Table II, the (100) wall energy is lower than the (220) wall energy, and we find that $\Delta(\ln\sigma)/\Delta\phi \simeq 4\%$. On the other hand, the continuum theory[4] of the angular dependence of the 180° domain-wall energy yields $\Delta(\ln\sigma)/\Delta\phi \simeq 2\times10^{-4}\%$. The reason for this large discrepancy must stem from the inadequacy of applying a continuum theory to a domain wall that is vanishingly thin.

IV. SUMMARY

The domain-wall energies and thicknesses of the four possible 180° domain walls in $BaTiO_3$ were calculated according to a microscopic, energy-minimization scheme based on a model that treats the local fields self-consistently and accounts for the nonlinearity of the oxygen electronic polarizability; the $BaTiO_3$ lattice was approximated by linear chains of Ti and O_a ions, whose interaction is by far the dominant interaction in tetragonal $BaTiO_3$. The lowest energy walls perpendicular to ⟨100⟩ and ⟨110⟩ are the (100) and (220) walls, with energies of 1.52 and 10.3 erg/cm^2, respectively. The (220) wall energy is about an order of magnitude larger than the value obtainable from the Miller-Weinreich nucleation model, but this model is shown to be capable of correctly ordering the (100) and (220) wall energies when the proper minimum step along ⟨110⟩ is employed.

The anisotropy of these wall energies along ⟨100⟩ and ⟨110⟩ is in much better quantitative agreement with the estimates of Fousek and Šafránková than the earlier continuum theories; these experimental estimates were derived from studies of the equilibrium domain structure in $BaTiO_3$.

ACKNOWLEDGMENTS

The author is indebted to Dr. R. C. DeVries for introducing him to domain-wall problems in $BaTiO_3$ and for numerous stimulating discussions, and to Dr. Jan Fousek for kindly reading the typescript and offering valuable suggestions.

PHYSICAL REVIEW VOLUME 175, NUMBER 2 10 NOVEMBER 1968

Determination of the Electric-Field-Gradient Tensor at the Arsenic Site in KH_2AsO_4 by Proton Relaxation Measurements*

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(Received 6 June 1968)

Crossover contact of protons and arsenic in KH_2AsO_4 below the ferroelectric transition temperature $T_C=96°K$ makes a significant contribution to the proton spin-lattice relaxation rate. The decrease in proton relaxation time occurs at those values of the applied magnetic field and crystal orientation at which the proton transition frequency is equal to one of the arsenic transition frequencies. It is found that the observed crossover pattern can be reproduced with considerable precision by a calculation based on a model of the electric-field-gradient tensor at the arsenic site which is suggested by the crystal structure in the ordered state. The comparison with experimental data yields a value of the electric quadrupole coupling constant equal to 34.8 Mc/sec at 77°K. These results are difficult to determine by direct observation of the arsenic resonance because only the $\frac{1}{2}$ to $-\frac{1}{2}$ transition is observable. The orientation of the principal axes and the value of the asymmetry parameter are described.

I. INTRODUCTION

MEASUREMENTS by Bjorkstam[1] on the proton spin-lattice relaxation in ferroelectric KH_2AsO_4 revealed a sharp decrease in T_1 at the Curie temperature $T_C=96°K$. Similar measurements on the isomorphs of this crystal in which arsenic is not present did not exhibit this behavior. In particular, the relaxation time in samples of KH_2PO_4 which were available at the time of these earlier measurements disclosed no more than the usual relaxation which can be attributed to spin-diffusion effects in the presence of a moderately high density of paramagnetic impurity ions. The contrast between the two crystals from this point of view is well displayed for a particular sample of each in Fig. 1. No suggestion of a minimum in T_1 at the Curie temperature $T_C=123°K$ is to be found in KH_2PO_4.

These results suggest that the presence of arsenic is responsible for the proton relaxation at and below T_C in KH_2AsO_4. Some further evidence justifying this conclusion was found by Jones[2] when he observed a negative

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* Supported by the National Science Foundation.

[1] J. L. Bjorkstam, Ph.D. thesis, Department of Physics, University of Washington, Seattle, Washington, 1958 (unpublished).

[2] E. D. Jones, Ph.D. thesis, Department of Physics, University of Washington, Seattle, Washington, 1962 (unpublished).

frequency dependence as well as a frequency-dependent angular anisotropy for the proton relaxation time T_1 at temperatures well below T_C. In order to explain his results, Jones proposed that in addition to spin diffusion there is a second relaxation mechanism involving dipolar coupling of the protons to rapidly relaxing arsenic nuclei whose spectrum is determined by the magnitudes of both the applied magnetic field and the crystalline electric field gradient (EFG). He found that all of his observations could be moderately well explained if the electric quadrupole coupling constant of arsenic to the crystalline field was of the order of 37 Mc/sec.

Independent studies based on direct observations of the arsenic nucleus were not successful for some time. Repeated attempts to observe the pure quadrupole transitions had failed or at best led to ambiguous results. But, in 1964, Bjorkstam[3] succeeded in observing the $\frac{1}{2}$ to $-\frac{1}{2}$ arsenic Zeeman transition, first above the Curie temperature and then below it. On the basis of these observations he was able to deduce a value for the quadrupole coupling constant ν_Q at 77°K equal to about 33 Mc/sec, which is not in strong disagreement with the value predicted by Jones. Above T_C he found that the value of ν_Q is smaller by a factor of 10, increasing slowly as T_C is approached from above. The large jump in ν_Q at T_C does not disagree with expectation since one may anticipate that the combined effects of proton ordering and change of shape of the AsO_4 tetrahedron should lead to a large change in the EFG at the site of the arsenic nucleus.

These results on the value of ν_Q suggested the possibility of a more precise study based again on the observation of the proton relaxation. A quadrupole coupling constant of 30–40 Mc/sec would, in the presence of a strong magnetic field, lead to an energy level system for the arsenic nucleus with transition frequencies easily adjusted to be equal to the proton transition frequency by varying the strength of the magnetic field, the orientation of the crystal in the field, or both. Assuming sufficient strength of contribution to relaxation in the presence of other mechanisms, the proton relaxation rate would be expected to increase whenever its transition frequency was equal to one of the arsenic transition frequencies. Thus proton relaxation could be used as a monitor for detecting arsenic relaxation and in fact as the instrument for measuring the arsenic transition frequencies. The measurements are not qualitatively different than those performed by Jones[2] when he measured the frequency-dependent angular anisotropy of the proton T_1. But more perfect single crystals and improved measurement techniques led to new results and in fact to the first clear picture of what was actually happening.

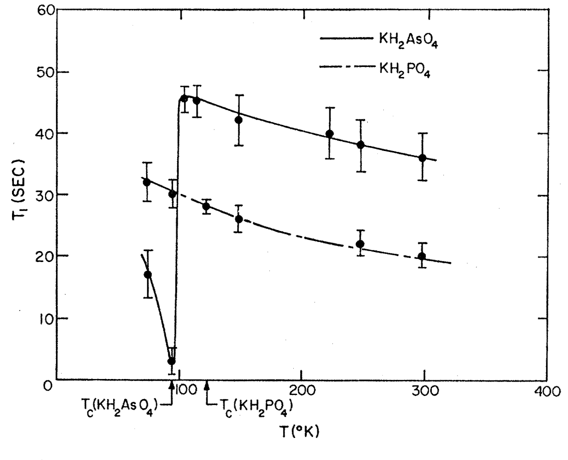

FIG. 1. Temperature dependence of proton relaxation time in KH_2AsO_4 and KH_2PO_4.

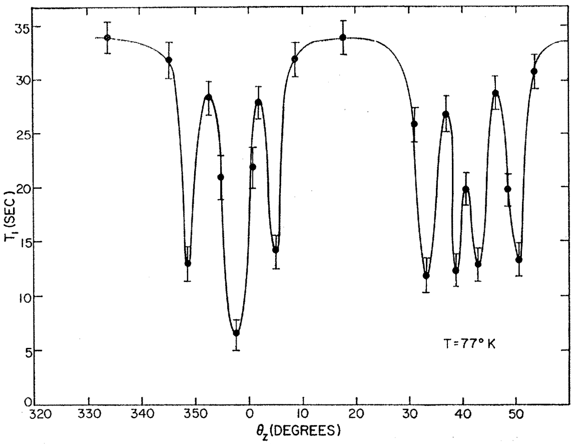

FIG. 2. Variation of T_1 as a function of crystal orientation. These are the crossover points in KH_2AsO_4 at 32 Mc/sec and 77°K.

Typical data for the variation of the proton T_1 as a function of angle of rotation of the crystal about a selected rotation axis in the presence of a constant magnetic field perpendicular to that axis are shown in Fig. 2. Such curves display a distinct pattern in terms of number of dips in a cycle of angular variation, magnitude of T_1 at the minima, and angular width of the relaxation rate peaks. It is the purpose of this paper to show that some features of these data, such as the location of the minima and the way in which the pattern of minima varies with the magnetic field, can be fitted quantitatively to predictions based on a unique choice of the EFG tensor. The quantitative fit is in fact sufficiently good that one obtains a quite satisfactory determination of the quadrupole coupling constant, the asymmetry parameter, and the EFG tensor orientation. Also, measurements as a function of temperature lead to a determination of changes in the quadrupole coupling constant over a range of temperatures extending from

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[3] J. L. Bjorkstam (private communication).

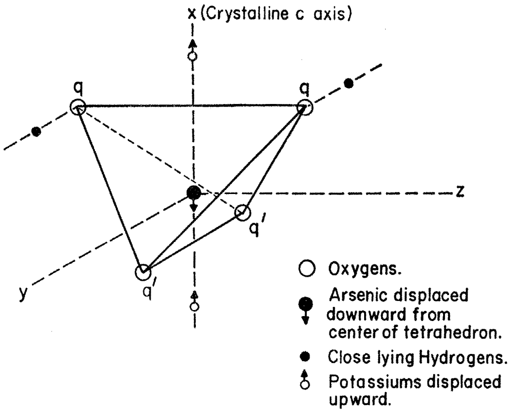

FIG. 3. Arsenate tetrahedron with four oxygen atoms surrounding one arsenic atom.

77°K to within 0.5°K of the transition temperature at 96°K.

The interpretation is based on a model of the EFG tensor which is suggested by the known crystal structure in the ordered state. These considerations and conclusions are described in Sec. II. Knowing the form of the EFG tensor, the energy levels of the arsenic spin in the presence of a magnetic field can be obtained. Since, however, the magnetic and electric quadrupole energies are comparable in this experiment, perturbation methods cannot be used. Therefore, in Sec. III the energy eigenvalue problem is solved numerically for the specific case of the arsenic spin and for various values of the ratio of magnetic and electric energy. Section III is concluded with a discussion of the basic elements which enter into the quantitative determination of the "crossover" pattern involving the arsenic and proton resonances. The discussion of crossover is continued in Sec. IV by noting that in KH_2AsO_4 there are several distinct orientations of AsO_4 groups each of which provides its own crossover pattern. The complete pattern is a superposition of four separate patterns. By refining the choice of numerical values on which the prediction of crossover frequencies depends, it is shown that complete agreement between theory and experiment can be obtained. It is now assumed that the correctness of the model has been established. It may then be used as a basis for measuring the temperature dependence of the electric quadrupole coupling constant. The procedure and results are described in Sec. V.

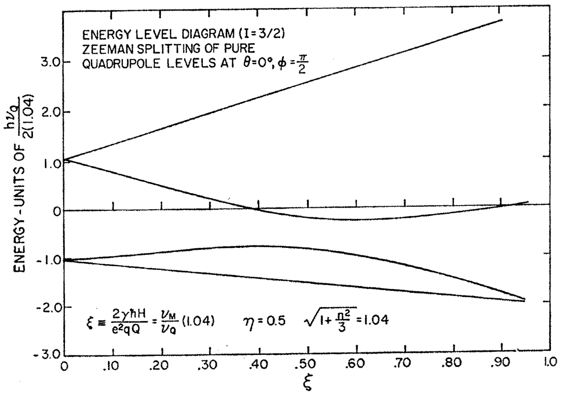

FIG. 4. Energy levels as a function of the ratio of magnetic and electric quadrupole energies.

No attempt is made here to explain the magnitude of the crossover relaxation rate. This and other problems are mentioned more explicitly in Sec. VI.

II. EFG TENSOR

It will be assumed that the EFG tensor at the site of the arsenic nucleus in KH_2AsO_4 is determined by gross features in the crystal structure which are known from x-ray[4] and neutron-diffraction[5] measurements. In the ferroelectric phase, the crystal has a spontaneous polarization along its c axis. Taking the positive direction upward, the results of x-ray and neutron-diffraction studies which are of present interest may be summarized as follows: (a) The two protons in hydrogen bonds at the top edge of the AsO_4 tetrahedron are in equilibrium positions that are adjacent to the tetrahedron while the protons at the bottom edge are more remote; (b) the As atom is displaced downward from the center of the tetrahedron; and (c) the K atoms lying in the same vertical axis as the As are displaced upward. A schematic diagram of charges and displacements is shown in Fig. 3.

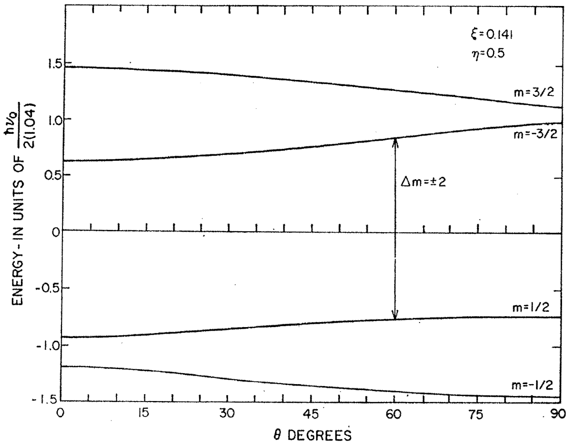

FIG. 5. Angular dependence of the energy levels.

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[4] Benjamin Chalmers Frazer and Ray Pepinsky, Acta Cryst. **6**, 273 (1953).

[5] S. W. Peterson, Henri A. Levy, and S. H. Simonsen, J. Chem. Phys. **21**, 2084 (1953); G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A230**, 359 (1955).

The principal contributions to the EFG at the As will be assumed to come from the ordering of protons and the displacement of the As, the former because the hydrogens close to oxygens decrease the electron charge around those oxygens, and the latter because it requires evaluation of the EFG tensor at an off-center position. The small displacement (of about 0.05 Å) of the distant K cannot contribute appreciably to the EFG tensor at the As.

Qualitative features of the EFG tensor based on the two major contributions are easily described. The first contribution coming from unequal charges q and q' at the top and bottom oxygens lead to an EFG tensor of the form $V_{zz}=-V_{yy}$, $V_{xx}=0$, where the coordinate system is that illustrated in Fig. 3. Thus two of the principal axes lie along the horizontal tetrahedral edges and the third axis is parallel to the crystalline c axis (the spontaneous polarization axis). However, the component of the EFG tensor along the third axis is zero, and the asymmetry parameter η defined by the relation

$$\eta=(V_{xx}-V_{yy})/V_{zz},$$

where, as usual, we take $|V_{zz}|\geq|V_{yy}|\geq|V_{xx}|$, is $\eta=1$. Now we add the contribution of the As displacement. Its principal consequence is to make a contribution to V_{xx} and thus to reduce η to a value less than 1. We will for the present disregard the magnitude of the effect, which for the observed As displacement (of about 0.03 Å) is very small. It is sufficient for the present to note that an EFG tensor with its two largest components in the horizontal plane and nearly parallel to the tetrahedral edges lying in this plane and with an asymmetry parameter less than unity, and as small as 0.5 if needed, is not inconsistent with the crystal structure in the ordered state.

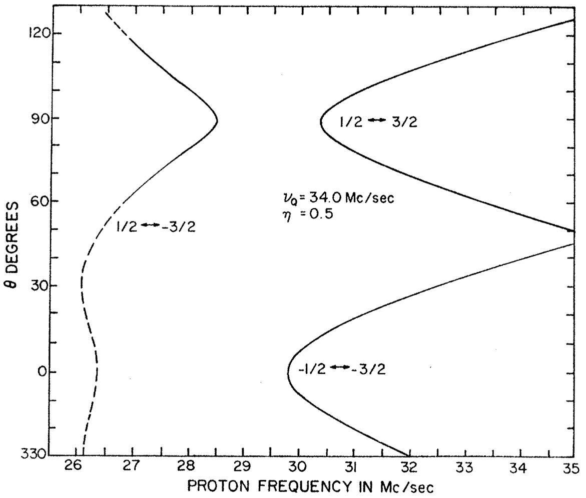

FIG. 6. Theoretical crossover pattern for one arsenate group, one domain, and the specified values of parameters.

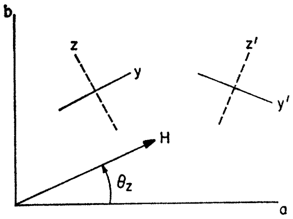

FIG. 7. Schematic showing the crystalline a and b axes, the top and bottom edges of two differently oriented AsO_4 tetrahedra, and the orientation of the magnetic field H.

III. CROSSOVER PATTERN OF As AND H RESONANCES

The Hamiltonian for the interaction of a nuclear spin with $I>\frac{1}{2}$ in combined electric and magnetic fields has been described by many authors.[6] A formulation of the problem which is valid for arbitrary ratios of magnetic and electric energies has been given by Dean.[7] Following his procedure, we find that for the case of As with $I=\frac{3}{2}$ the energy eigenvalues E can be determined exactly by numerical solution of the equation

$$\begin{aligned}E^4&-(2+\tfrac{2}{3}\eta^2+10\xi^2)E-(16\xi^2-24\xi^2\sin^2\theta\\&+8\xi^2\eta\sin^2\theta\cos2\phi)E+1+\tfrac{2}{3}\eta^2+\tfrac{1}{9}\eta^4-10\xi^2+12\xi^2\sin^2\theta\\&+9\xi^4+2\eta^2\xi^2-4\xi^2\eta^2\sin^2\theta+8\eta\xi^2\sin^2\theta\cos2\phi=0,\qquad(1)\end{aligned}$$

where θ is the angle between the magnetic field H and the largest EFG component (the z axis of Fig. 3), ϕ is the azimuthal angle between H and the smallest EFG component (the x axis of Fig. 3), E is in units of $\frac{1}{4}e^2qQ$, Q is the electric quadrupole moment of the nuclear spin, $eq\equiv V_{zz}$, and ξ is a parameter proportional to the ratio of magnetic and electric energies, $h\nu_M$ and $h\nu_Q$, and is equal to

$$\xi=2\gamma hH/e^2qQ=(\nu_M/\nu_Q)(1+\tfrac{1}{3}\eta^2)^{1/2}.\qquad(2)$$

Numerical solutions of Eq. (1) for a number of discrete orientations of the magnetic field and as a function of ξ and η have been obtained.[8] Figure 4 shows the variation of energy values as a function of ξ for $\theta=0$, $\phi=\frac{1}{2}\pi$ and $\eta=0.5$. The choice of $\phi=\frac{1}{2}\pi$ puts H in the y-z plane, i.e., perpendicular to the crystalline c axis. Similar curves for other values of θ then provide the basis for plotting curves of the type shown in Fig. 5. The latter shows the arsenic levels as a function of θ (with $\phi=\frac{1}{2}\pi$ and $\eta=0.5$) for a particular value of ξ. We must have such curves for various values of ξ over a suitable range. The next step is to make a provisional choice of ν_Q, the arsenic coupling constant, and to relate

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[6] R. V. Pound, Phys. Rev. **79**, 685 (1950); M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 321; T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic Press Inc., New York, 1958).

[7] C. Dean, Phys. Rev. **96**, 1053 (1954).

[8] P. Kelly, Department of Electrical Engineering, University of Washington (private communication). We are grateful to Mr. Kelly for communicating his results to us.

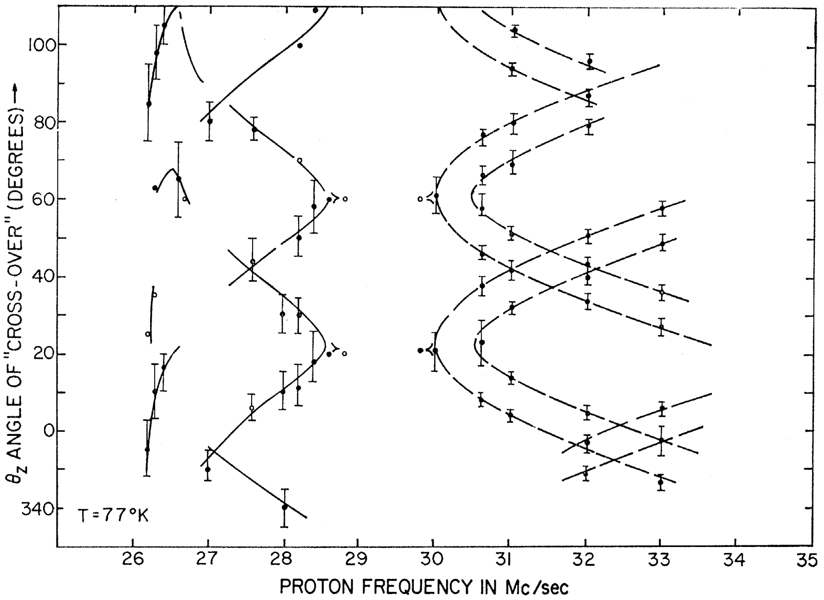

FIG. 8. Comparison of theoretical cross-over pattern with experiment. The cross-over pattern is shifted to make $\theta_z=0$ when the magnetic field is parallel to the *a* or *b* axis.

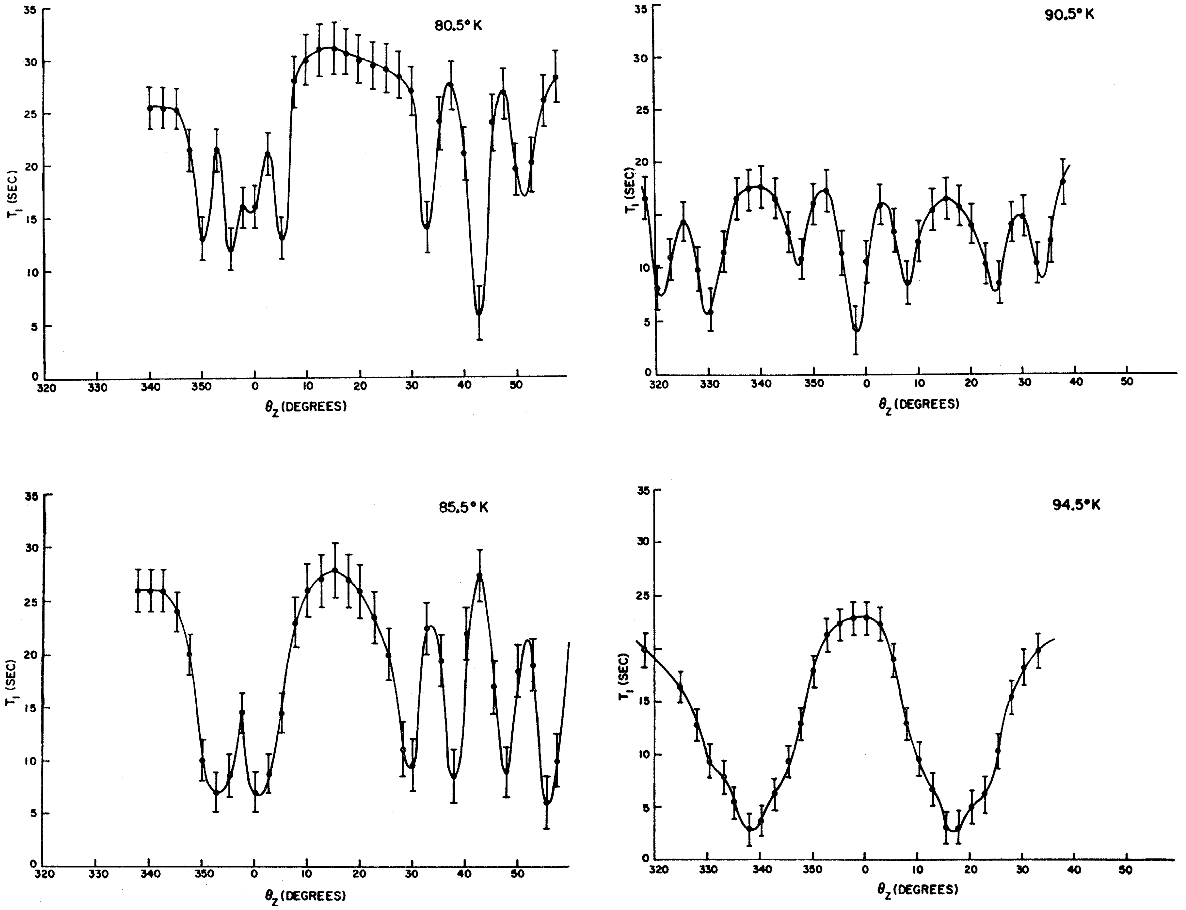

FIG. 9. Temperature dependence of T_1 minima at 32.0 Mc/sec.

the associated value of H to the proton nuclear resonance frequency. By locating the angles at which various arsenic transition frequencies are equal to a given proton frequency in the same magnetic field H, curves of the type shown in Fig. 6 are obtained. The curves plotted in this figure are for $\nu_Q = 34.0$ Mc/sec and $\eta = 0.5$. They show that for a magnetic field perpendicular to the c axis of the crystal there are ranges of proton frequencies within which this frequency will be equal to one of the arsenic transition frequencies at some definite value of θ. The curve for the $-\frac{1}{2}$ to $+\frac{1}{2}$ transition is not plotted since it lies at too high a proton frequency to be accessible in this experiment. The curve for the $\frac{1}{2}$ to $-\frac{3}{2}$ transition is in two sections since for this transition exact coincidence of As and proton frequencies is possible only over a restricted range of θ as represented by the solid-line portion of the curve. The choice of ν_Q and η are still provisional. They are based on the measurements of Jones[2] and of Bjorkstam[3] and the first attempts of the present experiment to fit the crossover data. As shown in Sec. IV, the accumulated data and the accuracy of the fit between measured and theoretical points permitted a rather accurate determination of ν_Q at a value somewhat different than the first choice.

IV. MATCHING OF EXPERIMENTAL AND THEORETICAL PATTERNS

Figure 6 gives the crossover pattern for one particular arsenate group. There are, however, four distinct groups leading to a crossover pattern which may be obtained from Fig. 6 by two successive doublings with an appropriate shift in angle. The first doubling is a consequence of the fact that there are two orientations[9] of the arsenate tetrahedra which differ from each other by a rotation of approximately 32° about the crystalline c axis. The second doubling comes from the fact that there are two domains of polarization in the crystal which can be reduced to a single domain only by the application of an appropriate electric field. This was not done in this experiment. In one domain the spontaneous polarization is directed in the upward direction along the crystalline c axis and the close-lying protons as described above are at the top horizontal tetrahedral edge. In the other domain the polarization is downward and it is the bottom horizontal tetrahedral edge at which the close-lying protons are to be found. Consequently, the principal axis of the EFG tensor in one domain is at an angle of 90° to the principal axis in the other. The complete pattern is then obtained by the addition to Fig. 6 of a duplicate set of curves displaced from the first by an angle corresponding to the rotation of the EFG tensor about the c axis in going from one AsO_4 group to the other and then adding a full set of curves by displacing what has just been obtained through 90°. Since there are two distinctly oriented AsO_4 groups, it is more convenient to measure θ from a crystalline a or b axis than from the direction of a principal axis of one of the EFG tensors. The way in which the two principal-axes systems, the crystalline a and b axes, and the direction of H, all lying in the same plane, are related to each other is shown in Fig. 7. The angle which measures the direction of H is now denoted by θ_z. The solid lines labeled y and y' represent the top edges of the two AsO_4 tetrahedra and the dashed lines represent the bottom edges. The angle between the top (or bottom) edges and the a (or b) axes, respectively, are ±16°.

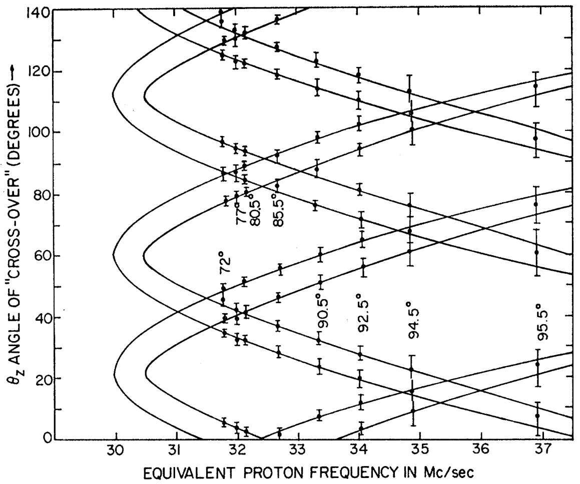

FIG. 10. Fitting the T_1 minima at various temperatures and 32 Mc/sec to the crossover pattern.

Successive attempts to fit the observed crossover points for several different values of the proton resonance frequency led, by trial and error, to a refinement in the selection of numerical values of parameters on which the final theoretical crossover patterns are based. The provisional curves already mentioned turn out to be quite good. The only changes required are in the magnitude of ν_Q, the electric quadrupole coupling constant, and in the angle between the principal EFG axes belonging to the two differently oriented arsenate groups. This angle turns out to be 38° instead of the structural value of nearly 32°. The final value of the coupling constant is $\nu_Q = 34.8$ Mc/sec. The best value of the asymmetry parameter is $\eta = 0.5$, but the choice is not critical. The final curves are shown in Fig. 8 together with the experimental points representing all of the observed minima in proton T_1 at 77°K over the range of frequencies indicated. Note the shift in zero of θ_z compared with θ of Fig. 6 as described above.

All of the observed minima in T_1 including those in the region of near crossovers at low proton frequencies lie very nearly on the predicted curves, and in addition

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[9] J. West, Z. Krist. **74**, 306 (1930). A c-axis projection showing the orientations and taken from the data of West has been reproduced many times; see, e.g. V. Hugo Schmidt and Edwin A. Uehling, Phys. Rev. **126**, 447 (1962) (see Fig. 10).

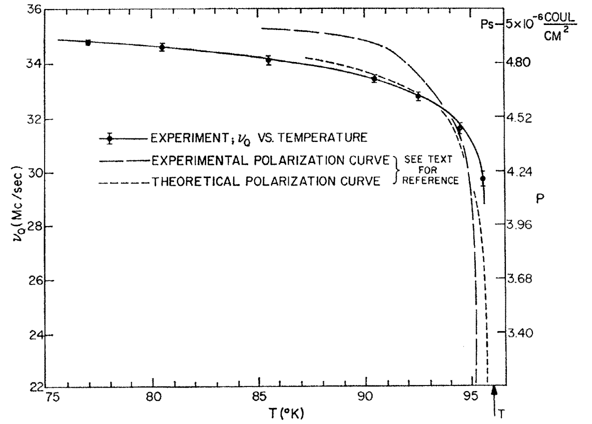

FIG. 11. Temperature dependence of the quadrupole coupling constant and the spontaneous polarization.

the minima of greater than normal depth are observed to correspond to crossovers in which two As transition frequencies are equal to the proton frequency. This is shown in particular by the data of Fig. 2, which may be brought into correspondence with the 32-Mc/sec points of Fig. 8 by a trivial shift in θ_z of 90°.

V. TEMPERATURE DEPENDENCE OF QUADRUPOLE COUPLING CONSTANT

We will now assume that the EFG tensor retains its form throughout the ferroelectric region, i.e., that the principal axes lie along the directions described in the previous sections and the asymmetry parameter η retains its value of approximately 0.5. Then only the coupling constant changes and one would expect it to change most rapidly just below T_C. Consequently, a measurement of the coupling constant in the temperature range extending upward from 77°K at which all previous measurements were made to $T_C=96$°K is useful.

Under the assumption of no change in the form of the EFG tensor, this can be accomplished using the curves of Fig. 8. For a fixed value of η the angle at which a crossover occurs corresponds to a particular value of ξ which by Eq. (2) is proportional to the ratio of magnetic and electric energies, and hence to the ratio of the proton frequency ν_p and the electric quadrupole coupling constant ν_Q. Thus a change in the latter may be observed as an apparent change in the former. The procedure for finding $\Delta\nu_Q$ as a function of temperature is to measure the crossover patterns at various temperatures using a single proton frequency. The curves of Fig. 9 are typical of such measurements for four different temperatures. The proton frequency is 32 Mc/sec, the same as in the measurements leading to Fig. 2. The crossover points at different temperatures may now be referred to the crossover curves of Fig. 8 by finding the equivalent proton frequency at which all crossover points can be made to fall on the curves. The results are shown in Fig. 10. The good fit of the data to the theoretical curves tends to support the initial assumption that the EFG tensor does not change its form appreciably over the range of temperatures considered.

The measured values of ν_Q as a function of temperature are shown in Fig. 11, in which is plotted also the experimentally determined spontaneous polarization curve[10] as well as a theoretical curve[11] based on what is generally regarded as a moderately successful model. There is, however, no reason to think that changes of coupling with temperature should agree with changes in spontaneous polarization, and the data are presented here without comparison with any theory of the EFG tensor.[12]

VI. CONCLUSION

It is believed that these results are of interest for two reasons. They demonstrate in a somewhat different way than has been described previously the usefulness of crossover methods in certain situations where direct observations of a particular resonance are difficult or impossible. Also, in this instance new and old results of greater accuracy on an EFG tensor of rather special interest have been obtained. There remain, however, a number of unanswered questions. One question is concerned with the magnitude of the crossover relaxation. Using the half-widths of the $1/T_1$ peaks at crossover as a basis for estimating the arsenic relaxation time, we obtain a prediction of proton relaxation greatly in excess of the measured value. A second problem is concerned with the EFG tensor. While the argument based on crystal structure which was used in Sec. II was useful as a guide, further consideration shows that it would be difficult to arrive quantitatively at a tensor of the magnitude and shape which we actually observe, at least on the basis of a point-charge model. We find it difficult to account for an asymmetry parameter as small as 0.5 in view of the small displacements[4] of the As and K along the c axis, and the result of an evaluation of the magnitude of the EFG components based on a point-charge model is too small by a large factor. These and other problems are being investigated further.

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[10] G. Busch, Helv. Phys. Acta **11**, 296 (1938).

[11] H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. **133**, A165 (1964).

[12] *Note added in proof:* A direct measurement of the AS quadrupole coupling constant in the ordered state has been reported recently by A. P. Zhukov *et al.*, Phys. Status Solidi **27**, K129 (1968). The results are in close agreement with those reported here.