Ferroelectric Transition in KD_2PO_4

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The ferroelectric transition in KD_2PO_4 has been investigated both experimentally and theoretically. Coherent neutron scattering by fluctuations associated with the transition was studied both above and below the transition temperature. None of the optic-phonon modes was found to change in frequency near the Curie temperature, in contrast with materials such as $SrTiO_3$. The ferroelectric fluctuations gave rise to quasi-elastic scattering, increasing in intensity as the transition was approached. The intensity distribution showed that the pattern of displacement of the atoms in these fluctuations was similar to that which relates the crystal structures of KH_2PO_4 above and below the transition temperature. It was found that the macroscopic electric field plays a large part in determining the probability distribution of the fluctuations. The results have been analysed in terms of an Ising model with one "spin" per unit cell. The intensity of the scattering is shown to be consistent with a relation connecting the dielectric and scattering properties. The implications of these results for the theory of ferroelectricity in KH_2PO_4 and KD_2PO_4 are discussed.

I. INTRODUCTION

Ferroelectrics are often classified in two groups: displacive ferroelectrics such as the perovskites and order-disorder ferroelectrics such as KH_2PO_4 (KDP). The theory of the former class has been developed in terms of an instability against one of the normal modes of vibration, as suggested by Cochran[1] and Anderson,[2] and this has found a considerable degree of confirmation in experiments on $SrTiO_3$,[3] $BaTiO_3$,[4] and $KTaO_3$.[5] The theory of other ferroelectrics is less developed. The first microscopic theories of KDP were put forward by Slater[6] and more recently extended by Silsbee and Uehling.[7] These models emphasize the ordering of the hydrogen atoms in the ferroelectric phase, which was confirmed experimentally by Bacon and Pease[8] using neutron diffraction. These theories however do not readily explain the strikingly large isotope effect in KDP—on deuteration the Curie temperature is increased[9] by a factor of about 1.9. To account for this, the concept of proton tunneling between two possible sites was introduced by Pirenne[10] and Blinc.[11] More recently an elegant spin formalism to describe the motion of the hydrogens has been introduced by de Gennes[12] and further developed by Brout *et al.*,[13] Tokunaga and Matsubara,[14] Tokunaga,[15] and others. One prediction of these theories is a collective motion (tunneling mode) of the hydrogens which becomes unstable at the phase transition.

That this is an over-simplified picture is apparent from the fact that while the motion of the hydrogen atoms is nearly in the *ab* plane, the ferroelectric axis is the *c* axis. Consideration of the motion of the other ions is therefore essential to explain the ferroelectric properties. This is borne out by the displacements of the ions at the phase transition, determined by Bacon and Pease.[8] Cochran[16] has also emphasized the need to consider all the atoms, and suggested their pattern of displacement in the "ferroelectric mode."

Unstable or temperature-dependent modes have been sought in a number of optical experiments. Infrared measurements on KDP by Barker and Tinkham[17] showed a relaxation of the dielectric response at relatively low frequencies. Kaminow and Damen[18] using Raman scattering have detected a heavily damped mode which does however appear to have a resonant character and for which the undamped frequency was deduced to vary as $[(T-T_c)/T]^{1/2}$.

Earlier neutron scattering measurements have also mostly been made on KDP,[19] and have therefore involved incoherent scattering. The object of our experiments[20] was to study any modes associated with the ferroelectric transition, and to determine the dispersion relation for phonon modes by coherent scattering. Consequently we used a single crystal of KD_2PO_4 (usually abbreviated DKDP). Almost concurrently with this work, a similar experiment, although with different emphasis, has been reported by Skalyo *et al.*[21]

In Sec. II we describe the experimental arrangement and the results for the ferroelectric mode. It is shown that scattering from this mode occurs at frequencies which are low compared with typical phonon frequencies and are indeed too low to be resolved by the neutron spectrometer. This is consistent with the frequency dependence of the dielectric constant of DKDP determined by Hill and Ichiki,[22] from which one can deduce that the mode does not have a resonant character. In Sec. III we use a simple model for this mode, based on the Ising model for an order-disorder transition. The results of this analysis are discussed in Sec. IV, where we show that the observed intensity gives the Curie temperature of the free crystal, that its magnitude is consistent with an expression[23] connecting the scattering

TABLE I. Experimental conditions in the two sets of experiments and the results of fitting the parameters to the measured resolution function. The units are degrees and are the full widths at half-height.

	Expt. I Nominal	Expt. II Nominal	Expt. II Fitted
Horizontal collimations			
α_0 before monochromator	0.8	0.8	
α_1 monochromator-specimen	0.75	0.127	0.078
α_2 specimen-analyzer	0.67	0.30	0.28
α_3 analyzer-detector	4.0	10.0	
Vertical collimations			
β_1 before monochromator	1.0	1.0	Gaussian
β_2 monochromator-specimen	2.0	1.0	(standard deviation =
β_3 specimen-analyzer	6.0	6.0	0.022 recip-
β_4 analyzer-detector	6.0	1.0	rocal-lattice units)
Crystals			
M	0.48	0.25	0.12
A	0.35	0.35	0.29
Monochromator	(111) Al	(111) Ge	
Analyzer	(111) Ge	(111) Ge	

and dielectric properties of the crystal, and that its dependence on wave vector is qualitatively of the form to be expected for fluctuations in a ferroelectric crystal. In Sec. V we discuss the implication of these results for the theory of ferroelectricity in these crystals. We suggest that our observations are of the tunneling mode, strongly coupled with a phonon normal mode.[24,25] However, at least within the framework of the random-phase approximation, the isotope effect on the Curie temperature is not accounted for quantitatively by the change in the value of the tunneling integral in going from KDP to DKDP.

II. EXPERIMENTAL RESULTS

A. Experimental Details

In the paraelectric phase DKDP has the space group $I\bar{4}2d$ and its lattice parameters at room temperature are $a=b=7.468$ Å and $c=6.974$ Å. The single crystal used in these experiments was a cylinder whose axis was approximately along the c axis, of 1-in. diameter and 2 in. in length. The crystal was mounted in a metal cryostat with the ac plane horizontal. The temperature could be held constant for long periods to 0.1°K and measured with an accuracy of 0.2°K. Measurements were made at temperatures between 307 and 213°K, and the transition temperature was found to be 223.1°K.

The neutrons scattered by the crystal were studied with the aid of a triple-axis crystal spectrometer controlled in the constant-**Q** or constant-E modes of operation.[26] The experiments were made with two different arrangements of the experimental equipment. In the initial set of experiments[20] an aluminium monochromator crystal and squeezed germanium analyzer crystal[27] were used with fairly large angular collimations, as set out in Table I. A further set of experiments has now been completed using squeezed germanium crystals as both monochromator and analyser and with much less divergence in the collimators, as also shown in Table I. Both sets of measurements were made with the triple-axis crystal spectrometer at the $C5$ facility of the NRU[26] reactor, Chalk River.

B. Phonon Measurements

Measurements were made of some of the low-frequency branches of the phonon dispersion relation for wave vectors along the a and c directions of the tetragonal cell and will be described in detail in a later publication. The result of interest for present purposes is that none of the undamped modes is directly associated with the ferroelectric transition. Their frequencies are essentially independent of temperature, as shown in Fig. 1 for the optic mode of lowest frequency with $q=0$, and for the mode with lowest frequency at the zone boundary in the c direction. There is thus no well-defined peak, in the frequency spectrum of neutrons scattered from DKDP, whose position moves towards

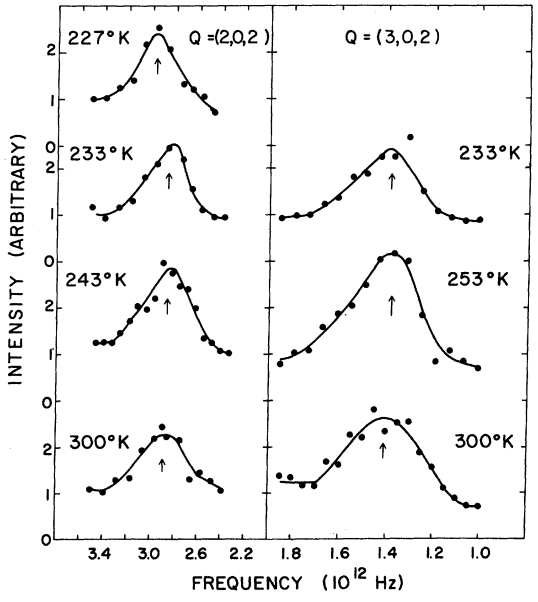

FIG. 1. Neutron intensity from two of the normal modes of vibration as a function of temperature. The wave-vector transfer **Q** is shown at the top of the figure in reciprocal-lattice units $2\pi(1/a, 1/a, 1/c)$. The arrows indicate the estimated centers of the neutron groups.

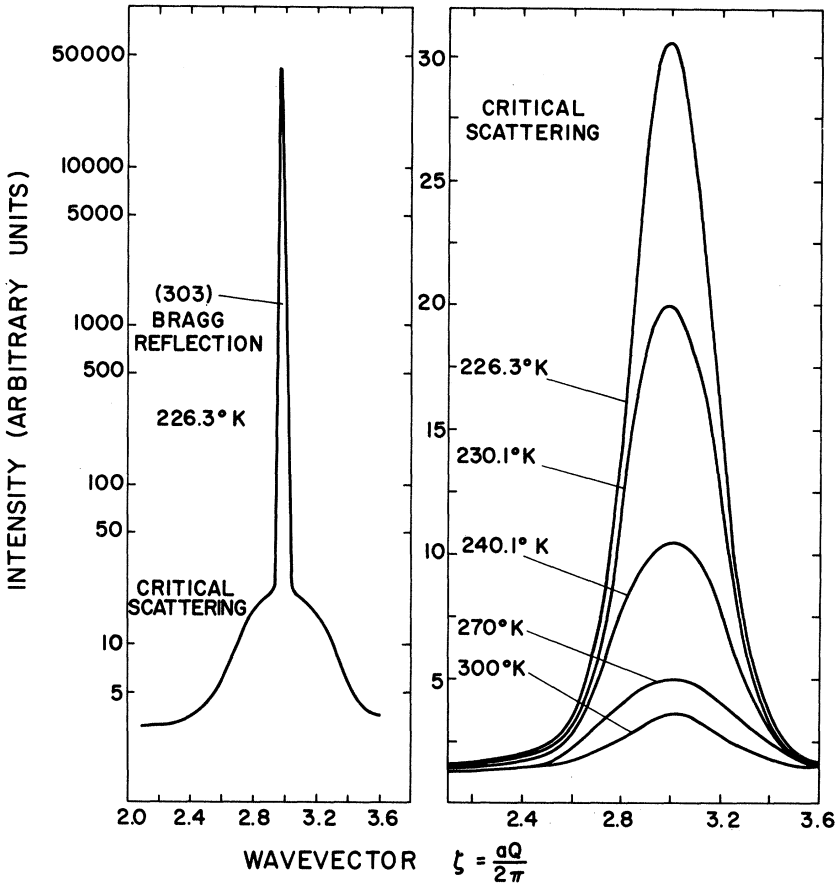

FIG. 2. Intensity of the quasi-elastic scattering along the line $(\zeta, 0, 3)$. The left-hand side shows the ferroelectric scattering and the (303) Bragg reflection. The right-hand side shows the temperature dependence of the ferroelectric scattering.

zero frequency as the ferroelectric transition is approached. This contrasts with the behavior found for $SrTiO_3$ [3] and $KTaO_3$,[5] but resembles the results obtained by Kaminow and Damen[18] in light-scattering experiments on KDP.

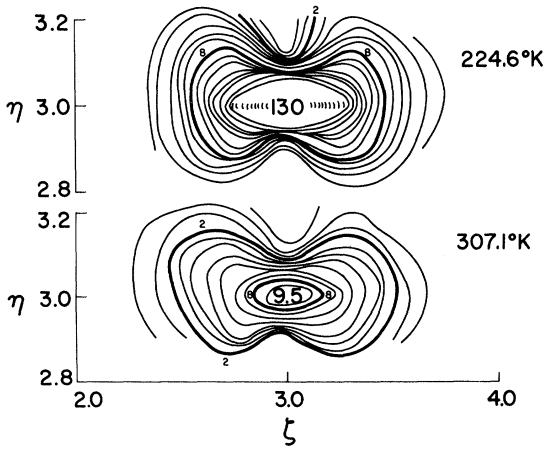

FIG. 3. Momentum distribution of the ferroelectric scattering as shown by contour maps in the (010) plane. Near the center of the distribution for 224.6°K, only the intercepts of the contours with the a^* axis were obtained from the data.

C. Quasi-Elastic Scattering

Quasi-elastic scattering was observed which was strongly temperature and wave-vector dependent. The intensity had a similar distribution in the neighborhood of each reciprocal-lattice point but varied greatly in magnitude from one reciprocal-lattice point to another. A distribution obtained by scanning along the line $(\zeta, 0, 3)$ through the lattice point $(3, 0, 3)$ is shown in Fig. 2. The sharp peak arises from the Bragg reflection and could be fairly readily subtracted. The background at large wave vectors arises from incoherent elastic scattering and may reasonably be expected to vary only slowly with temperature and wave vector. This was more difficult to subtract accurately but typical distributions in wave vector at two temperatures are shown in Fig. 3.

Measurements were made of the shape and temperature dependence of the scattering with both sets of experimental conditions, Table I. The excellent agreement obtained shows that the instrumental resolution does not greatly influence the results. The spread in frequency of the quasi-elastic scattering was such that no increase in width over and above the instrumental resolution, 0.12×10^{12} Hz. (full width at half-maximum)

TABLE II. Squared structure factors of the ferroelectric fluctuations as measured at various lattice points and as calculated using the displacements obtained by Bacon and Pease (Ref. 8). The goodness of fit is given by the χ value. The components of Q are given in reciprocal-lattice units.

Q	$F(\mathbf{Q})^2$ Expt.	Calculated from KDP displacements
(0, 0, 2)	0±0.03	0
(0, 0, 4)	0.4±0.05	0.29
(1, 0, 1)	0±0.03	0.08
(1, 0, 3)	0.05±0.04	0
(2, 0, 0)	0.01±0.03	0
(2, 0, 2)	0.02±0.03	0
(2, 0, 4)	0.21±0.07	0.01
(3, 0, 1)	0.30±0.03	0.99
(3, 0, 3)	1.0±0.1	0.95
(4, 0, 0)	0±0.03	0
(4, 0, 2)	0.01±0.03	0.03
Fit χ	···	7.4

was observed. From the results of Hill and Ichiki[22] on the frequency dependence of the dielectric constant, the predicted width is about 0.04×10^{12} Hz at room temperature and is less at lower temperatures. This would scarcely have been detectable. Thus the ferroelectric fluctuations occur on a time scale which is greater than the vibrational periods of all but the longest-wavelength acoustic phonons.

The variation in the intensity of quasi-elastic scattering with temperature and wave vector was studied most extensively around the reciprocal-lattice point (3, 0, 3). The magnitude associated with each reciprocal-lattice point $(h, 0, l)$ was obtained by taking the difference between the intensity at $(h\pm0.15, 0, l)$ and $(h, 0, l\pm0.15)$, as a means of eliminating background. Measurements were made at several different temperatures and under both sets of experimental conditions, and are summarized in column 2 of Table II. They are consistent with the more extensive measurements of this kind made by Skalyo *et al.*[21]

A comparison of the intensity of the quasi-elastic scattering with the integrated intensity of any normal mode of vibration enables the former to be put on an absolute scale, since the latter may be calculated when the eigenvectors are known. The quasi-elastic scattering $\mathcal{S}$ at a momentum transfer of (2.85, 0, 3) was therefore compared with that observed for the transverse-acoustic mode $\mathcal{S}_a$ of the same wave vector at four different temperatures under the same experimental conditions. We define a factor which we expect to be independent of temperature,

$$R=\mathcal{S}_a(T)/\mathcal{S}(T)(T-T_c), \tag{2.1}$$

where $T_c(q=0.15)$ was taken to be 218.5°K. This factor was found to be 0.016, 0.02, 0.023, and 0.021 at 307, 254, 233, and 224.9°K, respectively; that is, it is constant at 0.020±0.003, within the experimental error.

III. ANALYSIS OF EXPERIMENTAL RESULTS

In this section we give a description of the scattering by the ferroelectric fluctuations in terms of a phenomenological model. The model is an Ising model in which we assign a spin $S(l)=\pm1$ to each primitive unit cell which determines whether the dipole moment associated with the unit cell is along the positive or negative c axis. This model is similar to that used to describe the order-disorder transitions in $NaNO_2$[28] and in β brass.[29] If the interaction between the spins in the unit cells l and l' at $\mathbf{r}_l$ and $\mathbf{r}_{l'}$ is $V_{ll'}$, the Hamiltonian is

$$H=\tfrac{1}{2}\sum_{\mathbf{q}} V(\mathbf{q})S(\mathbf{q})S(-\mathbf{q}), \tag{3.1}$$

where

$$S(\mathbf{q})=(1/\sqrt{N})\sum_{l} S(l)\exp(-i\mathbf{q}\cdot\mathbf{r}) \tag{3.2}$$

and

$$V(\mathbf{q})=\sum_{ll'} V_{ll'}\exp(i\mathbf{q}\cdot(\mathbf{r}_l-\mathbf{r}_{l'})). \tag{3.3}$$

The neutron scattering by this model is given in the random-phase approximation by[30]

$$\mathcal{S}(\mathbf{Q})=N\,|\,F(\mathbf{Q})\,|^2\Gamma(\mathbf{q}), \tag{3.4}$$

where N is the number of unit cells in the crystal and $\mathbf{Q}$ is the scattering vector, related to $\mathbf{q}$ by the condition that $\mathbf{Q}-\mathbf{q}$ is a vector $\boldsymbol{\tau}$ to a reciprocal-lattice point. The correlation function $\Gamma(\mathbf{q})$ is given by

$$\Gamma(\mathbf{q})=[1+\beta V(\mathbf{q})]^{-1}=T/[T-T_c(\mathbf{q})], \tag{3.5}$$

where $\beta=1/k_BT$ and $k_BT_c(\mathbf{q})$ is defined as $-V(\mathbf{q})$. The structure factor is given by

$$F(\mathbf{Q})=\sum_k b_k\exp(-W_k(\mathbf{Q}))\sin(\mathbf{Q}\cdot\mathbf{u}_k)\exp(i\mathbf{Q}\cdot\mathbf{r}_k), \tag{3.6}$$

where b_k is the scattering length of the kth atom, $\exp(-W_k(\mathbf{Q}))$ its Debye-Waller factor, $2\mathbf{u}_k$ its displacement when $S(l)$ changes sign, and $\mathbf{r}_k$ its average position in the unit cell. The sum in (3.6) is taken over all atoms of one unit cell.

The interaction $V(\mathbf{q})$ was taken to involve a short-range interaction between a unit cell and its eight nearest neighbors, and a Coulomb interaction which was approximated by its singular form as $q\to0$. $V(\mathbf{q})$ is thus written as

$$V(\mathbf{q})=V_c\cos^2\alpha+J_0+8J_1[1-\cos(\tfrac{1}{2}aq_x)\times\cos(\tfrac{1}{2}aq_y)\cos(\tfrac{1}{2}cq_z)], \tag{3.7}$$

where α is the angle between $\mathbf{q}$ and the c direction. Comparing Eqs. (3.7) and (3.5) we see that the intensity diverges for $q_x\to0$, with q_y and q_z zero, at a tem-

TABLE III. Percentage change in the observed intensities when they are corrected for the instrumental resolution for $\mathbf{Q}=(2.85, 0, 3.0)$, columns a, and $(3.0, 0, 3.1)$, columns b.

Temperature (°K)	224.8	230.0	240.0		300.00
	a	*a*	*a*	*b*	*a*
103-point resolution function	···	−4.9%	−1.9%	+1.7%	−0.8%
13-point resolution function	−8.0%	−5.1%	−2.9%	+1.9%	−0.8%

perature given by $k_B T_c = -J_0$, thus relating J_0 to the Curie temperature of the transition.

The experimental results were analyzed using expressions of this form. Initially a check was made that the finite experimental resolution was not influencing the results. The resolution function was measured by scanning the spectrometer through the sharp (3, 0, 3) Bragg reflection and fitting the results to the expression derived for the resolution function by Cooper and Nathans.[31] The fit reproduced the measurements reasonably well ($\chi=4.1$) but the actual values of the parameters were significantly different from their nominal values, Table I. The effect of the finite resolution function was then calculated for the wave vectors (2.85, 0, 3) and (3, 0, 3.1) at the lowest temperatures where the effects are largest. The integration was performed using both 13 and 103 points to represent the resolution function; and, as shown in Table III, both calculations gave good agreement with one another, and corrections which were always less than 8%. We conclude that the effect of the resolution function on our results is quite small.

Two ways of analyzing the data taken around the reciprocal-lattice point (3, 0, 3) were used. A least-squares fit by computer to the measured intensity was made by varying the parameters V_c, J_0, and J_1 and allowing for a background contribution to the intensity which was assumed to be independent of $\mathbf{Q}$. The structure factor $F(\mathbf{Q})$ was also assumed to be independent of $\mathbf{Q}$. The parameters of the fit are given in Table IV, where it is seen that the value of J_0 corresponds to a temperature greater than the observed transition temperature by 5°K. A similar fit was made including the effects of the finite resolution function with little change in the parameters. A fit in which the short-range interaction was not restricted to nearest neighbors was also made but although the parameters changed considerably the goodness of fit did not improve.

TABLE IV. Parameters J_0, J_1, and V_c as deduced from a computer fit and a graphical analysis of the data (analysis A of Fig. 5).

	J_0 (°K)	J_1 (°K)	V_c (°K)
Computer fit	−228.5±0.7	10.90±0.05	258±1
Graphical analysis	−223.5±1.0	7.3±1.4	180±20

The other method of analyzing the data was to plot curves of the inverse intensity against the inverse temperature for various different wave vectors, assuming various different backgrounds (see Fig. 4). The intercept of these curves with the inverse temperature axis then gives $V(\mathbf{q})$ and the slope $V(\mathbf{q})/|F(\mathbf{Q})|^2$. The resulting $V(\mathbf{q})$ and $|F(\mathbf{Q})|^2$ are shown in Fig. 5 for $\mathbf{q}$ along the a axis and for two of the backgrounds employed. A value of V_c was then obtained by examining the intensity along the lines (2.6, 0, η), (2.7, 0, η), (2.8, 0, η), and (3.0, 0, η). For the value of the background given in analysis A the values of V_c from these different lines were all approximately equal but for analysis B the values were very different, varying between 4000 and 320°K. We list the parameters obtained from the analysis A in Table IV. The value of J_0 is now in agreement with the transition temperature. The values of J_1 and V_c are both smaller than the values obtained from the computer fit. This results in part from a different choice of background and in part because $|F(\mathbf{Q})|^2$ was held constant in the computer fits. The discrepancies give a measure of the uncertainties in these parameters.

The variation of the intensity, that is, of $|F(\mathbf{Q})|^2$, from one reciprocal-lattice point to another provides information about the pattern of displacements of the atoms in the ferroelectric fluctuation. The relative intensities have been calculated using for the $\mathbf{u}_k$ the displacements found by Bacon and Pease[8] at a temperature well below T_c in KDP and are compared with our measurements in Table II. Although there is a similarity between the measured and calculated values the discrepancies show that the displacements above T_c in DKDP do differ from these below T_c in KDP. Attempts were made to deduce better values of the $\mathbf{u}_k$ but these will not be reported since more extensive measurements and calculations have now been published by Skalyo *et al.*[21]

IV. DISCUSSION OF RESULTS

A. Value of J_0

The analysis of results in Sec. III gave $-J_0/k_B$ as greater than, or equal to, the transition temperature. For a piezoelectric crystal which makes a continuous transition, the transition temperature is equal to the Curie temperature of the "free" crystal, and this is higher than the Curie temperature of the "clamped"

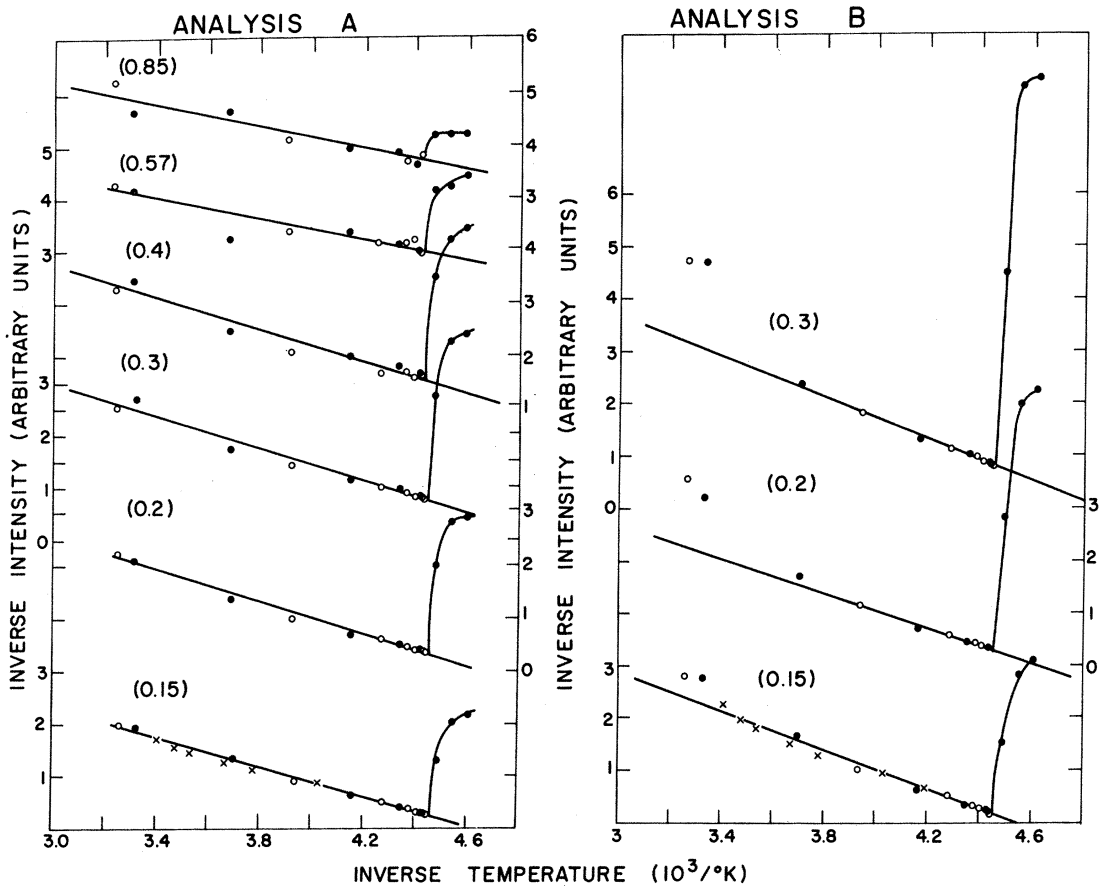

FIG. 4. Reciprocal intensity $(I-I_B)^{-1}$ plotted against reciprocal temperature for various wave vectors along the line $(\zeta, 0, 3)$. The open circles correspond to the results from the experimental arrangement I, the solid circles from experimental arrangement II, and the crosses were obtained with the conditions I, but not under constant temperature conditions. The analyses A and B were made with different backgrounds I_B. For analysis A, $I_B=0.040$; for analysis B, $I_B=0.008$, in the arbitrary units of the figure.

crystal.[9] We have already noted that for $\mathbf{q}$ in the a^* direction, $k_BT_c(q\to 0)=-J_0$. The question arises whether $T_c(q\to 0)$ should be the Curie temperature of the free or of the clamped crystal. Our measurements were made at wave vectors $\mathbf{q}$ sufficiently large that the frequencies in the spectrum of the ferroelectric mode were significantly lower than the frequency of the acoustic mode of the same wave vector. The acoustic mode can therefore follow the ferroelectric fluctuations, and conditions, extrapolated to zero wave vector, are those of the free crystal. Thus $-J_0/k_B$ *should* be equal to the transition temperature. In a Raman scattering measurement of ferroelectric fluctuations, the much smaller value of $\mathbf{q}$ results in conditions being reversed, and the intensity should involve $(T-T_c)^{-1}$, with T_c the Curie temperature of the clamped crystal, as confirmed by Kaminow and Damen[18] for KDP.

At comparatively large values of the wave vector the frequency of the acoustic mode corresponds to an elastic constant which is almost independent of temperature, whereas at very small wave vectors the frequency corresponds to an elastic constant which goes to zero at the transition temperature. Measurements which support this conclusion are shown in Fig. 6.[32]

B. Absolute Intensity of Scattering

The variation with temperature of the scattering is associated with the anomaly in the dielectric constant. If there is only one mode of motion present in the ferroelectric fluctuations, the dielectric susceptibility and the intensity are proportional. It has been shown[23] that

$$\lim_{q\to 0} S(\boldsymbol{\tau}+\mathbf{q})=(Nk_BT/vP_s^2)\,|\,F(\boldsymbol{\tau}+\mathbf{q})|^2\chi_{zz}(0), \qquad (4.1)$$

where the limit is taken with $\mathbf{q}$ perpendicular to the c axis (z direction). P_s is the spontaneous polarization,[9,33] and the static susceptibility is given by

$$\chi_{zz}(0)=C/4\pi(T-T_c), \qquad (4.2)$$

neglecting at this stage any contribution which is independent of temperature. The structure factor has already been defined, Eq. (3.6).

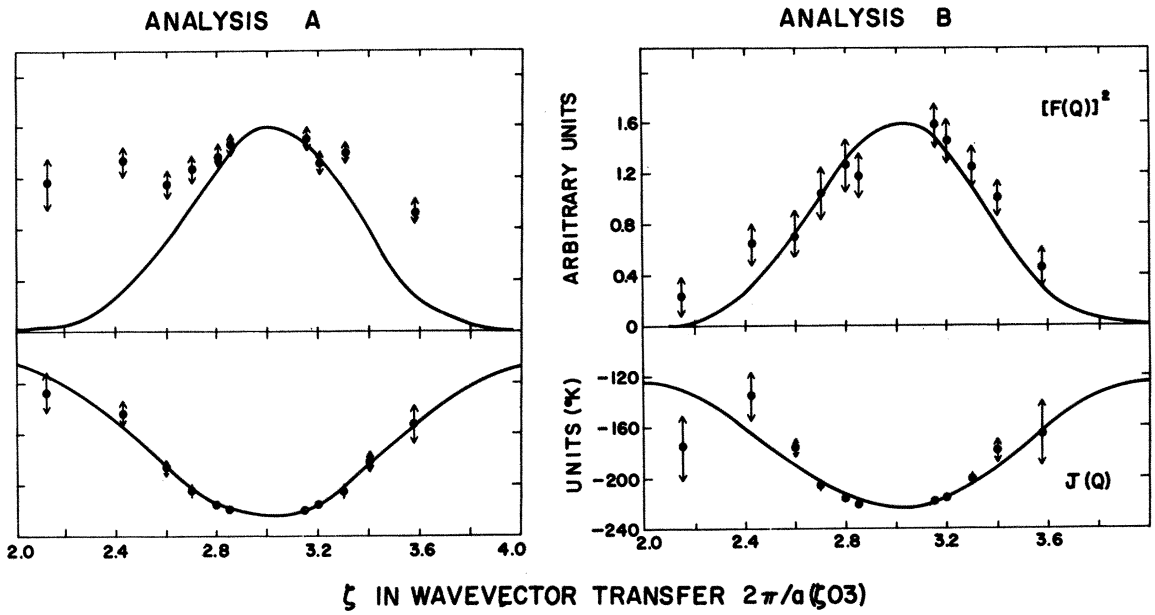

FIG. 5. Interaction $J(\mathbf{Q})$ and the structure factor $|F(\mathbf{Q})|^2$ as functions of the momentum transfer along the line $(\zeta, 0, 3)$. The different analyses were made with different values of the background (analyses A and B of Fig. 4).

The expression for the intensity scattered by an acoustic mode of the same wave vector, integrated over frequency, is

$$\mathcal{S}_a(\boldsymbol{\tau}+\mathbf{q})=[Nk_BT/2\omega_a^2(\mathbf{q})]\,|\,F_a(\boldsymbol{\tau}+\mathbf{q})|^2, \quad (4.3)$$

where ω_a is the frequency and F_a is the structure factor of the acoustic mode (defined in Sec. V). Now dividing $\mathcal{S}_a$ by $(T-T_c)$ we obtain an expression for the ratio R [Eq. (2.1)] for which an experimentally determined value was given in Sec. II C:

$$R=\frac{2\pi v F_a^2 P_s^2}{\omega_a^2 F^2 C}. \quad (4.4)$$

With $\omega_a/2\pi=(0.47\pm0.02)\times10^{12}$ Hz and $P_s=(1.50\pm0.05)\times10^4$ esu/cm²,[9] and taking the $\mathbf{u}_k$ of Eq. (3.6) to be as given by the structure analysis of Bacon and Pease[8] (Table V), we can now solve Eq. (4.4) for the Curie constant C, obtaining 4300 ± 700°K. This is in satisfactory agreement with the measured values[34,35] of 4040 and 3760°K, particularly as we have not distinguished in the above analysis between T_c appropriate to the susceptibility (223°K) and T_c appropriate to the neutron intensity which corresponds to $q=0.15(2\pi/a)$ and which was estimated in Sec. II C to be 218.5°K.

Equation (4.1) gives a relation between scattering and dielectric properties which is independent of a

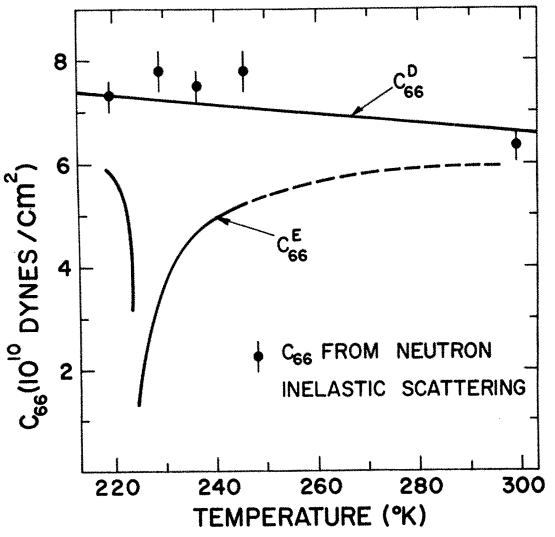

FIG. 6. Elastic constant C_{66} as a function of temperature. The solid lines are from ultrasonic results of Litov and Uehling (Ref. 35) and we have smoothly interpolated the dotted line to agree with the room-temperature measurement of Sliker and Burlage (Ref. 35).

TABLE V. Values of $\mathbf{u}_k$ deduced from the structure analysis of KDP.

Atom k	Components of $\mathbf{u}_k$ in Å	
	x	z
Phosphorus	0	+0.073
Potassium	0	−0.047
Oxygen	0	−0.007
Deuterium	0.20	0

particular model. On the other hand Eq. (3.4) predicts the absolute intensity of scattering, but is based on the random-phase approximation when Eq. (3.5) is used for the correlation function, and it depends of course on the one-spin-per-cell model. Dividing (4.3) by (3.4) we obtain for the predicted value of R on this model:

$$R=k_B F_a^2/2\omega_a^2 F^2. \tag{4.5}$$

This gives almost exact agreement with the measured value of R. The significance (or otherwise) of this is discussed in Sec. V.

C. Value of V_c

The coefficient of the singular part of the electrostatic interaction was written in Sec. III as V_c. The dipole moment in each unit cell of volume v is vP_s so that we expect

$$V_c=4\pi v P_s^2/\epsilon_L. \tag{4.6}$$

We are now taking the dielectric constant to be given more accurately than in Eq. (4.2) by

$$\epsilon_{zz}(0)=\epsilon_L+C/(T-T_c), \tag{4.7}$$

where ϵ_L is the combined lattice and electronic contribution to the dielectric constant, which we may estimate from the measurements of Barker and Tinkham[3] to be 8.7. Equation (4.6) then gives $V_c=450$°K, which is at least a factor of 2 greater than our experimental value, which two different methods of analysis gave as 258 and 180°K (Sec. III and Table IV).

There are a number of possible reasons for this discrepancy. First of all we have approximated $V_c(\mathbf{q})$ by a constant appropriate to its value at $q=0$ although intensities corresponding to relatively quite large values of q were involved in the analysis of Sec. III. Secondly we have been able to show that the structure factor $F(\boldsymbol{\tau}+\mathbf{q})$ [Eq. (3.6)] is singular as $\mathbf{q}\to 0$. This singularity arises because the coupling between the ferroelectric fluctuations and the other normal modes of vibration is altered by the macroscopic electric field[36] associated with the longitudinal part of the fluctuations. This singularity has not been allowed for in any of our computations so that the value of V_c may to some extent compensate for the failure to include the singularity in $F(\mathbf{q}+\boldsymbol{\tau})$.

D. Structure Factor

In Sec. III we deduced an expression for the structure factor of the ferroelectric fluctuations by assuming that the displacements of the atoms within any one unit cell are determined by the vectors, $\mathbf{u}_k$ and the spin $S(l)$. The resultant expression (3.6) is compared with the $|F(\mathbf{Q})|^2$ deduced from experiment in Fig. 5. This figure shows that whereas the theoretical expression gives zero at the zone boundary, the measured value is probably nonzero. This discrepancy is not surprising because the displacements of the atoms must vary smoothly from one unit cell to another where $S(l)$ changes sign. The effect of this may be simulated by multiplying the displacements by $\exp(i\mathbf{q}\cdot\mathbf{r}_k)$, when $|F(\mathbf{Q})|^2$ becomes almost constant within any Brillouin zone but is discontinuous at the zone boundary. In practice $|F(\mathbf{Q})|^2$ varies in a manner intermediate between these extremes as shown in Fig. 5.

V. NATURE OF FERROELECTRICITY IN DKDP

A. Order-Disorder or Damped Oscillator Model

The discussion so far has been in terms of an order-disorder model in which the dipole moment of each unit cell can be either up or down. It is however also possible to interpret the results in terms of a damped oscillatory phonon mode of the crystal. The intensity of neutron scattering by an anharmonic crystal[37] can be approximated by the result

$$\mathcal{S}(\mathbf{Q}\omega)=2N\hbar\omega[n(\omega)+1]\,|F_j(\mathbf{Q})|^2 \times\frac{2\gamma_j(\mathbf{q})}{[\tilde{\omega}_j^2(\mathbf{q})-\omega^2]^2+4\omega^2\gamma_j^2(\mathbf{q})}, \tag{5.1}$$

where the scattering by only one mode is considered. $\tilde{\omega}_j(\mathbf{q})$ is the quasiharmonic frequency of the mode and $\gamma_j(\mathbf{q})$ a damping constant. The structure factor for a phonon mode is given by

$$F_j(\mathbf{Q})=\sum_k b_k m_k^{-1/2}[\mathbf{Q}\cdot\mathbf{e}_j(\mathbf{q})]\exp(-W_k(\mathbf{Q})) \times\exp(i\boldsymbol{\tau}\cdot\mathbf{r}_k). \tag{5.2}$$

When the frequency is relatively low, $\hbar\omega[n(\omega)+1]$ can be replaced by k_BT. If the damping constant is relatively large, $2\gamma_j(\mathbf{q})\gg\omega_j(\mathbf{q})$, Eq. (5.1) reduces to an expression involving a Debye relaxation time:

$$\mathcal{S}(\mathbf{Q}\omega)=\frac{2Nk_BT\,|F_j(\mathbf{Q})|^2\tau_j(\mathbf{q})}{\tilde{\omega}_j^2(\mathbf{q})[1+\omega^2\tau_j^2(\mathbf{q})]}, \tag{5.3}$$

where

$$\tau_j(\mathbf{q})=2\gamma_j(\mathbf{q})/\tilde{\omega}_j^2(\mathbf{q}). \tag{5.4}$$

Integrating either Eq. (5.1) or Eq. (5.3) over frequency gives

$$\mathcal{S}(\mathbf{Q})=\int\mathcal{S}(\mathbf{Q}\omega)(d\omega/2\pi) =[Nk_BT\,|F_j(\mathbf{Q})|^2/\tilde{\omega}_j^2(\mathbf{q})]. \tag{5.5}$$

[This expression differs by a factor of 2 from that given as Eq. (4.3) because the latter involved an integration over positive ω only.] Equation (5.5) is independent of the damping constant or relaxation time. Comparing this result with those given in Sec. III, one finds that (5.5) and (3.4) are the same provided

$$\tilde{\omega}_j^2(\mathbf{q})=A[T-T_c(\mathbf{q})] \tag{5.6}$$

and the quantities $m_k^{-1/2}\mathbf{e}_{kj}(\mathbf{q})$ and $\mathbf{u}_k$ are taken to be proportional to one another. [In the range of $\mathbf{Q}$ covered by our measurements, $\mathbf{Q}\cdot\mathbf{u}_k$ could not be distinguished from $\sin(\mathbf{Q}\cdot\mathbf{u}_k)$.] To fit the measured intensity

requires

$$\tilde{\omega}_j(0)/2\pi = 0.14(T-T_c)^{1/2}(10^{12}\text{ Hz}).$$

Although there is certainly no direct evidence for the existence of such an undamped frequency, it is consistent with the experimental results to assume that the quasi-elastic scattering arises either from a heavily overdamped phonon mode, an extreme example of the situation which occurs for $BaTiO_3$,[4] or alternatively to assume that all phonon modes are almost independent of temperature and the basic phenomenon is an ordering process such as occurs in $NaNO_2$.[28] A way to distinguish these two possibilities would be to detect experimentally and enumerate the optic phonons in the paraelectric phase having the same symmetry as the ferroelectric mode. Group theory shows that there are six such optic phonons, so that if six were detected the order-disorder model would be favored and conversely. Unfortunately a more careful consideration of anharmonic effects in piezoelectric crystals[38] shows that even this test might not be conclusive. The large displacements of the hydrogen atoms at the phase transition ($2\mathbf{u}_H = 0.4$ Å) do, we believe, favor the order-disorder model.

B. Tunneling Model

There has been considerable discussion in the literature concerning the application of the tunneling model to the ferroelectric transition in KDP and DKDP.[10–15] The original theories assumed only one hydrogen atom per unit cell and neglected coupling between phonons and the tunneling modes involving the hydrogen atoms. Both of these features have now been incorporated into the theory.[25,39] In what follows we use essentially the same notation as in a review by one of us.[23] In particular, subscript j distinguishes different phonon modes and subscript i different tunneling modes of the same wave vector. For KDP, $i = 1 \cdots 4$ since there are four hydrogen atoms per unit cell. The frequency of a pure tunneling mode is given in the random-phase approximation by

$$\hbar^2\omega_i^2(\mathbf{q}) = 2\Omega[2\Omega - \tfrac{1}{2}J_i(\mathbf{q})\tanh\beta\Omega], \qquad (5.7)$$

where 2Ω is the tunneling integral and $J_i(\mathbf{q})$ is a measure of the direct interaction between hydrogen atoms in this mode. Coupling between the tunneling mode and phonon modes of the same symmetry results in mixed modes. Assuming that $\omega_i(\mathbf{q})$ is small compared with the relevant $\omega_j(\mathbf{q})$ one of the mixed modes has predominantly the character of a tunneling mode and its frequency is given by

$$\hbar^2\omega_i^2(\mathbf{q}) = 2\Omega[2\Omega - \tfrac{1}{2}\hat{J}_i(\mathbf{q})\tanh\beta\Omega], \qquad (5.8)$$

where

$$\hat{J}_i(\mathbf{q}) = J_i(\mathbf{q}) + 4\sum_j [|G_{ij}(\mathbf{q})|^2/\omega_j^2(\mathbf{q})]. \qquad (5.9)$$

In Eq. (5.9), $G_{ij}(\mathbf{q})$ is a measure of the coupling between a phonon and a tunneling mode. From Eq. (5.8) we see that the modified tunneling mode may become unstable at a temperature $T_c(\mathbf{q})$ given by

$$\tanh[\Omega/k_BT_c(\mathbf{q})] = 4\Omega/\hat{J}_i(\mathbf{q}). \qquad (5.10)$$

Comparison of Eqs. (5.7) and (5.8), using (5.9), shows that the Curie temperature is raised by the interaction through the lattice. When $k_BT_c(\mathbf{q})$ is large compared with Ω, the Curie temperature becomes independent of the precise value of Ω, being given by

$$k_BT_c(\mathbf{q}) = \tfrac{1}{4}\hat{J}_i(\mathbf{q}), \qquad (5.11)$$

and Eq. (5.8) reduces to

$$\hbar^2\tilde{\omega}_i^2(\mathbf{q}) = 4\Omega^2[T - T_c(\mathbf{q})]/T. \qquad (5.12)$$

For a ferroelectric transition $q = 0$, and we shall use the subscript $i = f$ to distinguish the ferroelectric mode.

The Raman scattering spectrum of KH_2PO_4 has been interpreted by Kaminow and Damen[18] in terms of a damped mode, giving a cross section for light scattering similar in form to Eq. (5.1) for neutron scattering. The temperature dependence of the frequency of this mode was found to be as predicted by Eq. (5.12). Numerically their results give $2\Omega/h = 3.0\times10^{12}$ Hz or $\Omega = 1.0\times10^{-14}$ erg. The damping constant $\gamma_f(0)$ was found to be independent of temperature; numerically we have

$$\gamma_f(0)/2\pi = 2.5\times10^{12}\text{ Hz}.$$

The theoretical significance of the damping constant is not clear. If, however, we assume it to have the same value in DKDP as in KDP, we can use the results of Hill and Ichiki[22] to estimate that Ω must be at least an order of magnitude smaller in the former material. While this large decrease is plausible, it does not provide a ready explanation of the increase of T_c from KDP to DKDP. Using subscripts H and D appropriately, and making the plausible assumption that $\hat{J}_f(0)$ is the same for both materials, we have from Eqs. (5.10) and (5.11) that

$$\Omega_H/k_BT_D = \tanh(\Omega_H/k_BT_H). \qquad (5.13)$$

Using the value $\Omega_H = 10^{-14}$ erg and $T_H = 120°$K gives T_D only a few degrees greater than T_H, contrary to observation.

A possible explanation is that $\hat{J}_f(0)$ is largely determined by the interaction through the lattice and not by $J_f(0)$ [Eq. (5.9)]. This is certainly found to be the case if all the optic-phonon modes are approximated by a single mode.[23] The interaction between the lattice and the tunneling mode might then be quite different if that interaction were calculated by averaging the interaction over the hydrogen and deuterium wave functions as is done in the self-consistent phonon approximation.[40] It is, however, probably unwise to place so much reliance on formulas which involve the random-phase approximation. Cochran[23] has given the cross section for neutron scattering (integrated over ω, and

assuming Ω relatively small) for the tunneling model of DKDP as

$$S(\mathbf{Q}) = \tfrac{1}{4}N \mid F(Q) \mid^2 \Gamma(\mathbf{q}). \qquad (5.14)$$

The structure factor is as defined in Eq. (3.6). The factor $\frac{1}{4}$ originates in the four equivalent pseudospins per unit cell. If the correlation function is taken to be as given by the random-phase approximation [Eq. (3.5)], Eq. (5.14) gives a predicted intensity too small by a factor of 4 to agree with observation (see Sec. IV B). The Curie constant C predicted by this approach is also too small by nearly the same factor. We do not consider that this disproves the tunneling model (which for DKDP reduces to an Ising model because of the relatively small value of Ω), rather that the random-phase approximation cannot be relied on to give correct numerical predictions, as distinct from giving the correct temperature dependence for quantities such as $\Gamma(\mathbf{q})$ and $\tilde{\omega}_f^2(0)$. Further work is clearly needed to allow for the correlations in the motion of the hydrogen or deuterium atoms, and to incorporate "damping effects" in a more satisfactory way.

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