

Ferroelectric displacement of atoms in Rochelle salt

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The crystal structure of Rochelle salt in the ferroelectric phase is studied by means of x-ray diffraction. The structures of the two paraelectric phases are also redetermined to obtain the displacements of the atoms owing to the phase transitions. Cooperative displacements of the atoms responsible for the appearance of the spontaneous polarization are obtained. The displacements consist of the movements of the tartrate molecules and the water molecules in a frame composed of K and Na ions. During the successive phase transitions there are several interatomic distances maintained constant. The direction of planes made of carbons of the tartrate molecules is practically unchanged throughout the phase transitions.

I. INTRODUCTION

Rochelle salt, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (abbreviated as RS) is a well-known ferroelectric. This crystal exhibits ferroelectric properties between 255 and 297 K, and the spontaneous polarization P_s appears along the a axis.^{1,2} The symmetry of the crystal structure in the two paraelectric phases is orthorhombic (space group $P2_12_12$), and that in the ferroelectric phase is monoclinic (space group $P2_111$).³

X-ray structure analysis of RS was first reported by Beevers and Hughes.⁴ They have pointed hydrogen bonds running among tartrate molecules and water molecules, and they intended to account for the ferroelectric behavior. They have particularly emphasized the significance of the hydrogen bond between O(1) and O(10), which lies parallel to the direction of the spontaneous polarization. In order to determine the locations of the hydrogen atoms assumed by Beevers and Hughes, Frazer, Mckeown, and Pepinsky⁵ carried out the investigation of two-dimensional neutron diffraction on deuterated RS in the ferroelectric phase. They reported that an orientational motion of the hydroxyl group O(5)-D is possibly responsible for the appearance of the spontaneous polarization.

On the other hand, Shiozaki and Mitsui⁶ have commented by x-ray study that the electron density peak, which is located on the position of the hydrogen atom of O(5)-H in RS is sharp in the two paraelectric phases, and it seems that O(5)-H make the intramolecule hydrogen bond to O(2). Recently, Iwata, Mitani, and Shibuya^{7,8} have carried out neutron-diffraction studies on deuterated RS ($\text{NaKC}_4\text{O}_6\text{H}_2\text{D}_2 \cdot 4\text{H}_2\text{O}$) in the two paraelectric phases ($T=313$ and 78 K). They have shown that there is no indication of the reorientational or the anisotropic motions of O(5)-D. They have especially commented on the existence of the flip-flop motion of the water molecule $\text{D}_2\text{O}(8)$. Their results show that the hydroxyl group has no important role on the phase transitions.

It is essential to observe directly the structure of the ferroelectric phase in order to clarify the structural change. Since the crystal in the ferroelectric phase has domain structures,⁹ the preparation of the crystal of the monodomain state is required for the diffraction study. The use of the sample having the domain structure results in the measurements of

mixed Bragg intensities of the two independent quadrants in the monoclinic crystal system. It seems that many works have not attained the true structure because of ignorance of the domain structure.

We have studied the crystal structure of RS in the ferroelectric phase ($T=273$ K) as well as the two paraelectric phases ($T=243$ and 308 K) in order to clarify the precise structural changes associated with the spontaneous polarization. The x-ray diffraction study in the ferroelectric phase ($T=273$ K) has been performed under a monodomain state; the spontaneous polarization has the maximum value at the temperature. The monodomain state is realized by the application of the dc field.

In the paper, we report the atomic displacements giving the spontaneous polarization and show the collective displacements composed of the tartrate molecules and water molecules observed in the phase transition. Discussions are made together with the dielectric, NMR studies.

II. EXPERIMENTAL AND LEAST-SQUARES REFINEMENTS

Single crystals were grown in saturated aqueous solution of RS (the purity of the reagent exceeds 99.5%) at room temperature after three cycles of recrystallization. A sample crystal was prepared in a cylindrical shape the length of which was about 2.0 mm and diameter of which was about 0.7 mm. The cylindrical axis was parallel to the ferroelectric a axis. Silver paste was used as electrodes for the purpose of maintaining a monodomain state by applying a dc bias field, and the sample was sealed in a glass capillary tube to avoid dehydration and deliquescence. A nitrogen-gas flow system was used to control the temperature of the sample. In all cases, the temperature stability was better than 1.0 K. In the ferroelectric phase (at $T=273$ K), the applied dc electric field was 200 V/cm: the coercive field E_c at this temperature is about 130 V/cm. A four-circle diffractometer (Rigaku AFC-5R) with pyrolytic graphite-monochromated Mo- $K\alpha$ radiation ($\lambda=0.71073$ Å) was used. During the collection of intensity data in the ferroelectric phase, the reflection (050) was monitored: the intensity of the reflection (050) is very sensitive to the temperature.¹⁰

The reflections with $F_o > 3\sigma(F_o)$ were used for the least-

TABLE I. Summary of the data collections and structure refinements of RS at the three temperatures.

Temperature (K)	243	273	308
Number of reflections measured	1157	4301	2330
Number of unique reflections observed	1012	2690	1310
[$F_o > 3\sigma(F_o)$]			
Bravais lattice	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12$	$P2_111$	$P2_12_12$
Number of formula unit in the unit cell	4	4	4
Number of parameters refined	183	361	183
R^a	0.0490	0.0744	0.0912
wR^b	0.0593	0.1140	0.1297
Lattice constants ^c			
a (Å)	11.860	11.882	11.927
b (Å)	14.244	14.268	14.292
c (Å)	6.215	6.222	6.225

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}. \text{ The weighting function is } w^{-1} = \sigma^2(F_o) + (0.05F_o)^2.$$

^cReference 15.

squares calculations, where F_o is the observed structure factor and $\sigma(F_o)$ is the standard deviation estimated by the statistics of counts of x rays. The observed intensities were corrected for the irradiated crystal volume as well as Lorentz polarization and absorption. A summary of the data collections and the refinements at the three temperatures is given in Table I. In the least-squares refinements of the paraelectric phases, the positional parameters reported by Beevers and Hughes⁴ were used as initial ones except for hydrogen atoms. Those of the hydrogen atoms were obtained from the difference Fourier maps. In the ferroelectric phase, the refinements were started by using the parameters obtained by Mitani *et al.*¹¹ In the ferroelectric phase, the origin was fixed on K(1) during the refinement. The full-matrix least-squares calculations were accomplished by RADIEL,¹² and in the course of the refinements the correction for isotropic secondary extinction was carried out. The least-squares calculations were made by minimizing the functions $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o) + (aF_o)^2$, where w is weighting function, F_c is the calculated structure factor, and a is an adjustable parameter. We have chosen $a = 0.05$ in the way that the value of $\sum w(|F_o| - |F_c|)^2$ remains constant when the reflections are grouped in $|F_o|$ or $\sin \theta/\lambda$ intervals. The atomic scattering factors and anomalous scattering factors were taken from *International Tables for X-ray Crystallography*.¹³ The thermal parameters of hydrogen atoms were treated as if they had a common value U_H : the value $U_H = 0.025$ gave the minimum R factor. Finally, R factors at $T = 308$ K, $T = 273$ K, and $T = 243$ K were 0.0912, 0.0744, and 0.0490, respectively. The final results of the atomic positions and the equivalent thermal parameters at 273 K is given in Table II.

III. STRUCTURE DESCRIPTION OF THE FERROELECTRIC PHASE, $T = 273$ K

A. Relative displacements associated with the phase transitions

In the ferroelectric phase, the two-fold screw axis, which is parallel to the b axis of the paraelectric phase, disappears. Thus, the space group changes from $P2_12_12$ to $P2_111$, and the asymmetric unit in the ferroelectric phase becomes twice that in the paraelectric phase (Fig. 1). In this paper, the numbers assigned to the atoms in the ferroelectric phase are suffixed A or B . The atoms suffixed A are related to those suffixed B by the twofold screw axis parallel to the b axis in the paraelectric phase.

The obtained result can be used to calculate the relative displacements between two molecules in the asymmetric unit. In the ferroelectric phase, the two molecules are related by a pseudo- $2_1[010]$ operation. The pseudosymmetry operation is applied to the atomic coordinate (x_B, y_B, z_B) , and the resulting coordinate is compared with the atomic position (x_A, y_A, z_A) . The differences between these positions are defined: $\delta x = a(x_A + x_B - 0.5)$, $\delta y = b(y_A - y_B + 0.5)$, $\delta z = c(z_A + z_B - 1.0)$, and $\Delta = (\delta x^2 + \delta y^2 + \delta z^2)^{0.5}$ (Table III). In those calculations, the lattice constants by the Bronowska¹⁵ have been used. The large relative displacements of atoms were obtained for O(10), O(3), O(8), O(6), and O(4) ($\Delta > 0.06$ Å). Those displacements of the oxygens except O(6) have large components along the a axis. Also the displacement of C(4) is large along the a axis ($\delta x > 0.03$ Å). It is clarified that the carboxylate anion O(3)-C(4)-O(4) in the tartrate molecule has a large relative displacement

TABLE II. Final positional parameters in fraction and the equivalent thermal parameters for the nonhydrogen atoms of Rochelle salt at $T=273$ K: $U_{eq}=(1/3)\sum U_{ij}a_i^*a_j^*a_i\cdot a_j$.

	x	y	z	$U_{eq} (\times 10^4 \text{ \AA}^2)$
Na(A)	0.2684(4)	0.4933(1)	0.4763(4)	223(15)
Na(B)	0.2322(4)	0.9932(2)	0.5200(5)	242(15)
K(1)	0	1.0009(1)	0.0460(3)	510(11)
K(2)	0.0000(3)	0.5011(1)	0.1595(2)	286(7)
C(1A)	0.1544(6)	0.1880(4)	0.2825(11)	187(28)
C(1B)	0.3449(6)	0.6883(4)	0.7184(9)	180(27)
C(2A)	0.1252(6)	0.2741(4)	0.4218(10)	182(27)
C(2B)	0.3755(7)	0.7734(4)	0.5764(9)	191(28)
C(3A)	0.1787(6)	0.2639(4)	0.6416(9)	167(26)
C(3B)	0.3225(6)	0.7638(4)	0.3527(10)	182(28)
C(4A)	0.1538(7)	0.3516(4)	0.7764(8)	204(28)
C(4B)	0.3494(7)	0.8508(4)	0.2212(10)	236(31)
O(1A)	0.1202(5)	0.1087(3)	0.3498(9)	239(24)
O(1B)	0.3805(5)	0.6093(3)	0.6517(8)	213(22)
O(2A)	0.2091(6)	0.2036(3)	0.1173(7)	265(25)
O(2B)	0.2894(6)	0.7028(3)	0.8801(8)	261(25)
O(3A)	0.2353(6)	0.4049(3)	0.8122(9)	338(30)
O(3B)	0.2700(7)	0.9072(4)	0.1892(10)	368(31)
O(4A)	0.0549(6)	0.3628(4)	0.8445(9)	299(28)
O(4B)	0.4489(6)	0.8601(4)	0.1520(8)	301(28)
O(5A)	0.1617(7)	0.3574(3)	0.3217(10)	256(27)
O(5B)	0.3357(6)	0.8570(3)	0.6738(7)	222(23)
O(6A)	0.2957(6)	0.2484(4)	0.6212(9)	250(26)
O(6B)	0.2050(5)	0.7480(3)	0.3684(8)	239(25)
O(7A)	0.3953(6)	0.0825(3)	0.4844(10)	286(28)
O(7B)	0.1052(6)	0.5830(4)	0.5177(11)	313(30)
O(8A)	0.2400(8)	0.0395(4)	0.8828(8)	432(36)
O(8B)	0.2555(8)	0.5418(4)	0.1121(10)	433(38)
O(9A)	0.4376(7)	0.3009(6)	0.0358(14)	519(47)
O(9B)	0.0625(7)	0.8047(6)	0.9628(12)	465(44)
O(10A)	0.4256(7)	0.3993(5)	0.4183(15)	502(43)
O(10B)	0.0777(6)	0.8932(5)	0.5698(12)	425(38)

along the a axis, and the oxygen of the water molecule O(8) also has a large relative displacement in the opposite direction.

B. Change of interatomic distances in the ferroelectric phase

K(1) is coordinated by six oxygens, which are located within 3.2 Å. The distance K(1)-O(10) is so large that the K(1) atom is not strongly interacting with O(10). The other potassium atom, K(2) is coordinated by eight oxygens, which are also located within 3.2 Å. The circumstances of K(1) differ largely from those of K(2).

In the ferroelectric phase, there are two kinds of the distances for K(1)-O(8) and also for K(2)-O(8) (Table IV). It shows that O(8A) approaches K(1) and O(8B) displaces away from K(1). The significant displacements of the atoms are observed around the cations, and they are responsible for the appearance of the spontaneous polarization of RS. The changes are most remarkable among many other changes.

The interatomic distances and angles in the tartrate molecules at three temperatures are practically unchanged. The

planarity and the direction of the plane made by C(1)-C(2)-C(3)-C(4) is not affected through the phase transitions. These results show that there is little deformation in the tartrate molecules with the phase transitions.

Two hydrogen bonds related to O(8) have different behaviors associated with the phase transitions. The distances O(8A)-O(3B) and O(8B)-O(3A), which are nonequivalent crystallographically in the ferroelectric phase, are almost same to those in the paraelectric phase. On the other hand, those of O(8A)-O(2A) and O(8B)-O(2B) are significantly different. O(10) has three hydrogen bonds; two are related to O(4) and O(1) in the carboxylate anions and one is related to O(6) in the hydroxyl group. Among the three bonds, the distance O(6)-O(10) is longer a little than the ordinary hydrogen bond length. In the ferroelectric phase, it becomes two significantly different mates [O(6A)-O(10A) and O(6B)-O(10B)]. These results show that the distances O(8)-O(2), O(9)-O(2), and O(6)-O(10), which connect the water molecules to the tartrate molecules with hydrogen bonds, make significant changes through the phase transitions.

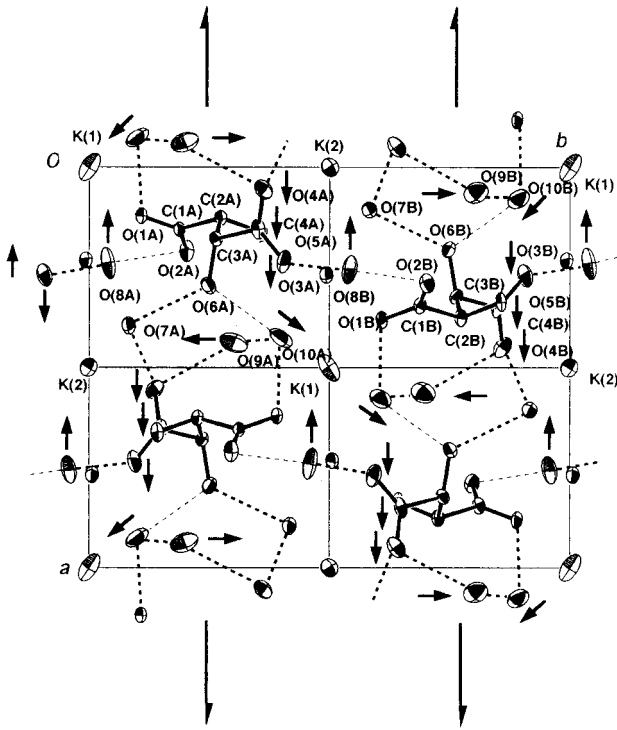


FIG. 1. Schematic view of the atomic displacements in the ferroelectric phase ($T=273$ K). Arrows indicate the directions of the displacements responsible to the appearance of the spontaneous polarization. Thick broken lines indicate the hydrogen bonds whose lengths are kept constant through the phase transitions. Thin broken lines indicate hydrogen bonds whose lengths are changed. ORTEPII (Ref. 14) was used.

IV. RESULTS AND DISCUSSIONS

The characteristic features are summarized as follows (see Fig. 1). Several interatomic distances change through the phase transitions. Among them there are interatomic distances that split into two significantly different ones in the ferroelectric phase: K(1)-O(8A) and K(1)-O(8B), and K(2)-O(8A) and K(2)-O(8B). Also it should be pointed that there are two distances between oxygens to split into significantly different pairs through the phase transitions; the pairs of O(8A)-O(2A) and O(8B)-O(2B), and also O(6A)-O(10A) and O(6B)-O(10B).

The oxygen O(8) behaves as a common nearest neighbor atom of Na, K(1), and K(2). It is situated at almost the middle point between K(1) and K(2) and has the large thermal motion directed to them. It is considered that the interactions between O(8) and the two K atoms cause the strong anisotropic thermal motion.

In the process of the ferroelectric phase transition, O(8) makes the considerably large displacement along the a axis, while C(4), O(3), and O(4) atoms (carboxylate anion) displace in the opposite direction. These facts show that the displacement of O(8) is accompanied by the movement of the tartrate molecule keeping the distance between O(8) and O(3) constant. It is considered that the displacement of O(8) must have an important role for the ferroelectric phase transition; however, the sign of an order-disorder behavior is not detected. For the establishment of the phase transition

TABLE III. The relative displacements of atoms due to the appearance of the spontaneous polarization. They are defined as follows: $\delta x = a(x_A + x_B - 0.5)$, $\delta y = b(y_A - y_B + 0.5)$, $\delta z = c(z_A + z_B - 1.0)$, and $\Delta = (\delta x^2 + \delta y^2 + \delta z^2)^{0.5}$. In the paraelectric phase, the values of δx , δy , δz , and Δ are zero.

	δx (Å)	δy (Å)	δz (Å)	Δ (Å)
Na	0.009(9)	-0.001(4)	-0.022(5)	0.024(20)
C(1)	-0.007(14)	0.004(11)	0.005(12)	0.009(20)
C(2)	0.010(15)	-0.009(11)	-0.011(11)	0.017(27)
C(3)	0.014(14)	-0.002(11)	-0.034(11)	0.037(34)
C(4)	0.038(16)	-0.011(11)	-0.014(11)	0.042(42)
O(1)	0.008(11)	0.008(8)	0.010(10)	0.015(22)
O(2)	-0.015(14)	-0.012(8)	-0.016(9)	0.025(30)
O(3)	0.063(15)	0.032(9)	0.009(11)	0.071(52)
O(4)	0.046(14)	-0.037(11)	-0.021(10)	0.063(50)
O(5)	-0.029(15)	-0.005(8)	-0.027(10)	0.040(39)
O(6)	0.008(13)	-0.006(9)	-0.064(10)	0.065(40)
O(7)	0.007(14)	0.007(9)	0.013(13)	0.016(26)
O(8)	-0.052(19)	0.032(11)	-0.031(11)	0.068(58)
O(9)	0.001(16)	0.054(17)	-0.007(16)	0.054(46)
O(10)	0.040(15)	-0.086(14)	-0.073(16)	0.120(77)

mechanism, it is very important whether the order-disorder behavior is observed or not with diffraction study. The thermal parameter of O(8) does not have any special anomaly during the phase transition. The thermal parameters of all other atoms also has no anomalous behavior.

Our results can be supported by many other experimental facts as follows. The complex dielectric dispersion of RS at the microwave range has been measured by Sandy and Jones.¹⁶ They have found the critical slowing down phenomena at the two transition points in the frequency range from 4–12 GHz. The critical relaxation phenomena seem to be mainly originated in these collective motions and show the behavior of the cooperative dipole interaction between them. It is generally believed that such phenomena in this frequency range are an evidence of the presence of the relaxational motion of the orientation of molecules, and they are observed in other ferroelectrics such as TGS, NaNO₂, DSP, and (NH₄)₂SO₄, etc., which are considered to be of the order-disorder type. Blinc, Petkovsek, and Zupancic,¹⁷ and Miller and Casabella¹⁸ have shown that the displacements of O(8) and O(5)-H contribute to the temperature dependence of the electric-field-gradient (EFG) tensor around Na atoms. Our study shows not only that the displacements of O(8) and O(5) affect the EFG tensors but also those of all neighboring oxygen atoms surrounding Na atoms, especially O(3), affects because the octahedron constructed by the neighboring oxygen atoms displaces against the Na atoms in the ferroelectric phase. Trontelj¹⁹ have carried out NMR studies on flipping motions of the four water molecules. Their results show the flipping motions are not affected during the phase transition. The behavior does not contradict the fact obtained by our x-ray analysis that the thermal behaviors of the four oxygen atoms of the water molecules display no clear change with the phase transition.

Our study has revealed that the tartrate molecules and water molecules displace against the flame composed of potassium and sodium ions. Especially the displacements of

TABLE IV. Selected interatomic distances of the three phases.

$T=243$ K (paraelectric phase)		$T=273$ K (ferroelectric phase)		$T=308$ K (paraelectric phase)	
	Distance (Å)		Distance (Å)		Distance (Å)
Na-O(3)	2.460(4)	Na(A)-O(3A)	2.473(7)	Na-O(3)	2.465(8)
		Na(B)-O(3B)	2.438(7)		
Na-O(8)	2.368(5)	Na(A)-O(8B)	2.376(7)	Na-O(8)	2.382(8)
		Na(B)-O(8A)	2.355(6)		
K(1)-O(8)	3.102(5)	K(1)-O(8A)	3.078(9)	K(1)-O(8)	3.121(10)
		K(1)-O(8B)	3.127(9)		
K(1)-O(10)	3.398(7)	K(1)-O(10B)	3.465(8)	K(1)-O(10)	3.363(11)
		K(1)-O(10A)	3.341(9)		
K(2)-O(8)	3.117(5)	K(2)-O(8B)	3.105(10)	K(2)-O(8)	3.130(11)
		K(2)-O(8A)	3.154(10)		
O(8)-O(2)	2.757(6)	O(8A)-O(2A)	2.783(7)	O(8)-O(2)	2.747(10)
		O(8B)-O(2B)	2.743(8)		
O(8)-O(3)	2.692(5)	O(8A)-O(3B)	2.707(8)	O(8)-O(3)	2.697(10)
		O(8B)-O(3A)	2.712(8)		
O(9)-O(2)	3.134(8)	O(9A)-O(2A)	3.090(11)	O(9)-O(2)	3.113(21)
		O(9B)-O(2B)	3.107(11)		
O(6)-O(10)	2.892(7)	O(6A)-O(10A)	2.935(10)	O(6)-O(10)	2.927(11)
		O(6B)-O(10B)	2.856(10)		

O(8), O(9), and O(10) around K(1) are large (see Fig. 1), and those oxygen atoms and K(1) have large thermal motion in all phases. We cannot explain well the relation between the mechanism of the phase transition and the displacements of O(9) and O(10).

It was recently reported by far-infrared transmission and reflection spectra and Raman spectra studies²⁰ that the type of the phase transition in RS is a mixture of displacive and

order disorder. It would be necessary to clarify what atoms have the order-disorder features by crystallographic work.

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