BRILLOUIN-SCATTERING STUDY OF THE FERROELECTRIC TRANSITION IN KH_2PO_4†

Edward M. Brody* and Herman Z. Cummins
Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 30 August 1968)

The Brillouin-scattering spectrum of KH_2PO_4 has been studied over the temperature range $118°K < T < 300°K$ with particular emphasis on the region close to the ferroelectric transition at 122°K. Results in the paraelectric phase are analyzed in terms of the piezoelectric coupling of the acoustic X_y shear mode to the ferroelectric soft mode. Results in the ferroelectric phase indicate that the transition is better described by the Slater-Takagi-Senko model than by Cochran's model.

The ferroelectric phase transition in potassium dihydrogen phosphate (KH_2PO_4) which occurs at 122°K[1] is generally considered to result from an ordering of the protons which occupy double-minima potential wells, a mechanism first suggested by Slater in 1941.[2] In 1963, de Gennes showed that there are collective excitations of the system of interacting tunneling protons above the partially polarized ground state. His pseudospin formalism was extended to the temperature dependent problem by Brout et al. who found that the frequency of the long-wavelength ($q \sim 0$) collective excitations exhibit the Cochran behavior $\omega_0^2 \propto (T-T_0)$ as $T \to T_0$ from above.[3]

Blinc and Kobayashi included the effects of coupling between the tunneling protons and lattice distortions.[4] The coupled collective excitation which they predict, a mixed tunneling proton-optical phonon mode, still exhibits the $\omega_0^2 \propto (T-T_0)$ behavior, but with a transition temperature T_0 which is higher than that for the rigid lattice model. The existence of a "soft" ferroelectric mode in KH_2PO_4 with this temperature dependence was also predicted independently by Cochran from lattic-dynamics considerations.[5]

Recently, Kaminow and Damen have observed a heavily damped feature in the Raman spectrum of KH_2PO_4 which they have identified as the ferroelectric soft mode.[6] If we let ω_P, the complex angular frequency of the soft mode, be the roots of

$$\omega_P^2 - \omega_0^2 - 2i\omega_P\Gamma = 0$$

then their data give $\omega_0/2\pi = (99\ \mathrm{cm}^{-1})[(T-T_0)/T]^{1/2}$, $\Gamma/2\pi = 85\ \mathrm{cm}^{-1}$, and $T_0 \simeq 117°K$.

As $T \to T_0$ from above, the soft-mode frequency ω_P would cross the acoustic-mode frequencies. Since KH_2PO_4 is piezoelectric, the soft mode (which includes polarization P_z) is linearly coupled to the X_y transverse acoustic modes. The coupling produces a "level repulsion," or anticrossing interaction, which drives the acoustic mode frequency to zero causing the transition to occur at a temperature T_C which is higher than T_0, a fact which has been pointed out by Cochran.[5] The resultant softening of the X_y elastic constant C_{66}^E of the shorted crystal was first observed by Mason in 1946.[7] Although Mason's resonance method clearly exhibited the softening effect, it did not permit detailed study of C_{66}^E in the immediate vicinity of the phase transition.

Experiment.—In this paper we present the results of a Brillouin-scattering experiment in which the y-polarized transverse phonons propagating along the x axis were observed over a large range of temperatures both above and below the transition. A one-half-inch cube of single-crystal KH_2PO_4[8] with edges parallel to the crystallographic xyz axes was mounted with its y axis perpendicular to the scattering plane. The wave vector of the incident light $\vec{k}_i$ was along (101) and $\vec{k}_S$ was along ($\bar{1}01$) so that $\vec{q} = \vec{k}_i - \vec{k}_S$ was along the x axis. The incident light (from a Spectra Physics model 125 He-Ne laser) was y polarized. In this configuration, only the X_y shear mode scatters light polarized in the scattering plane (VH) so that this mode can be easily isolated in the Brillouin spectrum.[9] Gold films were evaporated onto the (001) faces to provide electrodes for establishing the electrical boundary conditions.

The crystal was mounted in a copper thermostat filled with a fluid (2-methyl butane) which was suspended within a large liquid nitrogen Dewar. The crystal temperature was measured with a platinum resistance thermometer with 0.001°K precision and 0.1°K absolute accuracy. T_C, the temperature at which $C_{66}^E(E=0) \to 0$, was measured as 122.0°K. Temperature stability at the sample was 0.002°K/h.

The scattered light was analyzed with a pressure-scanned plane Fabry-Perot interferometer and "photon counting" electronics. The observed Brillouin shifts ($\omega_2/2\pi$) and the derived elastic

constant of the shorted crystal $C_{66}^E(E=0)$ are plotted in Fig. 1. As T approaches T_C from above, the Brillouin shift approaches zero and the Brillouin components are distorted by the large parasitic central component. Between 122.2 and 122.0°K, the accuracy decreases from ±2 to ±30%. For $T < T_C$ the accuracy is ±2%.

In a second-order transition, $C_{66}^E(E=0)$ would extrapolate to zero at the same temperature at which the transition occurs. From our data, the transition appears to be of second order within the limits imposed by temperature stability and possible thermal gradients. As $T \to T_C$ from above, the smallest $\omega_2/2\pi$ measured was 0.02 cm^{-1} at $T = 122$°K, corresponding to an elastic constant $C_{66}^E(E=0)$ of 0.07×10^{10} dyn/cm².[10] No hysteresis effects were observed when the zero-field condition was carefully maintained, and the rise in C_{66}^E below T_C, although extremely rapid, was continuous. First-order behavior, if present, is limited to a maximum temperature interval of 0.03°, and produces a maximum discontinuity in C_{66}^E of 0.5×10^{10} dyn/cm².

A lower limit of 1.0×10^{10} dyn/cm² for C_{66}^E at $E = 1500$ V/cm was observed in recent ultrasonic measurements on the deuterated crystal KD_2PO_4.[11]

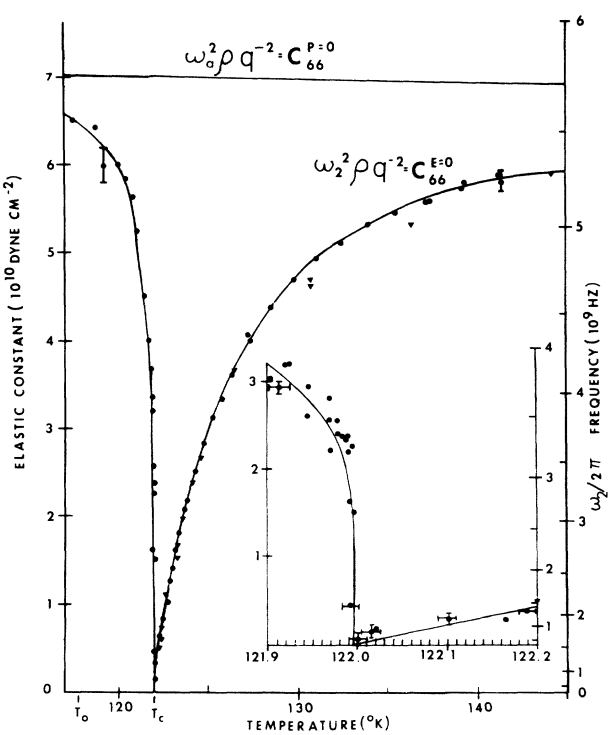

FIG. 1. The elastic constants C_{66}^E and C_{66}^P. Solid circles: Brillouin shifts ($\omega_2/2\pi$). Solid triangles: ultrasonic measurements of C_{66}^E (see Ref. 10). C_{66}^P is from piezoelectric resonance data (see Refs. 7 and 14).

The KD_2PO_4 transition was interpreted as first order, although the possible effect of the field on the minimum C_{66}^E was not explored. We have studied the Brillouin spectrum of KH_2PO_4 with applied electric fields of between 500 and 4000 V/cm, and find that C_{66}^E is strongly field dependent within 1°K of T_C. With $E = 1500$ V/cm, the smallest observed value of C_{66}^E was approximately 1.3×10^{10} dyn/cm².

Theory: $T > T_C$.—The equations of motion of the coupled ferroelectric and acoustic modes can be derived from the Lagrangian density.[12] The ferroelectric mode will be characterized by a weighted atomic displacement coordinate Q, an effective charge e and effective mass m (per dipole unit), and an effective force constant K. The dipole moment per unit volume $P = NeQ$, where N is the number of dipole units per unit volume.

The potential and kinetic energy densities for the ferroelectric mode are $U_P = \frac{1}{2}NKQ^2$ and $T_P = \frac{1}{2}Nm\dot{Q}^2$. If we define an "equivalent mass density" $m^* = m/Ne^2$, and let $\chi = K/Ne^2$, then $U_P = \frac{1}{2}\chi P^2$, and $T_P = \frac{1}{2}m^*\dot{P}^2$. (Note that $\chi/m^* = K/m = \omega_0^2$, where ω_0 is the undamped frequency of the ferroelectric soft mode.)

The total elastic potential energy density is $U_a = \frac{1}{2}C_{ij}^P x_i x_j$ where the x_i are symmetrized strains. The elastic kinetic energy density is $T_a = \frac{1}{2}\rho\dot{u}^2$ where u is the local displacement and ρ is the density. For excitations propagating along the X axis, the elastic problem is diagonal, and we need only consider the Y-polarized transverse acoustic modes since only these can couple to the ferroelectric soft mode. Thus, $u = u_y \times \exp[i(qx-\omega t)]$, $x_6 = iqu$, $U_a = \frac{1}{2}C_{66}^P x_6^2$, and $T_a = \frac{1}{2}(\rho/q^2)\dot{x}_6^2$. All other optic and acoustic modes will be ignored since they do not participate in the transition.

Inserting the piezoelectric coupling term $U_{aP} = a_{36}Px_6$, we have

$$U = \tfrac{1}{2}\chi P^2 + \tfrac{1}{2}C_{66}^P x_6^2 + a_{36}Px_6,$$
$$T = \tfrac{1}{2}m^*\dot{P}^2 + \tfrac{1}{2}(\rho/q^2)\dot{x}_6^2. \qquad (2)$$

The equations of motion, including a phenomenological damping term $-2m^*\Gamma\dot{P}$ in the equation for P, are

$$\ddot{x}_6 = -(q^2/\rho)C_{66}^P x_6 - (a_{36}q^2/\rho)P,$$
$$\ddot{P} = -(a_{36}/m^*)x_6 - (\chi/m^*)P - 2\Gamma\dot{P}. \qquad (3)$$

If the coupling constant a_{36} were zero, the equations would separate and would have as solutions a temperature-independent acoustic mode x_6

$\propto \exp(i\omega_a t)$, where $\omega_a{}^2 = q^2 C_{66}{}^P/\rho$, and a polarization mode $P \propto \exp(i\omega_P t)$ with ω_P, the soft-mode frequency, given by the roots of Eq. (1).

Harmonic solutions to the coupled Eqs. (3) are given by the roots of the secular equation

$$(\omega^2-\omega_a{}^2)(\omega^2-\omega_0{}^2-2i\Gamma\omega)-(q^2 a_{36}{}^2/\rho m^*)=0. \quad (4)$$

Since $\omega_0 \gg \omega_a$, the solutions of (4) separate into a high-frequency "mostly polarization" pair essentially identical to the uncoupled ferroelectric modes, and a low-frequency "mostly acoustic" pair which are closely approximated by

$$\omega_2{}^2 = \omega_a{}^2 - (q^2 a_{36}{}^2/\rho m^* \omega_0{}^2), \quad (5)$$

$$m^*\omega_0{}^2 = (a_{36}{}^2 q^2)/(\omega_a{}^2-\omega_2{}^2). \quad (6)$$

Equation (5) is formally equivalent to the equation derived by Mason from thermodynamic considerations.[7] It predicts that as ω_0 approaches zero, the low-frequency coupled mode ω_2 will fall from the uncoupled acoustic-mode frequency ω_a to zero, in good agreement with the experiment.[13]

From our measurements of ω_2 and the known values of the other quantities in Eq. (6),[1,7] we have computed $m^*\omega_0{}^2$ as a function of T (isothermal rather than adiabatic values of a_{36} were used). The results, shown in Fig. 2, were computer fitted with a linear function of temperature which gave

$$m^*\omega_0{}^2 = 4.14\times 10^{-3}(T-117.7). \quad (7)$$

Arbitrarily setting our result equal to Kaminow and Damen's[6] at $T = 140°$K and assuming that there is one dipole unit per phosphate group gives $m^* = 1.62\times 10^{-27}$ sec^2, and $m/e^2 = 2.34$ (proton mass)/(electron charge)^2. The linear function $\omega_0{}^2 \propto (T-T_0)$ gives a better fit to our data

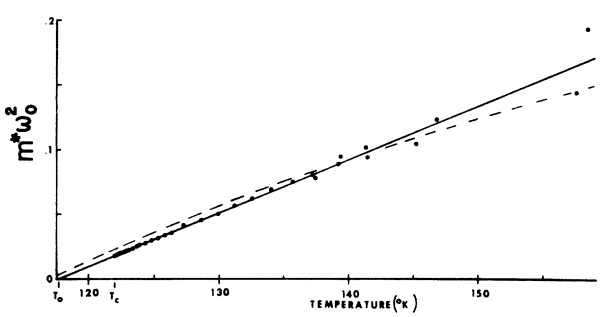

FIG. 2. $m^*\omega_0{}^2$ from Eq. (6) and the data of Fig. 1. Solid line: fit with linear function of T. Dashed line: fit with $m^*\omega_0{}^2 \propto (T-T_0)/T$ matched at 140°K.

than the function $\omega_0{}^2 \propto (T-T_0)/T$ found by Kaminow and Damen.

If we ignore the difference between adiabatic and isothermal constants, the potential energy density U of Eq. (2) is identical to the Helmholtz free energy density A from which we can find the dielectric constant at constant strain, ϵ_χ, and at constant stress, ϵ_σ: $\epsilon_\chi = 4\pi/\chi$, $\epsilon_\sigma = 4\pi/(\chi - a_{36}{}^2/C_{66}{}^P)$. Using our $\chi = m^*\omega_0{}^2$ result [Eq. (7)], we then find $\epsilon_\chi = 3030/(T-117.7)$, $\epsilon_\sigma = 3030/(T-122.0)$. The Curie constant is in good agreement with the observed value of 3122.[7] The difference of 4.3° between the Curie points of the clamped and free crystals agrees with the observations of Baumgartner[14] and mirrors the difference in the temperatures T_0 and T_C which mark the zeros in the frequencies of ω_P and ω_0, respectively.

Theory: $T < T_C$.—Since $\chi < 0$ when $T < T_0$, we must add another term $F(P)$ to the potential energy to stabilize the ferroelectric phase. If the transition were basically of the lattice displacement type,[5] $F(P)$ would be determined by the anharmonic lattice forces and would be of the Devonshire form[1]: $F(P) = (\xi/4)P^4 + (\zeta/6)P^6$. Letting both ξ and ζ be positive gives a second-order transition with the buildup of both spontaneous polarization and ω_2 below T_C much less rapid than what is observed. A better fit to the spontaneous polarization data[1] is obtained with $\xi < 0$ (e.g., $\xi = -2.1\times 10^{-10}$, $\zeta = 4.2\times 10^{-18}$ esu). The transition is then first order in agreement with Reese's calorimetric observations,[15] but the predicted maximum of the dielectric constant is then at least an order of magnitude too small. Furthermore, with this choice the transition is predicted to occur approximately 0.5°K above T_C, the extrapolated intercept of ω_2, whereas from our data T_C occurs at most 0.03° below the transition. Alternatively, the transition could be controlled by the statistical mechanics of the order-disorder transition of the protons as Slater proposed.[2] Although in Slater's theory the transition is too rapid, later modifications by Tagaki and Senko which were reviewed by Silsbee, Uehling, and Schmidt[16] (SUS) provide considerable flexibility to the theory.[17]

We have utilized the dielectric data for $T > T_C$ and the spontaneous-polarization and elastic-constant data for $T < T_C$ to determine the three energy parameters in the SUS equations. Reasonable preliminary fits were obtained with $\epsilon_0/k = 52.1°$, $\epsilon_1/k = 400°$, and $\beta/k = 20°$. However, with this choice the transition is first order by approximately 0.08°, a somewhat larger gap than the

Brillouin or dielectric data permit.

In conclusion, our results for $T > T_C$ are well described by the simple coupled-oscillator model and support the existence of a soft ferroelectric mode. The apparent agreement between the extrapolated zeros of ω_2 and the transition temperature indicate that the transition is of second order or very close to second order. Finally, the SUS equations fit the observations well over most of the range, but there is a region of about 0.1° below the transition which is not yet fully understood.

†Work supported by the Advanced Research Projects Agency (Project DEFENDER), monitored by the U. S. Army Research Office (Durham).

*National Aeronautics and Space Administration Trainee.

[1]F. Jona and G. Shirane, Ferroelectric Crystals (The Macmillan Company, New York, 1962).

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

[3]P. G. de Gennes, Solid State Commun. 1, 132 (1963); R. Brout et al., ibid. 4, 507 (1966).

[4]R. Blinc, Phys. Letters 26A, 8 (1967); K. Kobayashi, ibid. 26A, 55 (1967).

[5]W. Cochran, Advan. Phys. 10, 401 (1961).

[6]I. P. Kaminow and T. C. Damen, Phys. Rev. Letters 20, 1105 (1968).

[7]W. P. Mason, Phys. Rev. 69, 173 (1946).

[8]Obtained from the Isomet Corporation, Palisades Park, N. J.

[9]H. Z. Cummins, in Ferroelectricity, edited by E. F. Weller (Elsevier Publishing Company, Inc., Amsterdam, The Netherlands, 1967), p. 197.

[10]A similar lowest value was found in recent ultrasonic measurements in the paraelectric phase: C. W. Garland and D. B. Novotny, to be published.

[11]E. Litov and E. A. Uehling, Phys. Rev. Letters 21, 809 (1968).

[12]A similar discussion of the transition in $BaTiO_3$ was given by V. Dvorak, Phys. Rev. 167, 525 (1968).

[13]Slight broadening is also observed close to the transition which is predicted by an exact computer solution to the quartic Eq. (4).

[14]H. Baumgartner, Helv. Phys. Acta 23, 651 (1950), and 24, 326 (1951).

[15]W. Reese, Bull. Am. Phys. Soc. 13, 504 (1968).

[16]H. B. Silsbee et al., Phys. Rev. 133, A165 (1964).

[17]Slater's theory predicts a rather extraordinary transition which is second order in the sense that $\partial^2 A/\partial P^2$ goes to zero at the transition so that there is no range of temperatures over which $A(P)$ has three coexisting minima, but which is first order in the sense that both the polarization and the entropy undergo large discontinuous changes at T_C. The inclusion of Takagi's one- or three-proton configurations and Senko's polarization energy in the free energy expression of SUS produces a transition which may be either first or second order depending on the values of the energy parameters.

DIRECT HIGH-ENERGY PHOTOPROTONS FROM ^{12}C†

G. Manuzio, G. Ricco, and M. Sanzone
Istituto di Fisica dell'Università di Genova, Genova, Italy

and

L. Ferrero
Istituto di Fisica dell'Università di Torino, Torino, Italy
(Received 18 September 1968)

The energy spectra of fast photoprotons from ^{12}C have been measured for a bremsstrahlung energy between 50 and 80 MeV. The analysis of the obtained cross section shows a strong direct emission from the $1p$ shell.

Although a few experiments have been performed in the energy region just above the giant resonance,[1-3] still neither the experimental situation nor the theoretical expectations are clear. The existing data can be in fact interpreted both in terms of a "quasi deuteron interaction," i.e., absorption of the photon by a proton-neutron pair in the nucleus, and direct interaction with nucleons in single-particle states.[1,3] The investigation of the existence and relative importance of each process is therefore the main experimental problem necessary for a better understanding of the photonuclear process above the giant resonance in complex nuclei.

In the experiment presented in this Letter we have measured the energy distribution of fast photoprotons from ^{12}C in order to investigate the possibility of direct emission of high-momentum nucleons from light nuclei.[4-5]

In the particular kinematics involved in photonuclear reactions in this energy range, where the photon brings high energy but relatively small