Preston, and D. H. Vincent, Phys. Rev. Letters 4, 513 (1960).

[33] See Table V given by A. J. Freeman and Richard E. Watson, in *Magnetism*, Vol. IIa, edited by George T. Rado and Harry Suhl (Academic, New York, 1965); many additional references are quoted therein.

[34] W. Marshall, Phys. Rev. 110, 1280 (1958).

[35] D. A. Goodings and V. Heine, Phys. Rev. Letters 5, 370 (1960).

[36] R. M. Sternheimer, Phys. Rev. 86, 316 (1952).

[37] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961); and references cited therein.

[38] Conyers Herring, J. Appl. Phys. 31, 3S (1960).

[39] A. J. Freeman and R. E. Watson, Phys. Rev. Letters 5, 498 (1960); R. E. Watson and A. J. Freeman, J. Appl. Phys. Suppl. 32, 118 (1961).

[40] Toshinosuke Muto, Syoiti Kobayasi, and Hiroko Hayakawa, J. Phys. Soc. Japan 20, 388 (1962).

[41] G. Gaspari, Wei Mei Shyu, and T. P. Das, Phys. Rev. 134, A852 (1964).

[42] D. Ikenberry (private communication).

[43] A. Dalgarno, Advan. Phys. 11, 281 (1962); Proc. Roy. Soc. (London) A251, 282 (1959).

[44] K. J. Duff and T. P. Das [Phys. Rev. 168, 43 (1968)] report a calculation for Fe^{3+} which is qualitatively similar to the present system. Although the EP method was used, a subsequent calculation by D. Ikenberry (private communication) using the MP Dalgarno method gave almost exact agreement, shell by shell, with the EP calculation. The estimates of the corrections discussed for the EP method should therefore apply to the present MP calculation.

[45] P. D. De Cicco and A. Kitz, Phys. Rev. 162, 486 (1967).

[46] Mary Beth Stearns, Phys. Rev. 147, 439 (1966).

[47] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954); T. Kasuya, Progr. Theoret. Phys. (Kyoto) 16, 45 (1956); K. Yosida, Phys. Rev. 106, 893 (1957).

[48] A. W. Overhauser and M. B. Stearns, Phys. Rev. Letters 13, 316 (1964).

[49] T. Kushida and J. C. Murphy, Phys. Rev. 178, 433 (1969).

[50] H. P. Kelly, Phys. Rev. 131, 684 (1963); 136, B896 (1964); 144, 39 (1966).

[51] E. S. Chang, R. T. Pu, and T. P. Das, Phys. Rev. 174, 1 (1968); H. P. Kelly, *ibid.* 173, 142 (1968); 180, 55 (1969); N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. Letters 21, 1139 (1968); Phys. Rev. 177, 33 (1969); J. D. Lyons, R. T. Pu, and T. P. Das, *ibid.* 178, 103 (1969); 186, 266 (1969); T. Lee, N. C. Dutta, and T. P. Das, Phys. Rev. A 1, 995 (1970).

[52] R. K. Nesbet, Phys. Rev. 155, 51 (1967); 155, 56 (1967); 175, 2 (1968).

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Dynamics of Ferroelectric Rochelle Salt

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A quantum theory of ferroelectricity in Rochelle salt is developed which is an extension of the two-sublattice model of Mitsui. The isotope effects on deuteration are explained in a natural way, and the spontaneous polarization, the polarization of the two sublattices, and the dielectric constant are obtained as functions of temperature. The dynamics of the system is investigated for the case of deuterated Rochelle salt and is found to exhibit a two-mode relaxational behavior. The correlation time of one of these two modes is proportional to the static dielectric constant and thus exhibits a critical slowing-down on approaching the two Curie temperatures in agreement with the experimental data.

I. INTRODUCTION

Though Rochelle salt has been the first ferroelectric crystal to be discovered,[1] it is still not understood very well from a microscopic point of view. The shifts of the upper Curie point towards higher temperatures and of the lower towards lower temperatures on deuteration demonstrate the role of the hydrogen atoms in its ferroelectric behavior, but no theoretical explanation of these isotope shifts which increase the ferroelectric range by about 40% has been proposed so far. Whereas the lattice dynamics of both hydrogen-bonded "order-disorder"-type ferroelectrics and of "displacive" ionic ferroelectrics seems to be basically well understood, this is not the case for Rochelle salt.

It is the purpose of this note to present a quantum theory of ferroelectricity in Rochelle salt which is capable of describing the isotope effects on deuteration as well as the dynamics of dipole moment reversal in this crystal. The theory is essentially a quantum extension of Mitsui's model[2] along the lines used[3,4] to describe quantum effects in KH_2PO_4-type ferroelectrics. It is based on recent neutron-diffraction[5] and magnetic-resonance studies[6,7] and assumes that the ferroelectric dipoles move in asymmetric double-well crystalline potentials and form two interpenetrating sublattices[2] (Fig. 1). The asymmetric double-well potentials for the two sublattices are mirror images of each other, and the ground state is nonpolar due to the antiparallel arrangement of the dipoles.

The Hamiltonian of the problem can be conveniently expressed in terms of quasi-spin-$\frac{1}{2}$ operators,[3] where $S_z = +\frac{1}{2}$ designates a dipole in the "right" equilibrium site and $S_z = -\frac{1}{2}$ in the "left" equilibrium site:

$$\begin{aligned}\mathcal{H} = &- \sum_{ij} \left[J_{ij}(S^{(1)}_{z,i} S^{(1)}_{z,j} + S^{(2)}_{z,i} S^{(2)}_{z,j}) + K_{ij} S^{(1)}_{z,i} S^{(2)}_{z,j}\right] \\ &- 2\Omega \sum_j (S^{(1)}_{x,j} + S^{(2)}_{x,j}) - \Delta \sum_j (S^{(1)}_{z,j} - S^{(2)}_{z,j}) \\ &- 2\mu E \sum_j (S^{(1)}_{z,j} + S^{(2)}_{z,j}) \, . \end{aligned} \tag{1}$$

The indices (1) and (2) refer to the two sublattices, J and K are the effective interaction constants of dipoles belonging to the same and different sublattice, respectively, Δ is a measure of the asymmetry of the local crystalline potential, μ is the magnitude of the dipole moment interacting with the external electric field E, and Ω is the tunneling integral which measures the amount of delocalization of the ferroelectric dipoles.

II. EQUILIBRIUM PROPERTIES

In the molecular field approximation, the Hamiltonian (1) becomes

$$-\mathcal{H} = H_{z1} \sum_j S^{(1)}_{z,j} + H_{z2} \sum_j S^{(2)}_{z,j} + H_x \sum_j (S^{(1)}_{x,j} + S^{(2)}_{x,j}), \tag{2}$$

where

$$H_{z1} = 2J\langle S^{(1)}_z \rangle + K\langle S^{(2)}_z \rangle + \Delta + 2\mu E \, , \tag{3a}$$

$$H_{z2} = 2J\langle S^{(2)}_z \rangle + K\langle S^{(1)}_z \rangle - \Delta + 2\mu E \, , \tag{3b}$$

$$H_{x1} = H_{x2} = H_x = 2\Omega \, , \tag{3c}$$

and where the bracket stands for a thermal average. The molecular field thus forms a vector $\vec{H}_i = (H_x 0, H_{zi})$, $i = 1, 2$ in our pseudo-spin-space, which interacts with the spin variables and which takes on different values for the two sublattices. The thermal expectation values of the two sublattice polarizations, $\langle S^{(1)}_z \rangle$ and $\langle S^{(2)}_z \rangle$, are obtained by solving the two coupled equations

$$\langle S^{(1)}_z \rangle = \tfrac{1}{2}(H_{z1}/|H_1|)\tanh(\tfrac{1}{2}\beta|H_1|), \tag{4a}$$

$$\langle S^{(2)}_z \rangle = \tfrac{1}{2}(H_{z2}/|H_2|)\tanh(\tfrac{1}{2}\beta|H_2|), \tag{4b}$$

where $\beta = 1/kT$. The spontaneous polarization is obtained from

$$P = N\mu(\langle S^{(1)}_z \rangle + \langle S^{(1)}_z \rangle) \, , \tag{5}$$

with N being the number of dipoles per unit volume, and the dielectric constant from

$$\epsilon_0(\epsilon - 1) = \left(\frac{dP}{dE}\right)_{E=0} = \frac{4N\mu^2\alpha}{1 - \alpha(K + 2J)} \, , \tag{6}$$

where $\epsilon_0 = 4\pi \times 10^{-12}$ A sec/V m and

$$\alpha = \frac{H_x^2}{2H_1(0)^3} \tanh\left[\tfrac{1}{2}\beta|H_2(0)|\right] + \frac{\beta H_{1z}^2(0)}{4H_1^2(0)} \frac{1}{\cosh^2[\frac{1}{2}\beta H_1(0)]} \, , \tag{7}$$

with $H_i(0) = H_i(E = 0)$. The two Curie temperatures, $T = T_{C1}$ and $T = T_{C2}$, where $\epsilon \rightarrow \infty$, are obtained as solutions of the equation

$$1 - \alpha(K + 2J) = 0 \, . \tag{8}$$

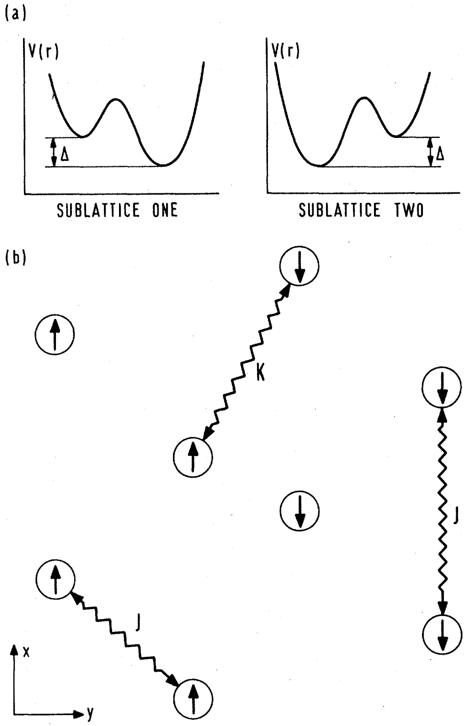

FIG. 1. Hypothetical asymmetric double-well potential for the motion of the ferroelectric dipoles (a), and assumed arrangement of the dipoles in the two sublattices of Rochelle salt (b).

Using $\Delta = 873$ cm^{-1}, $K = 1560$ cm^{-1}, $J = 144$ cm^{-1}, $\Omega = 0$, and $\mu = 4.9$ D, a rather good agreement between the experimental and theoretical Curie temperatures, dielectric constant, and polarization values for deuterated Rochelle salt can be obtained. The isotope shifts on replacing hydrogen for deuterium are then obtained by introducing a nonzero value of the tunneling integral $\Omega \approx 30$ cm^{-1}. Though the numerical values of these constants are only estimates and may not be unique, it is nevertheless encouraging that all equilibrium dielectric properties of normal and deuterated Rochelle salt can be described by such a simple model.

Figure 2 shows the temperature dependence of the two sublattice polarizations and of the reduced spontaneous polarization for deuterated Rochelle salt. For $T < T_{C1}$, we have $\langle S_z^{(1)}\rangle = -\langle S_z^{(2)}\rangle$, so that the polarizations of the two sublattices cancel each other, and the low-temperature phase is antipolar. It should be noted that according to Fig. 2, the low-temperature phase is not completely ordered. In the intermediate polarized phase, we have $\langle S_z^{(1)}\rangle \neq -\langle S_z^{(2)}\rangle$. The temperature dependence of the two sublattice polarizations show here some similarity with the temperature dependence of the electric-field-gradient tensor at the Na sites.[6] In the high-temperature phase $T > T_{C2}$, the sublattice polarizations again cancel each other, $\langle S_z^{(1)}\rangle = -\langle S_z^{(2)}\rangle$, but the disorder is significantly larger than for $T < T_{C1}$.

III. DYNAMIC BEHAVIOR

Let us now investigate the dynamic behavior of this system in the random-phase approximation (RPA). For sake of simplicity we put $\Omega = 0$, thus limiting ourselves to the case of deuterated Rochelle salt. The dipolar system is supposed to be in thermal contact with a large heat bath. Following the treatment of the Ising model by Kubo and Suzuki,[8] we assume that a master equation exists which can be written as

$$\frac{d}{dt}P(S_{z1},\cdots S_{zN},t) = -\sum_j W_j(S_{zj})P(S_{z1},\cdots S_{zN},t) + \sum_j W_j(-S_{zj})P(S_{z1},\cdots -S_{zj},\cdots S_{zN},t)\,, \tag{9}$$

where $P(S_{z1},\cdots S_{zN},t)$ is the probability of finding the quasispins in the configuration $(S_{z1}\cdots S_{zN})$, and the transition probability $W_j(S_{zj})$ can be expressed[8] as

$$W_j(S_{zj}) = (1/2\tau_0)(1 - 2S_{zj}\tanh\tfrac{1}{2}\beta H_j)\,, \tag{10}$$

where τ_0 is the correlation time of a noninteracting dipole, H_j is the local field at the spin j expressed in energy units, and

$$\langle S_{zj}(t)\rangle = \sum_{\{S_z\}} S_{zj}P(S_{z1}\cdots S_{zN},t)\,, \tag{11}$$

with the sum being taken over all quasi-spin-configurations. Introducing the collective coordinates as Fourier components

$$\delta S_{z,\vec{q}}^{(K)} = N^{-1/2}\sum_j \delta S_{z,j}^{(K)} e^{i\vec{q}\cdot\vec{R}_j}\,, \quad K = 1, 2 \tag{12}$$

of the small deviations from the molecular field solution $\langle S_z^{(K)}\rangle$

$$\delta S_{z,j}^{(K)} = \langle S_{zj}^{(K)}(t)\rangle - \langle S_z^{(K)}\rangle \tag{13}$$

and using

$$J(q) = \sum_j J_{ij} e^{i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)}\,, \tag{14}$$

one gets from (9) the relaxation equations in the RPA as

$$\tau_0\frac{d}{dt}\delta S_{z,\vec{q}}^{(1)} = -\delta S_{z,\vec{q}}^{(1)} + \tfrac{1}{4}\beta[2J(\vec{q})\delta S_{z,\vec{q}}^{(1)} + K(\vec{q})\delta S_{z,\vec{q}}^{(2)}] \times\{1 - \tanh^2[\tfrac{1}{2}\beta H_{1z}(0)]\}\,, \tag{15}$$

$$\tau_0\frac{d}{dt}\delta S_{z,q}^{(2)} = -\delta S_{z,q}^{(2)} + \tfrac{1}{4}\beta[2J(\vec{q})\delta S_{z,\vec{q}}^{(2)} + K(\vec{q})S_{z,\vec{q}}^{(1)}] \times\{1 - \tanh^2[\tfrac{1}{2}\beta H_{2z}(0)]\}\,. \tag{16}$$

Looking for solutions of the form

$$\delta S_{z,\vec{q}}^{(1)} = a\,e^{-t/\tau_{\vec{q}}}\,, \quad \delta S_{z,q}^{(2)} = b\,e^{-t/\tau_{\vec{q}}}\,, \tag{17}$$

we get a system of homogeneous linear equations for a and b, which has a nontrivial solution only if

$$\frac{\tau_0}{\tau_{1,2;\vec{q}}} = 1 - \frac{\beta J(\vec{q})}{4\cosh^2[\frac{1}{2}\beta H_{1z}(0)]} - \frac{\beta J(\vec{q})}{4\cosh^2[\frac{1}{2}\beta H_{2z}(0)} \pm\left[\frac{[\beta K(\vec{q})]^2}{16\cosh^2[\frac{1}{2}\beta H_{1z}(0)]\cosh^2[\frac{1}{2}\beta H_{2z}(0)]} + \frac{[\beta J(\vec{q})]^2}{16}\times\left(\frac{1}{\cosh^2[\frac{1}{2}\beta H_{1z}(0)]} - \frac{1}{\cosh^2[\frac{1}{2}\beta H_{2z}(0)]}\right)^2\right]^{1/2}, \tag{18}$$

so that the general solution is a linear combination of these two solutions

$$S_{z,\vec{q}}^{(1)} = Aa_1 e^{-t/\tau_{1\vec{q}}} + Ba_2 e^{-t/\tau_{2\vec{q}}}\,, \tag{19a}$$

$$S_{z,\vec{q}}^{(2)} = Ab_1 e^{-t/\tau_{1\vec{q}}} + Bb_2 e^{-t/\tau_{2\vec{q}}}\,, \tag{19b}$$

where A and B are relative weights of the two solutions which depend on the initial conditions.

The system thus exhibits a two-mode relaxation behavior for each $\vec{q}$. Of particular interest is the polarization relaxation time which is obtained in the limit $\vec{q} = 0$. In the unpolarized phase ($P = 0$) we then obtain

$$\frac{\tau_0}{\tau_1} = 1 + \frac{\beta(K - 2J)}{4\cosh^2[\frac{1}{2}\beta H_{1z}(0)]}\,, \tag{20a}$$

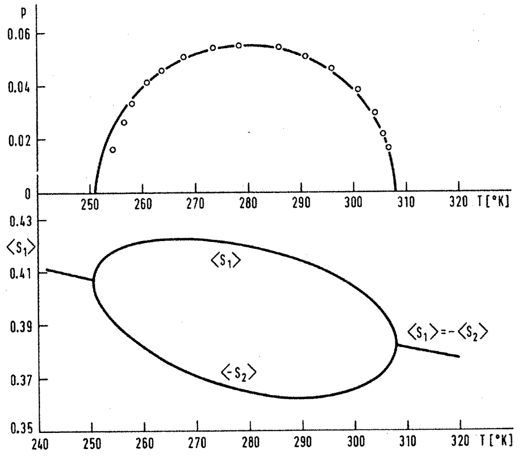

FIG. 2. Temperature dependence of the two sublattice polarizations and the reduced spontaneous polarization in deuterated Rochelle salt. Experimental data (Ref. 1) – circles – are included for comparison.

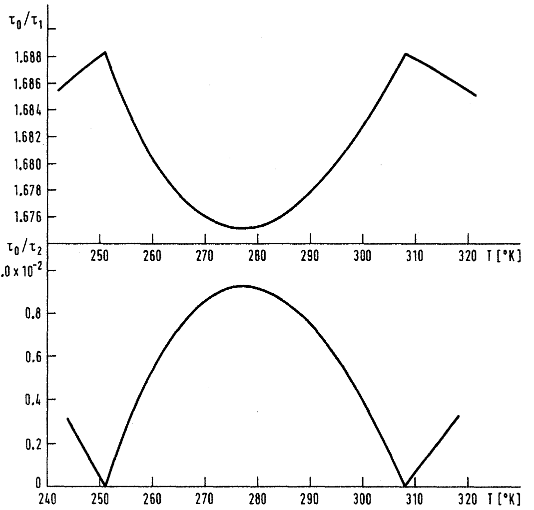

FIG. 3. Temperature dependence of the two relaxation times τ_0/τ_1 and τ_0/τ_2 for deuterated Rochelle salt in the limit $q = 0$.

$$\frac{\tau_0}{\tau_2} = 1 - \frac{\beta(K+2J)}{\cosh^2[\frac{1}{2}\beta H_{1z}(0)]} \; . \tag{20b}$$

Since for $T = T_C$,

$$\beta_C(K+2J) = 4\cosh^2[\tfrac{1}{2}\beta_C H_{1z}(0)] \; , \tag{21}$$

τ_0/τ_2 exhibits a critical slowing down ($\tau_0/\tau_2 \to 0$) as T_{C1} or T_{C2} is approached from either side, whereas τ_0/τ_1 exhibits no significant anomaly and stays high.

The temperature dependences of the two relaxation times are shown in Fig. 3. It is obvious that τ_0/τ_2 exhibits the same anomalous temperature dependence as the dielectric relaxation time measured by Sandy and Jones[9] and Akao and Sasaki.[10]

The fact that a monodispersive dielectric relaxation behavior is experimentally observed can be easily understood in the following way: In the unpolarized phase both sublattices are equivalent and are equally disturbed, when the system is placed in a constant electric field, so that the initial condition for polarization relaxation is

$$\delta S^{(1)}_{z,0}(0) = \delta S^{(2)}_{z,0}(0) \; . \tag{22}$$

From Eqs. (19) and (22) we have

$$\delta S^{(1)}_{z,0}(0)/\delta S^{(2)}_{z,0}(0) = Aa_1 + Ba_2/Ab_1 + Bb_2 = 1 \; . \tag{23}$$

For the unpolarized phase we can get, solving Eqs. (15) and (16),

$$a_1/b_1 = -1, \quad a_2/b_2 = 1 \; , \tag{24}$$

so that $A = 0$, $B \neq 0$ and we have a single-mode polarization relaxation behavior

$$\delta S^{(1)}_{z,\vec{q}=0} = a_2 e^{-t/\tau_2}, \quad \delta S^{(2)}_{z,\vec{q}=0} = b_2 e^{-t/\tau_2} \tag{25}$$

characterized by τ_2.

For the polarized phase the two sublattices are not equivalent, and the ratios $\delta S^{(1)}_z(0)/\delta S^{(2)}_z(0) \neq a_1/b_1$, a_2/b_2 are temperature dependent and are generally not equal to ±1. Thus $A \neq 0$ and $B \neq 0$ and a two-mode polarization relaxation results. But as $\tau_2 \gg \tau_1$ and $A \ll B$ only a single-mode dielectric relaxation behavior is expected to be observed. This agrees rather well with the dielectric relaxation measurements of Sandy and Jones,[9] who find a single-mode relaxation behavior in the paraelectric as well as in the ferroelectric phase. What is even more important is that the predicted [Eq. (20b)] and observed[9] temperature dependences of τ_2 agree rather well.

The present theory thus seems to give an adequate description both of the equilibrium dielectric properties of Rochelle salt and of its dynamics.

The dynamics of undeuterated Rochelle salt is reserved for a subsequent paper.

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[1] See, e.g., F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962).

[2] T. Mitsui, Phys. Rev. 111, 1259 (1958).

[3] R. Blinc, J. Phys. Chem. Solids 13, 204 (1959).

[4] P. G. de Gennes, Solid State Commun. 1, 132 (1963).

[5] B. C. Frazer, J. Phys. Soc. Japan Suppl. 17, 376 (1962).

[6] R. Blinc, J. Petkovšek, and I. Zupančič, Phys. Rev. 136, A1684 (1964); N. C. Miller and P. A. Casabella, *ibid.* 152, 228 (1966).

[7] J. L. Bjorkstam and J. H. Wilmorth, *Magnetic Resonance and Relaxation* (North-Holland, Amsterdam, 1967), p. 728.

[8] M. Suzuki and R. Kubo, J. Phys. Soc. Japan 24, 51 (1968).

[9] F. Sandy and R. V. Jones, Phys. Rev. 168, 481 (1968).

[10] H. Akao and T. Sasaki, J. Chem. Phys. 23, 2210 (1955).