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This is a published version of an article that originally appeared in *Physical Review* in December 1964 .

Schmidt, . "Dynamical Effects of Deuteron Intrabond Jumping in D₂ . . . 4." *Physical Review* 164, no. 2 (December 1964): 4 . doi:[10.1103/physrev.164.4](https://doi.org/10.1103/physrev.164.4) .

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Dynamical Effects of Deuteron Intrabond Jumping in KD_2PO_4 †

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(Received 5 July 1967)

Deuteron jumps along hydrogen bonds in KD_2PO_4 associated with effective motion of Slater-Takagi DPO_4 and D_3PO_4 groups are related to the deuteron magnetic-resonance spectrum and relaxation both above and below the ferroelectric transition temperature T_c , and to the dielectric relaxation and the domain-wall mobility. Below T_c the deuterons assume ordered bond positions, but occasionally jump to the opposite positions. The correlation time for the electric-field-gradient fluctuations seen by a deuteron undergoing such motion is found to be short above T_c and even shorter below T_c . The rms amplitude of the fluctuations drops rapidly below T_c . These results are used to explain the temperature dependence of the splitting and lack of line broadening in the deuteron spectrum below T_c , and the rapid decrease of the spin-lattice transition probabilities below T_c . Relaxation data above T_c , which yielded the energies and fractional populations of DPO_4 and D_3PO_4 groups, are reanalyzed using the recently reported field-gradient tensors at the two bond positions. The dielectric relaxation is calculated, and good agreement with the high dielectric loss measured at microwave frequencies is found. The jump time for a DPO_4 or D_3PO_4 group is found to be near \hbar/kT , implying little correlation between successive jumps, in contrast to KH_2PO_4 . This jump time is used in a calculation of domain-wall mobility in KD_2PO_4 .

INTRODUCTION

THE ferroelectric transition in KH_2PO_4 -type crystals has been shown by neutron-diffraction studies¹ to be accompanied by occupation by the hydrogen ions of ordered off-center positions in their hydrogen bonds, as was predicted by Slater.² The ordering does not become complete immediately at the transition temperature T_c , as indicated by the increase in spontaneous polarization with decreasing temperature.³ The disorder below T_c will be shown to be dynamic, involving occasional brief excursions of each hydrogen to the wrong end of its bond. Similar dynamic disorder, but with equal time spent at each end of the bond, had previously been found⁴ above T_c . Because the electric-field-gradient (efg) tensors have different values at the two ends of a given bond relative to the crystal axes, as measured by Bjorkstam⁵ in KD_2PO_4 , the deuteron motions affect the deuteron magnetic resonance spectrum and spin-lattice relaxation by means of the interaction of the efg with the deuteron quadrupolar moment. This quadrupolar interaction is a perturbation on the Zeeman energies of the three m levels of the deuterons in the applied magnetic field, and causes a splitting of the two $\Delta m=1$ transition frequencies. The amount of splitting is proportional to $\phi_{z'/z}$, an efg component in the laboratory reference frame in which z' is the direction of the magnetic field H_0 . The efg tensor was determined by Bjorkstam and Uehling^{5,6} by observing the splittings as a function of crystal orientation relative to H_0 . The $\Delta m=1$ and $\Delta m=2$

transition probabilities for deuteron spin-lattice relaxation have been studied⁴ as functions of orientation, temperature, and magnetic field. Quadrupolar relaxation due both to slow interbond jumping and fast intrabond jumping of deuterons was found. The activation energy found⁴ for the intrabond motion was identified as the energy of the DPO_4 and D_3PO_4 groups which were postulated by Takagi⁷ in extending the Slater² theory. In a subsequent extension⁸ of the Slater-Takagi theory, expressions for the fractional populations of these groups and the Slater D_2PO_4 groups were obtained, as well as expressions for the spontaneous polarization and static dielectric susceptibility as functions of temperature.

This paper deals with four dynamical effects of deuteron intrabond motion in KD_2PO_4 , namely, an additional splitting of the deuteron magnetic resonance spectrum below T_c , a contribution to deuteron spin-lattice relaxation, dielectric relaxation at microwave frequencies, and domain-wall motion. An expression for the autocorrelation of the efg fluctuations, valid both above and below T_c , is obtained and is used to explain the splitting and spin-lattice relaxation. The complex dielectric constant is then calculated and compared with experiment.^{3,9} The mean time between successive effective motions of DPO_4 and D_3PO_4 groups is evaluated from the spin-lattice and dielectric relaxation measurements. This time replaces an arbitrary parameter in the theory¹⁰ of domain-wall mobility in KD_2PO_4 . The significance of the magnitude of this time relative to the drastic differences in intra-

† Work supported in part by the National Institutes of Health.

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

² J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

³ R. M. Hill and S. K. Ichiki, Phys. Rev. **132**, 1603 (1963).

⁴ V. H. Schmidt and E. A. Uehling, Phys. Rev. **126**, 447 (1962). This paper will be referred to subsequently as SU.

⁵ J. L. Bjorkstam, Phys. Rev. **153**, 599 (1967).

⁶ J. L. Bjorkstam and E. A. Uehling, Phys. Rev. **114**, 961 (1959).

⁷ Y. Takagi, J. Phys. Soc. Japan **3**, 273 (1948).

⁸ H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. **133**, A165 (1964). This paper will be referred to subsequently as SUS.

⁹ Ts.-Zh. Ludupov, Kristallografiya **11**, 468 (1966) [English transl.: Soviet Phys.—Cryst. **11**, 416 (1966)].

¹⁰ V. H. Schmidt, in Proceedings of the International Meeting on Ferroelectricity, Prague, 1966, Vol. II, p. 97, (unpublished).

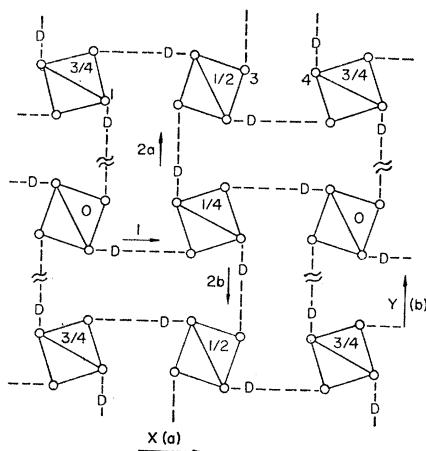


Fig. 1. $C(Z)$ axis projection of crystal structure of KD_2PO_4 .

bond motion exhibited by KH_2PO_4 and KD_2PO_4 ^{11,12} is discussed.

NATURE OF MOTION

The c -axis projection of the structure of KD_2PO_4 in the ordered phase is shown in Fig. 1. Potassium ions alternate with PO_4 groups in chains running along c (Z in the crystal coordinate system). The chains are linked to each other by hydrogen bonds nearly parallel to X and Y (X and Y bonds). Each deuteron is at the end of its bond nearest the top of a PO_4 tetrahedron, forming D_2PO_4 groups of one of the two zero-energy types indicated in Fig. 2. A region composed of groups having the other zero-energy configuration is a domain of the opposite polarization.

If the deuteron indicated by arrow 1 in Fig. 1 moves along its bond, a pair consisting of a DPO_4 and a D_3PO_4 group is formed at a cost of energy $2\epsilon_1$.¹³ The D_3PO_4 group can in effect move by means of either of the deuteron motions shown by arrows $2a$ and $2b$, to a position higher in the c direction. Its former site is then occupied by a Slater D_2PO_4 group of energy ϵ_0 . For each subsequent move, the D_3PO_4 group can move to either

Configuration	Energy		Fractional Population
	0	μ_0	X_2
	0	$-\mu_0$	X_{-2}
	ϵ_0	0	X_0 each
	ϵ_1	$\mu_0/2$	X_1 each
	ϵ_1	$-\mu_0/2$	X_{-1} each

Fig. 2. Schematic representation of PO_4 ions and their close hydrogens.

¹¹ J. L. Bjorkstam and R. E. Oettel, in Proceedings of the International Meeting on Ferroelectricity, Prague, 1966, Vol. II, p. 91 (unpublished).

¹² R. Blinc and S. Svetina, Phys. Rev. **147**, 430 (1966).

¹³ In SU, ϵ_1 was mistakenly described as the pair energy.

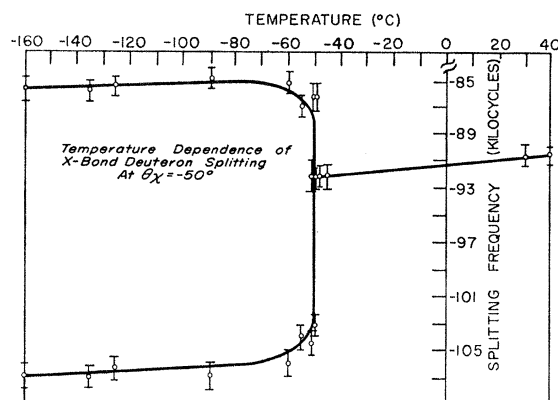


Fig. 3. Measured (Ref. 5) X-bond deuteron quadrupolar splitting in KD_2PO_4 at $\theta_x = -50^\circ$ compared with splitting proportional to spontaneous polarization (solid curves).

of two positions higher along c at a cost of energy ϵ_0 , or it can move to its previous position at a gain of energy ϵ_0 . The same statements apply to the DPO_4 group, except that its choice of new positions is in the negative c direction. Such motions thus create a string of Slater ϵ_0 groups running in the general direction of c , with a Takagi D_3PO_4 group at the upper end and a DPO_4 group at the lower end. These strings continually form, grow and shrink, and disappear. A deuteron jumps to the wrong end of its bond when a string grows past it, and jumps back when the string shrinks past it a short time later. With rising temperature the strings get longer, intersect, and finally destroy all long-range order at the Curie point.

The mean time T_0 required for a Takagi DPO_4 or D_3PO_4 group to jump to an adjacent site will be shown

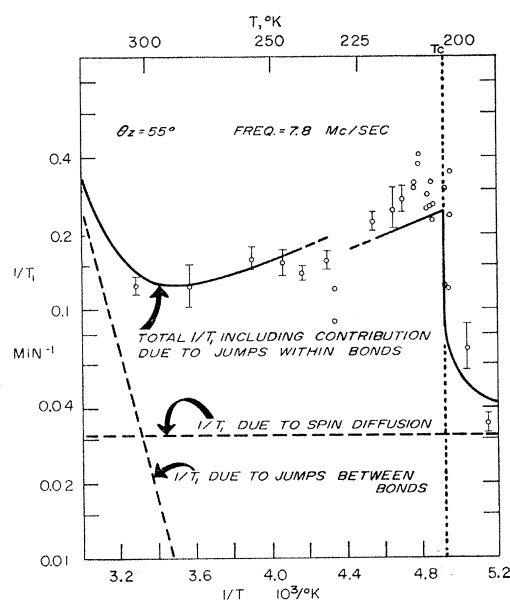


Fig. 4. Measured (Ref. 4) and calculated deuteron spin-lattice relaxation in KD_2PO_4 at $\theta_z = 55^\circ$.

TABLE I. P_1 and P_2 for X-bond deuterons.

$T(^{\circ}\text{K})$	Orientation	P_1 (min^{-1})		P_2 (min^{-1})	
		Calc.	Meas. (Ref. 4)	Calc.	Meas. (Ref. 4)
105	$\theta_z=90^{\circ}$	0.030	0.011 ± 0.002	0	0.027 ± 0.015
205	90°	0.046	0.032 ± 0.004	0	0.016 ± 0.009
210	90°	0.122	0.130 ± 0.011	0	0.036 ± 0.017
215	90°	0.114	0.102 ± 0.008	0	0.001 ± 0.003
215	45°	0.073	0.054 ± 0.003	0.084	0.094 ± 0.022
215	0°	0.030	0.050 ± 0.006	0.169	0.067 ± 0.011
307	0°	0.044	0.046 ± 0.003	0.034	0.021 ± 0.003
215	$\theta_x=90^{\circ}$	0.114	0.082 ± 0.008	0	0.065 ± 0.009
296	90°	0.061	0.034 ± 0.004	0.010	0.049 ± 0.003
343	90°	0.051	0.043 ± 0.003	0.256	0.282 ± 0.032

to be very short, comparable to a lattice vibration period, so T_0 is assumed to be independent of temperature in the absence of definite experimental evidence to the contrary. In calculating the spectral density of the efg fluctuations it will be assumed that deuteron intrabond jumps are governed by jump probabilities, with no correlation between successive jumps. Correlated motions do occur because a given Takagi group in its random motion may switch a given deuteron back and forth in its bond several times in rapid succession. Such correlated motions occur at a faster rate than the uncorrelated motions, so for given T_0 the frequency spectrum of these motions is broadened. This broadening increases the spectral density at the deuteron transition frequency, which is well below the peak frequency of the spectral density. This effect of the correlated motions is approximated by using an effective jump time T_{0e} which is greater than T_0 .

The density of Takagi groups as given in SUS is $4(x_1+x_{-1})N/V$, where x_1 and x_{-1} are fractional populations defined in Fig. 2, so the effective jump rate per unit volume is $4(x_1+x_{-1})N/VT_{0e}$. There are $(1+p)N/V$ deuterons per unit volume at correct positions and $(1-p)N/V$ at wrong positions, where p is the fractional spontaneous polarization. Accordingly, a given deuteron in a correct position has probability $2(x_1+x_{-1})/(1+p)T_{0e}$ per unit time of jumping to a wrong position, with the contrary probability having $1-p$ in the denominator. Using these probabilities, and given an ensemble of deuterons having arbitrary density N_c/V of deuterons in correct positions,

$$\begin{aligned} \frac{dN_c}{dt} &= \left(-\frac{N_c}{1+p} + \frac{2N-N_c}{1-p} \right) \frac{2(x_1+x_{-1})}{T_{0e}} \\ &= [N_c - N(1+p)] \frac{4(x_1+x_{-1})}{(1-p^2)T_{0e}}, \end{aligned} \quad (1)$$

so the density approaches its equilibrium value $(1+p)N/V$ exponentially. The effective time constant T_{we} , which also governs the density of deuterons in wrong positions, is given by

$$T_{we} = \frac{1}{4}(1-p^2)T_{0e}/(x_1+x_{-1}). \quad (2)$$

SPECTRAL DENSITY OF efg FLUCTUATIONS

Let an efg component have value ϕ_{ij} at the correct end of the bond, and value $\phi_{ij} + \Delta\phi_{ij}$ at the wrong end. The efg fluctuation felt by a given deuteron can be described by $\Delta\phi_{ij}F(t)$, where $F(t)=1$ during the fraction $\frac{1}{2}(1-p)$ of the time that the deuteron is at the wrong end, and $F(t)=0$ at other times. The autocorrelation function $G(\tau)$ for $F(t)$ is given by

$$\begin{aligned} G(\tau) &= \langle F(0)F(\tau) \rangle_{av} \\ &= \frac{1}{2}(1-p) \left[\frac{1}{2}(1-p) + \left[1 - \frac{1}{2}(1-p) \right] \exp(-\tau/T_{we}) \right] \\ &= \frac{1}{4}(1-p)^2 \exp(-\tau/T_{we}) + \frac{1}{4}(1-p)^2, \end{aligned} \quad (3)$$

using the previous result that an ensemble of deuterons initially all at wrong positions will approach the equilibrium distribution with time constant T_{we} . The constant term in $G(\tau)$ will be ignored because it does not contribute to the spectral density. The autocorrelation function is then characterized by a correlation time T_{we} and a pre-exponential coefficient $\frac{1}{4}(1-p^2)$ which varies rapidly with temperature below the Curie point.

Above the Curie point, $p=0$ and $G(\tau)$ reduces to

$$G(\tau) = \frac{1}{4} \exp(-\tau/T_{we}), \quad (4)$$

a result obtained previously for a "random telegraph signal" by Kenrick.¹⁴ The autocorrelation function of Eq. (4) applies also for deuteron jumps between X and Y bonds, if T_{we} is replaced by the time constant T_{XY} for mixing of populations of deuterons in X and Y bonds. The relation of this interbond motion to electrical conductivity and spin-lattice relaxation is discussed in SU.

To evaluate $G(\tau)$ as a function of temperature, it is necessary to calculate the fractional population $4(x_1+x_{-1})$ of Takagi groups from the expressions given in SUS, using the measured^{3,15} fractional spontaneous polarization p . For the Takagi group energy ϵ_1 , the activation energy measured⁴ for deuteron spin-

¹⁴ G. W. Kenrick, Phil. Mag. 7, 176 (1929). Dr. C. K. Rushforth has informed me that the result of Eq. (3) for biased random motion has also been previously derived, but apparently has not been published.

¹⁵ B. Zwicker and P. Scherrer, Helv. Phys. Acta 17, 346 (1944).

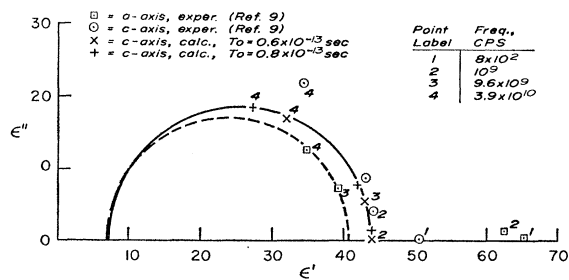


FIG. 5. Cole-Cole plot for KD_2PO_4 at room temperature.

lattice relaxation due to intrabond jumps above T_c is used. This value of $\epsilon_1/k=900^\circ\text{K}$ gives the best fit to the measured spontaneous polarization curve, as shown in Fig. 6 of SUS, if one chooses β/k as 20°K and ϵ_0/k as 116°K . The parameter β is associated with long-range polarization forces. In the notation of SUS, the fractional Takagi group population is

$$4(x_1+x_{-1}) = 8K \exp(-\epsilon_1/kT) \cosh \lambda \\ \simeq 2 \operatorname{sech} \lambda \exp(-\epsilon_1/kT), \quad (5)$$

where

$$K = \frac{1}{4} [\cosh^2 \lambda + 2 \exp(-\epsilon_1/kT) \cosh \lambda \\ + \exp(-\epsilon_0/kT) - \frac{1}{2}]^{-1} \simeq \frac{1}{4} \operatorname{sech}^2 \lambda$$

because the last two terms inside the parentheses almost cancel near the Curie point, and the second term is small. The parameter λ is obtained from the relation $p = \tanh(\lambda - \beta p/kT)$. In Eq. (2) the fairly rapid drop in Takagi group population below T_c tends to increase the correlation time T_{we} , but $1-p^2$ drops even more rapidly, so there is a relatively slow decrease in T_{we} as temperature drops below the Curie point.

SPLITTING OF DEUTERON SPECTRUM BELOW T_c

The temperature dependence of the splitting of the X -bond deuteron magnetic resonance in the X -rotation observed by Bjorkstam⁵ can be explained in terms of this correlation time. Above T_c , as pointed out by Bjorkstam, the deuterons jump back and forth randomly in their bonds with a correlation time so short that the efg's at the two ends of the bond are averaged. Below T_c the correlation time becomes even shorter, so the efg's felt by each deuteron will still be averaged. However, the biased nature of the motion below T_c will make the average efg approach the efg at the correct end of the bond. The splitting occurs because one end of the bond is correct for half of the deuteron sites, and the other end is correct for the remaining sites. The ratio of the splitting to the maximum splitting is the ratio p of the polarization to the maximum polarization. Figure 3 shows that a splitting proportional to p agrees within experimental error with the measured splitting. Bjorkstam explained the splitting

and lack of line broadening by assuming that below T_c the time between jumps abruptly increases to above 10^{-3} sec and inferred from this abrupt increase that the transition is first order and that the potential function for the deuteron in the bond changes abruptly at T_c . The present explanation also indicates that the transition is of first order because of the discontinuities in the temperature dependences of the splitting and the spontaneous polarization (see SUS), but this explanation, being based on a model in which the energies of the Slater and Takagi groups are unchanged across the transition, does not assume any change in bond potential function at the transition. The 7% increase in quadrupolar coupling constant below T_c indicates at least a small change in the bond potential function.

DEUTERON SPIN-LATTICE RELAXATION

Deuteron spin-lattice relaxation in KD_2PO_4 was discussed in SU in terms of three contributions: deuteron jumping between bonds, deuteron jumping within bonds, and spin diffusion to paramagnetic impurities. For relaxation due to spin diffusion, an estimate of 0.03 min^{-1} was made for the $\Delta m=1$ transition probability P_1 , independent of orientation and temperature. The $\Delta m=2$ transition probability P_2 is zero for this process.

The efg fluctuations seen by the moving deuterons are much more effective in causing relaxation than are the accompanying fluctuations in magnetic field. If the efg fluctuations are represented by $\Delta\phi_{ij}F(t)$, each quadrupolar transition probability can be expressed as the product of the spectral density of $F(t)$ at the transition frequency with the matrix elements for appropriate combinations of the $\Delta\phi_{ij}$. The spectral density for the autocorrelation function of Eq. (3) at frequency ω is

$$J(\omega) = \frac{1}{2} (1-p)^2 \tau_c / (1+\omega^2 \tau_c^2). \quad (6)$$

For relaxation due to intrabond motion, τ_c is the correlation time T_{we} . For interbond motion, τ_c is the time constant T_{XY} for mixing of X and Y bond deuteron population, and the factor $1-p^2$ must be omitted. The transition probabilities are

$$P_1 = \frac{e^2 Q^2 [(\Delta\phi_{x'z'})^2 + (\Delta\phi_{y'z'})^2] (1-p^2) \tau_c}{16 \hbar^2 (1+\omega^2 \tau_c^2)}, \quad (7)$$

$$P_2 = \frac{e^2 Q^2 [(\Delta\phi_{x'x'} - \Delta\phi_{y'y'})^2 + 4(\Delta\phi_{x'y'})^2] (1-p^2) \tau_c}{32 \hbar^2 (1+4\omega^2 \tau_c^2)}, \quad (8)$$

where $\omega/2\pi$ and $2\omega/2\pi$ are the $\Delta m=1$ and $\Delta m=2$ transition frequencies, respectively. These expressions are smaller than those given in Eqs. (34) and (35) of SU by a factor of $\frac{1}{4}$ for $p=0$ because in SU the rms amplitudes of the efg fluctuations were taken as the differences $\Delta\phi_{ij}$ in the gradient components at the two

deuteron sites, whereas the correct rms amplitude is $\frac{1}{2}\Delta\phi_{ij}$.

For relaxation due to interbond motion, $\omega T_{XY} \gg 1$ at all temperatures and magnetic fields at which measurements were made, so the transition probabilities are proportional to ω^{-2} or equivalently H_0^{-2} , and by reducing the magnetic field H_0 it was possible to make interbond motion the dominant relaxation mechanism over a considerable temperature range. The results shown in Fig. 7 of SU agree quite well with the expressions for P_1 and P_2 given in SU, so the corrected expressions in Eqs. (7) and (8) above predict values about $\frac{1}{4}$ as great as the experimental values. Because considerably more measurements were made of relaxation time than of T_{XY} , this discrepancy is probably due mostly to error in measurement of T_{XY} .

For intrabond motion, $\omega\tau_c = \omega T_{we} \ll 1$ in Eqs. (7) and (8). The $\Delta\phi_{ij}$ in the laboratory system are found from the difference in efg at the two ends of the bond below T_c as measured by Bjorkstam.⁵ This difference is used also above T_c in calculating the relaxation, although the efg changes somewhat at T_c as indicated in Fig. 3. Crystal symmetry allows nonzero components $\Delta\phi_{XY}$ and $\Delta\phi_{YZ}$ in the crystal system for this difference tensor, but Bjorkstam found only one nonzero component, $\Delta\phi_{YZ} = (21.0 \text{ kc/sec}) 2h/3eQ$. The expressions for P_1 and P_2 for X-bond deuterons and for \bar{P}_1 and \bar{P}_2 averaged over all deuterons given in Eqs. (12), (13), and (15) through (18) of SU are still valid if $A = \Delta\phi_{XY} = 0$, $B = \Delta\phi_{YZ}$, and $C = (1-p^2)e^2Q^2T_{we}/32\hbar^2$. The averages \bar{P}_1 and \bar{P}_2 must be used near 240°K and above because interbond jumps mix the X and Y bond deuteron population, while below about 220°K this mixing is slow enough to be unimportant.

Below T_c the transition probabilities drop rapidly with temperature, mostly because the factor $\frac{1}{4}(1-p^2)$ which is proportional to the square of the rms efg fluctuations is dropping rapidly, but also because T_{we} is decreasing somewhat. This decrease in T_{we} runs counter to the intuitive notion that since intrabond motion tends to disappear below T_c , the motion is slowing down and its correlation time should increase. The explanation is that T_{we} is roughly the time a deuteron remains at the wrong end of its bond below T_c . The time which a deuteron remains at the correct end of the bond, which is longer than T_{we} by a factor of about $(1+p)/(1-p)$, does increase rapidly with decreasing temperature below T_c . This time does not enter into the exponential part of the autocorrelation function which defines the correlation time. It does affect the relaxation strongly because its rapid increase relative to T_{we} causes the rapid decrease in the rms values of the efg fluctuations.

Best agreement between theory and experiment is obtained by setting the one adjustable parameter T_{0e} to 0.8×10^{-13} sec. Comparison between theory and experiment is made in Table I and Fig. 4. Here P_1 due

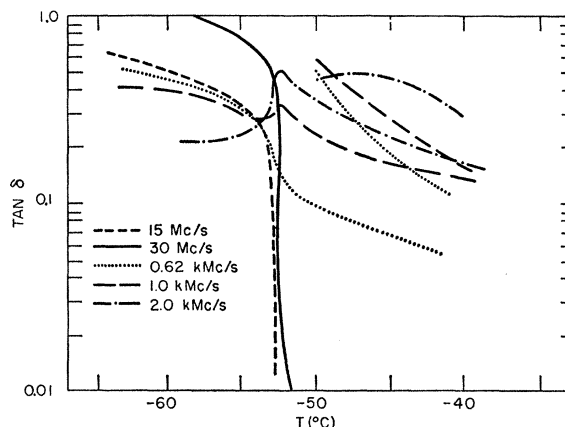


Fig. 6. Dielectric loss tangent in KD_2PO_4 near Curie temperature. Curves running from -50 to -40°C are calculated; other curves are experimental (Ref. 3).

to spin diffusion to paramagnetic impurities is taken as 0.03 min^{-1} , and P_1 and P_2 due to interbond jumps are the same as in SU. The agreement in Table I is not as good as in Table I of SU, because the ratio of $\Delta\phi_{XY}$ to $\Delta\phi_{YZ}$ is no longer an adjustable parameter. In particular, the prediction of $P_2 = 0$ for θ_X of 90° does not agree with experiment. Agreement could be improved by assuming that $\Delta\phi_{XY}$ is not quite equal to zero above T_c . Lattice vibrations are another possible source of nonzero P_2 in this orientation. Longitudinal vibrations in the hydrogen bonds, which have been postulated¹⁶ to be the source of the 400-cm^{-1} absorption band in KH_2PO_4 , would cause changes only in ϕ_{XX} , ϕ_{YY} , and ϕ_{ZZ} . Since the crystal and laboratory systems coincide for the $\theta_X = 90^\circ$ orientation, Eqs. (7) and (8) predict zero contribution to P_1 . An order-of-magnitude calculation indicates that such vibrations may make a significant contribution to P_2 . The transverse modes, which occur¹⁶ at 1030 and 1300 cm^{-1} in KH_2PO_4 , are at too high a frequency to cause appreciable relaxation. For the 0° and $90^\circ \theta_Z$ data at 215°K , some mixing of X and Y bond deuteron populations may account for some of the discrepancy between theory and experiment.

The data shown in Fig. 4 were obtained for the orientation at which the splitting disappears for X deuterons, for which relaxation involves only one time constant $T_1 = (P_{1X} + 2P_{2X})^{-1} \equiv P_X^{-1}$ at low temperatures. At higher temperatures $T_1 = [\frac{1}{2}(P_X + P_Y)]^{-1}$. The break in the theoretical curve corresponds to temperatures for which P_X^{-1} and P_Y^{-1} are comparable to T_{XY} , for which T_1 is undefined because relaxation involves two time constants as discussed in Appendix I of SU. Agreement with experiment is fairly good both above and below T_c .

¹⁶ Y. Imry, I. Pelah, and E. Wiener, J. Chem. Phys. **43**, 2332 (1965).

DIELECTRIC RELAXATION

The static dielectric susceptibility obtained by combining Eqs. (7) and (9) of SUS is given by

$$\chi_{dc} = \alpha N \mu_0 \mu_1 / V k T + \chi_0,$$

$$\alpha = \frac{1}{2} \left[\frac{\exp(-\epsilon_0/kT) + \exp(-\epsilon_1/kT) - \frac{1}{2}}{1 + \exp(-\epsilon_1/kT)} - \frac{\beta}{kT} \right]^{-1}. \quad (9)$$

Here μ_0 is related to the electric dipole moments of the various configurations shown in Fig. 2, and is the magnitude of the change in dipole moment per intrabond jump, while $\mu_1 = \mu_0 + 2\beta\chi_0 V / N\mu_0$, when multiplied by electric field E , is the magnitude of the electrostatic energy change per jump for polarization small enough that the $N\beta p^2$ term in the energy is negligible.

If the polarization $P - \chi_0 E$ associated with the hydrogen configurations is zero, hydrogen jumps which increase, and jumps which decrease, polarization along E have the same *a priori* probability. The jump probabilities are thus proportional to the Boltzmann factors for the corresponding mean energy changes. The configuration energy $4N[x_0\epsilon_0 + (x_1 + x_{-1})\epsilon_1]$ is stationary with respect to p for $p=0$, so the energy changes per jump for the two types of jumps are simply $\pm\mu_1 E$. The mean energy change per jump is then $-\mu_1 E \tanh(\mu_1 E/kT) \simeq -\mu_1^2 E^2/kT$. The ratio of polarization change to energy change for constant E is $-\mu_0/\mu_1 E$, so the mean polarization change per jump is $\mu_0 \mu_1 E/kT$. The jump rate per unit volume is $4N(x_1 + x_{-1})/VT = N/V T_w$, where $T_w/T_{we} = T_0/T_{0e}$, so for zero polarization the rate of change of polarization is

$$d(P - \chi_0 E)/dt \Big|_{p=0} = N \mu_0 \mu_1 E / V k T T_w. \quad (10)$$

For small fields the rate of change is proportional to the difference between the polarization and its equilibrium value for that E field, giving the following differential equation for $P - \chi_0 E$:

$$\frac{V k T T_w}{N \mu_0 \mu_1} \frac{d}{dt} (P - \chi_0 E) + \frac{P - \chi_0 E}{\chi_{dc} - \chi_0} = E. \quad (11)$$

For sinusoidal applied field $E = E_0 e^{j\omega t}$, $P - \chi_0 E$ can be written as $(\chi - \chi_0) E_0 e^{j\omega t}$. The complex susceptibility then is found to be

$$\begin{aligned} \chi - \chi_0 &= \frac{\chi_{dc} - \chi_0}{1 + j\omega k T T_w (\chi_{dc} - \chi_0) V / N \mu_0 \mu_1} \\ &= \frac{\alpha \mu_0 \mu_1 N / V k T}{1 + j\alpha \omega T_w}. \end{aligned} \quad (12)$$

The complex dielectric constant $\epsilon' - j\epsilon'' = 1 + 4\pi\chi$ ac-

cordingly has the following real and imaginary parts:

$$\epsilon' = 1 + 4\pi\chi_0 + \frac{4\pi\alpha\mu_0\mu_1 N / V k T}{1 + (\alpha\omega T_w)^2}, \quad (13)$$

$$\epsilon'' = \frac{4\pi\alpha^2\mu_0\mu_1\omega T_w N / V k T}{1 + (\alpha\omega T_w)^2}. \quad (14)$$

These expressions will be evaluated for T_0 's of 0.6 and 0.8×10^{-13} sec, using the parameters $\chi_0 = 0.5$, $\epsilon_0/k = 116^\circ\text{K}$, $\epsilon_1/k = 900^\circ\text{K}$, and $\beta/k = 20^\circ\text{K}$ which were chosen in SUS as giving the best fit to the experimentally observed high-temperature susceptibility and the spontaneous polarization. For the saturation spontaneous polarization, a value of 6.0×10^{-6} C/cm² is used, in accord with measurements of Hill and Ichiki³ and of Oettel and Bjorkstam.¹⁷ These calculated values are compared with the quantities measured at room temperature by Ludupov⁹ in the Cole-Cole plot of Fig. 5. A T_0 of 0.6×10^{-13} sec gives the best agreement and there appears to be a frequency-independent contribution to ϵ_c'' of about 4 in the high-frequency range. The good agreement with experiment, using only one adjustable parameter T_0 which has almost the same value as the corresponding parameter T_{0e} for deuteron relaxation, is regarded as convincing evidence that the dielectric relaxation at these high frequencies is due mostly to intrabond deuteron motion. Some additional support for this conclusion is given in Fig. 6, in which the calculated loss tangent ϵ_c''/ϵ_c' is shown to be in qualitative agreement with the values measured by Hill and Ichiki³ at three frequencies at temperatures slightly above T_c .

Figure 5 shows evidence for a peak in ϵ_a'' at nearly the same frequency as the peak in ϵ_c'' . The Cole-Cole plot indicates that only about half of the dc dielectric constant is associated with hydrogen configurations. This is consistent with Bantle's¹⁸ observation that below T_c the dc dielectric constant along the a axis drops from 100 to 50. The configurations responsible for this contribution to ϵ_a must be the Slater D_2PO_4 groups of energy ϵ_0 , which then must have dipole moments perpendicular to c of magnitude comparable to μ_0 , as was suggested by Slater.²

DOMAIN-WALL MOBILITY

Domain-wall motion in KD_2PO_4 has recently been explained¹⁰ in terms of effective motion of the Takagi DPO_4 and D_3PO_4 groups. The mean time between successive moves of a given group was taken as h/kT , or 2.4×10^{-13} sec at 200°K . Using instead the mean time T_0 of 0.6×10^{-13} sec obtained from the dielectric relaxation, the domain-wall mobility is 6.8×10^{-5} cm²/V-sec at 200°K , in better agreement with the values measured by Oettel and Bjorkstam¹⁶ than was the value based on h/kT .

¹⁷ J. L. Bjorkstam (private communication).

¹⁸ W. Bantle, *Helv. Phys. Acta* **15**, 373 (1942).

DISCUSSION

Four different phenomena in KD_2PO_4 have been explained quantitatively in terms of deuteron intrabond jumps associated with the effective motion of the thermally created DPO_4 and D_3PO_4 groups postulated by Takagi⁷ in his modification of the Slater² theory of KH_2PO_4 -type crystals. These phenomena are the deuteron magnetic resonance splitting below the ferroelectric transition temperature T_c , the deuteron spin-lattice relaxation due to intrabond motion both above and below T_c , the dielectric relaxation at high frequency, and the ferroelectric domain-wall mobility. The mean time T_w found for motion of a deuteron along its bond has been used together with the fractional population of the Takagi groups to calculate the mean time T_0 per effective move of a Takagi group. The result that T_0 is comparable to \hbar/kT implies little correlation between successive deuteron jumps associ-

ated with Takagi group motion. This is in interesting contrast to the intrabond motion in KH_2PO_4 , which Blinc and Svetina¹² describe as correlated proton tunneling associated with effective motion of HPO_4 and H_3PO_4 groups, in order to explain the result of Bjorkstam and Oettel¹¹ that domain-wall mobility in KH_2PO_4 is several orders of magnitude greater than in KD_2PO_4 .

ACKNOWLEDGMENTS

Helpful discussions with Professor J. A. Ball and Professor K. L. Nordtvedt, Jr. of Montana State University, and Professor J. L. Bjorkstam and Professor E. A. Uehling of the University of Washington are gratefully acknowledged. Professor Bjorkstam kindly supplied me with experimental results prior to publication.

β -Uranium Hydride: Heat Capacities from 1.4 to 23°K and Some Derived Properties*

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(Received 16 June 1967)

The heat capacity of the metallic, ferromagnetic compound $\beta\text{-UH}_3$ was determined from 1.4 to 23°K. An attempt was made to fit the data at the lowest temperatures by an equation of the form $C_p = \gamma T + AT^3 + BT^{3/2}$, where γT is the contribution of the conduction electrons, AT^3 is the lattice contribution, and $BT^{3/2}$ is the magnetic contribution. The coefficient γ is $29 \pm 1 \text{ mJ } ^\circ\text{K}^{-2} \text{ mole}^{-1}$. Because of uncertainty in the magnetic contribution, no reliable estimate of A or of the Debye Θ could be made. The thermodynamic functions S° , $(H^\circ - H_0^\circ)/T$ and $(G^\circ - H_0^\circ)/T$ were reevaluated as 63.67 ± 0.13 , 30.24 ± 0.06 , and $-33.43 \pm 0.07 \text{ J } (^\circ\text{K mole})^{-1}$, respectively, at 298.15°K.

INTRODUCTION

THE β crystalline modification of UH_3 is the usual phase formed when the hydride is prepared from the elements at 200°C or higher temperatures. The unit cell has cubic symmetry with $a_0 = 6.644 \text{ \AA}$, and contains eight uranium atoms arranged as in α tungsten, i.e., 2U_I at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and 6U_{II} at $\pm(\frac{1}{4}, 0, \frac{1}{2})$.^{1,2} Each U_{II} atom has two U_{II} atoms as nearest neighbors at 3.322 Å and four U_I atoms as next-nearest neighbors at 3.714 Å; each U_I atom has twelve U_{II} atoms as nearest neighbors at 3.714 Å. According to the neutron-diffraction study reported by Rundle,² the hydrogen atoms in $\beta\text{-UD}_3$ are in the center of a deformed tetrahedron and are equidistant (2.32 Å) from four uranium atoms. It was concluded by Rundle^{1,2} that the $\beta\text{-UD}_3$ structure is held together principally by U-D bonds rather than U-U bonds.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

¹ R. E. Rundle, *J. Am. Chem. Soc.* **69**, 1719 (1947).

² R. E. Rundle, *J. Am. Chem. Soc.* **73**, 4172 (1951).

The additional information that $\beta\text{-UH}_3$ has an electrical conductivity of the same order of magnitude as that of uranium metal³ and that it is ferromagnetic below about 173°K^{4,5} increases the interest in the low-temperature properties of this unusual compound.

The heat capacities of $\beta\text{-UH}_3$ ⁶ and $\beta\text{-UD}_3$ ⁷ have been previously determined from 5 to 350°K in this laboratory. From these results⁷ the entropy associated with the ferromagnetic transitions of $\beta\text{-UH}_3$ and $\beta\text{-UD}_3$ were found to be 1.19 and 1.18 cal deg⁻¹ mole⁻¹, respectively. These heat capacities were known to be increasingly uncertain below 20°K due to adsorption of He⁴ exchange gas on the samples. In this paper we report

³ F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns, and A. H. Daane, *Nucleonics* **4**, 4 (1949).

⁴ (a) W. Trzebiatowski, A. Sliwa, and B. Stalinski, *Roczniki Chem.* **26**, 110 (1952); (b) **28**, 12 (1954).

⁵ M. K. Wilkinson, C. G. Shull, and R. E. Rundle, *Phys. Rev.* **99**, 627 (1955).

⁶ H. E. Flotow, H. R. Lohr, B. M. Abraham, and D. W. Osborne, *J. Am. Chem. Soc.* **81**, 3529 (1959).

⁷ B. M. Abraham, D. W. Osborne, H. E. Flotow, and R. B. Marcus, *J. Am. Chem. Soc.* **82**, 1064 (1960).