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Deuteron Magnetic Resonance Spectrum and Relaxation in KD_2 PO_4*†

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The electric field gradient (EFG) tensor at the site of the deuteron in the hydrogen bond of KD_2PO_4 and the relaxation times of the deuteron have been studied. The measured quadrupole coupling constant is 119 kc/sec, the asymmetry parameter is 0.049, and the major principal axis of the tensor is along the bond direction. None of these features of the EFG tensor change appreciably with temperature over the entire range studied, which range includes the ferroelectric Curie point T_c. An interesting additional splitting in the spectral lines below T_c is observed however. The thermal relaxation time of the deuteron has been studied carefully only at room temperature. One obtains $T_1=6.5$ minutes at a particular orientation of the crystal decreasing by a factor of 2 at other particular orientations. T_2 is of the order 5×10^{-4} second. All deuterons have the same relaxation as a function of crystal orientation although falling into distinct categories from the point of view of relative orientation of electric field gradient tensor and applied magnetic field. This interdependence of deuterons in different environments and the possible causes of relaxation are discussed.

I. INTRODUCTION

ALTHOUGH neutron diffraction measurements[1] indicate that the direct contribution to spontaneous polarization by the protons in KH_2PO_4 is very small, the remarkable isotope effect observed[2,3] gives clear evidence that transition to the polarized phase is strongly influenced by the nature of the hydrogen bond. Various properties of the hydrogen bond and their dependence on temperature have already been studied in this and other crystals. The presently available information is based mainly on neutron diffraction[1] and infrared[4,5] studies.

Nuclear magnetic resonance studies should provide additional information. Since the proton in the hydrogen bond may be replaced by a deuteron and the deuteron possesses an electric quadrupole moment, these studies are capable of providing information on the electric field gradient at the position of the deuteron in the hydrogen bond and they may lead also to information about the state of motion of the deuteron. The first type of information would be obtained from a study of the magnetic resonance spectrum and its dependence on crystal orientation. A primary objective would be to obtain this information as a function of temperature and, particularly, at temperatures just above and below the ferroelectric Curie temperature. The second kind of information would be obtained as a possible consequence of experimental data on nuclear magnetic relaxation and its interpretation in terms of previously measured electric quadrupole, and possibly other, interactions. The principal objective of the present study is to obtain the indicated experimental information.

We will find that the thermal relaxation time is long and that the line width is narrow. Consequently, the deuteron resonance is easily saturated and previous attempts to find this resonance have been unsuccessful. In order to observe the deuteron resonance and to obtain information on the spectrum and on the relaxation time at all crystal orientations with sufficient precision to permit quantitative interpretations, we have had to use excitation fields which are not much in excess of a milligauss in amplitude.

In order to interpret the data we must make some use of the structural properties of the crystal. A three-dimensional drawing[6] of the KH_2PO_4 structure in the unpolarized phase is shown in Fig. 1(a). This high-temperature phase belongs to the tetragonal symmetry class $D_{2d}^{12}-I\bar{4}2d$. Spontaneous polarization in the Z (c) direction which occurs upon cooling below the Curie temperature T_c is accompanied by a spontaneous shear χ_y^0 when the crystal acquires orthorhombic symmetry $C_{2v}^{19}-Fdd$. A simultaneous shift of the proton (deuteron) from an elongated distribution in the center of the bond to a position displaced along the bond toward the "upper" oxygen (the one furthest along the polarization axis) has been confirmed by the neutron diffraction experiments.[1] Essential features of the hydrogen bond system in the polarized phase are shown in the Z (c) axis projection of Fig. 1(b). The bonds are nearly but not quite perpendicular to the Z (c) axis, making angles of 0.5° with respect to the plane formed by the equivalent X (a) and Y(b) axes.

A schematic drawing of the spontaneous shear χ_y^0 which occurs in the polarized phase together with orientation of the orthorhombic and tetragonal axes

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[1] G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A230**, 359 (1955).

[2] W. Bangle, Helv. Phys. Acta **15**, 373 (1942).

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[6] J. West, Z. Krist. **74**, 306 (1930).

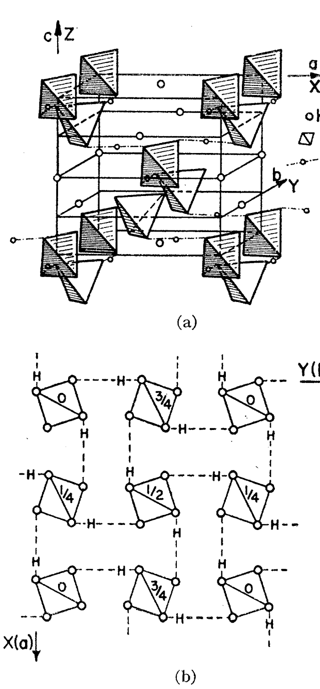

FIG. 1 (a). Structure of KH_2PO_4 (unpolarized phase. (b) c-axis projection of KH_2PO_4.

is shown in Fig. 2. Changes in the deuteron magnetic resonance spectrum which occur when the crystal polarizes will be related to this shear.

II. EXPERIMENTAL PROCEDURE

The deuteron resonance was observed with a Pound-Knight spectrometer modified for operation at a low rf level. Relaxation time measurements were made using a saturation method described by Linder.[7] Basically the method was to allow the spin system to reach equilibrium in the applied magnetic field and at the desired temperature when no external nuclear excitation was present. With the spectrometer operating at a relatively high rf level the resonance condition was brought about quickly by varying either the magnetic field or the spectrometer frequency. A large signal decaying to a smaller equilibrium value which depends on the rf level chosen is then observed. The decay rate and the final equilibrium signal level may be related to the relaxation time T_1.

Temperature measurements were made by enclosing the sample within a radiation shield coupled to a large heat leak. The entire assembly was placed in a Dewar flask and cooled to liquid nitrogen temperature. The excess nitrogen was poured off and the assembly allowed to warm up. The temperature changed from liquid nitrogen temperature to 200°K in approximately 10 hours allowing sufficient time for all desired measurements.

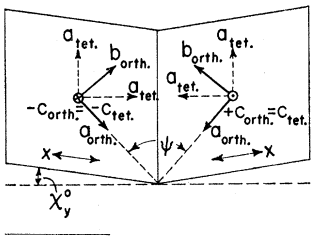

FIG. 2. Schematic domain structure of KH_2PO_4.

III. THE ELECTRIC FIELD GRADIENT TENSOR

Typical deuteron resonance spectra are shown in Figs. 3 and 4 corresponding to two different orientations of the crystal in the applied magnetic field. In order to understand these spectra we first note that each deuteron exhibits two lines in its spectrum which differ in frequency from the unperturbed Zeeman frequency ν_0 by an amount which depends on the electric quadrupole energy. The electric quadrupole splitting is indicated schematically in Fig. 5.

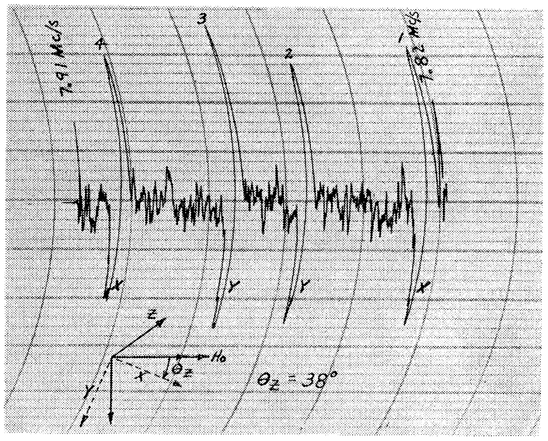

FIG. 3. Deuteron magnetic resonance lines in the Z rotation.

Since the perturbation due to the electric quadrupole interaction depends on the relative orientation of the electric field gradient (EFG) tensor and the applied strong magnetic field, the frequencies $\nu(-1\leftrightarrow 0)$ and $\nu(0\leftrightarrow 1)$ depend on crystal orientation. Furthermore nonequivalent deuterons will be differently oriented and there will be as many pairs of lines as there are nonequivalent deuterons in the crystal barring accidental degeneracies. Referring to Figs. 1(a) and 1(b), we observe that from the point of view of relative orientation of the EFG tensor and the applied magnetic field the bonds directed along the X (a) and Y (b) axes (X and Y bonds, respectively) are not equivalent. In addition we find that there are two kinds of X bonds and two kinds of Y bonds because of the 0.5° angle between the direction of these bonds and the plane formed by the X and Y axes. We denote the different bonds by X_+, X_-, Y_+, and Y_-, the + and − subscripts denoting whether the "upper" end of a bond is in the positive X (or Y) direction or in the negative direction.

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[7] S. Linder, J. Chem. Phys. **26**, 900 (1957).

Since there are four different bonds and consequently four nonequivalent deuterons, there are in general eight lines in the deuteron spectrum of KD_2PO_4 in the high-temperature phase. It is not difficult to show that lines corresponding to deuterons in the X_+ and X_- bonds will coalesce for all angles of rotation about the X and Z axes when the magnetic field is perpendicular to the rotation axis. An analagous statement can be made for the Y bonds. Consequently, only four lines are observed in the Z axis rotation shown for a particular angle of this rotation in Fig. 3. In Fig. 4 six lines are observed because only the Y bond lines coalesce for all angles of rotation about the Y axis whereas the X_+ and X_- bonds yield different lines in this rotation at all angles except θ_Y near 0° and 90°.

There is an additional splitting in the low-temperature phase which will be discussed later. It arises from the previously mentioned shear which accompanies spontaneous polarization. As a consequence of this shear there are several types of X_+, etc., bonds from the point of view of orientation with respect to a magnetic field.

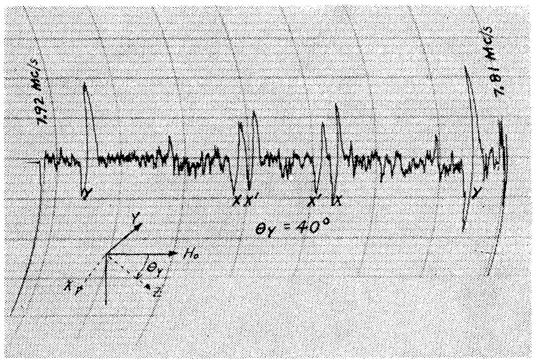

FIG. 4. Deuteron magnetic resonance lines in the Y rotation.

We consider now the determination of the electric quadrupole coupling constant, the asymmetry parameter and the orientation of the principal axes of the EFG tensor. In order to determine the EFG tensor, it is necessary to observe the frequencies corresponding to a particular bond and observe these frequencies as a function of orientation of the crystal with respect to the applied magnetic field. The frequencies are measured and the separation frequency $2\Delta\nu = \nu(-1 \leftrightarrow 0) - \nu(0 \leftrightarrow 1)$ is obtained. When, as is the case here, only first order effects in the quadrupole perturbation are observable it is necessary, in general, to obtain complete data on $2\Delta\nu$ as a function of rotation about three independent axes. Various methods for determining the EFG components and the associated parameters have been described by Volkoff and co-workers,[8] Itoh *et al.*,[9] and Brown and Williams,[10] These methods are summarized in a review article by Cohen and Reif.[11]

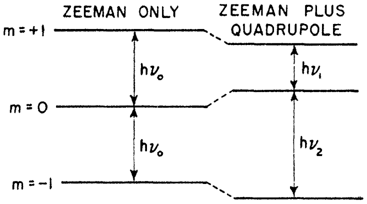

FIG. 5. The effect of quadrupole perturbation on the energy levels for a spin-1 nucleus.

One easily shows that in first order the separation frequency defined above is given by

$$2\Delta\nu = K\phi_{z'z'}, \tag{1}$$

where $K = 3eQ/2h$, Q is the quadrupole moment of the deuteron, x', y', z' is a fixed laboratory coordinate system with the magnetic field directed along z', and $\phi_{z'z'}$ is a component of the electric field gradient tensor in that coordinate system. If we now consider rotations of the coordinate system X, Y, Z representing the previously defined principal crystallographic axes we obtain for each choice of rotation axis and angle of rotation, a connection between the tensor components in the laboratory system and the components in the crystal system. The relation for $\phi_{z'z'}$ in terms of ϕ_{XY} etc., may then be substituted into Eq. (1). Consider for example, the rotation which is described in Fig. 6 which we call the X rotation.

For this rotation the transformation between coordinate systems leads to an expression for $2\Delta\nu$ which we call $(2\Delta\nu)_X$ and which is

$$(2\Delta\nu)_X = A_X + B_X \cos 2\theta_X + C_X \sin 2\theta_X, \tag{2}$$

where

$$A_X = \tfrac{1}{2}K(\phi_{YY} + \phi_{ZZ}) = -\tfrac{1}{2}K\phi_{XX},$$
$$B_X = \tfrac{1}{2}K(\phi_{YY} - \phi_{ZZ}),$$
$$C_X = -K\phi_{YZ}.$$

By cyclic permutations of the subscripts in Eq. (2) similar relations are obtained for rotations about the Y and Z axes, denoted as Y and Z rotations, respectively.

The experimental data on the frequency splitting as a function of the rotation angles are given in Figs. 7,

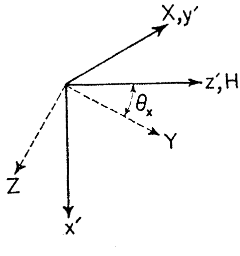

FIG. 6. Orientation of crystalline and laboratory axes in the X rotation.

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[8] G. M. Volkoff, Can. J. Phys. **31**, 820 (1953); Petch, Cranna, and Volkoff, Can. J. Phys. **31**, 837 (1953); Phys. Rev. **88**, 1201 (1952).

[9] Itoh, Kusaka, and Yamagata, J. Phys. Soc. Japan **9**, 209 (1954).

[10] L. C. Brown and D. Williams, J. Chem. Phys. **24**, 751 (1956); Phys. Rev. **95**, 1110 (1954).

[11] M. H. Cohen and F. Reif, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

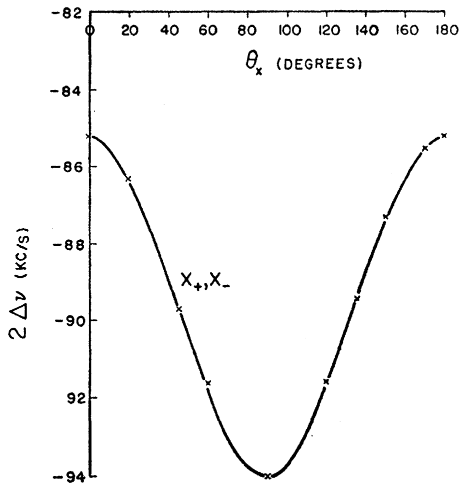

FIG. 7. X rotation data.

8, and 9. The information contained in these figures may be substituted directly into Eq. (2) and its analogs for the Y and Z rotations to determine all of the tensor components. A simpler procedure in this case is as follows: Reference to Figs. 1(a) and 1(b) will show that the Y axis is a twofold rotation axis for deuterons located at the center of an X bond. Consequently, the potential function in the neighborhood of the midpoint of an X bond possesses the property that

$$\phi(-X, Y, -Z)=\phi(X,Y,Z).$$

Therefore $\phi_{YX}=-\phi_{YX}$ and $\phi_{YZ}=-\phi_{YZ}$ or $\phi_{YX}=\phi_{YZ}=0$. The immediate consequence of the vanishing of these two tensor components is that the Y axis is a principal axis of the EFG tensor. A second principal axis is now determined experimentally by using the Y rotation and determining the angle of maximum splitting. From the data on the basis of which Fig. 8 is plotted, this angle is $\theta_Y=90.5°$ for X_+ bonds and $\theta_Y=89.5°$ for X_- bonds. Consequently, the second principal axis lies along the bond directions[12] which deviate by ±0.5° from the direction of the X axis. The maximum splitting is $2\Delta\nu=179.2$ kc/sec. This splitting is furthermore the absolute maximum for all crystal orientations. Consequently one concludes on the basis of Eq. (1) that

$$K\phi_{zz}=179.2 \text{ kc/sec},$$

where ϕ_{zz} is the largest (in absolute value) of the three components of the diagonalized EFG tensor and the z axis of the principal axis system (x,y,z) is along the bond direction.

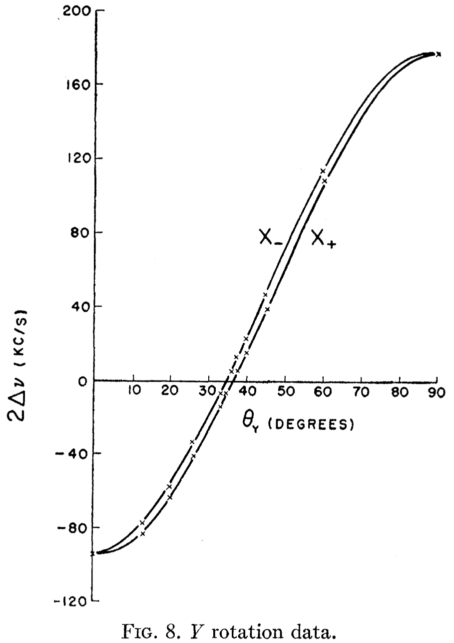

FIG. 8. Y rotation data.

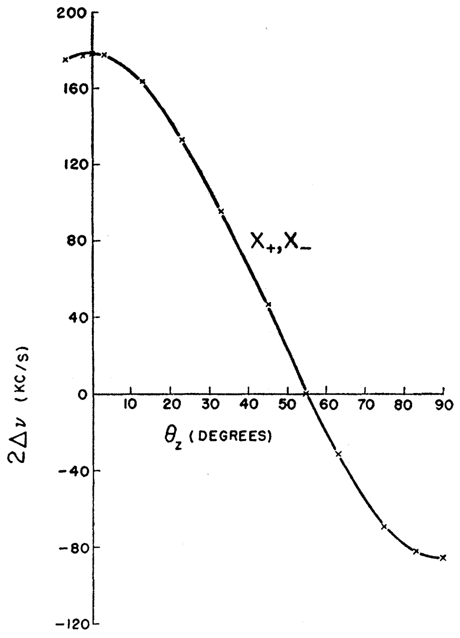

FIG. 9. Z rotation data.

The third principal axis of the EFG tensor is perpendicular to the Y axis and to the bond direction and thus makes an angle of 0.5° with the crystalline Z axis. We can now determine the other two diagonal components of the EFG tensor by using a single equation of the type of Eq. (2) and the data corresponding to a single rotation. Since the X, Y, Z crystalline axes coincide

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[12] There is a small discrepancy involved here which should be studied more closely. Figure 8 shows that the angular displacement of the spectra for the X and Y bonds in this rotation is approximately ±1° rather than ±0.5°. A more careful examination of the original observations shows that the displacement is ±0.75°; i.e., definitely larger than the reported deviation of X and Y bonds from the X-Y plane. Consequently, there may be a small deviation between the bond direction and the principal axis of the EFG tensor.

very nearly with the z, x, y principal axes of the EFG tensor it will be sufficiently accurate for our present purpose to identify ϕ_{XX} with our already determined ϕ_{zz}. Then using Eq. (2), the data of Fig. 7, and setting $\phi_{YZ}=0$ and $K\phi_{XX}=179.2$, one obtains

$$K\phi_{YY}=-85.2 \text{ kc/sec},$$
$$K\phi_{ZZ}=-94.0 \text{ kc/sec}.$$

Expressing these results in the x, y, z principal axis system of coordinates, we have

$$\begin{aligned} K\phi_{zz}&=179.2 \text{ kc/sec},\\ K\phi_{yy}&=-94.0 \text{ kc/sec},\\ K\phi_{xx}&=-84.2 \text{ kc/sec}. \end{aligned} \tag{3}$$

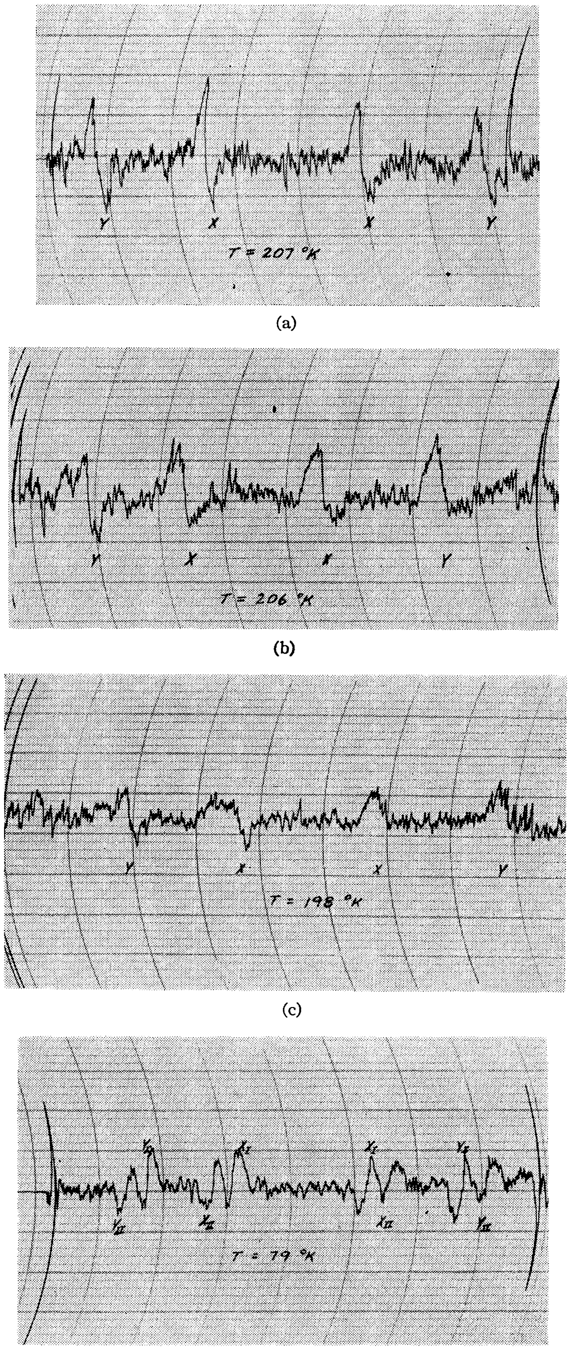
The asymmetry parameter and quadrupole coupling constant are then given by

$$\begin{aligned} \eta&=(\phi_{xx}-\phi_{yy})/\phi_{zz}=0.049,\\ |eQ\phi_{zz}/h|&=\tfrac{2}{3}K\phi_{zz}=119.5 \text{ kc/sec}. \end{aligned} \tag{4}$$

Since the deuteron quadrupole moment is 2.77×10^{-27} cm^2, the maximum EFG component is $\phi_{zz}\sim0.6\times10^{15}$ esu/cm^3. This is approximately the value to be expected on the basis of the essentially ionic character of the hydrogen bond coupling.

We now consider possible changes in the hydrogen bond as a consequence of spontaneous polarization. Changes in the EFG tensor as the crystal is taken through the Curie temperature should be a sensitive indicator of physical changes in the hydrogen bond structure. But no such changes are observed. In particular no appreciable shift in the midpoint of the spectral lines is observed as the temperature varies between values above and below T_c. Consequently, there is no change within the experimental errors of our measurements in the EFG tensor. This is in distinct contrast to the results of measurements in non-hydrogen-bonded types of ferroelectric crystals; in particular, the results of Cotts and Knight[13] on the Nb resonance in $KNbO_3$. As the temperature is lowered from 20°C they observe changes in the quadrupole coupling constant from a value of 23.1 Mc/sec at the higher temperature to a value of 16.0 Mc/sec at the lower temperature and a change in the asymmetry parameter η from a value of 0.8 to 0.0. Our results are not inconsistent, however, with the results of infrared measurements on KH_2PO_4. The "stretching frequencies" should also be a sensitive indicator of changes in the structure of the hydrogen bond. However, no change in these frequencies on passing through the Curie temperature has been observed.[14]

We turn now to changes in the structure of the resonance lines on passage through the Curie temperature. Such changes are observed and are illustrated in Figs. 10(a), (b), (c), and (d). The crystal orientation is with the magnetic field perpendicular to the Z axis and $\theta_Z=49°$. Reference to Fig. 9 shows that the lines from the X_+ and X_- (and similarly the Y_+ and Y_-) bonds coalesce and that the splitting of the $Y_\pm$ bonds in this orientation is greater than the splitting of the



(a)

(b)

(c)

(d)

FIG. 10(a), (b), (c), (d). Temperature dependence of the deuteron line shape in KD_2PO_4.

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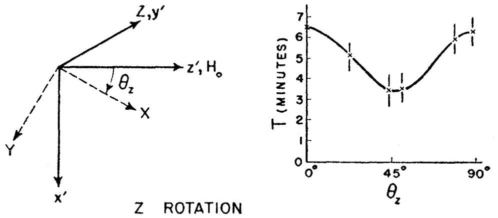
[13] R. M. Cotts and W. D. Knight, Phys. Rev. **96**, 1285 (1954).

[14] J. Schaffhauser, Dipomlarbeit (1949), P. Baer, Diplomarbeit (1950), and K. Brugger, Diplomarbeit (1951), Swiss Federal Institute, Zurich (unpublished).

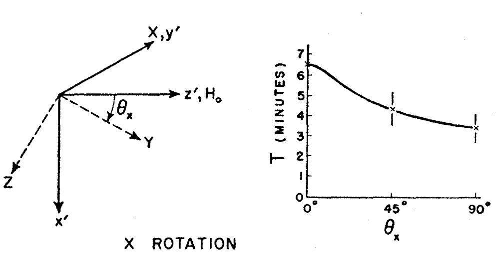
$X_{\pm}$ bonds. We now follow the changes in the spectrum as the temperature is lowered through T_c in a few discrete steps. Starting with a temperature of 207°K in Fig. 10(a), all lines are first observed to broaden as the temperature is lowered. They then become indistinct and finally after a considerable lowering of the temperature ($T = 79°$ K in these particular measurements) each line has been split into two lines. This process has not been studied in detail. But the observations are sufficient to suggest that the principal contribution to the further splitting is the spontaneous shear which accompanies spontaneous polarization. We can illustrate this quantitatively by reference to Fig. 2 and the data of Fig. 9. The shear χ_y^0 indicated in Fig. 2 is known to be 27 min for KH_2PO_4 at 103° K. Consequently, it is reasonable to assume that an angle of the order of 1° will exist between the projections on the xy plane of like bonds in two adjacent domains. If we now refer to Fig. 9, we find that this assumption is not inconsistent with what one would expect on the basis of the observed splitting and the measured rate of change of frequency with angle. The rate of change of $(2\Delta\nu)_Z$ at $\theta_Z = 49°$ is about 4.5 kc/sec degree. The measured splitting of the X bond line in Fig. 10(d) is 8 kc/sec. Consequently, the relative orientation of two bonds leading to the split line is about 1.5° or a little larger. This result does not differ very much from the estimate based on the known shear. It is possible that other slight rearrangements of the bond angles may accompany the shear. In any case further data will be required before a more quantitative interpretation is possible.

The extreme broadening of the lines observed in Figs. 10(b) and 10(c) is probably the result of simultaneous existence of the polarized and unpolarized phase in the crystal. This is similar to the result of Cotts and Knight[13] for the Nb resonance in $KNbO_3$.

It will be noted that changes in the spectra which have just been discussed occur at temperatures which are well below $T_c = 213°$ K for an ideal deuterated crystal. Nevertheless, we interpret these changes as occurring at T_c and below. We assume that our crystal is not completely deuterated and that T_c is consequently lower than 213° K. We have not, however made the measurements which a more careful study of these aspects of the problem would require.



Z ROTATION



X ROTATION

FIG. 11. Orientational dependence of D relaxation time for the X bond in KD_2PO_4.

IV. THE RELAXATION TIMES

The deuteron spin-lattice relaxation time T_1 has been measured at room temperature for various orientations of the crystal. The principal results are shown in Fig. 11. The relaxation time is long and has a strong angular dependence.

The most striking features of these results are not immediately obvious from the curves. One feature is that the relaxation times of X-bond and Y-bond deuterons are equal to each other for all orientations of the crystal. That this is the case for the Z rotation follows from the fact that T_1 as a function of θ_Z is symmetric about $\theta_Z = 45°$ where the X and Y bonds make the same angle with respect to the applied magnetic field. But it is also true in the X and Y rotations where, for example, the X bond lies along the rotation axis (actually 0.5° off the rotation axis) and consequently its direction with respect to the applied magnetic field does not change appreciably in the rotation. However, the relaxation time changes by a factor of 2, and simultaneous measurements of T_1 for the Y bond, the direction of which is changing in the rotation, shows that T_1 is the same for both bonds for all values of θ_X.

The interdependence of the two types of bonds which manifests itself in the equality of T_1 for all orientations is also exhibited in the saturation behavior. Referring again to Fig. 3, we notice that the amplitudes of the four resonances vary from one to another. It is suggested by these data that the act of sweeping a resonance of one bond disturbs the population in the other bond. A more quantitative investigation shows that this is in fact the case. We can, in the first place, reduce the excitation to a value sufficiently low that no appreciable saturation occurs. The amplitudes of the various resonances are then equal within the error of measurement. Secondly, we can increase the excitation level and deliberately saturate a given resonance at will. If, for example, we saturate resonance 1 in Fig. 3 we observe not only an enhancement of resonance 4 but also a change in the intensities of resonances 2 and 3, one of which is enhanced and the other decreased. The latter effect is a consequence of the interdependence of X and Y bonds.

Since we do not have an adequate theory of these effects, we shall present only the results of certain order of magnitude arguments that are suggestive of further experiments. The first is concerned with the magnitude of T_1. If we regard the relaxation as due to the electric quadrupole interaction and use the theory of random fluctuations[15] to describe the time variation of the EFG components, we obtain a theory of relaxation in which T_1 is made to depend on the magnitudes of the EFG components and a correlation time τ_c. Since all quantities except τ_c have been measured, we use this theory to determine τ_c. One obtains $\tau_c = 5\times 10^{-3}$ sec. This time is very long compared to the reciprocal of the quadrupole splitting frequency ($2\Delta\nu \sim 10^5$), and it is rather long compared to the reciprocal of the half-width of the individual lines which we have measured to be $\Delta\nu_{\frac{1}{2}} = 0.7\times 10^{+3}$. But it is not long compared to the reciprocal of $\Delta\nu_{\frac{1}{2}}$ which comes from the mutual dipolar interaction of deuterons alone.

Without specifying in greater detail the mechanism by which a given spin orientation first finds itself in the EFG configuration of one bond and then after a time of order τ_c in that of another, we have sought to describe both the saturation effect and the dependence of T_1 on orientation by using for the mean square value of the time-varying functions the average of the mean square values in the X and Y bonds. An outline of successive steps in the calculation is given in the Appendix. The principal results are as follows: (*a*) In the Z rotation T_1 is symmetric about $\theta_Z = \pi/4$ where it has a minimum value which is $\frac{2}{5}$ of the value at 0 and $\pi/2$ (the experimental ratio is $\frac{1}{2}$); (*b*) In the X (or Y) rotations, T_1 decreases from a maximum value at $\theta_X = 0°$ to a value at $\theta_X = \pi/4$ which is $T_1(\pi/4) = (4/9)T_1(0)$ and then rises to a value at $\theta_X = \pi/2$ which is $T_1(\pi/2) = \frac{1}{2}T_1(0)$. The experimental result is a monotonically decreasing function between the same two extremes at $\theta_X = 0$ and $\pi/2$. As discussed previously, the correlation time τ_c is the only adjustable parameter in the theory.

We have not completely ruled out the possibility that other mechanisms play some role in the phenomena we are discussing. It is known[16] for example that protons in KH_2PO_4 are relaxed by spin diffusion to paramagnetic impurity ions which are present in sufficient concentration in all crystals studied so far to provide relatively short relaxation times. Assuming that our deuterated crystal possesses an impurity concentration equal to the lowest which has been observed in any of the nondeuterated crystals, we can easily obtain a lower limit to the magnitude of T_1 for deuterons if relaxation is solely by diffusion to impurity ions. The spacing of like neighbors is equal for the protons and deuterons and the spin diffusion process involves probabilities of mutual spin flips and energy exchanges with the impurity ion which are proportional to the square of the gyromagnetic ratio. Consequently, for this process

$$T_1(\mathrm{D})/T_1(\mathrm{H}) \sim \gamma_{\mathrm{H}}^2/\gamma_{\mathrm{D}}^2 \sim 45.$$

For our purest crystals and at a frequency of 8 Mc/sec corresponding to the deuteron measurements, $T_1(\mathrm{H}) = 10$ sec in KH_2PO_4 and 28 sec in KH_2AsO_4. Using the value of 28 sec, we obtain an expected value for deuterons of $T_1(\mathrm{D}) = 1300$ sec. This is only 3 times the value actually obtained at certain orientations. Furthermore, it is at these very orientations where the relaxation time in one of the two bonds would be very long if quadrupolar interactions alone were effective and if we had not incorporated the exchange mechanism between bonds.

Somewhat similar uncertainties are present with respect to the role of lattice vibrations in the relaxation process. Instead of discrete jumps at random intervals described by a correlation time, we now consider an entire spectrum of small amplitude oscillations. If we knew the spectrum of these oscillations and the way in which the EFG components vary as a function of ion displacement, we could predict the value of T_1. We have made some estimates of T_1 for our particular case based on a theory developed by Chang[17] and some additional estimates based on measured values of T_1 in other crystals and the ratios of measured quadrupole coupling constants. In general we obtain values of T_1 which are a factor of 10 and more too large. But we are undoubtedly underestimating the amplitude of motion of the hydrogen ion, and our model for the way in which the EFG components vary with displacement may be far from correct. For these reasons we cannot rule out the possibility that the motion associated with lattice vibrations is sufficient to provide the measured relaxation.

We are now using pulse methods in order to explore more fully the question of interdependence of X and Y bonds in relaxation. These and other measurements should also be made as a function of temperature in order to obtain better evidence in regard to the relaxation mechanism.

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[15] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948). The application here is to relaxation via dipolar interactions. The translation of this theory to electric quadrupolar interactions requires only the substitution of the matrix elements of the quadrupolar interaction for the dipolar interaction.

[16] John L. Bjorkstam and Edwin A. Uehling, Bull. Am. Phys. Soc. Ser. II, **3**, 166 (1958).

[17] C. H. Chang, Air Force Office of Scientific Research Report, 1955 (available from the Department of Physics, University of Washington, Seattle, Washington), unpublished.

APPENDIX

The results for the relaxation time quoted in Sec. IV of the text can be derived on the basis of a random fluctuation theory using a quadrupole interaction energy which is the mean square value of the two distinct bonds in the crystal. If $J(\nu)$ is the associated spectral density, the transition probability due to the fluctuations is

$$P=J(\nu)/\hbar^2, \tag{5}$$

where, under the assumption of a correlation time τ_c,

$$J(\nu)=|G(t)|^2\frac{2\tau_c}{1+(2\pi\nu\tau_c)^2}, \tag{6}$$

and $G(t)$ is the appropriate matrix element of the quadrupole interaction Hamiltonian.

The matrix elements are

$$\begin{aligned}(m\pm1|\mathcal{H}|m)&=\frac{eQ}{4I(2I-1)}(2m\pm1)\\&\quad\times[(1\pm m+1)(I\mp m)]^{\frac{1}{2}}\phi_{z'\mp},\\(m\pm2|\mathcal{H}|m)&=\frac{eQ}{8I(2I-1)}[(I\mp m)(I\mp m-1)\\&\quad\times(I\pm m-1)(I\pm m+2)]^{\frac{1}{2}}\phi_{\mp\mp},\end{aligned} \tag{7}$$

where

$$\phi_{z'\mp}=\phi_{x'z'}\mp i\phi_{y'z'},$$

$$\phi_{\mp\mp}=\phi_{x'x'}-\phi_{y'y'}\mp 2i\phi_{x'y'}.$$

If we take the absolute value square of Eq. (7) in order to obtain $|G(t)|^2$ and insert the results into Eqs. (5) and (6), we obtain for the transitions probabilities

$$P_{m\to m-1}=\frac{e^2Q^2(2m-1)^2(I-m+1)(I+m)}{16I^2(2I-1)^2\hbar^2}\times(\phi_{x'y'}{}^2+\phi_{y'z'}{}^2)\frac{2\tau_c}{1+(2\pi\nu\tau_c)^2}, \tag{8}$$

$$P_{m\to m-2}=\frac{e^2Q^2(I+m)(I+m-1)(I-m+1)(I-m+2)}{64I^2(2I^2-1)^2\hbar^2}\times[(\phi_{x'x'}-\phi_{y'y'})^2+4\phi_{x'y'}{}^2]\frac{2\tau_c}{1+(4\pi\nu\tau_c)^2}, \tag{9}$$

where ν is the frequency corresponding to the transitions $\Delta m=\pm1$ and where such quantities as $\phi_{x'y'}{}^2$, etc., are to be evaluated as arithmetic averages in the two distinct bonds. The primes indicate that the tensor components themselves are to be evaluated in the laboratory system. Using the table

Bond	$K\phi_{XY}$	$K\phi_{YY}$	$K\phi_{ZZ}$
X	179.2 kc/sec	−85.2 kc/sec	−94.0 kc/sec
Y	−85.2	179.2	−94.0

for the tensor components in the crystal system ($K=3eQ/2h$), we transform to the laboratory system for two rotations, X and Z, and obtain for the arithmetic averages

$$\begin{aligned}&\langle\phi_{x'z'}{}^2\rangle_{\text{Av}}+\langle\phi_{y'z'}{}^2\rangle_{\text{Av}}=(a+b)^2\cos^2\theta_Z\sin^2\theta_Z,\\&\langle(\phi_{x'x'}-\phi_{y'y'})^2\rangle_{\text{Av}}+\langle4\phi_{x'y'}{}^2\rangle_{\text{Av}}\\&\qquad=\tfrac{1}{2}(a+b)^2[\sin^4\theta_Z+\cos^4\theta_Z]+(c-b)(c+a),\end{aligned} \tag{10}$$

for the Z rotation, and

$$\begin{aligned}&\langle\phi_{x'z'}{}^2\rangle_{\text{Av}}+\langle\phi_{y'z'}{}^2\rangle_{\text{Av}}\\&\quad=[c^2+\tfrac{1}{2}(a^2+b^2)+c(a-b)]\cos^2\theta_X\sin^2\theta_X,\\&\langle(\phi_{x'x'}-\phi_{y'y'})^2\rangle_{\text{Av}}+\langle4\phi_{x'y'}{}^2\rangle_{\text{Av}}\\&\quad=[c^2+\tfrac{1}{2}(a^2+b^2)+c(a-b)][1+\sin^4\theta_X]\\&\qquad\qquad-2[c^2+c(a-b)-ab]\sin^2\theta_X,\end{aligned} \tag{11}$$

for the X rotation, where

$$a=\frac{179.2}{K}\times10^3,\quad b=\frac{85.2}{K}\times10^3,\quad c=\frac{94.0}{K}\times10^3.$$

From the differential equations which describe the approach to equilibrium in a three-level system, we can write

$$1/T_1=2P_{1\to-1}+P_{1\to0}. \tag{12}$$

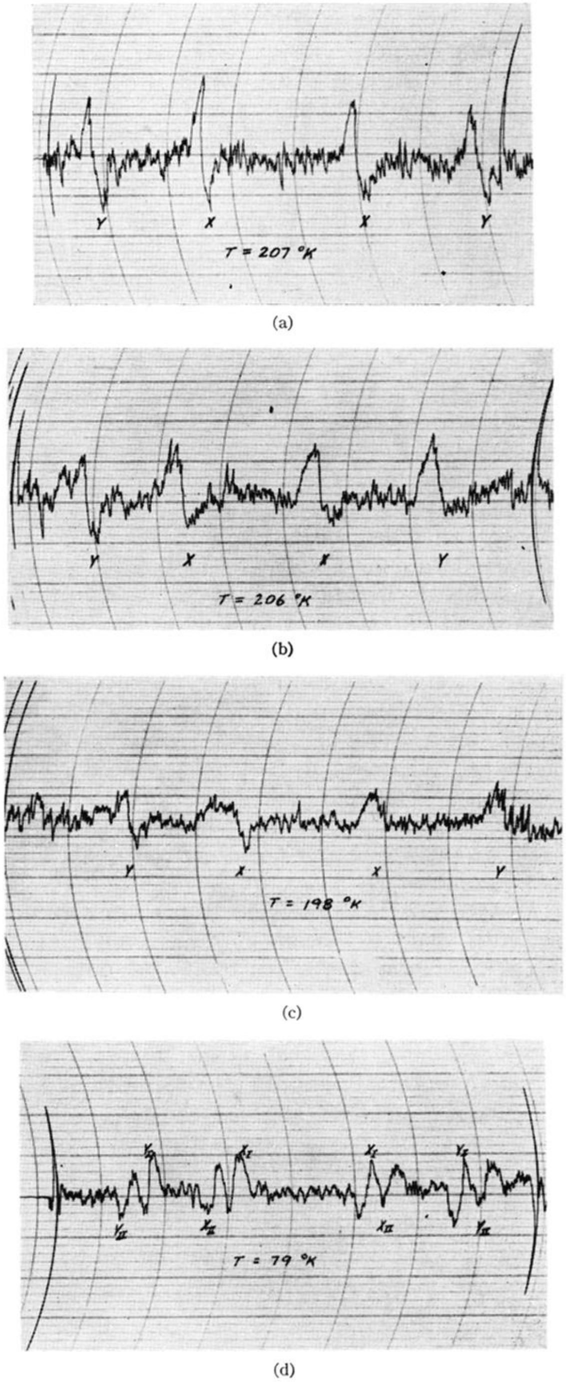
Also, since it will be found that $\tau_c\sim10^{-3}$ sec. we simplify our results by using the condition $\nu\tau_c\gg1$. One then obtains from Eqs. (8), (9), (10), (11), and (12)

$$\begin{aligned}\frac{1}{T_1}&=\frac{e^2Q^2}{32(h\nu)^2\tau_c}[6(a+b)^2\cos^2\theta_Z\sin^2\theta_Z\\&\qquad+(a+c)^2+(c-b)^2]\\&\cong\frac{e^2Q^2}{32(h\nu)^2\tau_c}(a+b)^2[6\cos^2\theta_Z\sin^2\theta_Z+1],\end{aligned} \tag{13}$$

for the Z rotation, and

$$\begin{aligned}\frac{1}{T_1}&=\frac{e^2Q^2}{32(h\nu)^2\tau_c}\{[a+b)^2+2(a+c)(b-c)]\sin^2\theta_X\\&\qquad+[a^2+b^2+2c(a-b+c)][1+3\cos^2\theta_X\sin^2\theta_X]\}\\&\cong\frac{e^2Q^2}{32(h\nu)^2\tau_c}(a+b)^2[1+\sin^2\theta_X\\&\qquad+3\cos^2\theta_X\sin^2\theta_X],\end{aligned} \tag{14}$$

for the X rotation.



(a)

(b)

(c)

(d)

FIG. 10(a), (b), (c), (d). Temperature dependence of the deuteron line shape in KD_2PO_4.

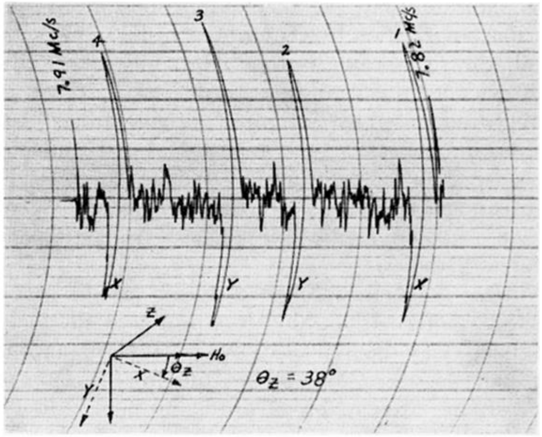


FIG. 3. Deuteron magnetic resonance lines in the Z rotation.

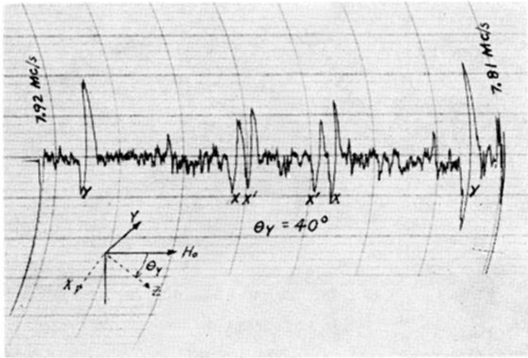


FIG. 4. Deuteron magnetic resonance lines in the Y rotation.