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Reorientation Frequencies of Ferroelectric Dipoles near a Paramagnetic Center in KH_2AsO_4 and KD_2AsO_4

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The frequency of exchange between the various "Slater"-type H_2AsO_4 dipolar configurations near a local paramagnetic center has been measured in the paraelectric phase of γ-irradiated KH_2AsO_4. The lifetime effects in the proton hyperfine structure of the EPR spectrum were used as a detector of the proton motion. Similar effects were also found in KD_2AsO_4. The results show the absence of an instability of the lattice against any "ferroelectric mode" involving proton displacements, and they favor the order-disorder model of ferroelectricity in this class of crystals.

INTRODUCTION

THOUGH KH_2PO_4-type ferroelectrics have received considerable attention in recent years, the microscopic nature of ferroelectricity in these compounds is not yet completely clear. Slater[1] introduced an order-disorder model of the ferroelectric transition in KH_2PO_4. He assumed that each hydrogen has two equilibrium sites in the H bond, connecting two neighboring PO_4 tetrahedra, so that the paraelectric phase consists of a random, and the ferroelectric phase of an ordered, arrangement of H_2PO_4 dipoles. One of the authors of the present paper later suggested[2,3] that the disorder in the paraelectric phase is a dynamic one and that hydrogens may tunnel from one equilibrium position in the H bond to another, thus producing a reorientation of the Slater H_2PO_4 dipoles. Uehling and Schmidt[4] were the first to demonstrate the existence of deuteron intrabond motion in KD_2PO_4 by deuteron spin-lattice relaxation time measurements. At about the same time, Cochran[5] explained the ferroelectric transitions in displacive ferroelectrics as a result of an instability of the crystal lattice against a "ferroelectric" lattice mode, and several authors tried to apply this model to KH_2PO_4-type ferroelectrics as well.

This paper reports a direct measurement of the frequencies of proton exchange between the six "Slater" H_2AsO_4 dipolar configurations near a paramagnetic center in KH_2AsO_4 (Fig. 1). The purpose of the work is: (i) to elucidate the dynamics of the ferroelectric dipoles in KH_2AsO_4, and (ii) to find out whether the phase transition in hydrogen-bonded KH_2PO_4-type crystals can be understood in terms of an instability of the lattice against a ferroelectric mode as in displacive ferroelectrics, or a modified Slater order-disorder model still applies.

The arsenates, and KH_2AsO_4 in particular, were found to be most suitable for such a study. McDowell[6] and others[7] have shown that in γ- or neutron-irradiated KH_2AsO_4 a stable paramagnetic center AsO_4^{4-} is formed by electron capture. No fundamental structural change seems to occur on formation of this center, which is hydrogen bonded to four other tetrahedron units in the crystal. The gross features of the electron-paramagnetic-resonance spectrum of this center are due to hyperfine interaction with the As^{75} nucleus and can be described by the following spin Hamiltonian[6]:

$$\mathcal{H}_0=\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}-g_n\beta_n\mathbf{H}\cdot\mathbf{I}. \qquad (1)$$

Proton hyperfine structure, however, has been detected on each of the four As^{75} lines.[6] In the present work the lifetime effects in the proton hyperfine structure have been used as a detector of the protonic motion. Since the odd electron enters an A_1-type molecular orbital localized on the AsO_4^{3-} ion,[6] the Fermi contact coupling is sensitive to even small amplitude motion—such as proton transfer from one equilibrium site in the H-bond to another—which takes the proton outside the unpaired spin-density cloud, though this motion does not significantly alter the magnetic dipolar coupling. Therefore in KH_2AsO_4 electron paramagnetic resonance is much better suited for a study of proton intrabond motion than for instance, proton magnetic resonance, which detects only changes in the magnetic dipole-dipole interactions.

RESULTS AND DISCUSSION

The crystal was oriented with the c axis parallel to the magnetic field so that all four protons in the hydrogen bonds linking the AsO_4^{4-} centers to the surrounding AsO_4^{3-} tetrahedra had the same magnetic dipolar coupling with the unpaired electron, and moreover, all AsO_4^{4-} sites in the unit cell were magnetically equivalent.

The experimental results for KH_2AsO_4 are shown in Figs. 2 and 3. The K-band, as well as the X-band, proton hyperfine structure of each of the four As^{75} lines was found to be a quintet from $+100°C$ down to $-50°C$, where it changed to a triplet (Fig. 2). The

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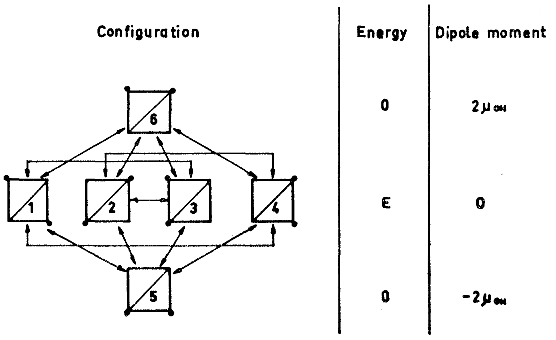

FIG. 1. Energies, z-component dipole moments, and rate-determining transitions between the six "Slater" proton configurations around an AsO_4 tetrahedron in KH_2AsO_4.

total width remained the same: The separation between two neighboring absorption maxima amounted in the quintet to 14.5 and in the triplet to 29 Mc/sec. The proton hyperfine structure (hfs) does not change at the Curie point ($T_c=-176$°C) and remains a triplet down to the lowest temperature where measurements were made (2.14°K) (Fig. 3). The application of a static electric field of 7 kV/cm parallel to the a or c axis does not change the spectra.

The results can be understood in terms of a dynamic order-disorder model, where rapid exchange of protons in different spin states occurs between the six Slater dipolar configurations shown in Fig. 1. When the exchange frequency, which modulates the contact coupling $a_i(t)$ in the proton part of the spin Hamiltonian

$$\mathcal{H}-\mathcal{H}_0=\sum_{i=1}^{4} a_i(t)\mathbf{I}_i\cdot\mathbf{S}+\sum_{i=1}^{4} g_N\beta_N\mathbf{H}_0\cdot\mathbf{I}_i+\sum_{i=1}^{4} B_i(\mathbf{I}_i\cdot\mathbf{S}-3I_{z,i}S_z), \quad (2)$$

is larger than the difference ($a_{\rm cl}-a_{\rm f}$) in the contact coupling constants belonging to the sites "close" ($a_{\rm cl}$) and "far away" ($a_{\rm f}$) from the AsO_4^{4-} radical in a given H bond, the electron "sees" only the time average of the hyperfine field

$$\langle a_i(t)\rangle_{\rm Av}=\tfrac{1}{2}(a_{\rm cl}+a_{\rm f})\cong\tfrac{1}{2}a_{\rm cl}. \quad (3)$$

Since all four protons are now equally coupled to the electron, the resulting hyperfine structure is a quintet

$$\omega_{M_I}=\omega_0-(\bar{a}-2\bar{B})M_I, \qquad M_I=-2,\,-1,\,0,\,+1,\,+2. \quad (4)$$

When the frequency is lower than $a_{\rm cl}-a_{\rm f}$, the electron sees the instantaneous fields, and since $a_{\rm f}\approx 0$, $a_{\rm cl}=29$ Mc/sec, and $a_{\rm cl}\gg B_{\rm cl}\approx B_{\rm f}\approx\bar{B}$, only the two close protons contribute to the hyperfine structure, which is a triplet

$$\omega_{M_{I'}}=\omega_0-a_{\rm cl}M_{I'}+2\bar{B}M_I, \qquad M_{I'}=-1,\,0,\,+1 \quad (5)$$

with an increased linewidth due to the unresolved dipolar splitting $\bar{B}$.

No change of the spectrum can occur at the temperature of the order-disorder transition $T_c=-176$°C—where the time the AsO_4 unit spends in the polar Slater configurations equals to the time it spends in the nonpolar ones—because the odd electron sees the "instantaneous" proton hyperfine field already in the paraelectric phase below -50°C.

The temperature dependence of the spectrum in the intermediate region can be calculated from the modified Bloch equations[8]

$$(dG_j/dt)j+\alpha_jG_j=-i\gamma H_1M_{0j}+\sum_k(\tau_{kj}^{-1}G_k-\tau_{jk}^{-1}G_j), \quad (6)$$

where $G_j=u_j+iv_j$, and u and v are the transverse components of magnetization M parallel and perpendicular to the rotating field H_1, $\alpha_j=T_{2j}^{-1}-i(\omega_j-\omega)$ with T_{2j} standing for the transverse relaxation time and ω_j for the hyperfine-coupling Larmor-frequency shift in the configuration j, (Table I), and with τ_{jk}^{-1} defining the transition probability per unit time for the proton jumps between the Slater configurations j and k shown in Fig. 1. Using the steady-state solution we obtain the following expression[9] for the intensity of absorption at the frequency ω:

$$I(\omega)=(1/\pi)\,\mathrm{Re}(-\mathbf{P}[i(\mathbf{\Omega}-\omega)+\mathbf{D}]^{-1}\mathbf{1}). \quad (7)$$

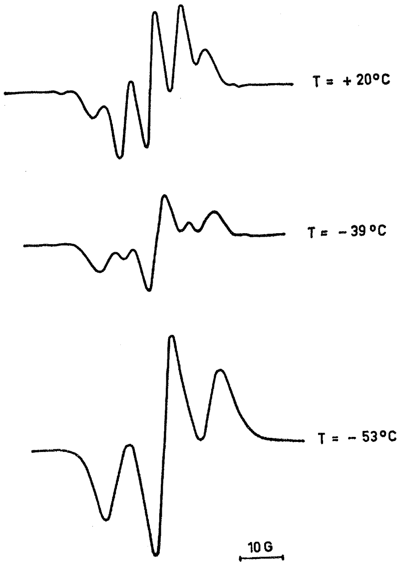

FIG. 2. Proton hyperfine structure of an As^{75} EPR line at different temperatures ($c \parallel \mathbf{H}_0$).

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Here **P** is a row matrix whose elements determine the occupation of the six Slater H_2AsO_4 configurations (Fig. 1)

$\mathbf{P}=K(e^{-m}, e^{-m}, e^{-m}, e^{-m}, e^{m}, e^{m})$, $\boldsymbol{\omega}$ is ω times the unit matrix, the matrix elements $\Omega_{ij}=\omega_i\delta_{ij}$ (where the values of ω_i are given in Table I) measure the contact coupling frequency shifts in the six Slater protonic configurations and D[9]

$$D=\tfrac{1}{4}\tau^{-1}\begin{pmatrix} 4\tau T_2^{-1}+2(1+e^{m}) & 0 & -1 & -1 & -e^{-m} & -e^{-m} \\ 0 & 4\tau T_2^{-1}+2(1+e^{m}) & -1 & -1 & -e^{-m} & -e^{-m} \\ -1 & -1 & 4\tau T_2^{-1}+2(1+e^{m}) & 0 & -e^{-m} & -e^{-m} \\ -1 & -1 & 0 & 4\tau T_2^{-1}+2(1+e^{m}) & -e^{-m} & -e^{-m} \\ -e^{m} & -e^{m} & -e^{m} & -e^{m} & 4(\tau T_2^{-1}+e^{-m}) & 0 \\ -e^{m} & -e^{m} & -e^{m} & -e^{m} & 0 & 4(\tau T_2^{-1}+e^{-m}) \end{pmatrix} \quad (8)$$

is the matrix determining the probabilities of exchange between the six configurations of Fig. 1 in the approximation that transitions, involving jumps of more than two protons can be neglected. $m=\epsilon/2kT$, and K is the normalization factor. The lifetimes

$$\tau_5=\tau_6=\tau e^{m}, \qquad \tau_1=\tau_2=\tau_3=\tau_4=2\tau(e^{+m}+1)^{-1} \quad (9)$$

of the Slater configurations at the AsO_4^{4-} center were obtained by a comparison of theoretical and experimental results. The data shown in Fig. 4 can be fitted to the equation $\tau=\tau_0\exp(E/kT)$ with $E=0.2$ eV and $1/\tau_0=4\mathrm{cm}^{-1}$. The value of the Slater parameter ϵ, which, however, does not critically influence the results, was estimated from dielectric properties[3] to be of the order of 6×10^{-3} eV, and $1/T_2$ was estimated to be about 10 Mc/sec. The activation energy obtained for proton exchange is similar to the one which seems to be found by NMR T_1 measurements[10] in undamaged KH_2PO_4, whereas the value of the pre-exponential factor is normal and significantly lower than the one obtained in the above-mentioned NMR study. It is even lower than the one found for deuteron intrabond transfer[4] in the paraelectric phase of undamaged KD_2PO_4. This reduction of the pre-exponential factor demonstrates the change in the potential field for hydrogen motion on formation of the AsO_4^{4-} center. Radiation-induced internal strains may also influence this result.

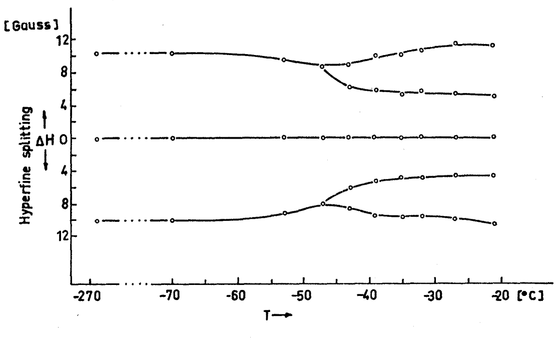

FIG. 3. Temperature dependence of the proton hyperfine splitting in the EPR spectrum of the AsO_4^{4-} center in KH_2AsO_4.

The persistence of the triplet hfs down to liquid-helium temperatures further shows that the potential field is not changed by electron capture to such an extent as to allow the formation of stable H_3AsO_4 centers. It should be pointed out that the absence of H_3AsO_4 effects in the EPR spectrum (i.e., the absence of a four-line proton hyperfine structure) does not mean that such configurations do not exist at all in KH_2AsO_4. It only means that the lifetimes of the various H_2AsO_4 configurations are much longer than those of the H_3AsO_4 configurations, which can therefore not be detected directly by EPR. The detailed mechanism of the transition from one H_2AsO_4 configuration to another is not yet clear, but it almost certainly requires the existence of a short-lived intermediate state which could be either a $HAsO_4$ or a H_3AsO_4 ionic defect.

A similar exchange between Slater dipolar configurations occurs as well in irradiated KD_2AsO_4 (Fig. 5), where a nine-line deuteron hfs with a frequency separation of 2.9 Mc/sec is discernible at room temperature. The unpaired electron is thus equally coupled to four deuterons, indicating that the frequency of deuteron exchange is larger than 10^6 cps at this temperature. At lower temperatures the hfs becomes smeared out and seems to change to a quintet of the same total width, indicating that the frequency of deuteron exchange becomes smaller than the difference in the deuteron contact coupling constants belonging to the sites close and far away from the AsO_4^{4-} center.

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[10] Unpublished work from this laboratory.

TABLE I. Hyperfine-coupling frequency shifts in the six Slater protonic configurations of the H_4AsO_4 tetrahedron.

Total proton-spin magnetic quantum number	Spin state	Frequency shift for a given Slater configuration					
		ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
$M_I=0$	1. $\alpha(1)\ \alpha(2)\ \beta(3)\ \beta(4)$	0	0	0	0	$-a$	a
	2. $\alpha(1)\ \beta(2)\ \alpha(3)\ \beta(4)$	0	0	a	$-a$	0	0
	3. $\alpha(1)\ \beta(2)\ \beta(3)\ \alpha(4)$	a	$-a$	0	0	0	0
	4. $\beta(1)\ \alpha(2)\ \beta(3)\ \alpha(4)$	0	0	$-a$	a	0	0
	5. $\beta(1)\ \alpha(2)\ \alpha(3)\ \beta(4)$	$-a$	a	0	0	0	0
	6. $\beta(1)\ \beta(2)\ \alpha(3)\ \alpha(4)$	0	0	0	0	a	$-a$
$M_I=1$	7. $\alpha(1)\ \alpha(2)\ \alpha(3)\ \beta(4)$	0	a	a	0	0	a
	8. $\alpha(1)\ \alpha(2)\ \beta(3)\ \alpha(4)$	a	0	0	a	0	a
	9. $\alpha(1)\ \beta(2)\ \alpha(3)\ \alpha(4)$	a	0	a	0	a	0
	10. $\beta(1)\ \alpha(2)\ \alpha(3)\ \alpha(4)$	0	a	0	a	a	0
$M_I=-1$	11. $\beta(1)\ \beta(2)\ \beta(3)\ \alpha(4)$	0	$-a$	$-a$	0	0	$-a$
	12. $\beta(1)\ \beta(2)\ \alpha(3)\ \beta(4)$	$-a$	0	0	$-a$	0	$-a$
	13. $\beta(1)\ \alpha(2)\ \beta(3)\ \beta(4)$	$-a$	0	$-a$	0	$-a$	0
	14. $\alpha(1)\ \beta(2)\ \beta(3)\ \beta(4)$	0	$-a$	0	$-a$	$-a$	0
$M_I=2$	15. $\alpha(1)\ \alpha(2)\ \alpha(3)\ \alpha(4)$	a	a	a	a	a	a
$M_I=-2$	16. $\beta(1)\ \beta(2)\ \beta(3)\ \beta(4)$	$-a$	$-a$	$-a$	$-a$	$-a$	$-a$

The hyperfine structure is not well resolved and no really reliable study of the kinetics of this change could be made. The estimate obtained for the activation energy of this process, $E=0.08$ eV, however, seems to be in a surprisingly good, and perhaps fortuitous, agreement with the value obtained by Uehling and Schmidt[4] for deuteron intrabond motion in KD_2PO_4 ($E=0.078$ eV). As in the case of KH_2AsO_4, the spectrum did not change on going through the Curie point.

It should be stressed that if the above behavior is representative for the undamaged crystal as well (which seems to be the case), then the present results exclude the possibility of the existence of a "ferroelectric mode" involving proton displacements, since in this case marked changes at the Curie point should be observed.

There are two classical models for the ferroelectric mode in KH_2PO_4-type crystals.[5] In the first, the protons are oscillating around the center of the hydrogen bond in the paraelectric phase and are displaced toward the AsO_4 units in the ferroelectric phase as a result of the instability of the lattice against the acoustic mode controlled by the elastic constant C_{66}^E. Since the odd electron would be equally coupled to four protons, the proton hfs in the paraelectric phase would thus be a quintet and would change to a triplet at the Curie point, where H_2AsO_4 dipoles would be formed.

According to the second model, which is closer to the order-disorder theory, the paraelectric phase is a random mixture of the six Slater-type H_2AsO_4 dipolar configurations (Fig. 1). The hydrogen-bond potential has two minima and the motion of the protons in the ferroelectric mode is essentially a small-amplitude vibration around the various equilibrium sites. The room-temperature frequency of this ferroelectric mode in KH_2PO_4 was estimated[5] to be about 84 cm^{-1}, decreasing to a minimum of 14 cm^{-1} at the Curie point, where the potential wells for the collective movement of hydrogens become flat-bottomed and the protons would move to form H_2AsO_4 groups with dipole moments

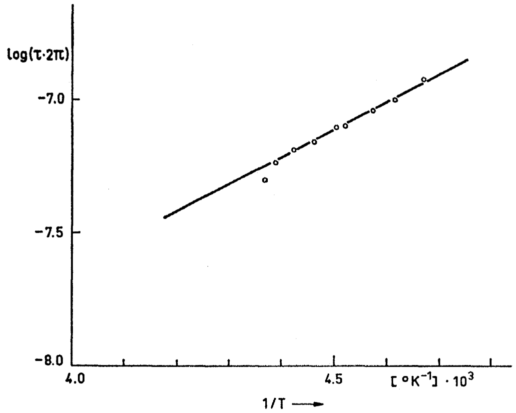

FIG. 4. Lifetime of the Slater protonic arrangements, calculated from the temperature dependence of the proton hyperfine structure.

FIG. 5. Deuteron hyperfine structure in the EPR spectrum of the AsO_4^{4-} center in KD_2AsO_4. Arrows indicate the position of the deuteron hyperfine absorption maxima.

pointing in the plus or minus directions of the ferroelectric axis. While one would expect to see a triplet in the ferroelectric and paraelectric phases, the hfs should change to a quintet in the vicinity of the Curie point. The instability of the lattice with the resulting large-amplitude protonic motion at a frequency which is still much higher than the hyperfine splitting—expressed in frequency units—should accordingly result in an averaging of the contact coupling constants over the protonic motion, so that in this region the electron would be equally coupled to all four surrounding protons.

None of these effects has been observed, and one may say that the present results support the dynamic proton order-disorder model of the ferroelectric transition in KH_2AsO_4 rather than the one involving proton displacements. The absence of such ferroelectric-mode phenomena in the proton hfs, however, does not necessarily imply that the rest of the crystal lattice does not become unstable against some collective mode as one approaches the temperature of the protonic order-disorder transition. The transition may well be an order-disorder one for hydrogens and a displacive one for the K ions.

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Energy Bands in Ferromagnetic Nickel*

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The energy bands in ferromagnetic nickel have been calculated within the framework of the unrestricted Hartree-Fock scheme, in which the exchange terms were approximated by a local potential. The augmented-plane-wave method was used to find the eigenvalues of the approximate Hamiltonian, and self-consistency was achieved after several iterations of this method. It was found that the use of the averaged free-electron exchange potential, i.e., $\bar{V}_x^{(s)} = -6(6\rho_s/8\pi)^{1/3}$, gave results in qualitative disagreement with experiment. Reducing the exchange potential by a factor of $\frac{2}{3}$ gave more realistic results. Comparisons with the experimental data are presented which show that the unrestricted Hartree-Fock scheme may be an acceptable model for the ground state of a ferromagnetic solid.

I. INTRODUCTION

EXPERIMENTAL information on the metallic properties of nickel, which are dependent on the electronic configuration, has recently become available, and with it some analyses that explain these properties on the basis of the energy-band model. Energy-band models have been presented[1–3] which attempt to explain empirically the available data on the electronic and optical properties. Also, within the last five years, several papers have appeared in the literature[4–8] which give the energy-band structure calculated from basic considerations, i.e., they present solutions for Schrödinger's equation in a crystal using some form of one-electron potential. This potential, in all cases, has been derived from an atomic calculation corrected for the effects of placing the atoms in a crystalline lattice.

Although these previous calculations are qualitatively quite similar, the arbitrariness of the potential used is enough to create differences between them which are large with respect to the experimental effects which are to be explained. The calculation described in this paper attempts to eliminate this dependence on an arbitrary potential by solving the equations self-consistently, in the same way as the Hartree-Fock method used in atomic calculations. In this way, it is possible to examine the validity of the approximations which must be made in order to solve the equations.

The case of ferromagnetic nickel turns out to be extremely sensitive to slight changes in these approximations. In particular, the form in which the exchange effects responsible for the ferromagnetic structure are inserted into the theory can radically change the final results. This effect was not pointed out in previous calculations on nickel or other materials, either because the solutions were not carried to self-consistency or because the particular case was not sensitive enough to show a definite discrepancy with experiment.

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