Ultrasonic Investigation of the Ferroelectric Transition Region in KH_2PO_4†

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The velocity and attenuation of 15-MHz ultrasonic shear waves have been investigated as a function of the temperature and the electric field applied along the polar axis of potassium dihydrogen phosphate single crystals. These data are analyzed to give the free dielectric susceptibility χ^X and the constant-stress polarization relaxation time τ_X. The χ^X values are in fairly good agreement both above and below T_c with the predictions of the Silsbee-Uehling-Schmidt model. However, the τ_X values show a temperature dependence which cannot be readily interpreted in terms of the Silsbee-Uehling-Schmidt model. Comparison with comparable data for KD_2PO_4 strongly suggests that proton tunneling plays an important role in KH_2PO_4.

INTRODUCTION

Potassium dihydrogen phosphate (KDP) is a uniaxial ferroelectric with a Curie temperature of 122°K. Since the completely analogous transition in KD_2PO_4(KD*P) occurs at ~222°K, there is an unusually large isotope effect associated with the ordering of the protons. In its paraelectric phase, KDP is tetragonal ($\bar{4}2m$) and the x_y mechanical strain is piezoelectrically coupled to the polarization along the ferroelectric z axis.[1] Therefore, the anomalous ultrasonic wave is a transverse wave propagating in the [100] direction with its polarization in the [010] direction.[2] There are two limiting values of the elastic constant related to this shear, depending on the electrical boundary conditions. One can specify the elastic stiffness at constant polarization (c_{66}^P) or at constant electric field (c_{66}^E). The limiting high-frequency wave velocity u_∞ is determined from $\rho u_\infty^2 = c_{66}^P$, where c_{66}^P exhibits a normal linear temperature dependence.[3] The velocity u and attenuation α at ultrasonic frequencies are related to the real and imaginary parts of the complex stiffness at constant field.

For crystals which are piezoelectric in both the ferroelectric and paraelectric phase, Dvorak[4] has analyzed the interaction of acoustic waves with polarization waves to show that the frequency and spatial dispersion of the effective elastic constants are directly related to the dispersion of the dielectric susceptibility. For the case of KDP,

$$c_{66}^* = c_{66}^P - a_{36}^2 \chi_{33}^x(\omega), \tag{1}$$

where a_{36} is the piezoelectric stress constant $(\partial E_3/\partial x_6)_P$ and $\chi_{33}^x(\omega)$ is the complex linear susceptibility of the clamped crystal. It will be shown that $\omega\tau \ll 1$ for KDP at ultrasonic frequencies. Thus the susceptibility can be represented in the form $\chi(\omega) = \chi(0) - i\chi(0)\omega\tau$, where $\chi(0)$ is the static value and the polarization relaxation time τ is given by either

$$\tau = \chi(0)/L \quad \text{(Landau model)} \tag{2}$$

or

$$\tau = 2\Gamma/\omega_0^2 \quad \text{(damped oscillator model)}. \tag{3}$$

In Eq. (2), L is the Landau phenomenological kinetic coefficient.[5] In Eq. (3), Γ is the damping constant for a ferroelectric soft mode of frequency ω_0, where ω_0 is much greater than the acoustic frequency ω.[6] Taking the real part of Eq. (1), one obtains

$$c_{66}^{P,S} - c_{66}^{E,S} = a_{36}^2 \chi^{x,S}(0), \tag{4}$$

or the thermodynamically equivalent form

$$s_{66}^{E,S} - s_{66}^{P,S} = b_{36}^2 \chi^{X,S}(0), \tag{5}$$

where b_{36} is the piezoelectric strain constant, $\chi^{X,S}$ is the free susceptibility, and s_{66} is the elastic compliance $(=1/c_{66})$. The superscript S has been added as a reminder that elastic properties determined at ultrasonic frequencies are adiabatic values. From the imaginary part of Eq. (1), one finds

$$\mathrm{Im}(c^*) \cong 2\rho u^3 \alpha/\omega = a_{36}^2 \chi^{x,S}(0)\omega\tau_{S,x}, \tag{6}$$

which can be rewritten with the help of Eq. (4) as

$$\alpha = \frac{(c_{66}^P - c_{66}^E)}{2\rho u^3}\omega^2\tau_{S,x}. \tag{7}$$

Since it is the *free* susceptibility at zero field which diverges at the transition temperature according to the Curie-Weiss law $\chi^X = C/(T - T_c)$, Eq. (2) indicates that it is τ_X rather than τ_x which should diverge at the Curie point (in the absence of any applied field). Thus, it is convenient to rewrite Eq. (7) as

$$\alpha = \frac{(c_{66}^P - c_{66}^E)}{2uc_{66}^P}\omega^2\tau_{S,X}, \tag{8}$$

where $\tau_{S,X}$ is the relaxation time at constant (zero) stress. This change is justified by the fact that the two relaxation times are simply related by $\tau_X/\tau_x = c^P/c^E = \chi^X/\chi^x$.

From the above, it is clear that ultrasonic measurements will yield information about both the static sus-

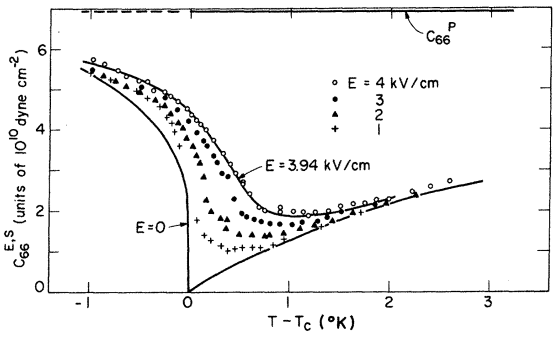

FIG. 1. Ultrasonic values of $c_{66}{}^{E,S}$ as a function of temperature for several constant values of the electric field parallel to the polar (z) axis. The smooth curves at $E=0$ and 3.94 kV cm^{-1} represent Brillouin data in the GHz range (see Ref. 14). The line labeled $c_{66}{}^P$ is taken from Mason (Ref. 15).

ceptibility and the polarization relaxation time. Garland and Novotny[7] have carried out such an investigation of KDP at zero applied field. However, their data were limited to temperature above T_c since strong domain scattering prevented acoustic measurements in the ferroelectric phase. In the case of KD*P, Litov and Uehling[8] have measured the velocity and attenuation in the both paraelectric and ferroelectric phase by applying a poling field of 1.5 kV cm^{-1} along the z axis. In the present investigation of KDP we have measured both the ultrasonic velocity and attenuation in external fields of 1, 2, 3, and 4 kV cm^{-1}. The elastic stiffness, the susceptibility, and the polarization relaxation time above and below T_c are compared with the values obtained in KD*P and are also discussed in terms of the Silsbee-Uehling-Schmidt (SUS) model.[9] This model, a modification of the order-disorder model of Slater[10] and Takagi,[11] includes long-range as well as short-range forces and introduces a temperature-independent jump rate for the motion of Takagi groups. The SUS model seems capable of giving a reasonable description of KD*P,[8] but one would not expect it to work as well for KDP since tunneling and specific interactions with the lattice are not included. Indeed, our data strongly suggest that proton tunneling is an important factor in KDP.

EXPERIMENTAL RESULTS

Most of the experimental techniques used in this investigation were the same as those used by Garland and Novotny[7] at zero field and very similar to those of Litov and Uehling.[8] Pulse-echo measurements were carried out with a single-transducer method using Matec ultrasonic equipment (model 120 synchronizer with a model 6000 pulsed generator/superheterodyne receiver and a model 666 pulse comparator). Oriented single crystals were obtained from the Harshaw Chemical Co. with dimensions of 0.75, 1.5, and 1.5 cm along the x, y, and z axes. A pair of gold electrodes were vacuum evaporated onto the faces perpendicular to the z axis, and a fused-silica buffer rod was inserted between the Y-cut quartz transducer and the KDP crystal in order to prevent the metallic surfaces of the transducer from distorting the uniformity of the electric field in the sample. A very stable applied electric field was obtained with a Fluke 410B power supply. Temperature stability during a measurement (i.e., during a period of about 30 min) was ± 0.002 deg. Since the electrocaloric effect is quite large in KDP,[12] velocity and attenuation measurements were carried out simultaneously as a function of temperature at fixed values of the applied field.

Data were obtained at the single frequency of 15 MHz. It is known that there is no velocity dispersion at zero applied field between ultrasonic ($\sim$5 MHz) and hypersonic ($\sim$5 GHz) frequencies,[13] and it will be shown below that this is also true in the presence of an applied field. As far as attenuation measurements are concerned, the ω^2 dependence of α has been demonstrated between 10 and 90 MHz for KDP [7] and between 5 and 45 MHz for KD*P.[8] Measurements at frequencies as low as 5 MHz are often complicated by high background loss due to beam spreading, while the α values at 25 MHz and above are too high to be measured throughout the transition region. We have chosen 15 MHz as a compromise value and have *assumed* that any noncritical background attenuation will be independent of temperature in the region from 120 to 140°K.

Velocity data. The values of $c_{66}{}^{E,S}=\rho u^2$, where ρ is the mass density, are shown in Fig. 1 as a function of temperature for four different applied fields. Above $\sim$125°K, any differences between Garland and Novotny's data[7] at $E=0$ and our highest-field data at $E=4$ kV cm^{-1} are comparable to the experimental uncertainty in c_{66} ($\sim 3\%$). Thus, we have only shown data points which are quite near the zero-field Curie point T_c. The data for $E=1$ kV cm^{-1} are the least reliable near T_c since this poling field is not large enough

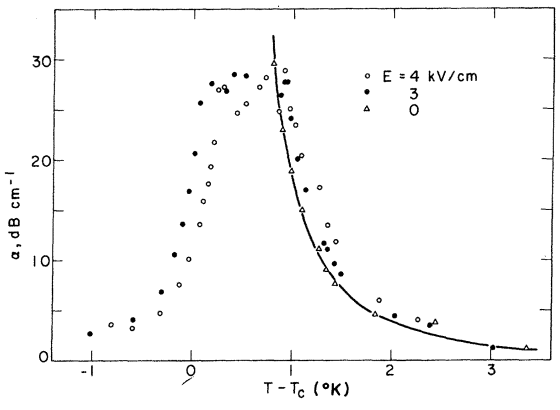

FIG. 2. Attenuation at 15 MHz as a function of temperature for several values of the poling field.

to produce a single-domain ferroelectric crystal. The smooth curves labeled $E=0$ and $E=3.94$ kV cm^{-1} represent Brillouin measurements at frequencies in the range 0.5–5 GHz.[13,14] The excellent agreement demonstrates the complete lack of dispersion and indicates that velocities measured at 15 MHz certainly correspond to the zero-frequency limit. Indeed, $\omega\tau$ must be small even at hypersonic frequencies (i.e., $\tau<3\times10^{-10}$). Also shown in Fig. 1 is the essentially normal variation of $c_{66}{}^{P}$ obtained by Mason.[15] His data can be represented by $c_{66}{}^{P}=[6.96-0.0044\,(T\text{-}122)]\times10^{10}$ dyn cm^{-2}; thus $c_{66}{}^{P}$ is effectively constant over the four-degree range of interest.

Attenuation data. The attenuation α at 15 MHz is shown as a function of temperature in Fig. 2. At an applied field of 1 kV cm^{-1} no reliable attenuation data could be obtained below T_c due to appreciable domain scattering. Even at $E=2$ kV cm^{-1} there was some indication that the α values were distorted by scattering losses. Therefore, Fig. 2 shows only the data obtained at 3 and 4 kV cm^{-1}, plus some zero-field data in the paraelectric phase. These data were obtained by a comparison of the echo amplitudes at any given temperature T to that observed at 140°K. This method was adopted since only a single echo could be detected close to T_c. The results are quite insensitive to the choice of 140°K as the reference temperature corresponding to zero critical attenuation since the background attenuation is constant between 130 and 142°K.

The large and rapidly varying attenuation in KDP is very difficult to measure accurately. The α values in the range from $T-T_c=-1$ to $+0.7$ could be reproduced to within $\pm15\%$ on several independent runs, but the values above $T-T_c=+0.7$ are much less certain. Although the attenuation in the paraelectric phase varied by $\pm35\%$ from one crystal to another, in every case it was observed that there was very little field effect. The data shown in Fig. 2 represent the *lowest* α values determined above T_c and are therefore considered to be the most reliable ones. However, it should be stressed that the principal result above about $T_c+0.7$ is the absence of any prominent effect due to the applied field.

In contrast to the asymmetric attenuation observed in KD*P, the KDP attenuation curves at 3 and 4 kV cm^{-1} are roughly symmetrical about the maximum value. This difference between KDP and KD*P is shown in Fig. 3, which presents the temperature variation of $\tau_{S,X}{}^{-1}$, the inverse adiabatic relaxation time at zero stress as determined from Eq. (8). For KD*P in the vicinity of the Curie temperature, Litov and Uehling[8] report that $(\partial\tau^{-1}/\partial T)_E=0.4\times10^{10}$ sec^{-1} deg^{-1} for $T>T_c$ and 3.0×10^{10} for $T<T_c$. For KDP at zero field, Garland and Novotny[7] report that $(\partial\tau^{-1}/\partial T)_E=4.2\times10^{10}$ in the paraelectric phase, whereas our limited present data give a slope of 2.8×10^{10} for $T>T_c$. Other values for $(\partial\tau^{-1}/\partial T)_E$ in KDP above T_c can be obtained from Eq. (3) and the Raman measurements of

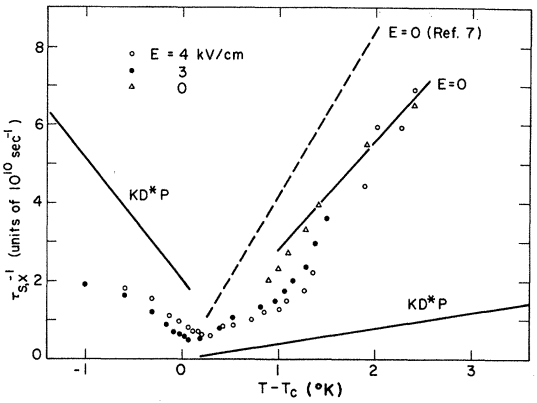

FIG. 3. Reciprocal adiabatic relaxation time $\tau_{SX}{}^{-1}$. The solid line for $E=0$ indicates the variation obtained from the present measurements; the dashed line represents the more extensive zero-field results of Ref. 7. The lines labeled KD*P represent data obtained in Ref. 8 on KD_2PO_4 at $E=1.5$ kV cm^{-1}. (It should be noted that a first-order discontinuity is observed in KD*P.)

Kaminow and Damen[16] ($\partial\tau^{-1}/\partial T\simeq1.5\times10^{10}$) and from the microwave transmission data of Gauss and Happ[17] ($\partial\tau^{-1}/\partial T\simeq8.5\times10^{10}$). In view of all these results, it is clear that there is a striking difference between the dynamic behavior of KDP and that of KD*P above T_c. On the other hand, the normal and deuterated salt have fairly similar dynamic behaviors in the ferroelectric phase. From the KDP data obtained in a limited range below T_c, we can roughly estimate that $(\partial\tau^{-1}/\partial T)_E\simeq1.6\times10^{10}$. It should also be noted that the field effect on τ^{-1} in the vicinity of T_c+1 is due almost completely to the variation of the c^E values with field rather than a direct effect on the α values.

DISCUSSION

The static aspects of this investigation will be discussed primarily in terms of the free susceptibility $\chi^{X,S}(0)$, which can be obtained from Eq. (5). The dynamic aspects will be presented in terms of the Landau kinetic coefficient L given in Eq. (2). This does *not* mean that our data indicate that the Landau model is preferable to a heavily damped harmonic-oscillator model. However, $L\equiv\chi(0)/\tau$ is a convenient way to compare the dynamic behavior with the static.

The results will also be compared with the predictions of the SUS order-disorder model.[9,18] In this model, the static properties are determined by the equilibrium arrangement of protons around the PO_4 groups. In addition to the various arrangements within Slater groups (two protons associated with a PO_4 ion), arrangements involving Takagi groups with one or three protons per PO_4 are also considered. The dynamical properties are determined by the average effective jump frequency of these Takagi groups. The basic parameters of the SUS model are the energy required to create a Takagi group ϵ_1, the energy required to rearrange the protons within

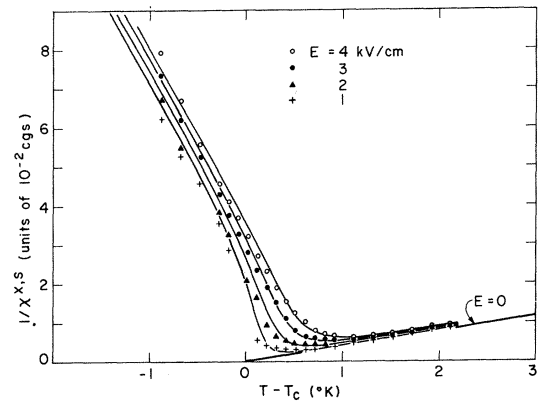

FIG. 4. Reciprocal of the free adiabatic susceptibility as a function of temperature. The straight line labeled $E=0$ represents directly measured dielectric data, which are characterized by a Curie constant of 259°K (Ref. 20). The smooth curves represent the predictions of SUS theory for the parameters of set 1.

a Slater group ϵ_0, and a long-range force parameter β.[9] Not all three of these parameters are independent since there is a relation among them involving the zero-field Curie temperature T_c. We have chosen ϵ_1 and ϵ_0 as the free parameters and have calculated β by using $T_c=122.085$ (the temperature at which our zero-field c_{66}^E values go to zero) and by assuming that the zero-field transition does not involve a first-order discontinuity. The small amount of first-order character indicated by Reese[12] would cause a negligible change in the calculated value of β.

Susceptibility. The reciprocal of the $\chi^{X,S}(0)$ values calculated from our elastic data with the aid of Eq. (5) are shown in Fig. 4. In determining these values, we have assumed that the piezoelectric strain constant is independent of applied electric field and have represented the weak temperature dependence by $b_{36}=[5.06-0.015(T\text{-}122)]\times10^{-7}$ cm dyn$^{-1/2}$.[19] The resulting values of $\chi^{X,S}$ can be compared above T_c with direct dielectric measurements by Baumgartner.[20] For fields of 1 and 2 kV cm^{-1}, the agreement is essentially perfect. For fields of 3 and 4 kV cm^{-1}, our $\chi^{X,S}$ values are slightly lower than Baumgartner's values close to T_c. Since Fig. 1 shows that our c_{66}^E values at 4 kV cm^{-1} are in excellent agreement with recent Brillouin data, the new $\chi^{X,S}$ values at high fields should be preferred over the older dielectric values. Below T_c one can obtain a Curie constant of 20.5°K by fitting the straight section of the $1/\chi^{X,S}$ curves at 2, 3, and 4 kV cm^{-1}. This value is to be compared with a direct dielectric value of 32°K determined at 1 kHz and 6.6 kV cm^{-1}.[14] Other values of C for $T<T_c$ can be obtained from Brillouin and microwave-transmission measurements at zero field: Brody[14] gives 22.8°K for $T_c>T>T_c-1$, Kaminow and Harding[21] give 17.5°K, and Gauss and Happ[17] give 17.0°K. It should also be noted that the ultrasonically determined C values are almost identical for KDP and KD*P: We find $C^+=259$°K and $C^-=20.5$°K while Litov and Uehling[8] report $C^+=(270\pm5)$°K and $C^-=22$°K. In both cases, the ratio C^+/C^- has the very high value ~12.5, in contrast to the mean-field prediction of 2.

For a SUS calculation of the free susceptibility, we begin by writing

$$\chi^T=\chi'+\chi_0, \tag{9}$$

where χ^T is the total isothermal susceptibility, χ' is SUS contribution due to the hydrogen and heavy-ion configurational changes, and χ_0 is a small additional contribution due to induction. The value of χ_0 is not well known, but we shall adopt the constant value of 0.5 which was used for KD*P[8] and was estimated for KDP at room temperature.[9] This choice is not very crucial since the χ values of interest lie in the range from 10 to 200. The quantity χ' is obtained from SUS Eq. (3b):

$$\frac{1}{\chi'}=\frac{2kT}{n\mu_0\mu_1}\frac{d\lambda}{dp}-\frac{1}{1-p^2}-\frac{\beta}{kT}, \tag{10}$$

where p is the fractional polarization; λ is a complicated function of p, T, E, and the SUS parameters ϵ_0 and ϵ_1 (we let $\epsilon_2=\infty$); μ_0 is the dipole moment associated with the saturation polarization ($\mu_0=P_s/n$, where n is number of PO_4 groups per cm^3); and μ_1 is a dipole moment which differs from μ_0 because of induced polarization and the effect of long-range forces.[9] At high temperatures, μ_0 and μ_1 are simply related to the Curie constant: $C^+=n\mu_0\mu_1/k$.

There is a difficulty associated with the choice of values for μ_0 and μ_1. For KD*P, the choice $\mu_0=1.8\times10^{-18}$ esu and $\mu_1=2.0\times10^{-18}$ esu is consistent with the other parameters and with the experimental value of both P_s and C^+.[8] However, in applying the SUS model to KDP it is not possible to choose μ_0 and μ_1 values which are consistent with both the experimental value of P_s and that of C^+. Thus we have tested two sets of values for μ_0 and μ_1. Set 1 is based on choosing μ_0 and μ_1 in a way consistent with the chosen β and χ_0 values and such that the experimental value of C^+ is reproduced by the model. In this case, the test of the model lies in the fit below T_c and in the magnitude of the field

TABLE I. SUS parameters used in calculating the free adiabatic susceptibility and the elastic constant c_{66}^E.

Quantity	Set 1	Set 2
χ_0 (cgs)	0.5	0.5
μ_0 (10^{-18} esu)	1.80	1.48
μ_1 (10^{-18} esu)	1.91	1.60
P_s (μC cm^{-2})	6.2 (calc)	5.12 (expt)
C^+ (°K)	259 (expt)	178 (calc)
ϵ_2/k (°K)	∞	∞
ϵ_1/k (°K)	450	450
ϵ_0/k (°K)	60	64
β/k (°K)	16.3[a]	13.9[a]

[a] Based on the experimental value $T_c=122.085$°K.

effect near T_c. Set 2 is based on choosing μ_0 by fitting the experimental value[22] of P_s, and then determining μ_1 from the chosen values of μ_0, β, and χ_0. In this case, the model is forced to fit well at low temperatures and the test of the model lies in the behavior near and above T_c. The two sets of choices for μ_0 and μ_1 are listed in Table I along with the value assumed for χ_0.

Once χ^T has been calculated, it is possible to obtain χ^S from the expression

$$\frac{1}{\chi^S}=\frac{1}{\chi^T}\left[1+\frac{T(\partial P/\partial T)_E^2}{\chi^T C_P}\right], \tag{11}$$

where C_P is the specific heat at constant polarization. The constant value 1.15 J deg^{-1} cm^{-3} was used for C_P,[23] and the SUS value was used for $(\partial P/\partial T)_E$. Calculated χ^S values were obtained for a wide choice of parameters in the range $\epsilon_1/k=350$–550°K and $\epsilon_0/k=55$–67°K, and the SUS parameters which yield the best fits are also listed in Table I. Figure 4 shows that the susceptibility can be fairly well represented using the parameters of set 1. No choice of parameters in set 2 did well at fitting $\chi^{X,S}$ values above T_c.

Another way to judge the SUS model is shown in Fig. 5 where the experimental c_{66}^E values are compared with the theoretical curves for both set 1 and set 2. Brody[14] has analyzed his Brillouin data in this way. Having tested only models like set 1 in which agreement with the experimental C^+ value is guaranteed, he reports a best fit for $\epsilon_1/k=475$°K and $\epsilon_0/k=63$°K. The small difference between our "best choice" of ϵ_0 and ϵ_1 and that reported by Brody is presumably due to the way in which he evaluated β and in the value chosen for C_P. In any case, a reasonably unique set of SUS parameters can be found to represent the static behavior. However, as we shall see, the SUS model is not adequate for the interpretation of the dynamical behavior in KDP.

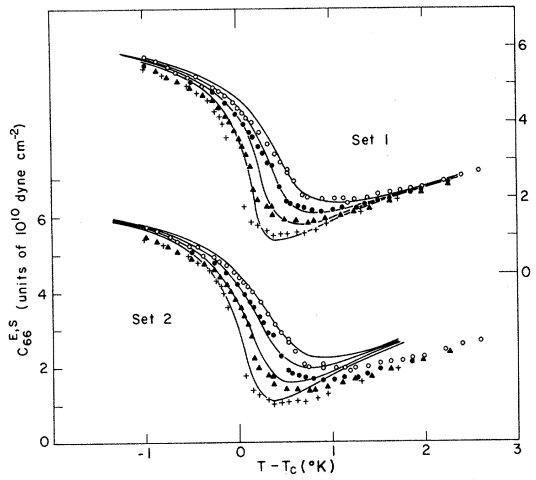

FIG. 5. Comparison of experimental $c_{66}^{E,S}$ values with those predicted by the SUS model. Values of the parameters used in set 1 and set 2 are given in Table I.

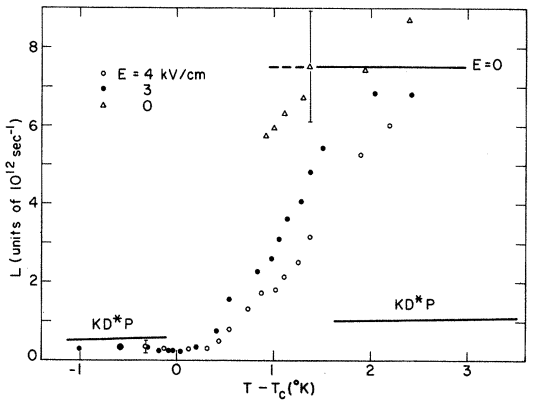

FIG. 6. Temperature dependence of the Landau kinetic coefficient $L\equiv\chi(0)/\tau$. The KD*P lines represents data from Ref. 8. The line labeled $E=0$ represents an estimate of the asymptotic value of L above T_c.

Polarization relaxation. Litov and Uehling[8] show that SUS theory predicts

$$\frac{1}{\tau_{S,X}}=\frac{n\mu_0\mu_1}{2\tau_c kT}\frac{1}{\chi^{X,S}}, \tag{12}$$

or, in terms of the Landau coefficient,

$$L=\frac{n\mu_0\mu_1}{2kT}\frac{1}{\tau_c}=\frac{n\mu_0\mu_1}{2kT}\frac{x_T}{\tau_0}. \tag{13}$$

The quantity τ_c is the correlation time for the motion of Takagi groups and equals τ_0/x_T, where x_T is the density of the Takagi groups and τ_0^{-1} is the mean effective jump frequency for a single Takagi group.

Figure 6 compares the experimental temperature dependence of the Landau kinetic coefficient L for KDP with that observed for KD*P. In the latter case, it was possible to choose a temperature-independent value of 1.6×10^{-14} sec for τ_0 and to explain the difference in the values of L above and below T_c in terms of changes in the density of the Takagi groups.[8] Such an interpretation of the data is not possible for KDP since the SUS model with a constant value of τ_0 cannot reproduce the strong temperature dependence shown in Fig. 6. The zero-field value of L inferred from Garland and Novotny's data over a 10 degree range in the paraelectric phase[7] is $(11\pm2)\times10^{12}$ sec^{-1}, which is in fair agreement with the asymptotic value of ~8 that we have found above T_c. Thus the rate of polarization relaxation in the disordered phase is approximately 10 times faster in the normal compound than in the deuterated compound. [Part of this difference may be explained by the somewhat larger value of x_T in KDP, but Eq. (13) would require that τ_0 have a value of $\sim0.3\times10^{-14}$ sec above T_c.]

Below T_c, the two compounds are more similar and it is possible to fit the L values for KDP with the SUS model by choosing $\tau_0=12\times10^{-14}$ sec for set 1 or 10×10^{-14} sec for set 2. These values would appear to be

rather high, but it should be pointed out that they are very sensitive to the choice of the parameter ϵ_1.[24] Roughly comparable τ_0 values have been obtained in KD*P from dielectric and domain-wall studies ($\tau_0 \sim 2\times 10^{-14}$ sec) and from deuteron spin relaxation measurements ($\tau_0 \sim 8\times 10^{-14}$ sec).[18]

The present results would suggest that proton tunneling plays a much more important role in KDP than deuteron tunneling does in KD*P. The use of the SUS order-disorder model to fit the behavior below T_c is based on the view that even in KDP one can neglect tunneling in the ordered phase. In that case, the parameters of set 2 would be the most appropriate choice and the failure of the model to predict C and L accurately above T_c could be explained by tunneling. This is an attractive view since one would expect appreciable tunneling to occur only when there is a symmetrical double minimum in the potential for the hydrogen motion.[25]

In recent years, there have been several theoretical treatments of the phase transition in KDP which explicitly include the tunneling of protons. The model proposed by Tokunaga and Matsubara[26,27] emphasizes the role of K^+ and $PO_4^=$ ionic displacements but includes an interaction between the ions and the proton tunneling motion. In this theory, the order-disorder arrangement of dipole moments associated with ionic displacements will lead to a transition even in the absence of a collective proton mode. On the other hand, Kobayashi[28] has proposed a model which takes ionic motion into account without assuming an order-disorder behavior. In his model the proton tunneling mode is strongly coupled with an optical lattice vibration along the z axis, and the frequency of one of the coupled modes goes to zero at T_c. This soft-mode model of Kobayashi has been used by Inoue[29] as the basis of a treatment of the critical sound attenuation in KDP. Inoue assumed that the acoustic phonon is coupled to the soft ferroelectric mode via third-order anharmonic interaction (which has the same form as an electrostrictive interaction) and also assumed a one-dimensional model. Thus his result can be applied only to the case of a sound wave propagating *parallel* to the polar axis and can not be used to interpret our present experiment. Hopefully, further theoretical work on critical attenuation in KDP will be stimulated by the presentation of these results on KDP and those of Litov and Uehling[8] on KD*P.

Note added in manuscript. After this paper had been submitted for publication, it was called to our attention that Harnik and Shimshoni[30] have recently studied the propagation of longitudinal ultrasonic waves along the ferroelectric axis in KDP. On the basis of zero-field attenuation and velocity data, they conclude that $(\partial\tau^{-1}/\partial T)_E = 4\times 10^{12}$ sec^{-1} deg^{-1} in the polar phase. This value is more than 2 orders of magnitude greater than the value which we have found at 3 and 4 kV cm^{-1} for $T<T_c$. The reason for this enormous discrepancy is not clear. The phenomenological approach used to analyze their data appears to be directly analogous to that used here. However, we note that the longitudinal velocity variation does not seem to follow the dielectric behavior in the same manner as do our shear velocities. Thus, the same relaxation formalism may not apply in both cases. The suggestion that proton tunneling is not very important in the polar phase is, of course, based on the similarity of the $\chi(0)\tau^{-1}$ values in KDP and KD*P for $T<T_c$ (see Fig. 6). The situation would be completely different if one adopted the relaxation times reported by Harnik and Shimshoni.

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