. The spontaneous strain x_5 has no temperature dependence, however, the intensities of superlattice reflections and several Bragg reflections change gradually with temperature. From this feature, we conclude that the order parameter of the phase transition of ARS is not the spontaneous strain because the temperature dependence of the intensities of the Bragg reflections reflects the evolution of the order parameter. It was reported that the direction of the polarization of ARS could not be reversed by electric field but reversed by mechanical stress. The behavior is observed in ferroelastic crystals, [9] however, our observation shows the temperature independent strain. We cannot simply conclude that ARS crystal is ferroelastic. To clarify the nature of the phase transition and the nature of the polar phase, precise studies are required.

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