NMR STUDIES OF PHASE TRANSITION IN DIELECTRIC MATERIALS

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ABSTRACT

A general review is given of recent results of the anomalous proton spin–lattice relaxation time concerning the order–disorder type ferroelectric $Ca_2Sr(C_2H_5COO)_6$ and dielectric $Ca_2Pb(C_2H_5COO)_6$ materials. Emphasis is placed on the role played by the dipole–dipole interaction between electric dipoles. The temperature dependence of an observed electric field gradient of ^{23}Na is related to that of the long-range order parameter by using the simplified model of the order–disorder type ferroelectric $NaNO_2$. Experimental results for $NaNO_2$, $AgNa(NO_2)_2$ and $RbDSO_4$ are given briefly.

1. INTRODUCTION

Nuclear magnetic resonance absorption and the spin–lattice relaxation time have played an important role in studies of the local behaviour of the phase transition. In magnetic materials, critical behaviour of the magnetic moment of an electron spin system directly affects the n.m.r. spectrum through hyperfine interaction. While dielectric materials have no magnetic property of the electron spins, the change of the relative position of nuclei exerts an influence upon the n.m.r. spectrum through the change of the local dipolar magnetic field or of the electric field gradient of the nucleus concerned. In this paper we present some applications of n.m.r. to the study of the phase transition in order–disorder type ferroelectrics and dielectrics which show a dielectric anomaly near the transition point. In section 2, we report the theoretical survey of the anomalous nuclear spin–lattice relaxation time emphasizing the effect of the depolarization field originating from the electric dipole–dipole interaction between electric dipoles and show our recent experimental results in dicalcium metallic propionates[1,2]. In section 3 we present that the temperature dependences of the electric field gradient of the ^{23}Na nucleus in $NaNO_2$ and $AgNa(NO_2)_2$, have the relation to those of the long-range order parameter[3-5]. Finally we report the ^{87}Rb and deuteron resonance spectra in $RbDSO_4$.

2. ANOMALY OF SPIN–LATTICE RELAXATION TIME T_1

In recent studies of the phase transition, anomalous increases and decreases of the physical quantities near the phase transition temperature have

been discussed in connection with the increase of fluctuations of the order parameter, which corresponds to an electric polarization in ferroelectric materials. The anomalous increase of the fluctuations leads to the concept of the so-called 'critical slowing down' of the order parameter, in other words since the electric polarization is the sum of microscopic electric dipoles this means that electric dipoles move slowly in a cooperative manner from one equilibrium position to the other one or vice versa. This is directly observed with experiments on dielectric dispersion in ferroelectric materials. In antiferroelectrics or other order–disorder type dielectrics, the conjugate force to the order parameter cannot be applied externally and indirect methods are needed, such as nuclear spin–lattice relaxation investigations.

Since the anomalous behaviour of the nuclear spin–lattice relaxation of ^{23}Na in sodium nitrite was reported by Rigamonti[6], measurements of anomalous spin–lattice relaxation have been made on various ferroelectric materials.[7,8].

Figures 1 and *2* show the temperature dependence of the inverse of the observed proton–lattice relaxation time for single crystals of $Ca_2Sr(C_2H_5COO)_6$ (abbreviated as DSP, hereafter) and $Ca_2Pb(C_2H_5COO)_6$

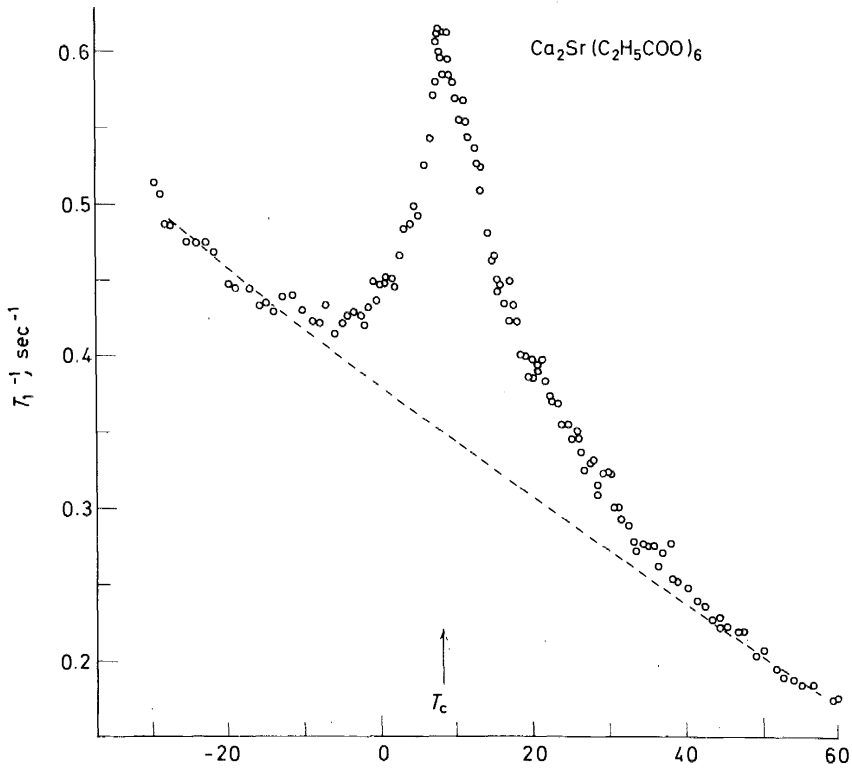


Figure 1. Observed spin–lattice relaxation time T_1^{-1} of ^1H in single crystal DSP versus $T - T_c$. The magnetic field is parallel to the c axis.

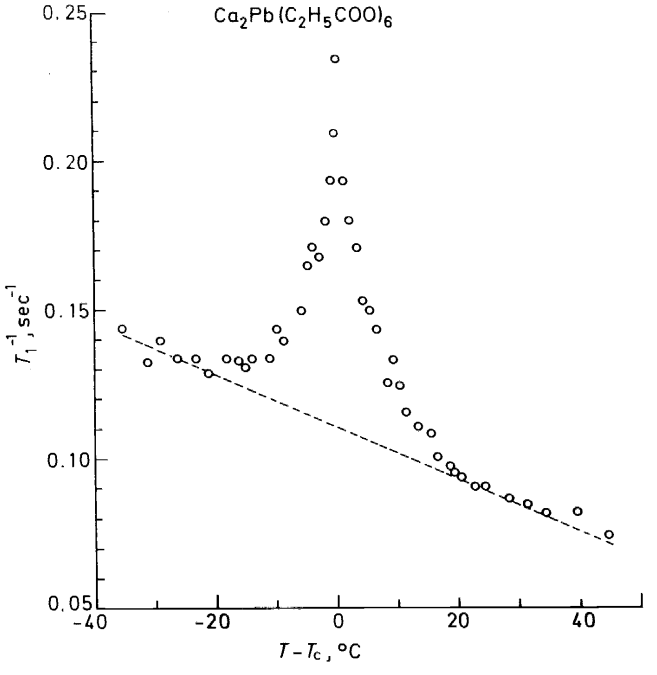


Figure 2. Observed spin–lattice relaxation time T_1^{-1} of ^1H in single crystal DLP versus $T - T_c$. The magnetic field is parallel to the c axis.

(DLP) under application of the magnetic field along the c axis of the single crystals[1,2]. DSP is ferroelectric below 8.5°C with the polar c axis[9] and DLP is not ferroelectric but shows a prominent dielectric anomaly along the c axis at 60°C[10]. The mechanism of the phase transition seems to be an order–disorder of C_2H_5COO in both materials. Now let us consider what relation exists between the critical index of T_1^{-1} and the dielectric anomaly in the order–disorder system.

Magnetic dipole–dipole interaction between ith spin and jth spin can be written formally as

$$\mathcal{H}_1 = \tfrac{1}{2} \sum_{i,j} \sum_{q=2}^{-2} F_{ij}^{(q)} A_{ij}^{(q)} \tag{1}$$

where the 'lattice functions' $F_{ij}^{(q)}$ are the random functions of the relative positions of the two spins and $A_{ij}^{(q)}$ are spin operators. Two magnetic moments are those of protons belonging to the same (C_2H_5COO) radical (hereafter abbreviated as o.d. unit) in the present case, that is, only intramolecular interactions are taken into account. The o.d. unit transfers stochastically between two equivalent positions corresponding to the plus and minus orientations of an electric dipole. The two eigenvalues of the nth Ising operator Z_n representing the orientation of the nth electric dipole correspond one to one to the two equilibrium positions of the nth o.d. unit. Thus $F_{ij}^{(q)}(t)$ takes alternately two different values $F_{ij}^{(q)}(+)$ and $F_{ij}^{(q)}(-)$ as the radius

vector between two protons changes stochastically. As $F_{ij}^{(q)}(+)$ and $F_{ij}^{(q)}(-)$ depend on the directions of the radius vector relative to the external magnetic field, they take two different values in general though it is possible that they take the same value for the special direction of the magnetic field in a single crystal having high symmetry. $F_{ij}^{(q)}(t)$ is expressed as[1, 11]

$$F_{ij}^{(q)}(t) = \tfrac{1}{2}\{F_{ij}^{(q)}(+) + F_{ij}^{(q)}(-)\} + \tfrac{1}{2}\{F_{ij}^{(q)}(+) - F_{ij}^{(q)}(-)\} Z_n = [F_{ij}^{(q)}]^{s} + [F_{ij}^{(q)}]^{a} Z_n(t) \qquad (2)$$

The correlation of the first term $[F_{ij}^{(q)}(t)]^{s}$ represents the contribution to the background relaxation rate, that is the reciprocal spin–lattice relaxation time $(T_1^{-1})_{base}$ due to the usual lattice vibrations and that of the second term $[F_{ij}^{(q)}]^{a} Z_n(t)$ gives the anomalous relaxation rate $(T_1^{-1})_{fluc}$ coming from the fluctuation of the electric dipoles. Since the observed relaxation rate $(T_1^{-1})_{obs}$ is expressed as

$$(T_1^{-1})_{obs} = (T_1^{-1})_{base} + (T_1^{-1})_{fluc} \qquad (3)$$

it is assumed that $(T_1^{-1})_{base}$ is determined from the value interpolated as shown by the dashed lines in *Figures 1* and *2* from the temperature region with no anomalous behaviour. The $(T_1^{-1})_{base}$ is caused by a relaxation mechanism different from $(T_1^{-1})_{fluc}$ and might be observed if it were not for the anomalous magnetic dipolar interaction. It is shown that $(T_1^{-1})_{fluc}$ can be written as

$$(T_1^{-1})_{fluc} \propto \sum_{qnij} \int_{-\infty}^{+\infty} dt \exp(i\omega_L q t) |[F_{ij}^{(q)}]^{a}|^2 \langle Zn(0) Z_n(t) \rangle \qquad (4)$$

Equation 4 shows that $(T_1^{-1})_{fluc}$ reflects the local motion of the individual electric dipole as the time correlation of the Ising operator corresponds one to one to that of the electric dipole. On the other hand, the critical slowing down is attributed to the divergent relaxation time of the fluctuation of the total electric polarization $P(t)$, which is proportional to $\Sigma_n Z_n(t)$ and the relaxation time is not equal to the relaxation time of the individual $Z_n(t)$.

As the temperature approaches the transition point the existence of interaction among electric dipoles changes the height of the double minimum potential barrier in time as well as in space, i.e. the relaxation time of electric dipoles takes various values stochastically. In other words, each motion of the electric dipole can be expressed as a superposition of various modes having the relaxation time τ_k. This picture is written in terms of the Fourier transformation of Z_n as follows

$$\langle Z_n(0) Z_n(t) \rangle = \frac{1}{N} \sum_k \langle Z_k Z_{-k} \rangle \exp\left(-\frac{t}{\tau_k}\right) \qquad (5)$$

where $\langle Z_k Z_{-k} \rangle$ means physically, so to speak, the probability of occurrence of a fluctuation having the wave vector k. Then $(T_1^{-1})_{fluc}$ is written as

$$(T_1^{-1})_{fluc} \propto |[F^{(q)}]^{a}|^2 \sum_{q=1,2} \sum_k \langle Z_k Z_{-k} \rangle \frac{2\tau_k}{1 + (q\omega_L \tau_k)^2} \qquad (6)$$

where

$$\sum_{ij} |[F_{ij}^{(q)}]^a|^2 \equiv |[F^{(q)}]^a|^2$$

The term $k = 0$ in equation 6 represents the time and space correlation of a uniform fluctuation extended over the crystal and corresponds to the imaginary part of the dielectric susceptibility in the present case, which increases anomalously as the temperature approaches the transition point. Since the expression given in equation 6 includes the summation over k, the anomalous behaviour of $(T_1^{-1})_{\text{fluc}}$ appears subdued in comparison with that of the dielectric susceptibility.

While $(q\omega_L\tau_k)^2$ in the denominator increases anomalously very near the transition point, let us consider the temperature region where the term $(q\omega_L\tau_k)^2$ is negligible compared with unity so that we may see the theoretical result for the critical index of $(T_1^{-1})_{\text{fluc}}$ in the region where the mean field theory is still accurate. Equation 6, then, is reduced to the form

$$\sum_{q=1,2} |[F^{(q)}]^a|^2 \sum_k \langle Z_k Z_{-k} \rangle \tau_k$$

which appears often in discussions of dynamical scaling laws and this form in fact is identical to the expression of T_1^{-1} of the ^{19}F nucleus in antiferromagnetic MnF_2 if the hyperfine coupling constant A and Heisenberg operator are used instead of $|[F^{(q)}]^a|^2$ and the Ising operator, respectively[12].

The relaxation time τ_k in the Ising spin system is proportional to $\langle Z_k Z_{-k} \rangle$, while $\langle Z_k Z_{-k} \rangle$ is proportional to $(k^2 + \kappa^2)^{-1}$ in the random phase approximation, where κ^{-1} is a correlation length having the temperature dependence of $|T - T_c|^{-\frac{1}{2}}$. Replacing the summation over k by integration in the k-space, the critical index of $(T_1^{-1})_{\text{fluc}}$ is as follows.

$$\begin{aligned}(T_1^{-1})_{\text{fluc}} &\propto \int_0^{k_d} \langle Z_k Z_{-k} \rangle^2 \, d\boldsymbol{k} \propto \int_0^{k_d} \left(\frac{1}{\kappa^2 + k^2}\right)^2 k^2 \, dk \int_{-1}^{+1} d(\cos\theta) \int_0^{2\pi} d\phi \\ &\propto \kappa^{-4} \int_0^{k_d} d\left(\frac{k}{\kappa}\right) \kappa^3 \left\{1 + \left(\frac{k}{\kappa}\right)^2\right\}^{-2} \left(\frac{k}{\kappa}\right)^2 \int_{-1}^{+1} d(\cos\theta) \int_0^{2\pi} d\phi \\ &\propto \kappa^{-1} \propto |T - T_c|^{-\frac{1}{2}} \end{aligned} \tag{7}$$

In order to compare the theoretical prediction with the experimental results, $(T_1^{-1})_{\text{fluc}}$ has been calculated using the observed values $(T_1^{-1})_{\text{obs}}$, the estimated values $(T_1^{-1})_{\text{base}}$ and equation 3. $(T_1^{-1})_{\text{fluc}}$ versus logarithmic $|T - T_c|/T_c$ plots for DSP and DLP are shown in *Figures 3* and *4*[1,2]. It should be noted that the anomalous behaviour of $(T_1^{-1})_{\text{fluc}}$ for both materials can be expressed as

$$(T_1^{-1})_{\text{fluc}} \propto \log|(T - T_c)/T_c| \tag{8}$$

This critical index is zero and is quite different from the value $-1/2$ predicted by equation 7.

The zero value of the critical index is obtained by considering the depolarization field due to the long-range dipole–dipole interaction between electric dipoles in addition to the interaction mechanism considered above; it is known that the fluctuations of the longitudinal polarization wave having the component of $\boldsymbol{k}$ along the electric polarization axis are suppressed by the

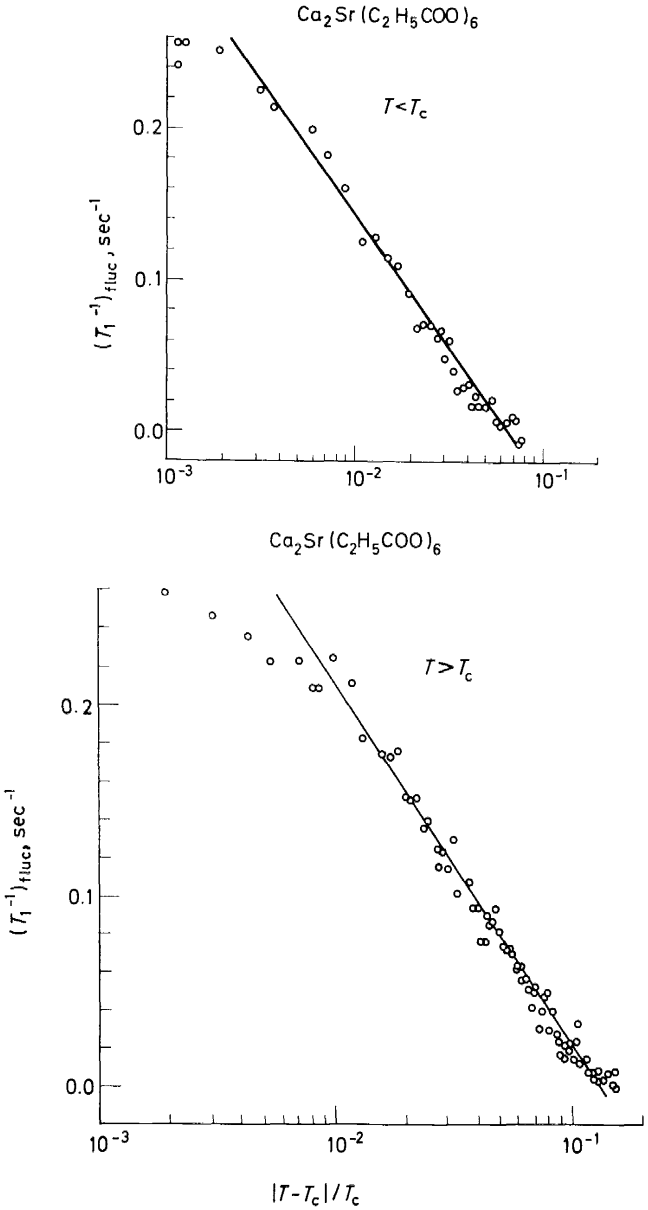
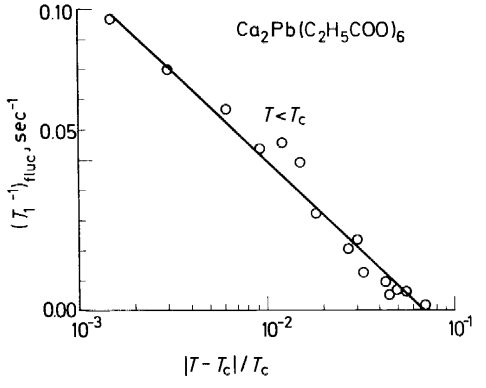


Figure 3. Semilogarithmic plot of the anomalous part of the inverse relaxation time $(T_1^{-1})_{\text{fluc}}$ versus $|T - T_c|/T_c$. (a) for $T < T_c$, (b) for $T > T_c$.

depolarization effect[13, 14]. Since not all terms in equation 6 describing the fluctuations with wave vector $\boldsymbol{k}$ contribute to the anomalous behaviour, it is expected that the critical index will take a value smaller than $-1/2$. The static correlation function with a very small $\boldsymbol{k}$ value, in fact, is written as



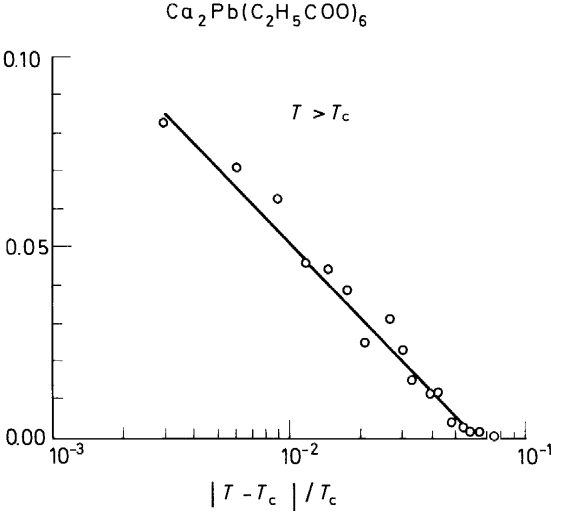


Figure 4. Semilogarithmic plot of the anomalous part of the inverse relaxation time $(T_1^{-1})_{fluc}$ versus $|T - T_c|/T_c$. (a) for $T < T_c$, (b) for $T > T_c$.

$$\langle Z_k Z_{-k} \rangle = \kappa^{-2} \left\{ 1 + \left(\frac{k}{\kappa} \right)^2 + \gamma \left(\frac{\cos \theta}{\kappa} \right)^2 \right\}^{-1} \tag{9}$$

where γ is constant and θ denotes the angle between $\boldsymbol{k}$ vector and the electric polarization axis. On substituting equation 9 into equation 7, the integral over k brings us the result

$$(T_1^{-1})_{fluc} \propto \kappa^{-4} \int_0^{k_d} \int_{-1}^{+1} \int_0^{2\pi} \left\{ 1 + \left(\frac{k}{\kappa} \right)^2 + \gamma \left(\frac{\cos \theta}{\kappa} \right)^2 \right\}^{-2} \kappa^4 \times \left(\frac{k}{\kappa} \right)^2 \mathrm{d}\left(\frac{k}{\kappa} \right) \mathrm{d}\left(\frac{\cos \theta}{\kappa} \right) \mathrm{d}\phi \tag{10}$$

The critical index $(T_1^{-1})_{\text{fluc}}$ can thus become zero in the present case. The rounding of the peak in $(T_1^{-1})_{\text{fluc}}$ can be explained as the result of the non-negligibility of $(q\omega_L\tau_k)^2$ compared with unity near the transition point.

The further possibility of including the effect of four-body correlation which appears as the result of interactions between protons in the different o.d. units has also been considered. According to the above effect, $(T_1^{-1})_{\text{fluc}}$ is proportional to $C_E^{\frac{1}{2}}$, where C_E is the specific heat at constant electric field. The contribution of the four-body correlation to $(T_1^{-1})_{\text{fluc}}$ is usually expected to be small when compared with that of the two-body correlation. However, if the static magnetic field is applied along the direction with respect to which the $[F_{ij}^{(q)}]^a$ in the nth o.d. unit is zero, the four-body correlation will be the main source of $(T_1^{-1})_{\text{fluc}}$. Such a direction of the magnetic field may be one of some special directions relative to the single crystal. Experiments have been carried out with DSP under the application of the magnetic field along the c axis, the a axis, and the direction of 45° with the a axis in the (001) plane. In all cases $(T_1^{-1})_{\text{fluc}}$ has shown a logarithmic divergence. These results and the fact that the relation $(T_1^{-1})_{\text{fluc}} \propto C_E^{\frac{1}{2}}$ does not hold may suggest that the logarithmic divergence is attributed to the depolarization effect of the long-range dipole–dipole interaction in addition to the two-body correlation.

3. ELECTRIC FIELD GRADIENT AND LONG-RANGE ORDER PARAMETER

The relation between the observed electric field gradient (hereafter abbreviated as e.f.g.) and the long-range order parameter S has been studied by several authors and it is reported that the temperature dependence of the e.f.g. is proportional to S or to the square of S without being given the physical meaning of the portionality constant except for deuteron spectra in the DKDP family. Moreover the long-range order parameter S itself, which reflects the degree of order of the alignment of atoms or molecules, is an important factor to give the temperature dependence of the e.f.g. However, the contribution caused by the temperature dependence of the lattice parameters cannot be neglected since S vanishes in the disordered phase and the e.f.g. still changes with the temperature. Therefore, if after making corrections due to the lattice parameters for the observed e.f.g. $\Phi_{zz}^{\text{obs}}(T)$, the temperature dependence of the e.f.g. still remains, it will be attributed to the temperature dependence of the long-range order parameter S.

In what follows, we have proposed a simplified model to explain the temperature dependence of the e.f.g. at the site of a ^{23}Na nucleus in ferroelectric sodium nitrite[3]. The properties of sodium nitrite are treated under the following assumptions: (a) the sodium nitrite crystal is an ionic crystal, (b) each ion has a unit point charge $\pm e$, (c) a negative charge $(-e)$ of the NO_2^- ion is localized at the middle of the O—O line, (d) in the ordered state, $S = 1$, all NO_2^- ions are arranged in the same direction along the b-axis and (e) in the disordered state, since all NO_2^- ions alternately take two equilibrium positions during a time which is short compared with the inverse of the quadrupole frequency, the charge is represented effectively by a unit charge placed at the middle point of the two equilibrium positions.

The crystal lattices in the ordered state for $S = 1$ and in the disordered state are shown in *Figures* 5(a) and (b), respectively. In the ferroelectric phase for $S < 1$, it is rather difficult to calculate $\Phi_{zz}^{ob}(T)$ as the probabilities of possessing the one of two equilibrium positions, solid and dashed positions in *Figure* 5(b), change according to the degree of long-range order. For

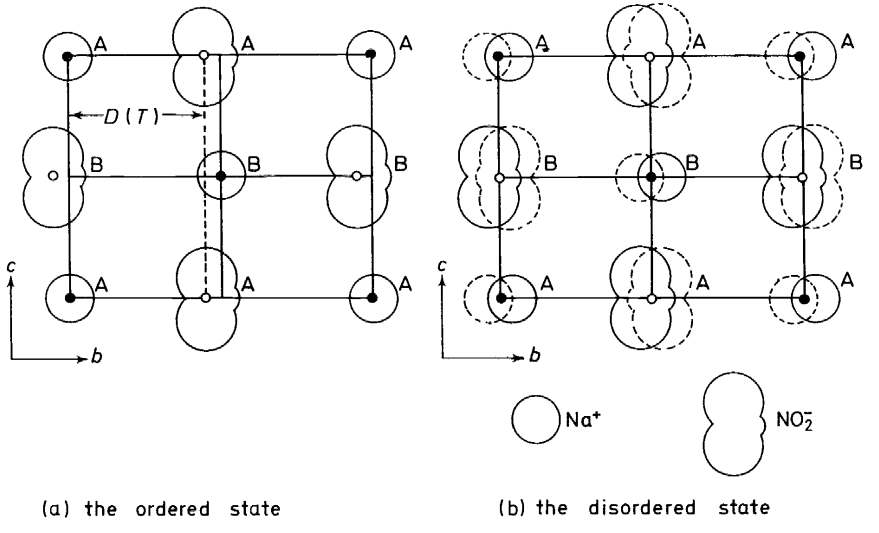


Figure 5. The crystal lattice which is composed of point charges in the two state: (left) the ordered state, (right) the disordered state. $D(T)$ is the distance between the ^{23}Na nucleus concerned and the effective point charge $-e$ located on the nearest NO_2^- ion along the b axis.

the present purpose, the following assumption is made; $\Phi_{zz}^{ob}(T)$ is obtained by superposition of $\Phi_{zz}^{o}(T)$ and $\Phi_{zz}^{D}(T)$, where $\Phi_{zz}^{o}(T)$ is calculated by using the actual lattice constants in the ferroelectric phase under the condition of the ordered state $S = 1$ and $\Phi_{zz}^{D}(T)$ is also calculated by using the fictitious lattice constants extrapolated into the ferroelectric phase from the paraelectric phase as if there were no phase transition under the condition of the disordered state $S = 0$. $\Phi_{zz}^{ob}(T)$ is, thus, written as the mean value of $\Phi_{zz}^{o}(T)$ and $\Phi_{zz}^{D}(T)$ with the probability of P_o and P_D, respectively

$$\Phi_{zz}^{ob}(T) = (\Phi_{zz}^{o}(T) \times P_o + \Phi_{zz}^{D}(T) \times P_D)/(P_o + P_D)$$
$$= (\Phi_{zz}^{o}(T) - \Phi_{zz}^{D}(T)) \times P_o + \Phi_{zz}^{D}(T) \qquad (11)$$

where $P_o + P_D = 1$ and P_o is none other than the long-range order parameter S in the present model, as may be seen easily. $\Phi_{zz}^{ob}(T)$ is finally written as

$$\Phi_{zz}^{ob}(T) = [\Phi_{zz}^{o}(T) - \Phi_{zz}^{D}(T)]\, S(T) + \Phi_{zz}^{D}(T) \qquad (12)$$

which is equivalent to a formula expanded formally in terms of the $S(T)$ to the first term with the temperature-dependent coefficients. In the calculation of $\Phi_{zz}^{o}(T)$, the distance between the ^{23}Na nucleus concerned and the effective point charge $-e$ located on the nearest NO_2^- ion along the b axis, the so-called y coordinate in the structural analysis, is needed at each temperature.

Since the distance was measured only at 20°C and 185°C, the interpolated values have to be used. Furthermore, the Sternheimer constant γ is found to be -3.77 at 20°C where the long-range order parameter S is nearly equal to unity and the value of γ is used to calculate $\Phi_{zz}^{ob}(T)$ from the n.m.r. spectrum through the whole temperature region. From equation 12 the temperature dependence of the long-range parameter may be calculated.

The results are shown in *Figure 6* together with the long-range order

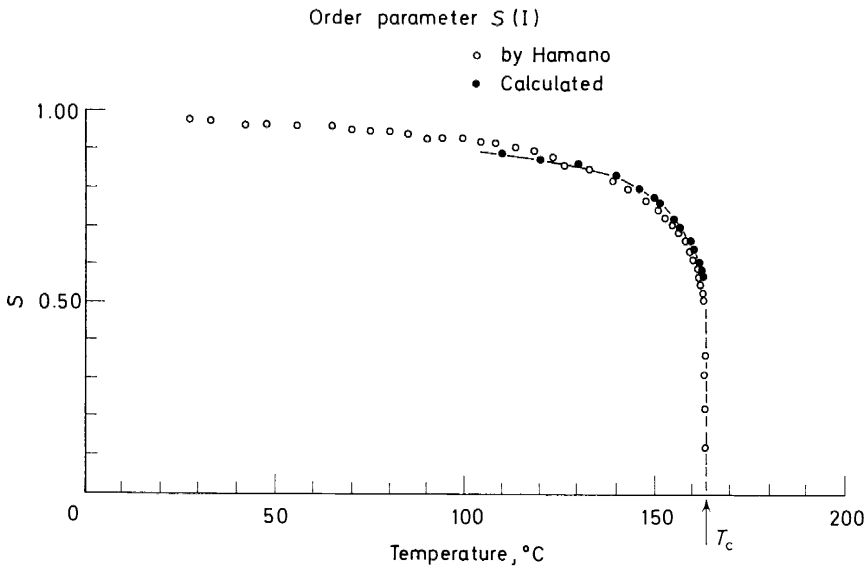


Figure 6. Temperature dependence of the long-range order parameter calculated by equation 12 and the observed one.

parameter obtained from the spontaneous electric polarization P_s measured by Hamano[15] in order to facilitate the comparison. Similar studies are made on e.f.g. of the ^{23}Na nucleus in $AgNa(NO_2)_2$, which seems to undergo an order–disorder ferroelectric transition caused by the NO_2^- ion. The agreement between the calculated $S(T)$ and the long-range order parameter obtained from P_s is fairly good in both cases except near the transition point, in spite of the simplified model and rather crude approximation mentioned above.

Recently, we studied ^{87}Rb and deuteron resonance spectra in $RbDSO_4$. Though the mechanism of the phase transition has not been clarified yet, order–disorder of sulphate groups seems to be a possible trigger. Each spectrum splits into two components below the transition point. The separation $\Delta\Phi_{ij}(T)$ can be written as

$$\Delta\Phi_{ij}(T) = \{[\Phi_{ij}^{o}(T)]_1 - [\Phi_{ij}^{o}(T)]_2\}\, S(T) \tag{13}$$

corresponding to equation 12. If the temperature dependence of $\{[\Phi_{ij}^{o}(T)]_1 - [\Phi_{ij}^{o}(T)]_2\}$ is ignored compared with that of $S(T)$, $\Delta\Phi_{ij}(T)$ should be

proportional to $S(T)$. It is found that $\Delta\Phi_{ij}(T)$ grows as $|T - T_c|^{\beta}$, where β for each separation is in the range of 0.28 to 0.39 for ^{87}Rb and 0.29 to 0.34 for deuteron[16, 17], which should be compared with the temperature dependence of spontaneous polarization.

ACKNOWLEDGEMENTS

We thank Dr K. Gesi of Japan Atomic Energy Research Institute for kindly measuring the spontaneous polarization of $RbDSO_4$. The authors are very grateful to their co-workers for assisting in data acquisition and discussion.

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