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Detection by Electron Paramagnetic Resonance and Electron-Nuclear Double Resonance of the Proton-Lattice Coupled Mode in KH_2AsO_4, KD_2AsO_4, and $NH_4H_2AsO_4$ (Ferroelectrics and Antiferroelectrics)

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The temperature dependence, over the range 4.2–343 °K, of the As^{75} and proton hyperfine structure in KH_2AsO_4 and $NH_4H_2AsO_4$, and of As^{75} in KD_2AsO_4 measured by electron-nuclear double resonance (ENDOR) and EPR is reported. Analysis of the results presents the first *direct* observation of evidence for the coupled proton-lattice motion in these crystals. The data allow the evaluation of the correlation times for the motions of the protons and the As^{75} nuclei. Plots of $\ln(1/\tau)$ vs $\ln(T-T_c)$ point to the existence of a power law of the form $\nu \propto (T-T_c)^n$, where ν is the exchange frequency $(1/\tau)$. These observations support the theoretical model proposed earlier by Kobayashi to explain the nature of the ferroelectric transition in these crystals.

The nature of the basic interactions in the KH_2PO_4-type ferroelectrics is not yet fully understood. One of the major problems concerns the role of the heavy ions. It is well known that the ferroelectric transition is triggered by a cooperative ordering of the protons but that the spontaneous polarization arises because of the accompanying displacements of the heavy ions.[1] Only recently has Kobayashi,[2] following others,[3-6] proposed a model which appears to be the most suitable one for explaining the ferroelectric transitions and several other properties. This model is, however, based critically on the postulate of the existence of a strongly coupled proton-lattice mode, and therefore most of the available experimental techniques have since been employed with a view to examining the validity of this assumption.[7-25] No clear picture has, however, emerged in particular for the crystals of the KH_2AsO_4 type.

We report here what we believe to be the first quantitative measurements of the temperature dependence of the motion of As^{75} in the paraelectric phases of the ferroelectrics KH_2AsO_4 and KD_2AsO_4 and also the antiferroelectric $NH_4H_2AsO_4$, using as microscopic probe the temperature dependence of the As^{75} $(I=\frac{3}{2})$ hyperfine structure in the electron paramagnetic resonance (EPR) of the AsO_4^{4-} center in these crystals. In addition, these studies appear to present rather *direct* evidence for the existence of the much-sought-after proton-lattice coupled motion in these materials. They also offer an explanation for certain, hitherto not understood, anomalies in the EPR spectra of these systems. The latter seems to be important in view of the fact that the EPR of the AsO_4^{4-} center was shown to be a potentially important microscopic probe for studying several properties in these crystals.[26-32] The conclusions are supported by the recent studies of the effects of electric fields on EPR spectra as well as the electron-nuclear double-resonance (ENDOR) measurements in the case of[30] KH_2AsO_4 and mixed[32] KH_2PO_4-KH_2AsO_4 crystals.

The basis of the present experiment can be described as follows: Previous EPR studies of the AsO_4^{4-} center in KH_2AsO_4 and KD_2AsO_4 have shown that in the ferroelectric phase four orientations for this center are, in general, observed.[29] Two of these sites were shown to be due to the existence of the two differently oriented AsO_4 tetrahedra in the unit cell of these crystals, whereas the other two were proved to arise from the existence of the two oppositely polarized domains.[30] If, therefore, the lattice is completely rigid in the paraelectric phase, the ferroelectric transition being entirely due to the ordering of protons in the hydrogen bonds—accompanied by the displacement of As and K ions along the *c* axis at the Curie point—then two sites are in general expected for all the orientations of the AsO_4^{4-} center. If, however, the K-AsO_4 system is in motion, according to the Kobayashi[2] or the Cochran[3] models, the number of sites for the AsO_4^{4-} center could be one or more, depending upon the state of the motion in the system. Moreover, the range of the anticipated frequencies, 10^{11} sec^{-1} or lower, falls in the range where the EPR is known to be the most suitable compared to other techniques.

The present study shows that only one site is observed for the orientation of the AsO_4^{4-} center at very high temperatures, 253 °K and above for the cases of KH_2AsO_4 and KD_2AsO_4, and 333 °K and above for the case of $NH_4H_2AsO_4$. At lower temperatures, even though still about 80 °K above the Curie points, the EPR spectra already reflect the symmetry of those sites expected and observed in ferroelectric phases of KH_2AsO_4 and KD_2AsO_4. This is clearly seen by examining Fig. 1 which shows the angular variation of the group of EPR lines

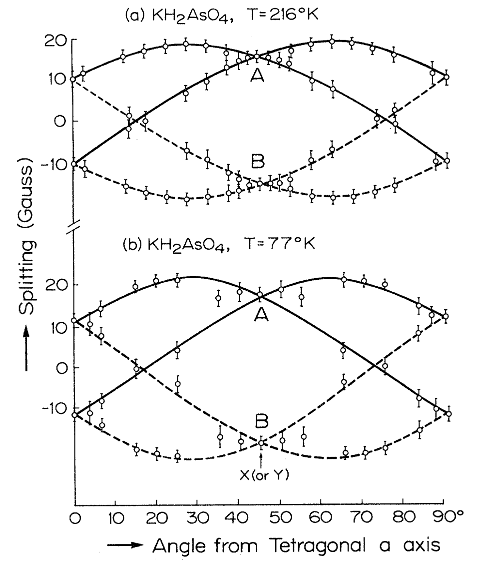

FIG. 1. Angular variation of the splitting observed on the lowest field As^{75} hyperfine component in the *ab* plane of KH_2AsO_4 at the indicated temperatures. (a) Paraelectric phase; the two differently oriented sites are indicated by the full and dashed lines. (b) Ferroelectric phase; the solid and dashed lines refer to the two different domains (Ref. 30).

(each arising from a distinct orientation of the AsO_4^{4-} center) associated with lowest-field hyperfine component ($m_I = \frac{3}{2}$) which alone shows this splitting, as explained previously.[30] For comparison the angular variation of the same group for the ferroelectric phase of KH_2AsO_4 at 77 °K is also included [see Fig. 1(b)]. It is further noted from the spectra recorded in the crystal *ab* plane that the range of temperatures at which these different orientations of the AsO_4^{4-} center become indistinguishable from each other is also the range of the temperature where the superhyperfine structure due to protons, on each of the As^{75} EPR lines, disappears. Moreover, as the temperature is raised further, the linewidth decreases from a value of 30–40 (at the coalescence temperature where the sites collapse) to a residual linewidth of 5 G at approximately 77 °K (almost corresponding to that of the individual components at very low temperatures). Similarly, as the temperature is lowered below that corresponding to the collapse of the individual components, the separation between the lines corresponding to the differently oriented AsO_4^{4-} centers increases until it reaches a maximum of about 35 G. This happens when the crystals are still in their high-temperature phase and is observed for the splittings of the As^{75} hyperfine interaction as well as those due to the proton hyperfine interactions. These results clearly rule out the rigid-lattice model for the ferroelectric transition in these crystals since they can only be explained in terms of the presence of motion of *both* As^{75} nuclei as well as protons, i.e., they demonstrate the existence of proton-lattice coupled modes as we shall show below.

According to the well-known theories of the effects of motion on the magnetic resonance spectra, the spectra will collapse when $\tau\Delta\omega \approx 1$, where τ is the correlation time for the particular type of motion involved and $\Delta\omega$ is the splitting between the spectral lines. When $\tau\Delta\omega > 1$, the individual lines become more and more resolved until, for $\tau\Delta\omega \gg 1$, the motion gets frozen and no further change is observed in the spectra.

The temperature dependence of the motion of As^{75} was studied from 4.2 to 343 °K with the Zeeman field $\vec{H}$ oriented along the tetragonal *a* (*b*) axis as well as along an orthorhombic axis, point *X* (or *Y*) in Fig. 1, where the EPR spectra are found to be the simplest. On the basis of the crystal structure it will be easily seen that for the case of $\vec{H} \parallel \vec{X}$, the lines due to the two differently oriented AsO_4 tetrahedra coincide,[30,33] and on the basis of the rigid-lattice model only one site is expected until (or very near) the Curie point when the arsenic nuclei get displaced and the two domains formed.[33] On the other hand, for the case of $\vec{H} \parallel \vec{a}$ (or $\vec{b}$), at any temperature, two and only two lines are expected because of the two differently oriented tetrahedra.[30] The isotropic spectra observed in the *ab* plane at high temperatures show that the AsO_4 groups undergo motion which is fast enough to smear out the distinction between the two types of tetrahedra. It must be mentioned further that for $\vec{H} \parallel \vec{X}$, no proton superhyperfine structure is resolved and this direction is thus more suitable for the study of the motional effects on the As^{75} hyperfine structure. On the other hand, the direction $\vec{H} \parallel \vec{c}$ was chosen for studying the motional effects in the proton superhyperfine structure because for that direction all the arsenic sites are equivalent, and thus the slowing of the As^{75} motion does not seem to affect the EPR spectra.

To evaluate the correlation times for the motion of As^{75} nuclei, as well as for the protons, a computer program based on the formalism of the modified Bloch equations[26] was used. For the case of the As^{75} motion, the splitting between the EPR lines due to the two AsO_4^{4-} centers belonging to the two oppositely polarized domains was measured to be 33 G, and $1/T_2$ was estimated to be 8 G. Although the actual line shapes were neither pure Lorentzian nor Gaussian, Lorentzian shapes were assumed for these calculations. For the case of the protons, the splittings for $\vec{H} \parallel \vec{c}$ for the case of both the "close" and "far" protons were measured to be 10.80 and 1.50 G respectively, using the ENDOR technique.[30] $1/T_2$ was estimated to be 3.5

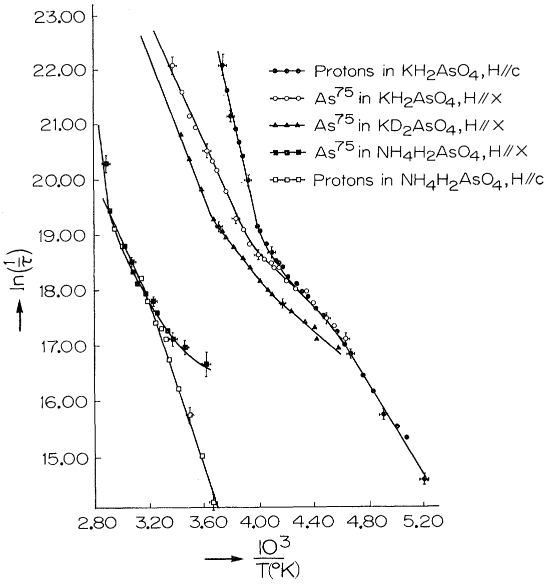

FIG. 2. Correlation times for the motion of As^{75} and of hydrogen protons calculated from the temperature dependence of As^{75} and proton hyperfine structure.

G and, contrary to Blinc's approach,[26] no allowance was made for those Slater configurations which give rise to zero dipole moment for an H_2AsO_4 group. This is because our EPR spectra show no clear evidence for such configurations, and also because the more recent infrared spectroscopic experiments on these compounds simply rule out the existence of these configurations.[13,16] By comparing the theoretical and the experimental spectra, the correlation times τ were obtained. The data are shown in Fig. 2 where $\ln(1/\tau)$ is plotted against $10^3/T$ °K.

Several important features can be noted from inspection of Fig. 2. First of all if we assume that the motions are thermally correlated, then the plot of $\ln(1/\tau)$ against $1/T$ should be linear, the slope being the activation energy of the potential-energy barrier to the motion. We notice that for the case of KH_2AsO_4, which could be studied the most extensively, both graphs can be broken into three linear regions with respective slopes (in electron volts) and preexponential factors (in hertz) of 0.25, 1.0×10^{13}; 0.12, 3.9×10^{10}; and 0.2, 3.2×10^{12} for the motion of As^{75}, and 0.5, 2.8×10^{18}; 0.15, 2.5×10^{11}; 0.2, 3.2×10^{12} for the motion of protons.

It is clear that the motion of As^{75} nuclei and protons are governed by different processes at higher temperatures but the same process governs the motion of both types of nuclei at lower temperatures. These studies thus present direct evidence for the existence of strong coupling between the motions of the protons and that of the As^{75} nuclei. Similar coupling is also observed for the case of $NH_4H_2AsO_4$. However, as is seen from Fig. 2, even after the crossover point the motion of the As^{75} nuclei is found to be slower than that of the protons, unlike the case of KH_2AsO_4, in the range of temperatures investigated. The activation energy and the preexponential factors for the As^{75} motion are, respectively, 0.5, 1×10^{12}; 0.25, 7.9×10^{10}; 0.12, 1.4×10^{9}; and those for the proton motion are 0.25, 7.9×10^{10}; 0.33, 8×10^{11}. The same quantities for the motion of As^{75} in KD_2AsO_4 were determined to be 0.3, 13.6×10^{13}; 0.13, 1×10^{11}; 0.09, 5×10^{9} for the case of $\vec{H} \parallel \vec{X}$. We have so far not been able to obtain correlation times for the motion of deuterons because of the lack of resolution in the EPR spectra. However, a comparison of the results for the deuteron intrabond motion in[24] KD_2AsO_4 with our results on As^{75} clearly shows that below about 250 °K the same process governs the motion of deuterons and As^{75}, and this may be taken as an evidence for the existence of the coupled-mode motion in this material also. $\nu = 1/\tau$ can be interpreted as the frequency of exchange of As^{75} and of protons in their respective double-minimum positions. For the protons this conclusion can be drawn in analogy with the NMR,[22-24,34] ESR,[26-28,30] infrared,[25,13,16] Raman-,[7,14] and neutron-scattering data.[8-10,21,33] For the case of As^{75}, although x-ray diffraction experiments point to preferential vibrations of heavy ions along the c axis,[33] no quantitative data are available, but this has been postulated recently by several authors.[2-6,35-37] We thus identify the observed motion of As^{75} as that of the K-AsO_4 or NH_4-AsO_4 systems along the c axis. Plots of ν vs $(T-T_c)^{1/2}$ were not linear over the entire region, but as $T \to T_c$, they became linear. Plots of ν against $[(T-T_c)/T]^{1/2}$ did not give any better fit in the high-temperature range. Only plots of the $\ln(1/\tau)$ vs $\ln(T-T_c)$ are nearly linear, indicating a power law of the form[38] $\nu \propto (T-T_c)^n$. This result is not contained in any of the existing theories of KH_2PO_4-like ferroelectrics. On the other hand, the slopes of the $1/\tau$ vs $(T-T_c)^{1/2}$ curves are quite different for KH_2AsO_4 and KD_2AsO_4—which further supports the Kobayashi model[2] against the Cochran model. At high enough temperatures, where the motion of protons and As^{75} nuclei is effectively decoupled, the exchange frequencies for the As^{75} motion are approximately the same for both KH_2AsO_4 and KD_2AsO_4. However, for $NH_4H_2AsO_4$, the motions of both As^{75} and protons are very much slower, as can be seen from Fig. 2.

In conclusion, the present studies are in better agreement with the Kobayashi model than any of the other models of the ferroelectric transition phenomena in these crystals. In particular they offer the first direct experimental evidence for the existence of the proton-lattice coupled mode for the KH_2AsO_4-

type ferroelectrics as well as antiferroelectrics. Our results also show that above T_c the tetragonal symmetry of these crystals as determined by the diffraction techniques[33] is only a time average of two orthorhombic ones, and that EPR and ENDOR spectra of AsO_4^{4-} centers can serve as sensitive microscopic probes for investigating the dynamics of the domain formation in such systems.[1,30,33] Analysis of similar results on RbH_2AsO_4 and mixed KH_2PO_4-KH_2AsO_4 and KD_2PO_4-KH_2AsO_4 crystals is in progress and will be reported soon.

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