define in a purely operational way the homopolar and ionic contributions to the effective energy gap by the relations $E_h^2 = E_g^2(1-f_i)$ and $C^2 = E_g^2 f_i$. Crystal structures predictions based on calculations of C and E_h for the 68 materials we have been considering are quite similar to the PV predictions,[3,6] though now there is a small overlap region on the ionicity scale between zinc-blende and rock-salt structures.

The reason for introducing a new definition of ionicity based on the experimentally determined dispersion energy is not to reproduce the PV successes but to provide a method which, potentially, may be extended to other classes of materials where the details of the PV analysis are not valid. In particular we have considered applications to metallic systems, work which is to be reported in a later paper.

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[1]J. C. Phillips, Phys. Rev. Lett. 20, 550 (1968), and 22, 645 (1969).
[2]J. A. Van Vechten, Phys. Rev. 182, 891 (1969).
[3]J. A. Van Vechten, Phys. Rev. 187, 1007 (1969).
[4]S. H. Wemple and M. DiDomenico, Jr., Phys. Rev. Lett. 23, 1156 (1969), and 24, 193(E) (1970).
[5]D. Penn, Phys. Rev. 128, 2093 (1962).
[6]J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ., London, England, 1964), Sec. 8.2.
[7]J. C. Phillips, "Bands and Bonds in Semiconductors," to be published.
[8]Wemple and DiDomenico actually confined their attention to fitting index of refraction data below the gap using (3) and did not imply this extension.
[9]E. W. Aslaksen, Phys. Rev. Lett. 24, 767 (1970).
[10]J. J. Hopfield, Bull. Amer. Phys. Soc. 15, 309 (1970), and to be published.
[11]Note that this model ϵ_2 implies an ϵ_1 which fits (3) precisely over only a limited energy range.
[12]R. M. Martin, Phys. Rev. B 1, 4005 (1970).

ELECTRON PARAMAGNETIC-RESONANCE AND ELECTRON-NUCLEAR DOUBLE-RESONANCE OBSERVATIONS OF DOMAINS IN THE IRRADIATED FERROELECTRICS KH_2AsO_4 AND KD_2AsO_4

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A direct observation of ferroelectric domains in x-irradiated KH_2AsO_4 and KD_2AsO_4 using electron paramagnetic resonance (EPR), and in the case of KH_2AsO_4 also using electron-nuclear double-resonance (ENDOR), is reported. The nature of the observed domain splittings and consequently the effects of an externally applied electric field on the EPR and ENDOR spectra are explained. Moreover, the higher resolution possible with the ENDOR technique, has, for the first time, made it possible to use protons as microscopic probes and to identify in general lines from individual domains in all directions.

Since the pioneering work of Slater, considerable progress has recently been made in the field of hydrogen-bonded ferroelectrics, but a number of basic problems still remain unsolved.[1] Among the several experimental techniques employed in these studies, the use of the EPR of AsO_4^{4-} as a detector of protonic motion in the KH_2AsO_4 type of ferroelectrics has already yielded significant results.[2,3] However, a complete analysis of the EPR spectrum of the AsO_4^{4-} center in the ferroelectric phase has not yet appeared (see, however, Hampton et al.[4]). We have therefore carried out this study which has proved essential for a clear understanding of the origin of the ferroelectric domain splitting in the EPR spectra of the AsO_4^{4-} center. Electron-nuclear double-resonance (ENDOR) studies of protons around the AsO_4^{4-} center have further confirmed our model of these ferroelectric domain splittings. The effects of an externally applied electric field on the domain splittings are observed[5] and explained. These studies have shown the feasibility of plotting a hysteresis loop using the EPR technique. This method could complement dielectric and other studies[5a] in those ferroelectrics containing a paramagnetic center.

At room temperature, KH_2AsO_4 (KDA) forms tetragonal ($I\bar{4}2d$) crystals with each tetrahedral AsO_4 group hydrogen-bonded to four neighboring AsO_4 groups.[6] The time-average position of each

hydrogen atom is located symmetrically between the upper oxygen of one AsO_4 tetrahedron and a lower oxygen of a neighboring AsO_4 tetrahedron, these two tetrahedra being related to each other by a rotation of approximately 32° about the tetragonal c axis of the crystal. In the ferroelectric phase, below 97°K, the symmetry of the crystal becomes orthorhombic ($Fdd2$); the fourfold axis in the c direction disappears, and the two other orthorhombic axes, X and Y, appear at 45° from the tetragonal a and b axes, respectively. The X and the Y directions are definite only in a single-domain crystal. Ferroelectric twinning (i.e., an interchange of X and Y axes) is found in multidomain or unpolarized crystals. Within each domain the hydrogens are ordered, the two protons associated with each AsO_4 unit occupying positions closer to the upper oxygens in one domain or closer to the lower oxygens in the other domain. KD_2AsO_4 (DKDA) is isomorphous with KDA, the Curie point for the DKDA being 162°K.

X irradiation of KDA[6] or DKDA[2] produces a stable, paramagnetic AsO_4^{4-} center. No significant structural change seems to occur on the formation of this center which is hydrogen-bonded to four other AsO_4 units in the crystal. The EPR spectrum at room temperature shows hyperfine interaction of an unpaired electron with the As^{75} ($I=\frac{3}{2}$) nucleus. The spin-Hamiltonian parameters reflect the expected tetragonal site symmetry about the c axis of the crystal.[4]

The present study of x-irradiated KDA and DKDA in the ferroelectric phase at 77 and 4.2°K shows that the general nature of the EPR spectrum is the same but that the details of the spectrum can be explained only by a rhombic spin Hamiltonian. The salient features of the EPR results are best described by following the angular variation of the spectrum of DKDA in the tetragonal ab plane. The lowest field As^{75} hyperfine component ($m_I=\frac{3}{2}$) alone shows a splitting into four lines in general, the other three As^{75} hyperfine components being unsplit. The angular variation of this group of lines associated with the lowest-field hyperfine component (Fig. 1) leads to the following results: The rhombic spin-Hamiltonian parameters are $g_z=2.0021\pm0.0001$, $g_x=2.006\pm0.0005$, $g_y=1.993\pm0.0005$; $A_z=3270\pm2$, $A_x=2960\pm3$, and $A_y=2901\pm3$ MHz. The z direction is the polar axis (c axis) direction while there are two possible orientations for x (i.e., two sites for the AsO_4^{4-} center) making angles ±16° with the crystallographic X direction.[7]

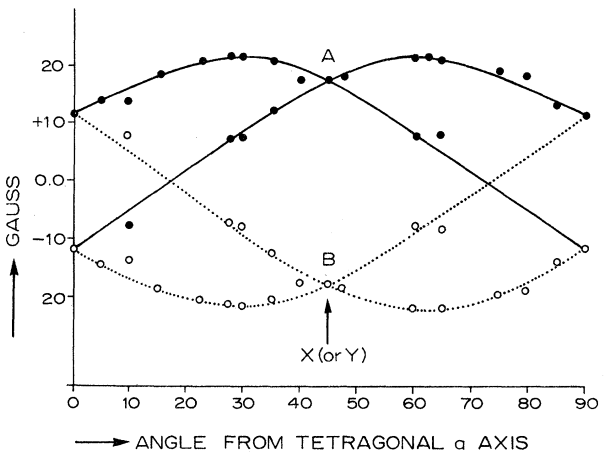

FIG. 1. Angular variation of the splitting observed on the lowest field As^{75} hyperfine component in the ab plane of KD_2AsO_4 at 77°K. The observed line is in general incompletely resolved and the points in the figure refer to the estimated centers of components into which the line could be decomposed. The full and the dotted lines refer to the two different domains.

If x and y are taken to coincide with the projections of the top and bottom edges of the AsO_4 tetrahedra, then these results show the tetrahedra to be rotated by ±16° on either side of the orthorhombic X (or Y) mirror plane.[6] In addition to the existence of these two sites for the AsO_4^{4-} center, in the unpolarized crystal, twinning (i.e., domain structure) is present and X and Y directions can be interchanged. This again doubles the number of sites for the AsO_4^{4-} center. Hence, four components are, in general, expected and observed (Fig. 1). It is seen from Fig. 1 that when H_0 (the external magnetic field) is along the X or the Y direction, the components arising from the two differently oriented tetrahedra coincide, the remaining splitting being entirely due to the domain structure. However, for $H_0 \| a$ or $H_0 \| b$, the components belonging to the two domains coincide, the remaining splitting now being entirely due to the two differently oriented AsO_4 tetrahedra. It is now easy to see that the presence of the orthorhombic site symmetry together with a large second-order effect in the As^{75} hyperfine structure is responsible for the other three As^{75} hyperfine lines remaining unsplit.

To confirm these results further, we repeated the EPR study on KH_2AsO_4 at 77°K in the ab plane with a polarizing dc electric field across the crystal parallel to its c axis. Variable electric fields up to ±12 kV/cm were used. When $H_0 \| X$ or $H_0 \| Y$ we could observe the expected variation

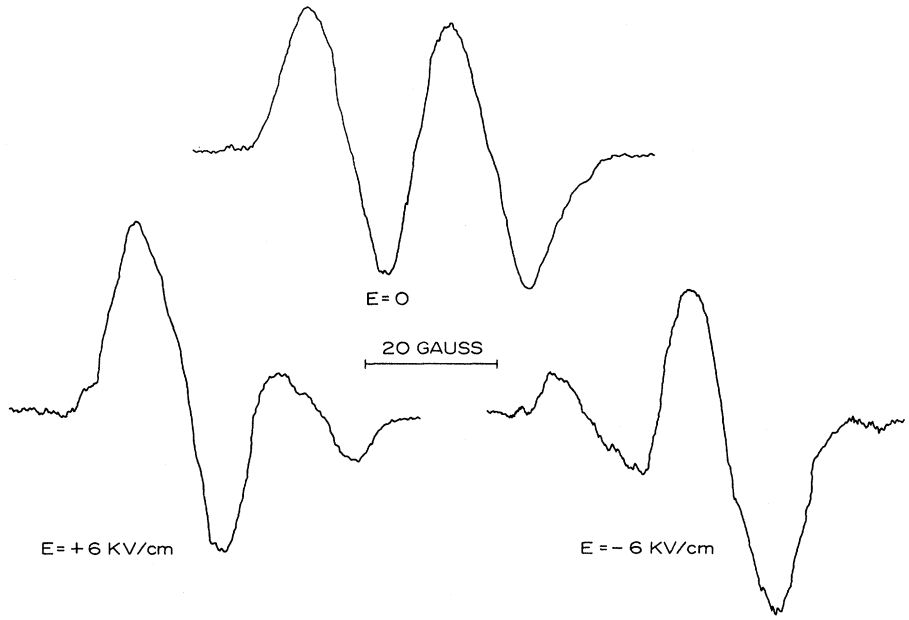

FIG. 2. Electric field effects on the lowest-field hyperfine component of As^{75} in KH_2AsO_4 at 77°K for $H_0 \| X$ or $H_0 \| Y$.

of the line intensities with the field strength and the direction of the applied electric field (Fig. 2). Also no electric-field effect could be seen for the case with $H_0 \| a$ or $H_0 \| b$—thus fully confirming our model. For the case of $H_0 \| X$ (or $H_0 \| Y$), we could plot the hysteresis loop for applied fields between ±12 kV/cm by taking the polarization in the crystal to be proportional to the difference in the intensities of the two lines. The hysteresis loop was found to be symmetrical and the coercive force determined to be 5.5 kV/cm. This value appears to be slightly higher than the average value of the coercive force for the undamaged crystal, in agreement with the observation that radiation damage increases the coercive force in ferroelectric crystals.[8] The exact mechanism for this is still not understood.[8] We believe, however, that this method of obtaining the hysteresis loop can be of special importance for studying the domain or the sublattice polarization.

We have also observed domain effects in the ENDOR spectra of protons for these hydrogen bonded ferroelectrics for the first time. These studies were initially undertaken with a view to understanding the part played by protons in the ferroelectric phenomenon[9] and have now been completed.[10] Certain results relevant to the observation of the domains and the electric field effects will be described briefly.

Figure 3 shows the angular variation of the ENDOR spectra for the nearest-neighbor protons

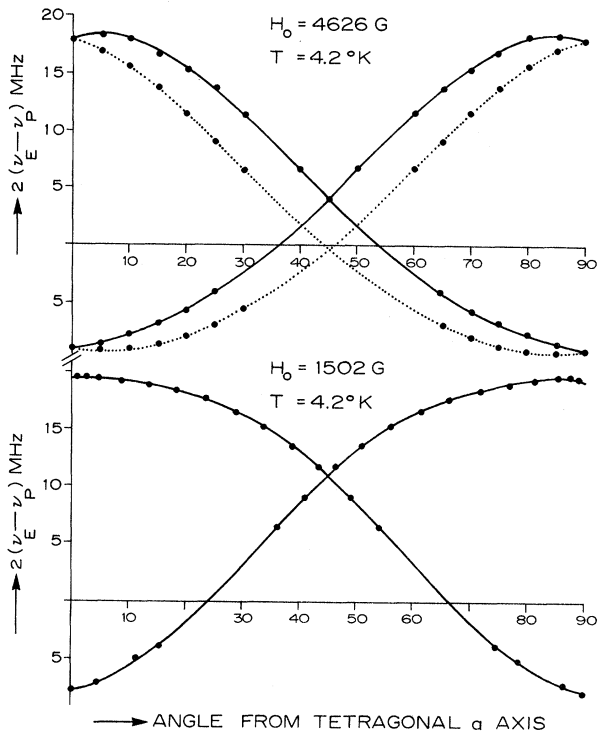

FIG. 3. Angular variation of the ENDOR lines of the nearest-neighbor protons in KDA for the highest field (H_0=4626 G) and the lowest field (H_0=1502 G) As^{75} hyperfine components. ν_E is the observed ENDOR frequency and ν_P is the free proton NMR frequency. A detailed analysis taking into account the change of H_0 shows that the continuous curves in the two diagrams refer to the same domain.

in the *ab* plane of KDA at 4.2°K when the lowest ($m_I = \frac{3}{2}$) and the highest ($m_I = -\frac{3}{2}$) field As^{75} EPR lines are saturated. In the first case the magnetic field H_0 is set to satisfy conditions corresponding to the point *A* in Fig. 1 and is kept constant throughout the angular variation study. It will be seen that for ENDOR the EPR condition is then satisfied mainly for the lines from the two sites in a single domain and two transitions are therefore expected and observed in the ENDOR experiments. Similarly by satisfying the EPR conditions corresponding to the point *B* in Fig. 1, two other ENDOR transitions (from two sites in the other domain) could be studied exclusively. For the highest field hyperfine transition, however, since the splittings due to the two sites or the domain structure remain unresolved in EPR, while performing the ENDOR experiment four transitions are in general expected and observed. By saturating this EPR line ($H_0 = 4626$ G), we have also observed the effects of polarizing electric fields on the ENDOR transitions. The crystal was polarized at 77°K and then cooled to 4.2°K. The polarizing electric field was then removed and the ENDOR transitions were observed. The expected changes in the ENDOR line intensities were clearly seen, thus lending further support to our model of the domain structure and the domain switching in the KDA-type of ferroelectrics.

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[1]R. Blinc, Advan. Magn. Resonance 3, 141 (1968).

[2]R. Blinc, P. Cevc, and M. Schara, Phys. Rev. 159, 411 (1967).

[3]D. J. Genin, D. E. O'Reilly, and T. Tung, Phys. Rev. 167, 445 (1968).

[4]M. Hampton, F. G. Herring, W. C. Lin, and C. A. McDowell, Mol. Phys. 10, 565 (1966).

[5]Two brief references to the observation of domain switching by EPR in this system have been made, although no analysis of the origin of the domain splitting has been given: (i) R. Blinc and P. Cevc, Solid State Commun. 6, 635 (1968); (ii) R. C. DuVarney and R. P. Kohin, Bull. Amer. Phys. Soc. 13, 4 (1968).

[5a]See, for example, J. L. Bjorkstam and R. E. Oettel, in *Proceedings of the International Meeting on Ferroelectricity, Prague, 1966,* edited by V. Dvořák, A. Fouskora, and P. Gilogán (Institute of Physics of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia, 1966), p. 91; V. H. Schmidt, *ibid.*, p. 97.

[6]G. E. Bacon and R. G. Pease, Proc. Roy. Soc., Ser. A 230, 359 (1955).

[7]Our results here do not agree with the axes used by W. Beezhold and E. A. Uehling, Phys. Rev. 175, 624 (1968), in their calculation of the electric field gradient tensor at As sites in KDA. A relabeling of Fig. 7 in their paper, by substituting *X* and *Y* axes for the tetragonal *a* and *b* axes, will remove the discrepancy.

[8]F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, England, 1962).

[9]N. S. Dalal, C. A. McDowell, and R. Srinivasan, Chem. Phys. Lett. 4, 97 (1969).

[10]N. S. Dalal, C. A. McDowell, and R. Srinivasan, to be published.