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Spin-Lattice Relaxation by Quasi-Spin-Waves in Order-Disorder-Type Ferroelectrics: Polarization Fluctuations in $Ca_2Sr(C_2H_5CO_2)_6$ †

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A theory of nuclear spin-lattice relaxation by unstable, overdamped quasi-spin-waves – or critical polarization fluctuations – in order-disorder ferroelectrics is developed. If relaxation due to competing processes is not too fast, such an unstable mode will dominate the magnetic dipolar or electric quadrupolar relaxation rate not only right at the Curie point, but also in its neighborhood. In such a case, the temperature dependence of T_1 is given by $T_1 \propto |T - T_C|^n$, where $0.5 \leq n \leq 2$, depending on the details of the interaction between the ferroelectric dipoles and the Brillouin-zone size. The theory is applied to the case of ferroelectric dicalcium strontium propionate. This crystal exhibits an anomalous dip in T_1 on approaching T_C which we believe is due to magnetic dipolar coupling to an overdamped, unstable quasi-spin-wave mode.

INTRODUCTION

The nature of the elementary excitations[1,2] in "order-disorder"-type ferroelectric crystals – which can be described as quasi-spin-waves[2] – has recently attracted a great deal of attention, but the experimental evidence is still rather scarce. It has been suggested[3,4] that nuclear spin-lattice relaxation might represent a useful new method to study elementary excitations and lattice instabilities in this type of system, and that the information obtained would be complementary to that from dielectric, ultrasonic, Raman, and neutron-scattering data. The reasoning goes as follows: The nuclear magnetic spin-lattice relaxation time T_1 of a nonequilibrium system is a macroscopic transport coefficient which is related to the statistical fluctuations in the equilibrium ensemble. The natural fluctuations, which occur in a system in equilibrium, are on the other hand related by the fluctuation-dissipation theorem to the imaginary part of the generalized dielectric susceptibility. In crystals undergoing ferroelectric phase transitions, the dominant contribution to the dissipative part of the susceptibility arises from that mode whose frequency approaches zero at the phase transition, while the frequencies of the other lattice modes stay comparatively high. If relaxation due to competing processes is not too fast, such an unstable ferroelectric mode will dominate the nuclear spin-lattice relaxation rate T_1^{-1} not only right at the Curie point but also in its neighborhood.

Though nuclear-magnetic-resonance techniques have been widely used for the study of ferroelectric phase transitions,[5] relatively little attention has been paid so far to the study of quasi-spin-waves or polarization fluctuations and unstable modes by T_1 measurements. It has been only in a few cases that critical polarization fluctuations were reported to dominate electric quadrupole[3] spin-lattice relaxation and in only one case[4] was it suggested that magnetic dipolar spin-phonon coupling to a ferroelectric mode is the rate determining relaxation mechanism.

In this paper, we wish to present a theory of spin-lattice relaxation by ferroelectric quasi-spin-waves for the case of large damping. The case of small damping will be treated in a subsequent paper. Further, we would like to report the observation of an anomalous decrease in the proton spin-lattice relaxation time on approaching the ferroelectric Curie point ($T_C = 8.5$ °C) in dicalcium strontium propionate, $Ca_2Sr(CH_3CH_2CO_2)_6$ (henceforth designated DSP), which we believe is due to magnetic dipolar coupling to an overdamped temperature-dependent "ferroelectric" mode.

EXPERIMENTAL RESULTS

Single crystals of DSP were grown from water solutions of $Ca_2Sr(CH_3CH_2CO_2)_6$ following Matthias and Remeika.[6] In agreement with the data of other investigators,[7] the paraelectric space group was found to be D_4^4 or D_4^8 and the lattice constants $a = 12.53$ Å and $c = 17.26$ Å. The ferroelectric space group[7] is C_4^2 or C_4^4, and the unit cell dimensions are[7] $a = 12.48$ Å and $c = 17.13$ Å. The crystal is polarized along the c direction. The ferroelectric transition at 8.5 °C seems to be a second-order one.[8]

The proton spin-lattice relaxation time T_1 was measured by the 90°-90° pulse method from -170 to $+90$ °C at 9, 15, and 23 MHz. The experimental data are presented in Fig. 1. From 90 °C down to room temperature, T_1 slowly decreases with decreasing temperature. The activation energy deduced from the curve of $\log T_1$ versus $1/T$ is about 0.1 eV. In the vicinity of the Curie point, a new relaxation mechanism becomes rate determining, resulting in an anomalous dip in the proton T_1. The shape of the dip does not depend on the Larmor frequency within the 9–23-MHz range. At still lower temperatures, the same mechanism which dominated T_1 above room temperature takes over again. T_1 slowly decreases with decreasing temperature until a broad minimum at about -173 °C is reached. The depth of the minimum agrees with the value expected for hindered rotation of CH_3 groups. As the correlation times deduced from the T_1 minimum nearly exactly coincide with the lifetime of the CH_3 protons at a given site, obtained from quasielastic neutron-scattering data,[9] one may safely ascribe this motion to hindered rotation of the $-CH_3$ group around its C_3 axis. The activation energy for CH_3 rotation does not significantly change at the Curie point demonstrating that $-CH_3$ rotation plays no role at the ferroelectric transition.

The T_1 data thus show that both at high and at low temperatures, $-CH_3$ rotation dominates the relaxation process, but that in the vicinity of the Curie point a new reorientational mechanism becomes rate determining.

Though the crystal structure of DSP has not yet been completely solved, it seems to be clear that polarization reversal in this crystal is accompanied by a reorientation of two out of the six $CH_3CH_2CO_2$ groups.[7] The twofold symmetry about the C_{carboxyl}-C_α axes in the paraelectric phase further suggests that above T_C the propionate groups are flipping between two equilibrium positions. The low value of the room-temperature proton second moment ($M_2 = 4.5$ G^2) of powdered DSP supports this model. This M_2 value cannot be explained by $-CH_3$ rotation alone – which would yield about 10 G^2 – and requires the existence of additional molecular motion which must be associated with the whole propionate group. The correlated fluctuations of these $CH_3CH_2CO_2$ dipoles may well form a kind of "quasi-spin"-wave dipolar ferroelectric mode,[1,2] the critical slowing down of which may be responsible for the observed dielectric dispersion[8] as well as the anomalous behavior of the proton T_1 in the vicinity of T_C.

THEORY OF NUCLEAR SPIN RELAXATION BY OVERDAMPED QUASI-SPIN-WAVE MODES

Let us calculate the anomalous relaxation rate T_1^{-1} due to the critical slowing down of an overdamped quasi-spin-wave mode, which modulates the interaction Hamiltonian[10]

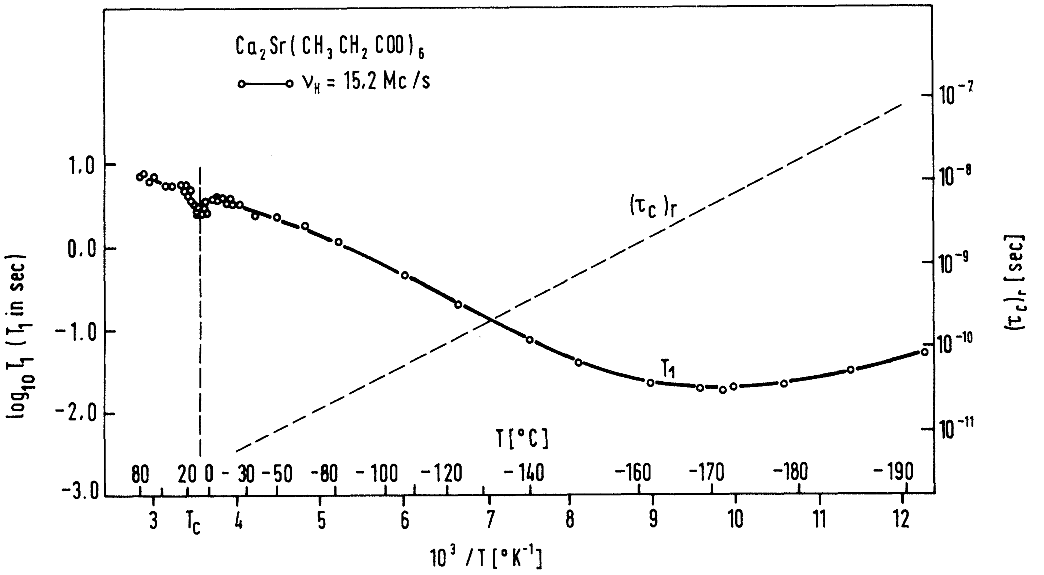

FIG. 1. Temperature dependence of the proton spin-lattice relaxation time in powdered DSP.

$$\mathcal{H}_I = \sum_{i<j} \sum_{k=-2}^{+2} F_{ij}^{(k)} A_{ij}^{(k)} . \qquad (1)$$

In the following, we shall assume that $\mathcal{H}_I$ stands for magnetic dipole-dipole interactions, but the extension to the case of electric quadrupole interactions is straightforward, and the predicted temperature dependence of T_1 is the same. Here $A^{(k)}$ are operators acting on spin variables, whereas the "lattice" functions $F^{(k)}$ are assumed to be implicit functions of time through their dependence on the eigenvectors of the quasi-spin-wave (or polarization) mode.

The total Hamiltonian of our problem is

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_I , \qquad (2)$$

where $\mathcal{H}_I$ is small compared to the Zeeman term $\mathcal{H}_z = -\gamma\hbar \vec{I} \cdot \vec{H}_0$. The spin-lattice relaxation rate will depend on the spectral density of the autocorrelation function of the matrix elements of $\mathcal{H}_I$ with respect to the eigenstates of $\mathcal{H}_z$:

$$G(t) = \langle\langle i|\mathcal{H}_I(0)|f\rangle\langle f|\mathcal{H}_I^{\dagger}(t)|i\rangle\rangle . \qquad (3)$$

If only one species of magnetic nuclei is present, we get in the spin temperature approximation

$$1/T_1 = \tfrac{3}{2}\gamma^4\hbar^2 I(I+1)(2/N')[J^{(1)}(\omega_L) + J^{(2)}(2\omega_L)] , \qquad (4)$$

where N' is the total number of spins in the sample. The spectral densities $J^{(k)}(\omega)$ which are defined as

$$J^{(k)}(\omega_k) = \sum_{i<j,\, i'<j'} \int_{-\infty}^{+\infty} \langle F_{ij}^{(k)}(0) F_{i'j'}^{(k)}(t)\rangle e^{i\omega_k t}\, dt \qquad (5)$$

can be – in the case of molecular crystals such as DSP – conveniently divided into an intramolecular and an intermolecular part:

$$\sum_{i<j} \langle F_{ij}(0) F_{ij}(t)\rangle = \sum_{\alpha<\alpha',\, \beta=\beta'} \langle F_{\alpha\alpha',\beta\beta'}(0) F_{\alpha\alpha',\beta\beta'}(t)\rangle + \sum_{\alpha,\alpha',\, \beta<\beta'} \langle F_{\alpha\alpha',\beta\beta'}(0) F_{\alpha\alpha',\beta\beta'}(t)\rangle . \qquad (6)$$

Here β represents the index of the molecular group, whereas α stands for the index of the nuclei within such a group. The brackets stand for the ensemble average. The first term in Eq. (6) thus represents a sum of the intramolecular and the second term a sum of the intermolecular contributions. This division makes sense if the distances between the nuclei within a group are much smaller than the distances between different groups.

We shall treat the case of a quasi-spin-wave with $S = \frac{1}{2}$ where the molecular group flips between two equilibrium positions, -1 or 2-, corresponding to $S_Z = \frac{1}{2}$ or $S_Z = -\frac{1}{2}$. The variation of $F_{ij}^{(k)}$ with time is in such a case determined by the time variation of the component μ of the group electric dipole moment along the ferroelectric axis:

$$\begin{aligned} F_{\alpha\alpha',\beta\beta'}(t) = {} & \tfrac{1}{2}[1 + p_\beta(t)] F_{\alpha\alpha',\beta\beta'}(1,1) \\ & + \tfrac{1}{2}[1 - p_\beta(t)] F_{\alpha\alpha',\beta\beta'}(2,2) \\ & \text{for} \quad \beta = \beta' , \end{aligned} \qquad (7a)$$

$$\begin{aligned} F_{\alpha\alpha',\beta\beta'}(t) = {} & \tfrac{1}{4}[1 + p_\beta(t)][1 + p_{\beta'}(t)] F_{\alpha\alpha',\beta\beta'}(1,1) \\ & + \tfrac{1}{4}[1 + p_\beta(t)][1 - p_{\beta'}(t)] F_{\alpha\alpha',\beta\beta'}(1,2) \\ & + \tfrac{1}{4}[1 - p_\beta(t)][1 + p_{\beta'}(t)] F_{\alpha\alpha'\beta\beta'}(2,1) \\ & + \tfrac{1}{4}[1 - p_\beta(t)][1 - p_{\beta'}(t)] F_{\alpha\alpha',\beta\beta'}(2,2) , \\ & \text{for} \quad \beta = \beta' \end{aligned} \qquad (7b)$$

where $p = \mu/|\mu|$ and 1 refers to the right and 2 to the wrong equilibrium site. Introducing the Fourier components of p_β

$$p_\beta(t) = (1/\sqrt{N}) \textstyle\sum_{\vec{q}} p(\vec{q}, t)\, e^{i\vec{q}\vec{r}_\beta} , \qquad (8)$$

where N is the number of molecular groups, we can express $J^{(k)}(\omega_k)$ in terms of the spectral densities of the Fourier components of the polarization fluctuations. In the random-phase approximation, we obtain

$$\begin{aligned} \sum_{i<j} \langle F_{ij}(0) F_{ij}(t)\rangle = {} & \text{const} + \tfrac{1}{4} \\ & \times \sum_{\alpha<\alpha',\, \beta=\beta'} |\Delta F_{\alpha\alpha',\beta\beta'}|^2 \frac{1}{N} \sum_{q} \langle p(\vec{q}, 0) p(-\vec{q}, t)\rangle \\ & + \frac{1}{16} \sum_{\alpha,\alpha',\, \beta<\beta'} \Big[P_{\alpha\alpha',\beta\beta'} \sum_{\vec{q}} \frac{1}{N} \langle p(\vec{q}, 0) p(-\vec{q}, t)\rangle \\ & + R_{\alpha\alpha',\beta\beta'} \sum_{\vec{q}} \frac{1}{N} \cos\vec{q}(\vec{r}_\beta - \vec{r}_{\beta'}) \langle p(\vec{q}, 0) p(-\vec{q}, t)\rangle \\ & + S_{\alpha\alpha;\beta\beta'} \sum_{\vec{q},\vec{q}'} \frac{1}{N^2} \langle p(\vec{q}, 0) p(-\vec{q}, t)\rangle \\ & \times \langle p(\vec{q}', 0) p(-\vec{q}', t)\rangle \left(1 + e^{i(\vec{q}+\vec{q}')(\vec{r}_\beta - \vec{r}_{\beta'})}\right)\Big] . \end{aligned} \qquad (9)$$

Here we have

$$|\Delta F_{\alpha\alpha',\beta\beta}|^2 = |F_{\alpha\alpha',\beta\beta}(1,1) - F_{\alpha\alpha',\beta\beta}(2,2)|^2 , \qquad (10a)$$

$$\begin{aligned} P_{\alpha\alpha',\beta\beta'} = {} & 2[F^2_{\alpha\alpha',\beta\beta'}(1,1) + F^2_{\alpha\alpha',\beta\beta'}(2,2) \\ & + 2F^2_{\alpha\alpha',\beta\beta'}(1,2) - 2F_{\alpha\alpha',\beta\beta'}(1,1) F_{\alpha\alpha',\beta\beta'}(2,2) \\ & - 2F_{\alpha\alpha',\beta\beta'}(1,2) F_{\alpha\alpha'\beta\beta'}(2,1)] , \end{aligned} \qquad (10b)$$

$$\begin{aligned} R_{\alpha\alpha',\beta\beta'} = {} & 2[F^2_{\alpha\alpha',\beta\beta'}(1,1) + F^2_{\alpha\alpha;\beta\beta'}(2,2) \\ & - 2F^2_{\alpha\alpha',\beta\beta'}(1,2) - 2F_{\alpha\alpha;\beta\beta'}(1,1) F_{\alpha\alpha',\beta\beta'}(2,2) \\ & + 2F_{\alpha\alpha',\beta\beta'}(1,2) F_{\alpha\alpha',\beta\beta'}(2,1)] , \end{aligned} \qquad (10c)$$

$$\begin{aligned} S_{\alpha\alpha',\beta\beta'} = {} & [F^2_{\alpha\alpha',\beta\beta'}(1,1) + F^2_{\alpha\alpha',\beta\beta'}(2,2) \\ & + 2F^2_{\alpha\alpha',\beta\beta'}(1,2) + 2F_{\alpha\alpha',\beta\beta'}(1,1) F_{\alpha\alpha',\beta\beta'}(2,2) \end{aligned}$$

$$-4F_{\alpha\alpha',\beta\beta'}(1,1)F_{\alpha\alpha',\beta\beta'}(1,2)$$
$$-4F_{\alpha\alpha',\beta\beta'}(2,2)F_{\alpha\alpha',\beta\beta'}(1,2)$$
$$+2F_{\alpha\alpha',\beta\beta'}(1,2)F_{\alpha\alpha',\beta\beta'}(2,1)] \;, \qquad (10d)$$

with $\beta \neq \beta'$.

If the division of the interactions into an intra- and an intergroup part is well justified – as is the case in DSP – the terms with P, R, and S are negligibly small as compared to the $|\Delta F|^2$ term in Eq. (9). In such a case, we get from (5)

$$J^{(k)}(\omega_k) = \frac{1}{4N} \sum_{\alpha<\alpha',\beta=\beta'} \left| \Delta F^{(k)}_{\alpha\alpha',\beta\beta'} \right|^2 \times \sum_{\vec{q}} \int_{-\infty}^{+\infty} \langle p(\vec{q},0) p(-\vec{q},t)\rangle e^{i\omega_k t}\, dt \;. \qquad (11)$$

Using the fluctuation-dissipation theorem, we can relate the spectral densities of the Fourier components of the polarization fluctuations to the imaginary part of the wave-number-dependent generalized dielectric susceptibility $\chi(\vec{q},\omega)$.

In the classical limit $kT \gg \hbar\omega$, we obtain

$$J^{(k)}(\omega_k) = A(kT/\omega_k) \sum_{\vec{q}} \chi''(\vec{q},\omega_k) \;, \qquad (12)$$

where

$$A = \tfrac{1}{4} \sum_{\alpha<\alpha',\beta=\beta'} \left|\Delta F^{(k)}_{\alpha\alpha',\beta\beta'}\right|^2 [V/(N\mu)^2] 2\epsilon_0$$

with $\epsilon_0 = 1/4\pi$ in cgs units. The dominant contribution to the dissipative part of the susceptibility arises from the mode whose frequency approaches zero at the phase transition. In view of the apparent overdamping of this quasi-spin-wave mode in many order-disorder ferroelectrics, we do not attempt to fit $\chi''(\vec{q},\omega)$ to a damped harmonic oscillator function, but rather use the Kubo expression[11] for an Ising model:

$$\chi(\omega,\vec{q}) = \beta C/[1-\beta J(\vec{q}) + i\omega\tau] \quad , \qquad (13)$$

where $\beta = (kT)^{-1}$ and $C = N\mu^2/(\epsilon_0 V)$. The dissipative part of the generalized dynamic susceptibility is then[11] obtained as

$$\chi''(\omega,\vec{q}) = \chi(\vec{q},0)\{\omega\tau_{\vec{q}}/[1+(\omega\tau_{\vec{q}})^2]\}, \qquad (14)$$

where for $T > T_C$

$$\tau_{\vec{q}} = \tau_0\, T/[T - T_C(\vec{q})] \;, \qquad (15a)$$

$$\chi(\vec{q},0) = \beta C\, T/[T - T_C(\vec{q})] \;, \qquad (15b)$$

and for $T < T_C$

$$\tau_{\vec{q}} \approx \tau_0 [1 + 2T_C(\vec{q})/T - 3T_C(\vec{q})/T_C]^{-1} \qquad (16a)$$

and

$$\chi(\vec{q},0) \approx \beta C [1 + 2T_C(\vec{q})/T - 3T_C(\vec{q})/T_C]^{-1} \;, \qquad (16b)$$

with $T_C(\vec{q}) = J(\vec{q})/k$ and $T_C = J(\vec{q}=0)/k$. Here τ_0 is the correlation time for the flipping motion of a noninteracting dipolar group and the factor $T/[T - T_C(\vec{q})]$ represents the critical slowing down of the quasi-spin-wave fluctuations with wave vector $\vec{q}$ due to the interaction

$$J(\vec{q}) = \sum_j J_{ij} e^{i\vec{q}\cdot\vec{R}_{ij}}$$

between the dipolar groups in the system.

A rough estimate of the sum occurring in Eq. (12) can be obtained by using

$$T_C(q) = T_C(1 - \alpha q^2) \qquad (17)$$

(where for nearest-neighbor interactions $\alpha = \frac{1}{6} d^{-2}$ with d being the nearest-neighbor distance between the dipolar groups) and by replacing the summation over all q values within the first Brillouin zone by an integration over a sphere:

$$\sum_q \chi''(q,\omega) = (V/2\pi^2) \int_0^{q_{\max}} q^2 dq\, \chi''(\omega,q) \;, \qquad (18)$$

where $q_{\max} = (6\pi^2/V)^{1/3}$. For the spectral density of the fluctuations of the lattice part of Hamiltonian (1) due to the ferroelectric quasi-spin-wave mode, one thus finds

$$J^{(k)}(\omega_k) = \frac{V}{4N} \sum_{\alpha<\alpha',\beta=\beta'} \left|\Delta F^{(k)}_{\alpha\alpha',\beta\beta'},\right|^2 \frac{\alpha^{-3/2}}{\pi^2} \times I(T, T_C, \alpha q_m^2, \omega\tau_0)\tau_0 \;, \qquad (19)$$

where, for $T > T_C$,

$$I = (T/T_C)^2 [T_C/(T-T_C)]^{1/2} \mathcal{K}(u_m, a) \;, \qquad (20)$$

whereas, for $T < T_C$,

$$I = \frac{[T/2(T_C - T)]^2}{[T/2(T_C - T) - 1]^{3/2}} \mathcal{K}(u_m, a) \;, \qquad (21)$$

$$\text{with} \quad K(u_m, a) = \int_0^{um} \frac{u^2 du}{(1+u^2)^2 + a^4} \;. \qquad (22a)$$

Here

$$u_m = [T_C/(T - T_C)]^{1/2} \alpha^{1/2} q_m \qquad \text{for } T > T_C \qquad (22b)$$

and

$$u_m = [T/2(T_C - T) - 1]^{1/2} \alpha^{1/2} q_m \qquad \text{for } T < T_C \;, \qquad (22c)$$

$$\text{whereas} \quad a = \omega\tau_0 T/(T - T_C) \qquad \text{for } T > T_C \qquad (22d)$$

$$\text{and} \quad a = \omega\tau_0 T/2(T_C - T) \qquad \text{for } T < T_C \;. \qquad (22e)$$

The general expression for $\mathcal{K}(u_m, a)$ is rather lengthy and is given in Appendix A. For $a \to 0$ (or, what is the same, $\omega\tau_0 \ll 1$), however, this expression becomes rather simple:

$$\mathcal{K}(u_m, 0) = \tfrac{1}{2}[\arctan u_m - u_m/(1 + u_m^2)] \;. \qquad (23)$$

To get a rough estimate of the temperature dependence of T_1 in the vicinity of the Curie point, we can now treat two limiting cases $u_m \rightarrow \infty$ and $u_m \rightarrow 0$. For $\alpha^{1/2} q_m \rightarrow \infty$, we have

$$I = \tfrac{1}{2}\pi[T_C/(T - T_C)]^{1/2} \quad \text{for } T > T_C \tag{24a}$$

and $$I = \tfrac{1}{2}\pi[T_C/2(T_C - T)]^{1/2} \quad \text{for } T < T_C . \tag{24b}$$

For $\alpha^{1/2} q_m \rightarrow 0$, on the other hand, we get

$$I = \tfrac{1}{3}(\alpha^{1/2} q_m)^3 [T_C/(T - T_C)]^2, \quad T > T_C \tag{25a}$$

and

$$I = \tfrac{1}{3}(\alpha^{1/2} q_m)^3 [T/2(T_C - T)]^2, \quad T < T_C . \tag{25b}$$

In the first of these two limiting cases, we thus obtain for the temperature dependence of T_1 near the Curie point

$$T_1 \propto |T - T_C|^{1/2}, \quad \alpha^{1/2} q_m \rightarrow \infty , \tag{26a}$$

whereas in the second case we get a result which was already obtained in a previous paper[4]:

$$T_1 \propto (T - T_C)^2, \quad \alpha^{1/2} q_m \rightarrow 0 . \tag{26b}$$

It should be stressed that very close to the Curie point we shall always be in the limit $u_m \rightarrow \infty$ so that T_1 will be proportional to $|T - T_C|^{1/2}$ if the Kubo expression for $\chi(q, \omega)$ is still valid.

APPLICATION TO DSP

Let us now apply these results to polycrystalline DSP where the flipping of two out of the six $CH_3CH_2CO_2$ groups in the unit cell gradually freezes in on approaching T_C from above.

For the case of a polycrystalline sample

$$\frac{1}{N'} \sum_{\alpha < \alpha', \beta \neq \beta'} |\Delta F_{\alpha\alpha', \beta\beta'}|^2 = \tfrac{1}{5} \sum_{\alpha < \alpha'} \langle |\Delta F_{\alpha\alpha', \beta\beta'}|^2 \rangle_{\text{av}}$$
$$\simeq \tfrac{1}{5} \langle |\Delta F_{\alpha\alpha'}(CH_2)|^2 \rangle_{\text{av}} + \tfrac{1}{5} \sum_{\alpha < \alpha'} \langle |\Delta F_{\alpha\alpha'}(CH_3)|^2 \rangle_{\text{av}} , \tag{27}$$

where the symbol $\langle \, \rangle_{\text{av}}$ designates an isotropic powder average over all possible orientations of the propionate groups with respect to the direction of the external magnetic field.

Since only two out of the six propionate groups are involved in the quasi-spin-wave mode and thus undergo the critical slowing down, one has

$$T_1^{-1} = (T_1^{-1})_a + (T_1^{-1})_n , \tag{28}$$

where $$(T_1^{-1})_a = \tfrac{1}{3}(2/5 T_1^{CH_2} + 3/5 T_1^{CH_3})_a \tag{29a}$$

and $$(T_1^{-1})_n = \tfrac{2}{3}(2/5 T_1^{CH_2} + 3/5 T_1^{CH_3})_n , \tag{29b}$$

with the index a standing for the anomalous "pure flipping" contribution and n for the normal contribution to T_1^{-1}. It is well known that

$$F^{(1)}_{\alpha\alpha'} = \sin\theta_{\alpha\alpha'} \cos\theta_{\alpha\alpha'} \exp(i\phi_{\alpha\alpha'}) r^{-3}_{\alpha\alpha'} \tag{30a}$$

and $$F^{(2)}_{\alpha\alpha'} = \sin^2\theta_{\alpha\alpha'} \exp(2i\phi_{\alpha\alpha'}) r^{-3}_{\alpha\alpha'} , \tag{30b}$$

with $r_{\alpha\alpha'}$ being the distance between the nuclei α and α' and with $\theta_{\alpha\alpha}'$ designating the angle between the internuclear vector and the direction of the external magnetic field, which is a function of time because of the flipping of the molecular group between the two equilibrium positions. As shown in Appendix B, we obtain for the case that the flipping axis is perpendicular to the H-H direction in the CH_2 group

$$\langle |\Delta F^{(1)}_{CH_2}|^2 \rangle_{\text{av}} = (1/r^6_{CH_2}) \times \tfrac{2}{5} \sin^2\beta \tag{31}$$

and $$\langle |\Delta F^{(2)}_{CH_2}|^2 \rangle_{\text{av}} = (1/r^6_{CH_2}) \times \tfrac{8}{5} \sin^2\beta , \tag{32}$$

where r_{CH_2} is the proton-proton distance in the CH_2 group and where β is the "flipping angle" of the molecular axis which is determined by the distance between the two equilibrium sites.

In contrast to the $-CH_2$ group case the intragroup magnetic dipolar interactions of the $-CH_3$ group protons are already partially averaged out because of hindered rotation around the C_3 axis. The flipping motion thus modulates only the residual part of the dipolar interactions. Assuming that the flipping motion of the propionate group and the $-CH_3$ group rotation are not correlated, we obtain for the flipping contribution to the $-CH_3$ spin-lattice relaxation rate (Appendix B)

$$\sum_{\alpha < \alpha'} \langle |\Delta F^{(1)}_{\alpha\alpha'}(CH_3)|^2 \rangle_{\text{av}} = (1/r^6_{CH_3}) \times \tfrac{3}{5} \sin^2\beta , \tag{33}$$

$$\sum_{\alpha < \alpha'} \langle |\Delta F^{(2)}_{\alpha\alpha'}(CH_3)|^2 \rangle_{\text{av}} = (1/r^6_{CH_3}) \times \tfrac{9}{10} \sin^2\beta , \tag{34}$$

if the flipping axis is perpendicular to the C_3 axis, and

$$(1/T_1^{CH_3})_a = \tfrac{3}{4}(1/T_1^{CH_2})_a \, r^6_{CH_2}/r^6_{CH_3} . \tag{35}$$

If the proton-proton distances in the $-CH_2$ and $-CH_3$ groups are about equal, we get from Eq. (29a) a simple expression for the ferroelectric quasi-spin-wave flipping mode contribution $(T_1)_a$ to the proton spin-lattice relaxation time in DSP:

$$(T_1)_a = 3.5(T_1^{CH_2})_a , \tag{36}$$

where according to Eqs. (4) and (19)

$$\left(\frac{1}{T_1^{CH_2}}\right)_\alpha = \frac{9}{32\pi^2} \alpha^{-3/2} \times \frac{V}{N} \frac{\gamma^4 \hbar^2}{r^6_{CH_2}} \sin^2\beta \, I(T, T_C, \alpha^{1/2} q_m) \tau_0 . \tag{37}$$

The dielectric correlation time τ_0 in DSP is known – from dielectric dispersion data (Fig. 2) – to behave like

$$\tau_0 = \tau_0^0 \exp(+E/kT), \tag{38}$$

where $E \approx 0.25$ eV and $\tau_0^0 = 5 \times 10^{-15}$ sec, so that

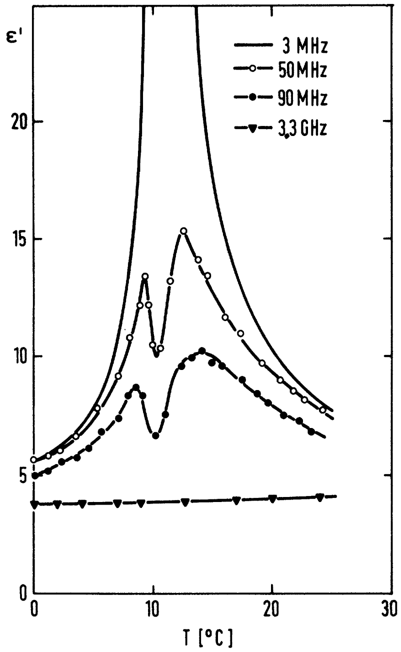

FIG. 2. Dielectric constant versus temperature at various frequencies in DSP, following Ref. (8).

$\tau_0(T \approx T_C) = 2.3\times10^{-11}$ sec justifying the approximation $\omega_L\tau_0 \ll 1$. From the unit cell dimensions we get $q_{\max} \approx 0.28$ Å^{-1} and $\alpha q^2_{\max} \approx 0.25$ for nearest-neighbor coupling. The temperature dependence of the anomalous contribution to the relaxation rate is now fixed, and the above model can be checked by comparing the observed and predicted relaxation rates due to the freezing in of the quasi-spin-wave mode.

The experimental relaxation rate due to the critical "flipping" is obtained by subtracting the "normal" relaxation rate from the observed total relaxation rate. Since the rotational minimum is far away from the region where the anomalous flipping contribution is observable, this separation can be done in a unique way. The resulting temperature dependence of $(T_1)_a$ is presented in Fig. 3.

Taking the r_{CH_2} distance as 1.8 Å and matching the experimental and theoretical T_1-versus-T curves at one temperature, we get for the flipping angle the rather reasonable value $\beta = 38°$. From the room-temperature value of the proton second moment, on the other hand, we obtain $\beta = 40°$ (Appendix B). What is even more satisfactory is the excellent agreement between the observed and theoretical temperature dependences of the "anomalous" spin-lattice relaxation time in the paraelectric as well as in the ferroelectric phase (Fig. 3).

It should be stressed that though the two equilibrium sites are not anymore equivalent below T_c, this asymmetry $\Delta E \approx 2\times10^{-3}$ eV is small compared to kT and its effect on $(T_1)_a$ can therefore be neglected.

If one, on the other hand, interprets the T_1 anomaly as a normal BPP minimum,[10] which occurs when the correlation time for the thermally activated molecular motion is of the order of the inverse Larmor frequency, one obtains an impossibly short value for τ_0^0 ($\approx 10^{-33}$ sec) and too large an activation energy $E_a = 1.3$ eV. Another deficiency of this interpretation is that it cannot explain the frequency independence of the T_1 anomaly.

The above results thus seem to show that the T_1 anomaly at T_C in DSP is indeed the result of magnetic dipolar spin-quasi-spin-wave coupling to a ferroelectric "flipping" mode, and that the theory presented in this paper is not a too unreasonable approximation.

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APPENDIX A

We wish to evaluate the integral [Eq. (22)]

$$\mathcal{K}(u_m, a) = \int_0^{u_m} \frac{u^2\,du}{(1+u^2)^2 + a^4} \tag{A1}$$

in its general form. Using

$$\mathcal{K}(u_m, a) = \int_0^{u_m} \frac{u^2\,du}{(1+u^2+ia^2)(1+u^2-ia^2)}$$

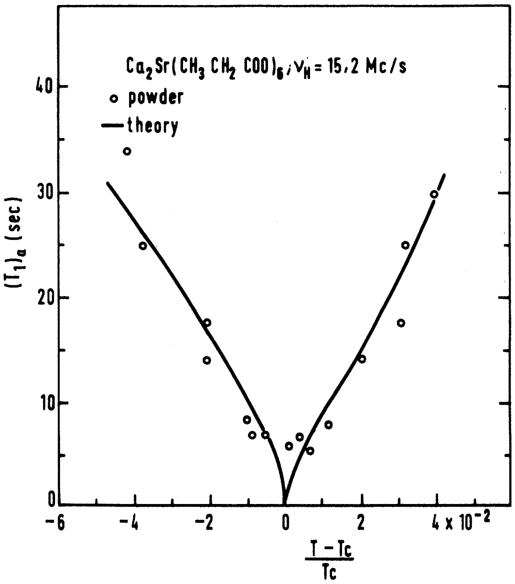

FIG. 3. Comparison of the theoretical (solid line) and experimental (circles) temperature dependences of the "anomalous" proton spin-lattice relaxation time in DSP near T_C.

$$=\frac{i}{2a^2}\int_0^{u_m}\left[\frac{1-ia^2}{1+u^2-ia^2}-\frac{1+ia^2}{1+u^2+ia^2}\right]du, \quad \text{(A2)}$$

we get

$$\mathcal{K}(u_m,a)=\frac{1}{4a^2}\Bigg(\{\tfrac{1}{2}[(1+a^4)^{1/2}+1]\}^{1/2}$$

$$\times\ln\frac{(1+a^4)^{1/2}+u_m^2+2u_m\{\frac{1}{2}[(1+a^4)^{1/2}-1]\}^{1/2}}{(1+a^4)^{1/2}+u_m^2-2u_m\{\frac{1}{2}[(1+a^4)^{1/2}-1]\}^{1/2}}$$

$$-2\{\tfrac{1}{2}[(1+a^4)^{1/2}-1]\}^{1/2}$$

$$\times\arctan\frac{\{2[(1+a^4)^{1/2}+1]\}^{1/2}u_m}{(1+a^4)^{1/2}-u_m^2}\Bigg). \quad \text{(A3)}$$

This reduces in the limit $a \rightarrow 0$ to Eq. (23).

APPENDIX B

Let us now sketch the derivation of Eqs. (31)–(34) as well as of the theoretical expression for the proton second moment of powdered DSP at room temperature.

Introducing the Euler angles ϑ, φ, and ψ [see Fig. 4(a)] – as described in Ref. 12 – one obtains from (30a) and (30b) for the case of the $-CH_2$ group

$$F_{\alpha\alpha'}(CH_2)=(e^{i\psi}/r^3_{CH_2})\{\sin\vartheta\sin\varphi(t)$$

$$\times[\cos\varphi(t)+i\cos\vartheta\sin\varphi(t)]\}\ , \quad \text{(B1)}$$

where ϑ is the angle between the direction of the external magnetic field and the flipping axis, and where φ is time dependent because of flipping between the two equilibrium sites: $\varphi(1)=\varphi, \varphi(2)=\varphi+\beta$. Hence,

$$\Delta F^{(1)}_{\alpha\alpha'}=F^{(1)}_{\alpha\alpha'}(r,\vartheta,\varphi,\psi)-F^{(1)}_{\alpha\alpha'}(r,\vartheta,\varphi+\beta,\psi) \quad \text{(B2)}$$

if the flipping axis is perpendicular to the interproton vector $\vec{r}_{CH_2}$ in the $-CH_2$ group. Inserting (B1) into (B2), squaring, and performing a powder average over ϑ and φ, we get Eq. (31):

$$\langle|\Delta F^{(1)}_{\alpha\alpha'}(CH_2)|^2\rangle_{av}=(1/r^6_{CH_2})\times\tfrac{2}{5}\sin^2\beta\ . \quad \text{(B3)}$$

Similarly, we have

$$F^{(2)}_{\alpha\alpha'}(CH_2)=(e^{2i\psi}/r^3_{CH_2})[\cos\varphi(t)+i\cos\vartheta\sin\varphi(t)]^2\ . \quad \text{(B4)}$$

Using the procedure described above, we get Eq. (32) from (B4) in a straightforward way.

In case of the CH_3 group because of simultaneous rotation and flipping, ϑ as well as φ are time dependent. Using a somewhat different set of Euler angles as before, where now ϑ and ψ are time dependent because of flipping, and φbecause of both flipping and hindered rotation [see Figs. 4(b) and 4(c)], we get

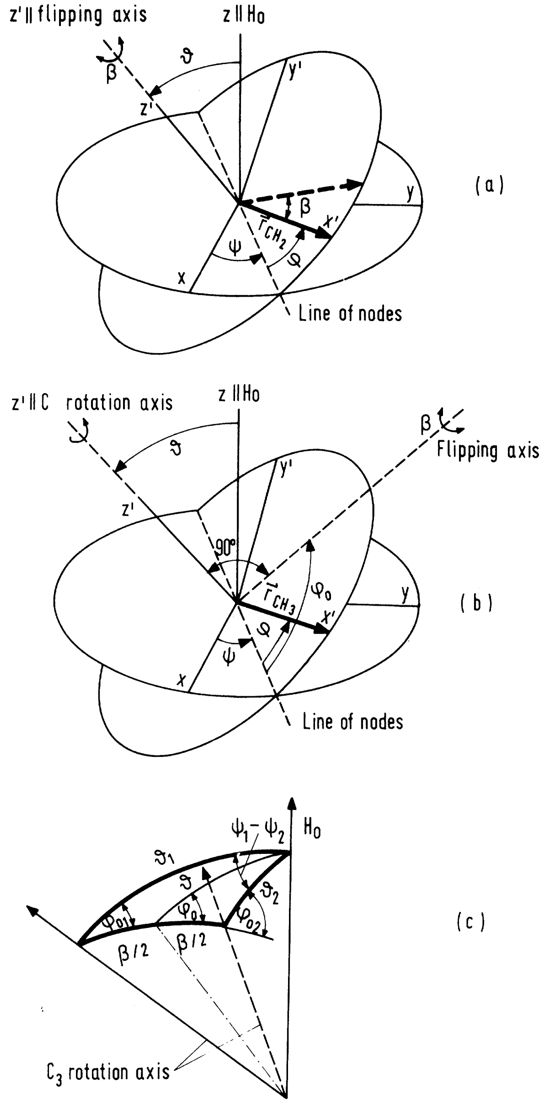

FIG. 4. Euler angles ϑ, φ, and ψ used for the description of the $-CH_2$ and $-CH_3$ motion.

$$F^{(1)}_{\alpha\alpha'}(CH_3)=\frac{e^{i\psi(t)}}{r^3_{CH_3}}\{\sin\vartheta(t)\sin\varphi(t)$$

$$\times[\cos\varphi(t)+i\cos\vartheta(t)\sin\varphi(t)]\} \quad \text{(B5)}$$

and

$$F^{(2)}_{\alpha\alpha'}(CH_3)=\frac{e^{2i\psi(t)}}{r^3_{CH_3}}[\cos\varphi(t)+i\cos\vartheta(t)\sin\varphi(t)]^2\ . \quad \text{(B6)}$$

Since the fluctuations due to flipping and rotation are not correlated, the autocorrelation function of $\Delta F^{(k)}_{CH_3}$ is given by a sum of products of the various autocorrelation functions for flipping and rotation. The pure flipping contribution is obtained in the limit of an infinitely short rotational correlation time as

$$\sum_{\alpha\alpha'}\langle|\Delta F^{(1)}_{\alpha\alpha'}(\mathrm{CH_3})|^2\rangle_{\mathrm{av}}=\frac{3}{16r^6_{\mathrm{CH_3}}}\times\langle|e^{i\psi_1}\sin 2\vartheta_1-e^{i\psi_2}\sin 2\vartheta_2|^2\rangle_{\mathrm{av}}\,, \qquad \text{(B7)}$$

$$\sum_{\alpha\alpha'}\langle|\Delta F^{(2)}_{\alpha\alpha'}(\mathrm{CH_3})|^2\rangle_{\mathrm{av}}=\frac{3}{4r^6_{\mathrm{CH_3}}}\times\langle|e^{2i\psi_1}\sin^2\vartheta_1-e^{2i\psi_2}\sin^2\vartheta_2|^2\rangle_{\mathrm{av}}\,, \qquad \text{(B8)}$$

where the angles ϑ_1, ϑ_2, ψ_1, and ψ_2 are defined in the Figs. 4(b) and 4(c). Using well-known relations for the spherical triangles to express ϑ_1, ϑ_2, and $(\psi_1-\psi_2)$ in terms of the flipping angle β, one obtains, after taking the powder average, Eqs. (33) and (34).

At room temperature, all propionate groups in DSP are flipping with a frequency which is large as compared to the rigid lattice proton linewidth.[13] The second moment of such a group is

$$M_2=\tfrac{3}{5}\langle\!\langle M_2(\mathrm{CH_3})\rangle\!\rangle+\tfrac{2}{5}\langle\!\langle M_2(\mathrm{CH_3})\rangle\!\rangle+\alpha^2\,, \qquad \text{(B9)}$$

where the symbol $\langle\,\rangle$ designates an average over molecular motion. $M_2(\mathrm{CH_3})$ and $M_2(\mathrm{CH_2})$ stand for the second moments of the isolated $-\mathrm{CH_3}$ and $-\mathrm{CH_2}$ groups, respectively, and α^2 is the intergroup contribution to the second moment. For the case of a polycrystalline sample, we have

$$\langle M_2\rangle=\tfrac{3}{2}\gamma^4\hbar^2(1/N)I(I+1)\sum_{j<k}\langle\langle\!\langle F^{(0)}_{jk}(t)\rangle\!\rangle^2\rangle_{\mathrm{av}}\,, \qquad \text{(B10)}$$

where $F^{(0)}_{jk}$ is

$$F^{(0)}_{jk}=(1-3\cos^2\theta_{jk})r^{-3}_{jk} \qquad \text{(B11)}$$

and N stands now for the number of nonequivalent nuclei in the group under consideration.

Introducing the Euler angles and using for the "flipping" average

$$\langle\!\langle F^{(0)}(t)\rangle\!\rangle=\tfrac{1}{2}[1+p]F^{(0)}(r,\vartheta,\varphi_1)+\tfrac{1}{2}[1-p]F^{(0)}(r,\vartheta,\varphi_2)\,, \qquad \text{(B12)}$$

we get for the $-\mathrm{CH_2}$ group contribution

$$\langle\!\langle M_2(\mathrm{CH_2})\rangle\!\rangle_{\mathrm{flip}}=\tfrac{3}{4}\gamma^4\hbar^2[I(I+1)/r^6_{\mathrm{CH_2}}]\times\tfrac{4}{5}[1-\tfrac{3}{4}(1-p^2)\sin^2\beta]\,. \qquad \text{(B13)}$$

In case of the $-\mathrm{CH_3}$ group, in addition to φ_1 the angles ψ and ϑ are also time dependent. We get

$$\langle\!\langle M_2(\mathrm{CH_3})\rangle\!\rangle_{\mathrm{flip+rot}}=\langle\!\langle M_2(\mathrm{CH_3})\rangle\!\rangle_{\mathrm{rot}}[1-\tfrac{3}{4}(1-p^2)\sin^2\beta]\,. \qquad \text{(B14)}$$

Assuming $r_{\mathrm{CH_2}}\approx r_{\mathrm{CH_3}}\approx 1.8$ Å, we get for the rigid lattice values of $M_2(\mathrm{CH_2})$ and $M_2(\mathrm{CH_3})$ 10 and 20 G^2, respectively. As $\langle\!\langle M_2(\mathrm{CH_3})\rangle\!\rangle_{\mathrm{rot}}=\frac{1}{4}M_2(\mathrm{CH_3})=5\ \mathrm{G}^2$, we can fit the experimental data with a flipping angle of $\beta=40^\circ$. The $-\mathrm{CH_2}$ and $-\mathrm{CH_3}$ contributions are then $\langle\!\langle M_2(\mathrm{CH_2})\rangle\!\rangle_{\mathrm{flip}}=6.3\ \mathrm{G}^2$ and $\langle\!\langle M_2(\mathrm{CH_3})\rangle\!\rangle_{\mathrm{rot+flip}}=3.2\ G^2$, so that $M_2\approx 4.5\ \mathrm{G}^2$, if α^2 is negligible.

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