

Uniaxial Stress Effect of ^{23}Na NMR and Spontaneous Polarization in Rochelle Salt

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Piezoelectric constants in Rochelle salt in the ferroelectric phase were determined at 276 K by a hysteresis bridge to be $d_{11} = -640 \pm 10 \text{ pC.N}^{-1}$ and $d_{13} = 75 \pm 5 \text{ pC.N}^{-1}$. The value of $d_{13} = 50 \pm 5 \text{ pC.N}^{-1}$ obtained by the NMR method was discussed by the Blinc model in terms of displacement of H(5) proton which is related to the change in the FFG tensor of Na at the phase transition.

§1. Introduction

Rochelle salt (RS) is a well-known substance for its unique dielectric behavior showing only a limited temperature range of ferroelectricity between 297 and 255 K. In order to investigate the microscopic origin of this interesting property, nuclear magnetic resonance (NMR) has been one of important tools. Blinc, *et al.*⁽¹⁾ and Miller, *et al.*⁽²⁾ studied ^{23}Na NMR in deuterated and ordinary RS and determined the values of displacement of some atoms associated with the phase transition. Fitzgerald and Casebella⁽³⁾ found that the spontaneous polarization P_s is proportional to the magnitude of site splitting in the satellite lines of ^{23}Na in the ferroelectric phase. Later, NMR was used to investigate the radiation effect on the ferroelectric properties and on the phase transition in RS, instead of hysteresis loop method in which unfavorable electrocaloric effect usually occurred.⁽⁴⁾ The microscopic origin of the ferroelectricity in RS has been ascribed to the ordering of OH(5) dipoles by a calculation of EFG tensor^(1,2) and by neutron diffraction studies.^(5,6)

In this report, some results of quadrupole effects of NMR and hysteresis loop measurements of a single crystal of RS under a uniaxial stress will be shown and a model for the microscopic origin of piezoelectric property in the ferroelectric phase will be discussed. There is a report⁽⁷⁾ on the effect of hydrostatic pressure on RS in which the transition shifts to higher temperatures with increasing pressure, but no appreciable change in P_s was observed. Hydrostatic pressure affects the crystal isotropically, while a uniaxial stress produces an aniso-

tropic effect on the lattice and may affect the spontaneous polarization in a different manner depending on its relative direction.

§2. Experimental Procedures and Results

Single crystals were grown from an aqueous solution at 310 K. Large crystals, typically $2 \times 3 \times 4 \text{ cm}^3$, were cut into a cylinder of 1.8 cm long and 1.2 cm across with its axis parallel to the crystallographic c axis for NMR experiments. Four thin plates were prepared for the a - and c -axis compression in hysteresis loop measurements. Planes on which uniaxial stress was applied were made parallel and polished.

2.1 Nuclear magnetic resonance of ^{23}Na

Sodium NMR was observed using an FET marginal oscillator by external magnetic field sweep. The frequency of oscillator was stable to within a few parts in 10^5 . There are four central and eight satellite lines in a general field direction in the paraelectric phase because there are four sodium sites in an orthorhombic unit cell of $P2_12_12$. If the field direction is perpendicular to one of the crystal axes, a , b , and c , two of these lines coalesce into a single line. In the ferroelectric phase this single line splits again into two except for the field perpendicular to the a axis because of lowering of the symmetry to $P2_1$. The magnitude of splitting varies with temperature in proportion to the spontaneous polarization along the a axis. The maximum splitting of 74 kHz was observed at 276 K in the field direction which makes an angle of 60° from the a axis in the ab plane. In this direction, one of the satellites occurs at the frequency of 10.033 MHz for the Larmor frequency 9.573 MHz. We ob-

served this line by field sweeping with and without uniaxial stress along the c axis.

A mechanical lever transduces stress on the crystal through a Teflon sheet up to $40 \text{ kg} \cdot \text{cm}^{-2}$. The natural linewidth was 7.1 kHz and we could not find any appreciable broadening of the line under stress. This indicates that inhomogeneity in strain over the size of crystal was negligible in the present experiments. The temperature was measured by a Chromel-P/Constantan thermocouple which was also used for temperature regulation to within 0.05 K . Figure 1 shows the result of uniaxial stress effect on NMR at temperatures 276 and 300 K . No remarkable broadening and shift of line could be seen with increasing or decreasing stress at 300 K . On the other hand a measurable shift was found at 276 K .

2.2 Dielectric hysteresis measurements

Spontaneous polarization was measured by a modified hysteresis bridge.⁸⁾ The experimental setup for uniaxial stress application was almost the same as that for the NMR experiments except that a boron nitride plate made by Nitto Denko Co. was used as a stress conducting medium in order to keep good electrical insulation and thermal conduction. Silver paste was used as the electrodes. The stress was applied along the a - and c -axis. The effect of the stress on the spontaneous polarization was observed in the following two different ways: (1) variation of P_s with stress at a fixed temperature of 276 K where P_s reaches its maximum value of $0.255 \times 10^{-2} \mu\text{C} \cdot \text{m}^{-2}$ and (2)

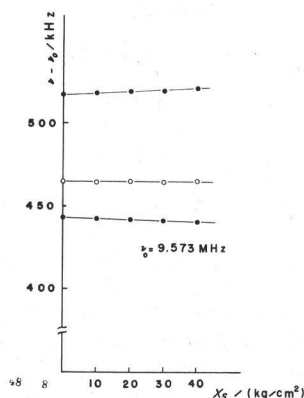


Fig. 1. Stress dependence of the site splitting of ^{23}Na at 300 K drawn by open circles and at 276 K by closed circles.

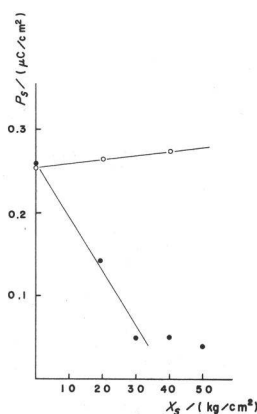


Fig. 2. Stress dependence of the spontaneous polarization P_s at 276 K . Stress is applied along the c axis shown by open circles and along the a axis by closed circles.

variation of P_s with temperature at a fixed uniaxial stress as shown in Figs. 3a and 3b. In Fig. 2, the compression along the a axis produces an appreciable decrease in P_s , while that along the c axis produces a slight increase in P_s . The change in P_s was linear in the stress up to $20 \text{ kg} \cdot \text{cm}^{-2}$ for the a axis and $40 \text{ kg} \cdot \text{cm}^{-2}$ for the c axis compression. Initial value of P_s was restored as much as 95% after removal of stress when the stresses were 20 and $40 \text{ kg} \cdot \text{cm}^{-2}$ for the a and c axes, respectively.

§3. Discussion

The components of piezoelectric modulus in the ferroelectric phase of RS are given by

$$\begin{array}{cccccc} d_{11} & d_{12} & d_{13} & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & d_{26} \\ 0 & 0 & 0 & 0 & d_{35} & d_{36} \end{array} \quad (1)$$

In the paraelectric phase, d_{11} , d_{12} , d_{13} , d_{26} , and d_{35} vanish because of the symmetry. The spontaneous polarization induced by piezoelectric effect in the ferroelectric phase is given by

$$P_s = d_{11}X_1 + d_{12}X_2 + d_{13}X_3 \quad (2)$$

under the present experimental conditions which enable us to ignore the effect of shear components in (1). From the measured value of the change in P_s under stress at 276 K by hysteresis bridge, $d_{11} = dP_s/dX_1 = -640 \pm 10 \text{ pC} \cdot \text{N}^{-1}$ and $d_{13} = dP_s/dX_3 = 75 \pm 5 \text{ pC} \cdot \text{N}^{-1}$ were determined. On the other hand, the value of d_{13} was derived from the results of NMR as

$$\begin{aligned} d_{13} &= dP_s/dX_3 = P_s d(\Delta\nu_s/\nu_s)/dX_3 \\ &= 50 \pm 5 \text{ pC} \cdot \text{N}^{-1} \end{aligned} \quad (3)$$

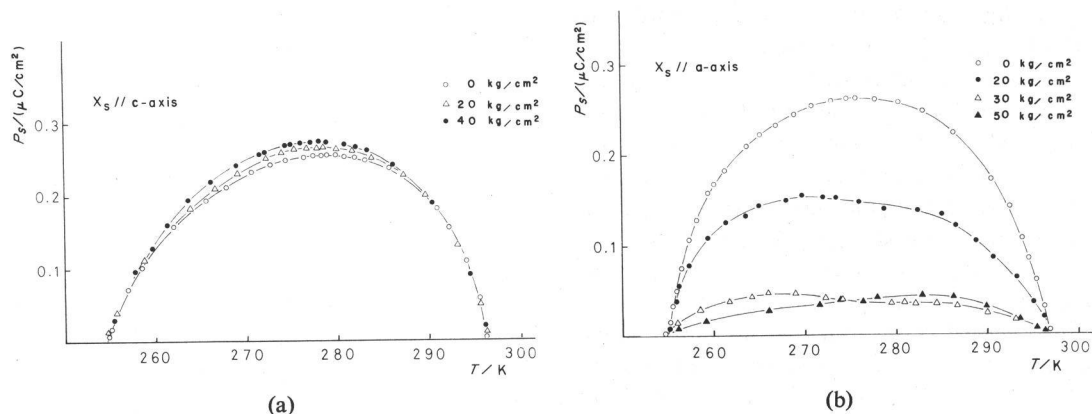


Fig. 3. Temperature dependence of P_s at the various stresses along the c axis (a) and along a axis (b).

where $\Delta\nu_s$ is a shift of frequency of satellite lines and ν_s is the initial site splitting. The value of d_{13} obtained by NMR as given in eq. (3) is more reliable than the value from the hysteresis method because parameters in NMR are not affected by macroscopic domains and inhomogeneous strain over the specimen while the value of P_s is very sensitive to these physical conditions. Our values of d_{11} and d_{13} are larger than the values of $d_{11} = -55 \text{ pC} \cdot \text{N}^{-1}$ and $d_{13} = 25 \text{ pC} \cdot \text{N}^{-1}$ extrapolated from the result by Schmidt⁹⁾ at 290 K under a bias field although the signs of d_{11} and d_{13} coincide with his.

The relation between EFG tensor and atomic displacements is given by Blinc, *et al.*¹⁾ in units of $10^5 \text{ Hz} \cdot \text{\AA}^{-1}$ by

$$\begin{aligned} & 2[\Delta(CV_{yy})_A - \Delta(CV_{yy})_B] \\ &= 0.33(2.32 \Delta X + 2.83 \Delta Y - 4.47 \Delta Z \\ & \quad + \text{the term for O(8) displacement, etc.}) \end{aligned} \quad (4)$$

where $\Delta X = 0.221$, $\Delta Y = 0.710$, and $\Delta Z = -0.028 \text{ \AA}$ were determined by Miller, *et al.*³⁾ for displacement of H(5) proton at the site A. Here we neglected the contribution from O(8) displacement because the value is small. The P_s can be expressed in terms of the displacement by

$$P_s = \sum_{\text{site A}} e_H \Delta X = 0.16 \mu\text{C} \cdot \text{m}^{-2}. \quad (5)$$

If a uniaxial stress of $40 \text{ kg} \cdot \text{cm}^{-2}$ induced a further displacement of H(5) at the site A by an amount of $10^{-2} \text{ \AA}$, our experimental result of NMR could be made accountable. This magnitude for the displacement is extremely large compared with that which is expected for an elastic deformation of the order of $10^{-4} \text{ \AA}$. The

static displacements proposed by Blinc, *et al.* can be considered to correspond to a weighted average of the sites identified by the double minima in the potential which are asymmetrically located at either side of the mean position, as given by

$$X = X_0(n_+ - n_-)_A - X_0(n_+ - n_-)_B \propto P_s \quad (6)$$

where X_0 is the distance between the double minima, $n_+/n_- = \exp(U/kT)$ with $U = 1248 \text{ K}^{10)}$ for the potential difference between double minima. If this value were modified by an amount of 20 K by application of $40 \text{ kg} \cdot \text{cm}^{-2}$ stress along the c direction, the above change in displacement by stress application would be accountable.

More detailed calculation is in progress based on this assumption.

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