SPIN-LATTICE RELAXATION BY THE FERROELECTRIC MODE IN KH_2PO_4†

R. Blinc*
Argonne National Laboratory, Argonne, Illinois

and

S. Zumer
The University of Ljubljana, Ljubljana, Yugoslavia

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The observed anomalous decrease in the P^{31} spin-lattice relaxation time on approaching the Curie point in a very pure KH_2PO_4 crystal is explained as being due to magnetic dipolar coupling to the temperature-dependent ferroelectric mode.

A great deal of attention has been devoted to theoretical studies of the nature of the elementary excitations in hydrogen-bonded ferroelectrics,[1,2] but the experimental evidence is still rather scarce.[2] Only recently Kaminow[3] has found in the Raman spectra of KH_2PO_4 a broad temperature-dependent band, which becomes stronger and narrower as one approaches the Curie point, and here we report the first observation of anomalous nuclear spin-lattice relaxation in KH_2PO_4 by what we believe is magnetic dipolar coupling to the ferroelectric lattice mode. The temperature dependence of our P^{31} relaxation times can be fitted to a simple damped-harmonic-oscillator-type ferroelectric mode, the characteristic freqeuncy of which becomes anomalously low as one approaches the Curie point. In contrast to Kaminow's data,[3] however, our results indicate that the damping of the ferroelectric mode is not constant but decreases in the vicinity of the Curie point.

It is generally assumed[4] that magnetic nuclear-spin–phonon coupling is a negligible relaxation mechanism in solids. The present results show that this is not always the case and that nuclear-spin–phonon relaxation may be in certain situations a powerful tool for the study of unstable lattice modes. The reasoning goes as follows: The nuclear magnetic spin-lattice relaxation time T_1 of a nonequilibrium system 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 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 certain conditions are met, such an unstable mode thus dominates the nuclear spin-lattice relaxation rate T_1^{-1} as well.

In the case of KH_2PO_4, the phosphorus relaxation rate $(1/T_1)_P$ is determined by the fluctuations of the proton-phosphorus magnetic dipolar interaction Hamiltonian

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

where as usual[5] the $F_{ij}^{(q)}$ are functions of the relative positions of the two spins and the $A^{(q)}$ are operators acting on the spin variables. In the spin temperature approximation[6] one finds

$$(1/T_1)_P=\hbar^2\gamma_P^2\gamma_H^2I(I+\tfrac{1}{2})(1/N_P)\times\{\tfrac{1}{12}J_{(\omega_H-\omega_P)}^{(0)}+\tfrac{3}{2}J_{(\omega_P)}^{(1)}+\tfrac{3}{4}J_{(\omega_H+\omega_P)}^{(2)}\},\tag{2}$$

where the spectral densities $J^{(q)}$ of the autocorrelation functions of $F_{ij}^{(q)}$,

$$J^{(q)}(\omega_\kappa)=\sum_{ij}\int_{-\infty}^{+\infty}\langle F_{ij}^{(q)*}(t)F_{ij}^{(q)}(t')\rangle\times\exp(i\omega_\kappa t)dt,\tag{3}$$

can be expressed in terms of the spectral densities of the mean-square-polarization fluctuations,

$$J^{(q)}(\omega_\kappa)=\tfrac{1}{4}\sum_{ij}|\Delta F_{ij}^{(q)}|^2\int_{-\infty}^{+\infty}\langle p_{ij}(t)p_{ij}(t')\rangle\times\exp(i\omega_\kappa t)dt.\tag{4}$$

The variation of F_{ij} with time is determined by the time variation of the fractional spontaneous polarization $p_{ij}(t)$:

$$F^{(q)}(t)=\tfrac{1}{2}[1+p(t)]F^{(q)}(1)+\tfrac{1}{2}[1-p(t)]F^{(q)}(2), \quad (5)$$

and

$$\langle F^{(q)*}(t)F^{(q)}(t')\rangle = \tfrac{1}{4}\langle p(t)p(t')\rangle\,|F^{(q)}(1)-F^{(q)}(2)|^2+\text{const}, \quad (6)$$

where $F(1)$ refers to the proton-phosphorus interaction term with the proton in the "right" and $F(2)$ to the term with the proton in the "wrong" equilibrium site in the H bond. Using the fluctuation-dissipation theorem,[7] we can relate the spectral densities of the long-wavelength polarization fluctuations to the imaginary part of the dielectric susceptibility $\chi''(\omega_K)$, so that Eq. (3) becomes

$$J^{(q)}(\omega_K)=\frac{N}{V}\frac{\hbar\epsilon_0}{4P_S^2}\coth\left(\frac{\hbar\omega_K}{2k_BT}\right) \times\sum_{ij}|\Delta F_{ij}^{(q)}|^2\chi''(\omega_K), \quad (7)$$

where P_S stands for the saturation value of the spontaneous polarization and all other symbols have their usual significance. In the vicinity of the Curie point, the dominant contribution to χ'' arises from the ferroelectric mode, so that one may use for χ a simple damped-harmonic-oscillator function, $\chi(\omega)=\omega_0^2\chi(0)/(\omega_0^2-\omega^2+i\omega2\Gamma)$. Since the nuclear Larmor frequencies ω_K are – except within 10^{-4} °K of T_C – much lower than the characteristic oscillator frequency ω_0 or the damping constant 2Γ of the ferroelectric mode, the imaginary part of χ in the ω_K frequency range equals

$$\chi''(\omega_K)\approx\omega_K\chi(0)2\Gamma/\omega_0^2, \quad (8)$$

and, since $\coth(\hbar\omega_K/2k_BT)\approx 2k_BT/\hbar\omega_K$, the spectral densities $J^{(q)}(\omega_K)$ become proportional to $\chi''(\omega_K)/\omega_K$ and hence frequency independent. Evaluating the lattice sums

$$\sum_{ij}|\Delta F_{ij}^{(q)}|^2=\tfrac{1}{2}NS^{(q)}$$

from the known crystal structure of KH_2PO_4 – $S^{(0)}=0.685\times10^{-3}$ Å^{-6}, $S^{(1)}=0.165\times10^{-2}$ Å^{-6}, $S^{(2)}=0.582\times10^{-2}$ Å^{-6} – and using the familiar Curie-Weiss law for the static susceptibility $\chi(0)=C/(T-T_C)$, one can obtain from the temperature dependence of $(T_1)_P$ the temperature dependence of $\omega_0^2/2\Gamma$:

$$(T_1)_P=A\frac{\omega_K}{\chi''(\omega_K)}=A\frac{\omega_0^2}{2\Gamma}\frac{T-T_C}{C}, \quad (9)$$

where $A=0.25\times10^{-6}$ sec^2 for KH_2PO_4.

In using Eq. (9), only the dipolar part of $(T_1)_P^{-1}$ has to be considered and the "background" contribution due to spin diffusion to paramagnetic impurities has to be subtracted (Fig. 1). Our data obtained both by pulse and "signal decay" methods on a very pure KH_2PO_4 single crystal show that for $T>T_C$ and $T<T_C$ the phosphorus relaxation time $(T_1)_P$ is not linear in $T-T_C$ but rather in $|T-T_C|^2$. This demonstrates that ω_0^2 is itself temperature dependent in agreement with the predictions of the quasi-spin-wave theories of order-disorder hydrogen-bonded ferroelectrics.[1,2] Except in the immediate vicinity of the Curie point, a good fit could be obtained using the quasi-spin-wave expression[1-3] $\omega_0^2=K\times(T-T_C)/T$ for the characteristic frequency of the ferroelectric mode and assuming that the damping Γ does not depend on temperature. Thus we get

$$(T_1)_P=A\frac{K}{2\Gamma}\frac{(T-T_C)^2}{CT}, \quad (10)$$

where $\sqrt{K}$ is the high-temperature value of ω_0 (Fig. 2).

In the immediate neighborhood of the Curie point, the curve of $\sqrt{T_1}$ vs $|T-T_C|$ does not follow

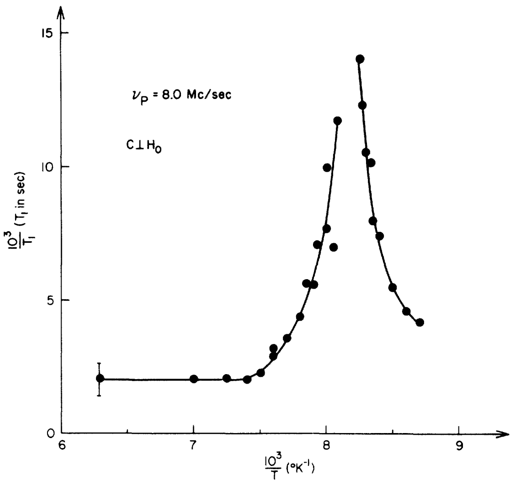

FIG. 1. Temperature dependence of the P^{31} spin-lattice relaxation rate in KH_2PO_4.

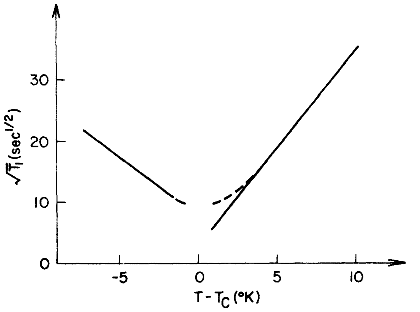

FIG. 2. Square root of the smoothed dipolar contribution to the P^{31} relaxation time in KH_2PO_4 as a function of $T-T_c$. The dashed line shows the influence of the T dependence of the damping.

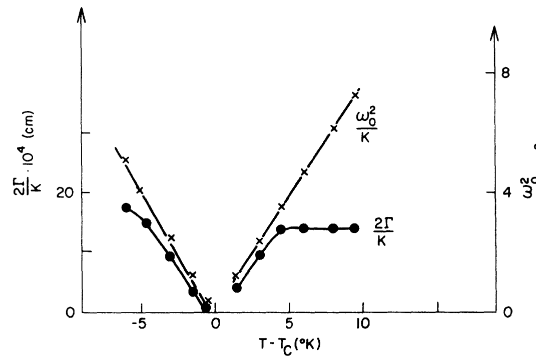

FIG. 3. Temperature dependence of the square of the characteristic frequency and of the damping of the ferroelectric mode in KH_2PO_4 expressed in units of °K.

expression (10) anymore but starts to round off, demonstrating an increase in $K/2\Gamma$. Since there is no reason why K should depend on temperature, this result indicates that the damping constant Γ decreases on approaching the Curie point. The temperature dependences of the square of the characteristic frequency and the damping constant of the ferroelectric mode as obtained from our T_1 data are presented in Fig. 3. Since the decrease in Γ is significant only in the immediate neighborhood of T_c and since Γ may be frequency dependent, our result does not necessarily contradict Kaminow's statement[3] that Γ does not depend on temperature. It should be mentioned that except for the narrow temperature range near T_c, the dipolar part of $(T_1)_P^{-1}$ strongly depends on the way one subtracts the background from the observed relaxation rate. The relative error in the absolute values of the parameters in Fig. 3 may be thus quite large for $T-T_c > 6$°C. What we would like to emphasize here is therefore not so much the exact values of the "ferroelectric" parameters, which can be obtained as well by other methods, but rather that the temperature dependence of $(T_1)_P$ gives for the first time clear evidence for the existence of magnetic dipolar spin-phonon coupling.

It should be stressed that the $(T_1)_P$ or $(T_1)_H$ data[8] (not shown here) cannot be quantitatively accounted for either by the simple Bloembergen-Purcell-Pound picture[9] of uncorrelated random proton motion or by the more refined Schmidt[10] model. If one tries to force the experimental data to fit the two above-mentioned models, one finds unreasonably high frequency factors, $\tau_0 \approx 10^{-25}$ sec, demonstrating that the neglect of correlation in the proton motion is not justified. Preliminary measurements in some other ferroelectric crystals as well seem to show anomalous spin-lattice relaxation via unstable lattice modes as predicted by expressions (7) and (10).

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*On leave of absence from the University of Ljubljana, Nuclear Institute "J. Stefan," Ljubljana, Yugoslavia.

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