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Crystal Structure of Rochelle Salt in the Paraelectric Phase

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Temperature dependence of crystal structure of Rochelle salt is studied by X-ray diffraction. As temperature decreased, the O(4) and O(3) atoms of the carboxylate anion have large displacement along the a-axis. The oxygen O(8) has large displacement in the direction opposite to the shift of the carboxylate anion, as in the same displacement observed in the paraelectric phase of $RS_{0.72}ARS_{0.28}$ mixed crystal.

I. INTRODUCTION

Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$, abbreviated as RS) has a ferroelectric phase between the two transition temperatures of $T_{c1} = 297$ K and $T_{c2} = 255$ K and its ferroelectric axis is along the a-axis. [1] On the other hand, ammonium Rochelle salt ($NaNH_4C_4H_4O_6 \cdot 4H_2O$, abbreviated as ARS) has one transition temperature at $T_c = 109$ K and its polar axis is the b-axis. RS and ARS are isomorphous in the paraelectric phase and they form a continuous series of mixed crystals over the whole range of the concentration. The mixed crystal system, $NaK_{1-x}(NH_4)_xC_4H_4O_6 \cdot 4H_2O$ (abbreviated as $RS_{1-x}ARS_x$), is divided into four compositional regions (I to IV) according to the type of the phase transition behavior.

Recently, Suzuki *et al.* [2] carried out X-ray diffraction studies on the mixed crystal $RS_{0.72}ARS_{0.28}$ in the paraelectric phase, and examined structural change with temperature. They had pointed out that the tartrate and the water molecules displace with decreasing temperature. The phase of the mixed crystal studied by them is the same phase as the paraelectric phase of RS, according to the phase diagram obtained by Takagi and Makita. [3] It is very attractive problem for the study of the phase transition mechanism of RS whether we are able to observe the similar displacement in the paraelectric phase as in the mixed crystal of the region III or not. For clarifying the structural changes of RS in the paraelectric phase, we have studied the crystal structure in the paraelectric phase below T_{c2}. The X-ray diffraction studies in the paraelectric phase have been made at the temperature range of 253−153 K. In this paper, we report the temperature dependence of the crystal structure in the paraelectric RS below T_{c2}. Comparison between RS and the mixed crystal are made.

II. EXPERIMENTAL

Experimental conditions of the X-ray study are summarized in Table I. Single crystal of RS was grown in saturated aqueous solution by slow cooling method. A sample crystal with diameter 0.30 mm was prepared. The sample was sealed in a glass capillary tube to prevent dehydration and deliquescence. A nitrogen-gas flow system was used to control the temperature of the sample. The temperature stability of the system was within 1.0 K.

Table 1. Experimental conditions of X-ray study

Crystal growth	Slow cooling method
Specimen shape	Sphere ($2r = 0.30$ mm)
X-ray	Graphite-monochromated Mo-$K\alpha$ ($\lambda = 0.70173$ Å) Rigaku-AFC5R
Scanning mode	ω ($2\theta < 30$ °) $2\theta - \omega$ ($2\theta \geq 30$ °)
Number of reflections	1626 (T=253 K) − 2417 (T=153 K)
Temperature	253, 248, 243, 238, 233, 223, 213, 203, 193, 173 and 153 K
Corrections	Lorentz Polarization Absorption $\mu r = 5.610$ at 253 K Anomalous scattering (Na, K, C and O) Isotropic secondary extinction [6]

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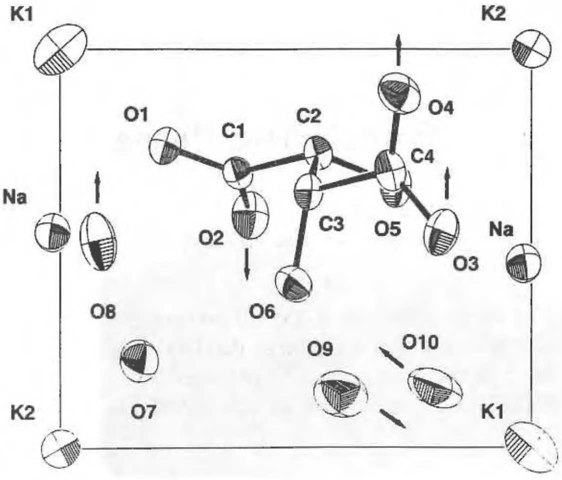

Fig. 1. Projection of the asymmetric unit of the crystal structure of the paraelectric phase of RS (T=153 K on (001)).

A four-circle diffractometer (Rigaku AFC-5R) with pyrolytic graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$Å) was used. The data were corrected for Lorentz, polarization, absorption and extinction effects. All of the reflections were used for least squares refinements. The number of reflections measured were about 2000. The discrepancy factor R and the weighted R factor are defined as $R = \sum \| F_o | - | F_c \| / \sum | F_o |$ and $wR = \left[\sum w\left(| F_o | - | F_c |\right)^2 / \sum w \mid F_o \mid^2\right]^{1/2}$,where F_o is the observed structure factor and F_c is the calculated structure factor. The weighting function is $w^{-1} = \sigma^2(F_o) + (0.01F_o)^2$. The lattice constant shows a nearly linear relationship with temperature. The positional and anisotropic thermal parameters of except H atoms were refined. The full-matrix least-squares calculations were carried out using the program RADIEL. [4] The selected crystal data are: (I) at T=253(1) K: R=0.0973, wR=0.0727, ND(Number of reflections)=1626, a=11.878(5), b=14.266(4), c=6.224(2)Å; (II) at T=153(1) K: R=0.0847, wR=0.0746, ND=2417, a=11.811(8), b=14.227(6), c=6.200(3)Å.

III. RESULT AND DISCUSSION

A. Relative displacements with decreasing temperature

ORTEP-plot [5] of the one-quarter of the unit cell at T=153 K is given in Fig.1. The fractional atomic coordinates at 253 K and 153 K are listed in Table II. The relative displacement of Na and K(1) atoms are obtained. The displacement of Na has component along the $+c$-axis, and that of K(1) has a slight amount of component along the $-c$-axis. These results represent the same feature as $RS_{0.72}ARS_{0.28}$ mixed crystal, but the displacement of K(2) as reported mixed crystal could not be found in this study.

Table 2. The fractional atomic coordinates at T=253 K and 153 K

Temp. K	253	153
Na		
x	0.2316(2)	0.2322(2)
y	0.9934(2)	0.9932(2)
z	0.5214(4)	0.5159(3)
K(1)		
x	0.0000	0.0000
y	0.0000	0.0000
z	0.0444(5)	0.0428(3)
K(2)		
x	0.0000	0.0000
y	0.5000	0.5000
z	0.1595(4)	0.1605(3)
C(1)		
x	0.1547(6)	0.1548(4)
y	0.1900(5)	0.1894(4)
z	0.2855(13)	0.2832(9)
C(2)		
x	0.1240(6)	0.1242(5)
y	0.2739(5)	0.2737(4)
z	0.4237(12)	0.4230(9)
C(3)		
x	0.1766(6)	0.1768(4)
y	0.2622(5)	0.2630(4)
z	0.6463(13)	0.6484(9)
C(4)		
x	0.1500(7)	0.1480(5)
y	0.3502(6)	0.3499(4)
z	0.7790(13)	0.7831(9)
O(1)		
x	0.1199(4)	0.1202(3)
y	0.1097(3)	0.1093(3)
z	0.3503(9)	0.3489(7)
O(2)		
x	0.2102(5)	0.2126(3)
y	0.2039(4)	0.2045(3)
z	0.1184(9)	0.1182(6)
O(3)		
x	0.2319(5)	0.2288(4)
y	0.4051(3)	0.4061(3)
z	0.8146(9)	0.8196(7)
O(4)		
x	0.0518(5)	0.0479(3)
y	0.3602(4)	0.3586(3)
z	0.8462(10)	0.8488(7)
O(5)		
x	0.1660(4)	0.1667(3)
y	0.3564(3)	0.3572(3)
z	0.3226(9)	0.3233(7)
O(6)		
x	0.2969(4)	0.2969(3)
y	0.2491(4)	0.2495(3)
z	0.6278(9)	0.6323(7)
O(7)		
x	0.3961(4)	0.3964(3)
y	0.0850(4)	0.0852(3)
z	0.4828(9)	0.4859(7)
O(8)		
x	0.2422(6)	0.2369(4)
y	0.0417(3)	0.0421(3)
z	0.8878(8)	0.8806(6)
O(9)		
x	0.4380(5)	0.4404(3)
y	0.3012(4)	0.3062(3)
z	0.0370(10)	0.0323(7)
O(10)		
x	0.4263(5)	0.4232(3)
y	0.3943(4)	0.3911(3)
z	0.4223(11)	0.4295(8)

For the tartrate molecules, there are no relative displacement of C(1), C(2), C(3) and C(4). The oxygens O(3) and O(4) of the carboxylate anion have large dis-

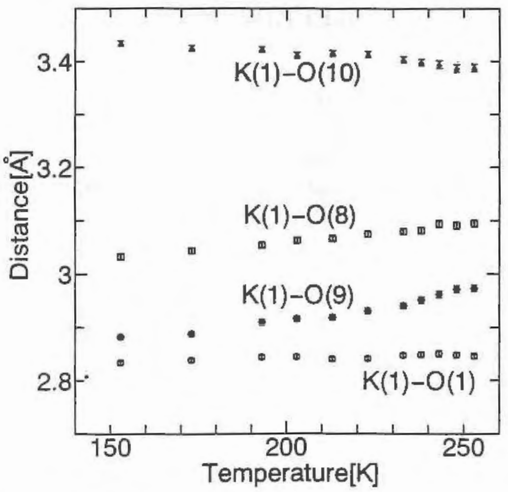

Fig. 2. Temperature dependence of interatomic distance between potassium (1) and oxygen atoms.

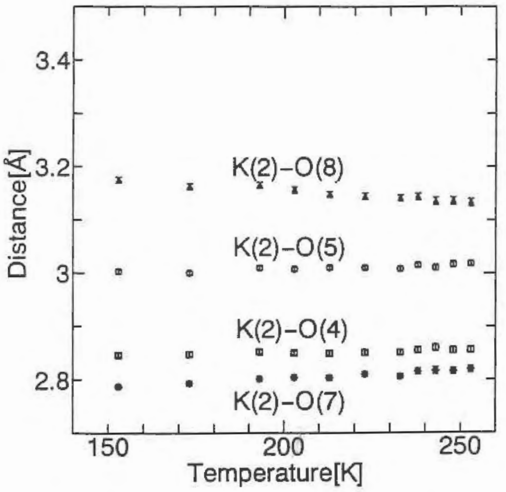

Fig. 3. Temperature dependence of interatomic distance between potassium (2) and oxygen atoms.

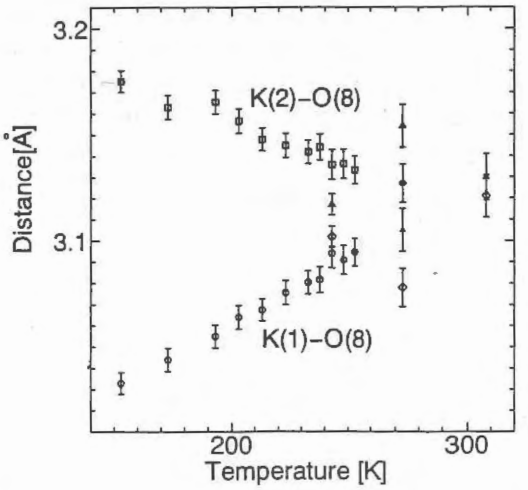

Fig. 4. Interatomic distance of K(1)-O(8) and K(2)-O(8). The values of the data at 308 K, 243 K and those of two at 273 K are cited from Ref.7.

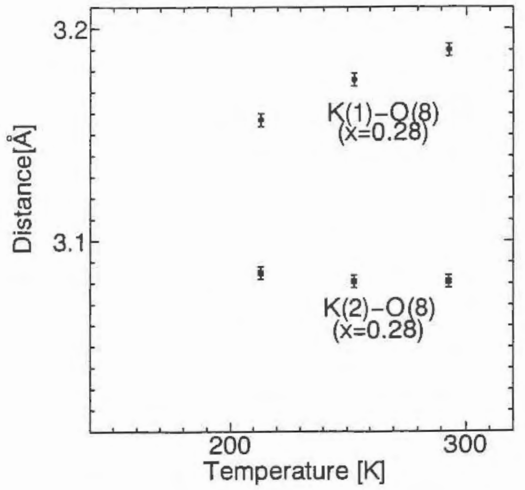

Fig. 5. Temperature dependence of K(1)-O(8) and K(2)-O(8) in $RS_{0.72}ARS_{0.28}$ mixed crystal. (Ref.2)

placement along the *a*-axis. The displacement of these atoms has the same direction obtained in $RS_{0.72}ARS_{0.28}$ mixed crystal.

The oxygen O(8), linked to O(3) and O(2) by the hydrogen bonds is displaced in the direction opposite to the shift of the carboxylate anion. The oxygens O(9) and O(10) have the large displacement. The oxygen O(9) moves toward K(1) with decreasing temperature. The oxygen O(10) moves away from K(1) and moves toward O(6) which are connected to O(10) by hydrogen bond. These structural changes are the same changes observed in $RS_{0.72}ARS_{0.28}$ mixed crystal.

B. Interatomic distance with decreasing temperature

As temperature decreased, the interatomic distances K(1)-O(8), K(1)-O(9) and K(2)-O(7) become short, but K(1)-O(10) and K(2)-O(8) become long (see Fig.2 and Fig.3). The distances K(1)-O(8), K(1)-O(9) and K(1)-O(10) represent the same feature in $RS_{0.72}ARS_{0.28}$ mixed crystal, but the change of the distance K(2)-O(8) are different. In $RS_{0.72}ARS_{0.28}$ mixed crystal, the distance K(2)-O(8) is constant, and does not exhibit temperature dependence. Figure 4 shows the temperature dependence of the interatomic distance K(1)-O(8) and K(2)-O(8). [7] Figure 5 shows temperature dependence of interatomic distances between potassium and oxygen, of which are exhibited in mixed crystal $RS_{0.72}ARS_{0.28}$. Na is surrounded by six oxygens. As the temperature is lowered, all Na-O distances become short as reported in $RS_{0.72}ARS_{0.28}$ mixed crystal.

For the interatomic distances between oxygens that form hydrogen bonds, the distances O(8)-O(2), O(8)-O(3) and O(10)-O(9) are kept constant, while those of O(6)-O(10) become short with decreasing temperature. The oxygens O(9) and O(10) have large displacement with temperature, but the distances between them are kept constant. These features show that the connection between these atoms are so strong and these features are observed in $RS_{0.72}ARS_{0.28}$ mixed crystal as well.

IV. CONCLUSION

In RS, the atoms which have large displacement with decreasing temperature are the same for $RS_{0.72}ARS_{0.28}$ mixed crystal, and the direction of the displacement with decreasing temperature are similar too. However, the relation between K(2) and O(8) is somewhat different from that in the mixed crystal.

REFERENCES

[1] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon. Oxford, 1962), Chap.VII.
[2] E. Suzuki, H. Kabasawa, T. Honma, R. Nozaki and Y. Shiozaki, to be published in Acta Cryst. **B52** (1996).
[3] Y. Takagi and Y. Makita, J. Phys. Soc. Jpn. **13**, 272 (1958).
[4] P. Coppens, T.N. Guru Row, P. Leung, E.D. Stevents, P.J. Becker, and Y.W. Yang, Acta Cryst. **B35**, 63 (1979).
[5] C.K. Johnson, *ORTEPII*, Report No. ORNL-5138 (1976).
[6] W.H. Zachariasen, Acta Cryst. **23**, 558 (1967).
[7] E. Suzuki and Y. Shiozaki, Phys. Rev. **B53**, 5217 (1996).