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As^{75} ELECTRIC-FIELD-GRADIENT FLUCTUATIONS IN KH$_2$PO$_4$-TYPE FERROELECTRICS*

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The electric-field-gradient tensor fluctuations at the As^{75} site in ferroelectric RbH$_2$AsO$_4$, RbD$_2$AsO$_4$, and KH$_2$AsO$_4$ have been studied as a function of temperature and applied electric field. The measurements allow a direct determination of the Slater short-range energy parameter ϵ and provide a test of the nature of the ferroelectric-mode–type elementary excitations.

Considerable progress has recently been made in the field of hydrogen-bonded ferroelectric crystals. On the one hand, an exact static solution of the two-dimensional Slater model in KH$_2$PO$_4$ has been obtained,[1] and approximate methods were developed[2] to take into account long-range interactions and tunneling effects. On the other, experimental[3] and theoretical[2] evidence was gathered for the existence of "ferroelectric-mode"–type elementary excitations in the paraelectric phase. A number of basic problems, however, are still unsolved. The "ferroelectric-mode"–type elementary excitations have not yet been related to the Slater model, which seems to be so helpful in understanding the equilibrium properties of these crystals. It is further not certain whether the observed "ferroelectric mode" represents a pure lattice mode which is not connected with the proton disorder, a quasi spin-wave type proton tunneling mode, or a mixed proton-lattice mode. Another unsolved problem is that the basic Slater short-range energy parameter ϵ (defined below) has so far not been directly measured.

In this note we report what we believe to be the first direct measurement of the Slater energy parameter ϵ as well as a critical test of both the validity of the Slater model and the nature of the elementary excitations in KH$_2$PO$_4$-type ferroelectric crystals. In addition we offer some preliminary results on a rather striking critical slowing down of polar atomic fluctuations into the megahertz range, the knowledge of which may be of some value for further refinements of the theory of hydrogen-bonded ferroelectrics.

We measured the temperature and electric field dependence of the pure nuclear quadrupole resonance (NQR) and quadrupole-perturbed NMR spectra of As^{75} in KH_2AsO_4 as well as in normal and deuterated RbH_2AsO_4, using the quadrupole moment of the As^{75} nucleus as a microscopic probe to study the dynamics of the electric-field-gradient (EFG) tensor fluctuations.

The Hamiltonian of our problem is

$$H = H_M + H_Q, \tag{1}$$

where H_M measures the Zeeman coupling[4] of the As^{75} nuclear spin ($I=\frac{3}{2}$) to the external magnetic field $\vec{H}_0$, and H_Q describes the interaction[4] of the nuclear quadrupole moment eQ with EFG tensor V_{ij} at the As^{75} site. In view of the covalent nature of the As-O bonds in KH_2AsO_4 and isomorphous crystals, V_{ij} is primarily determined by the AsO_4 bond structure, and only indirectly by the arrangement of the four hydrogens surrounding a given AsO_4 group. Since the frequency of modulation of V_{ij} by the "ferroelectric-mode"-type elementary excitations and the dynamic protonic disorder should be much larger than the instantaneous Larmor frequency of the As^{75} nucleus, the position of the As^{75} resonance lines is, for $T > T_c$, expected to be given by an effective, time-averaged Hamiltonian $H_0 = H_M + \langle H_Q \rangle_t$ ($\langle\ \rangle_t$ denotes a time average over the atomic motion and $\langle H_Q \rangle_t \ll H_Q$), whereas the linewidth should be determined by the fluctuating part of Hamiltonian in Eq. (1):

$$H_1(t) = H - H_0 = H_Q - \langle H_Q \rangle_t \simeq H_Q \tag{2}$$

and should therefore be a sensitive indicator of the mean time between atomic rearrangements in the H_2AsO_4 groups.

We first calculate the temperature dependence of the As^{75} NQR frequency $\nu_Q = eQV_{KK}/2h$ (where V_{KK} is the largest component of the diagonalized EFG tensor) for the case in which the "ferroelectric mode," which modulates H_Q and V_{ij}, is a "pure" lattice vibration. Expanding V_{ij} in powers of the normal coordinate of the ferroelectric mode $\xi(t)$ gives

$$V_{ij} = A_{ij} + B_{ij}\xi + C_{ij}\xi^2 + \cdots. \tag{3}$$

Taking into account that the constant A should be zero for a perfect tetrahedron, and that the time average of ξ vanishes for $T > T_c$, we find $\langle V_{ij} \rangle_t = C_{ij} \langle \xi^2 \rangle_t$. Using the fluctuation-dissipation theorem

$$\langle \xi^2 \rangle_t = \text{const} \times T\epsilon_{\text{ion}, z}(0) \tag{4}$$

[where $\epsilon_{\text{ion}, z}(0)$ is the ionic contribution to the static dielectric constant in the direction of the ferroelectric axis)] we obtain

$$\nu_Q = KT/(T - T_c). \tag{5}$$

T_c is the ferroelectric Curie temperature at which $\epsilon_{\text{ion}, z}(0) \to \infty$.

This result is significantly different from that obtained from the Slater model and the assumption of adiabatic proton-lattice coupling. It is now the dynamic disorder of hydrogens, moving between the two equilibrium sites in the O-H···O bonds, which modulates V_{ij}. Neglecting, for the sake of simplicity, tunneling effects (which should be a good approximation for RbD_2AsO_4), and replacing the time average by an ensemble average, we find

$$\langle V_{ij} \rangle_t = \sum_{l=1}^{6} \delta_l V_{ij}^{(l)}, \tag{6}$$

where the δ_l are weighting factors for the six "allowed" Slater H_2AsO_4 hydrogen arrangements and the V_{ij} are the corresponding EFG tensors. In view of their much higher excitation energy, the "defect" H_3AsO_4, etc. configurations make a negligible contribution to $\langle V_{ij} \rangle_t$.

Configurations (1) and (2) correspond to the case where both "close" hydrogens are at the "top" or "bottom" H_2AsO_4 oxygens if one looks along the ferroelectric C axis. The V_{ij} tensors for these two configurations should be proportional to those measured[5-8] in positive and negative domains [$V_{ij}(+P)$, $V_{ij}(-P)$] in the "perfectly" polarized ferroelectric phase:

$$V_{ij}^{(1,2)} = kV_{ij}(\pm P) \tag{7a}$$

with

$$\frac{eQ}{h} V_{ij}(\pm P) = \begin{bmatrix} 75, (-56) & 0 & 0 \\ 0 & -56, (75) & 0 \\ 0 & 0 & -19 \end{bmatrix} \text{MHz}, \tag{7b}$$

where the smallest principal axis V_{zz} is parallel to the C axis and the two major principal axes (V_{xx}, V_{yy}) are nearly parallel to the two AsO_4 tetrahedral edges lying in the a, b crystalline plane.[5,6] The proportionality factor K, which for the sake of simplicity is assumed to be a scalar, measures the strength of the proton-lattice coupling. In the four δ_0 configurations ($l = 3, 4, 5, 6$) one hydrogen is attached to the upper and one to the lower H_2AsO_4 oxygen so that the C component of the H_2AsO_4 dipole moment vanishes. In view of the proportionality of the As^{75} EFG tensor to the induced As^{75} displacement from its average paraelectric site, $\langle V_{ij}^{(1,2)}\rangle_t \gg \langle V_{ij}^{(0)}\rangle_t$ and

$$\langle V_{ij}\rangle_t = \delta_1(V_{ij}^{(1)} + V_{ij}^{(2)}), \tag{8}$$

where

$$\delta_1 = \frac{\delta_0(1+p)e^{\epsilon/kT}}{4(1-p)} \tag{9a}$$

and

$$\delta_0 = \left(1 + \frac{e^{\epsilon/kT}}{2}\,\frac{1+p^2}{1-p^2}\right)^{-1} \tag{9b}$$

with p the expectation value of the reduced spontaneous polarization and $\epsilon = kT_c \ln 2$ the Slater short-range energy parameter, which measures the positive energy difference between the $\delta_{1,2}$ and δ_0 hydrogen configurations ($\delta_1 = \delta_2$ for $p = 0$; i.e., $T > T_c$). At the Curie point $\delta_1 = \delta_2 = \frac{1}{4}$; so

$$(\langle\nu_Q\rangle_t)_{T=T_c} = (e^2QV_{zz}/2h)_{T=T_c} = \tfrac{1}{2}\nu_Q^{(1)} \tag{10}$$

and the strength of the proton-lattice coupling K can be determined from $K = 2(\langle V_{zz}\rangle_t)_{T=T_c}/V_{zz}(+P)$.

The Slater short-range energy parameter ϵ can be directly obtained from the temperature dependence of $\langle\nu_Q\rangle_t$ in the paraelectric phase [see Eq. (8)] as

$$[2(\langle\nu_Q\rangle_t)_{T=T_c} - \langle\nu_Q\rangle_t]/2\langle\nu_Q\rangle_t = e^{-\epsilon/kT}. \tag{11}$$

Below T_c, $p = \delta_1 - \delta_2$ and, depending on the sign of p, either V_{xx} or V_{yy} will correspond to the largest principal axis. The T dependence of ν_Q is then obtained as

$$\langle\nu_Q\rangle_t = (e^2Q/2h)[pV_{xx}^{(1)} + \delta_2(V_{xx}^{(1)} + V_{xx}^{(2)})] \simeq \nu_{Q,T=0}P, \tag{12}$$

whereas the asymmetry parameter

$$\eta = (\langle V_{zz}\rangle_t - \langle V_{yy}\rangle_t)/\langle V_{xx}\rangle_t \simeq 0.5 \tag{13}$$

should not depend on temperature for $p \geqslant 0.2$.

The difference between the "pure" lattice-mode model and the Slater model becomes most obvious if one expands Eq. (11) in powers of ϵ/kT (or equivalently in powers of T_c/T) and compares the predicted T dependences of ν_Q. The Slater model yields, up to first-order terms,

$$\langle\nu_Q\rangle_t = \nu_Q^{(1)}T/3(T - 0.45T_c), \tag{14}$$

a result which is very different from Eq. (5).

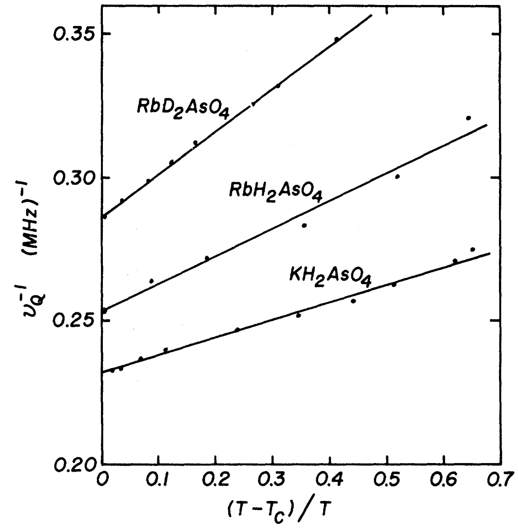

FIG. 1. Temperature dependence of the As^{75} nuclear quadrupole frequency in the paraelectric phase.

The experimental results on $\nu_Q = \nu_Q(T)$ (Fig. 1) are in much better agreement with the Slater model than with the "pure" lattice-mode description of the ferroelectric mode. The measured As^{75} NQR frequencies can be fitted[9] for $T > T_c$ by a Curie-Weiss law

$$\langle\nu_Q\rangle_t^{-1} = C(T - T_0)/T \tag{15}$$

with T_0 significantly lower than T_c. For RbD_2AsO_4, in particular, $T_0 = 0.36T_c$ in rather close agreement with the predictions of the Slater model. The value of the proton-lattice coupling parameter ($K = 0.75$ for RbD_2AsO_4) is also rather reasonable and shows that the As^{75} nuclei, as well as the deuterons, take part in collective atomic fluctuations on approaching T_c.

In the ferroelectric phase, ν_Q is roughly proportional[7] to the spontaneous polarization, and we find $\eta = 0.55$ [for $(T_c - T) > 0.2°C$)] in agreement with the predictions of Eqs. (12) and (13).

The value of the Slater short-range energy parameter ϵ—obtained from the slope of the plot of $\log[2(\langle\nu_Q\rangle_t)_{T=T_c} - \langle\nu_Q\rangle_t]/2\langle\nu_Q\rangle_t$ vs $1/T$—is $\epsilon/k = 122°K$ for RbD_2AsO_4, whereas the "theoretical" value obtained from $\epsilon = kT_c \ln 2$ equals 158°K. For RbH_2AsO_4, the NQR results give 71 and 54°K, whereas theory predicts 73 and 69°K.

The above results provide additional evidence for the essential correctness of the Slater-type description of KH_2PO_4-like hydrogen-bonded ferroelectrics, and for the existence of strong proton-lattice coupling in the paraelectric phase. In view of the neglect of tunneling and long-range interaction effects in our treatment, the above agreement between the Slater-model predictions and the experimental results is quite satisfactory.

It should be pointed out, however, that the "classical" Slater model cannot explain the isotope effects in ν_Q on going from RbH_2AsO_4 to RbD_2AsO_4. It predicts $(\nu_Q)_D > (\nu_Q)_H$ for $T > T_c$, whereas we find experimentally the opposite to be true. This prediction depends upon the fact that for $T < T_c$, $(\nu_Q)_D > (\nu_Q)_H$[7] while $\epsilon_D > \epsilon_H$. Preliminary calculations have shown that these discrepancies disappear when proton tunneling is taken into account.

The experimental results also show a critical broadening of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ and $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$ As^{75} lines as one approaches the Curie point from either side. Furthermore, the ferroelectric phase lines are considerably sharper than those in the paraelectric phase. These features are illustrated in Fig. 2. The broadening is strongly anisotropic and its angular dependence can be accounted for within the Slater model, demonstrating that the changes in the EFG principal-axis system during the fluctuations in the paraelectric phase are indeed roughly the same as on polarization reversal for $T < T_c$. The exact expression for the autocorrelation function of V_{ij} is rather lengthy. If, however, $V_{ij}^{(0)} \ll V_{ij}^{(1,2)}$ so that one deals with a "random" biased motion of the variable F between three values F_1, F_2, and $F_0 = 0$, the autocorrelation function $\overline{G}(t) = \sum_K \delta_K F_K \sum_l F_l p_l(t)$ becomes

$$\overline{G}(t) = \frac{\delta_1}{2} e^{-t/\tau_1}[F_1 - F_2]^2 + \frac{\delta_1\delta_2}{2(\delta_1 + \delta_0)}[F_1 + F_2]^2 e^{-t/\tau_2} + \text{const}, \qquad (16)$$

and the width of the $\frac{1}{2} \rightarrow \frac{3}{2}$ As^{75} transition is given by

$$(1/T_2)_{1/2 \rightarrow 3/2} = A_1\delta_1\tau_2 + [A_2 + A_3 \cos^2(2\theta_z)]\delta_1\tau_1 \qquad (17)$$

in agreement with the observed linear dependence of the linewidth on $\cos^2(2\theta_z)$. Here θ_z is the angle between $\vec{H}_0$ and the largest principal axis of the "ferroelectric" V_{ij}, τ_1 and τ_2 are correlation times which measure the approach to equilibrium of the difference $(p_1 - p_2)$ and the sum $(p_1 + p_2)$, respectively, of the populations of the 1 and 2 configurations, while F and A are appropriately transformed matrix elements of $H - \langle H_Q \rangle_t$ with respect to the eigenfunctions of H_Q. The data further show that τ_1 is of the order of 10^{-11} sec at room temperature and becomes longer as $T \rightarrow T_c$.

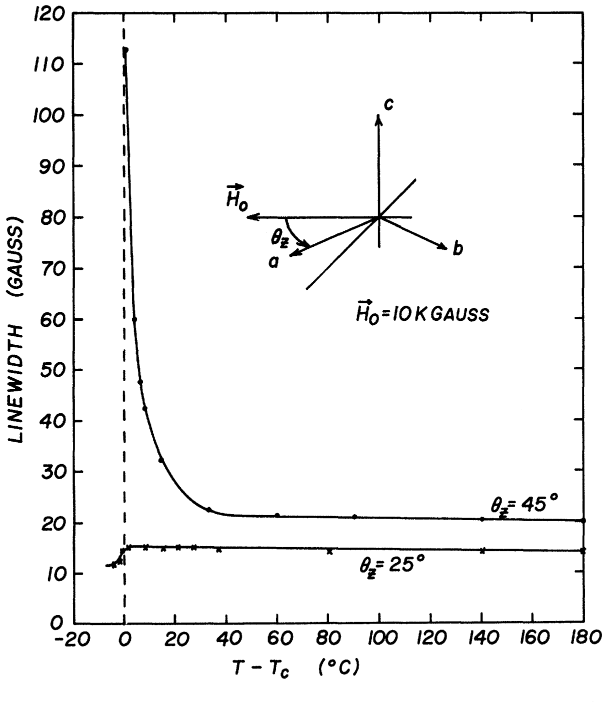

FIG. 2. Temperature dependence of the As^{75} $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ resonance linewidth in KH_2AsO_4 at two orientations. The tetragonal crystal axes are a, b, and c.

Finally we would like to mention that over a limited angular range (near the orientations where the δ_1 and δ_2 configurations of an H_2AsO_4 group lead to the same NQR splitting of the As^{75} NMR lines) one observes in KH_2AsO_4 in the C-axis rotation, in addition to the above mentioned $\eta = 0$, $\frac{1}{2} \rightarrow -\frac{1}{2}$ line (the position of which does not depend on θ_c), two new sharp $\frac{1}{2} \rightarrow -\frac{1}{2}$ lines whose frequencies depend on the angle between H_0 and the crystalline a axis (Fig. 3). These lines are strongest right above the Curie point, but they seem to be present up to $T \simeq T_c + 60°C$. They are well separated in frequency from the "ferroelectric" lines which can be simultaneously observed right at the Curie point. An applied electric field of 1000 V/cm along the C axis enhances one of these "sharp" lines while suppressing the other (and the $\eta = 0$ line as well). Reversing the direction of the field interchanges the enhancement. The field enhancement displays hysteresis. With less resolution this enhancement of one sharp line or the other might appear as an anomalously large shift in the peak of the resonance line with reversal of an applied electric field as has been reported.[10] Though the nature of these lines is

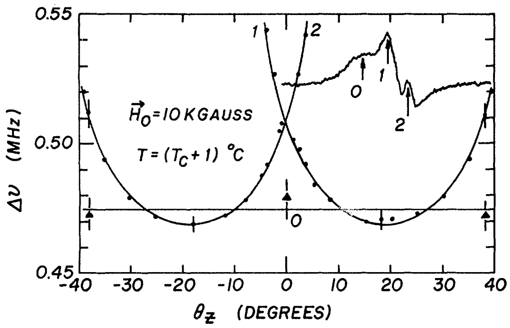

FIG. 3. Angular dependence of the As^{75} $\frac{1}{2}\longleftrightarrow\frac{1}{2}$ line and second-order shift $\Delta\nu$ in KH_2AsO_4. Inset shows a typical resonance with the broad $\eta=0$ line on which is superimposed the sharp lines designated 1 and 2. The pattern is repeated each 90°.

still not completely understood it seems clear that they are connected with a critical slowing down of polar atomic fluctuations into the megahertz range, which does not seem to be contained in any of the existing theories of KH_2PO_4-like ferroelectrics. Preliminary studies indicate the occurrence of similar effects in the Rb compounds.

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