not the characteristic mode of the order parameter in region I. In contrast to the magnetic system, the gas-liquid transition does not have a propagating critical mode $\omega^{\Psi}(\mathbf{k})$, either above or below the transition. The fluid system which is most closely analogous to magnetic systems (in particular, antiferromagnets) is superfluid helium, where the critical mode is *second* sound (analogous to spin waves) below T_λ, and a nonhydrodynamic relaxation mode $[\omega^{\psi}(0)\neq 0]$ above T_λ.

The scaling viewpoint gives a unified description of a wide variety of critical phenomena, both static and dynamic. Although it is too early to tell whether any of the new predictions of the dynamic theory are exactly correct, it is hoped that the qualitative picture can already be a useful guide to further experimental investigation. As more accurate experimental results become available, and more detailed microscopic and phenomenological theories are developed, their results can be compared to those of the scaling theory. The specific mathematical assumptions of dynamic scaling can then be put to a test, and the reasons for their success or failure investigated.

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Ultrasonic Velocity and Attenuation in KH_2PO_4†

CARL W. GARLAND AND DONALD B. NOVOTNY*

Department of Chemistry, Research Laboratory of Electronics, and Center for Materials Science and and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The velocity and attenuation of ultrasonic shear waves have been investigated at temperatures above $T_C=121.8_2$°K in single-crystal KDP. An elastic Curie-Weiss law, $(s_{66}^E-s_{66}^P)=D/(T-T_C)$, is obtained with an elastic Curie constant D equal to 6.31×10^{-11} dyn^{-1} cm^2 deg. The attenuation data are consistent with a cooperative relaxation time at constant stress τ which varies as $\tau=24\times10^{-12}/(T-T_C)$ sec.

INTRODUCTION

At a Curie temperature of ~122°K, potassium dihydrogen phosphate (KDP) undergoes a cooperative transition from a paraelectric to a ferroelectric phase.[1,2] There has been a great deal of current interest, both theoretical[3–7] and experimental,[8–11] in this transition and the analogous transition at ~223°K in KD_2PO_4. The present ultrasonic investigation involves the measurement of the anomalous shear velocity and attenuation at temperatures above T_C.

In its paraelectric phase, KDP is tetragonal $(m)\bar{4}2$ and the x_y mechanical strain is coupled to the polarization along the ferroelectric z axis. Therefore, a transverse ultrasonic wave propagating in the [100] direction with its polarization in the [010] direction is the shear wave of interest. The elastic constant related to this shear is called c_{66}, but there are two limiting values of this constant depending on the electrical boundary conditions. One can specify the elastic properties at constant dielectric displacement (c^D) or at constant electric field (c^E). Mason's low-frequency resonance measurements[12] on bare and on plated crystals show that c_{66}^D exhibits a normal linear temperature dependence above T_C, whereas c_{66}^E drops toward zero at the Curie point. Elastic shear constants of KDP measured at ultrasonic frequencies have been shown by Jona[13] to correspond to c^E; thus, we have determined $c_{66}^E=\rho U^2$, where ρ is the density and U is the ultrasonic velocity.

In addition to the rapid decrease in velocity, there is an anomalous increase in the attenuation of this shear wave as the temperature approaches the Curie point. Since KDP is still piezoelectric in its paraelectric phase, there is a strong coupling between the elastic wave and the polarization even above T_C. Thus, attenuation measurements provide a convenient way to determine the polarization relaxation time. As in other cases

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* Research Associate in Chemistry. Present address: Mechanics Division, National Bureau of Standards, Washington, D. C. 20234.

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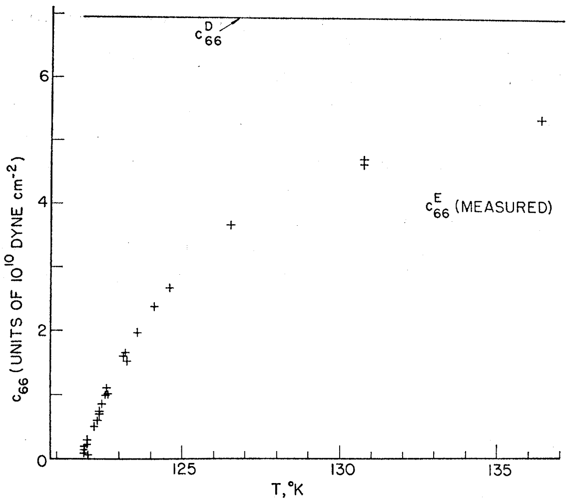

FIG. 1. Shear stiffness c_{66} versus temperature. $c_{66}{}^E$ values were obtained directly from ultrasonic velocity data; the smooth curve dependence of $c_{66}{}^D$ is taken from Mason (Ref. 12).

involving the relaxation of long-range order parameters in cooperative systems,[14] one expects a very rapid increase in the relaxation time near T_C. Recently, Geguzina and Krivoglaz[15] have discussed both the velocity and attenuation of ultrasound in a ferroelectric near its Curie point, and our experimental results will be compared with their predictions.

EXPERIMENTAL RESULTS

The ultrasonic equipment used in this work is essentially the same as that used previously for investigating ammonium chloride.[16] However, a new sample holder was constructed to permit two-transducer operation. This sample holder fitted inside a heavy copper cylinder wound externally with a heating coil. The entire assembly was suspended coaxially in a long Pyrex jacket, which was immersed in a Dewar of liquid nitrogen. The temperature of the sample assembly was set by adjusting the pressure of helium gas in the jacket and by regulating the current in the heating coil. Temperature stability of ±0.002°K was achieved with a Fisher Proportional Temperature Control by using a low-temperature thermister (Keystone Carbon Co.) as the thermal sensor. Temperatures were measured with a Rosemount Engineering Corp. platinum resistance thermometer (Model 146L-2), a 100-Ω calibrated standard resistance, and a Wenner potentiometer. The resistance thermometer was calibrated by Rosemount at five fixed points, including the ice point and the boiling point of nitrogen, and the absolute accuracy was reported to be ±0.02°K. The precision of our temperature measurements was ±0.001°K.

Oriented single crystals of KDP were obtained from the Harshaw Chemical Co. with $\sim$1 cm path lengths in the [100] direction. *Y*-cut quartz transducers were bonded to the KDP with *n*-propyl alcohol, and good echo patterns were obtained below its freezing point at 146°K. Attempts to use Nonaq stopcock grease or Dow-Corning 200 silicone fluid were unsuccessful since these bonds failed at about 190°K on cooling. Most of the data were obtained using 10-MHz transducers specially polished for overtone use, although velocity measurements within 0.5 deg of T_C were made with 1-MHz transducers because of the very high attenuation at 10 MHz. All velocity measurements were made by the pulse-echo method, which is quite adequate (less than 1% uncertainty in U) since the delay times are long (12–100 μsec). Attenuation measurements were made at 10, 30, 50, 70 and 90 MHz, and the differences between the amplitude of successive echoes were in reasonably good agreement (±10%). For high-frequency data close to T_C, the acoustic loss became greater than 30 dB/echo and only two echoes were measurable; in these cases the uncertainty in the attenuation values is probably greater.

Attempts were made to pole the KDP crystal by applying a field along the z axis, but these were not successful, and no echoes could be observed below T_C (presumably because of domain scattering). Above T_C, the results are given for zero applied field.

Unsmoothed data for the shear velocity at various temperatures were used to obtain the $c_{66}{}^E$ elastic-constant values shown in Fig. 1. The present values agree well with those reported by Mason,[12] and they extend much closer to the critical temperature (a value

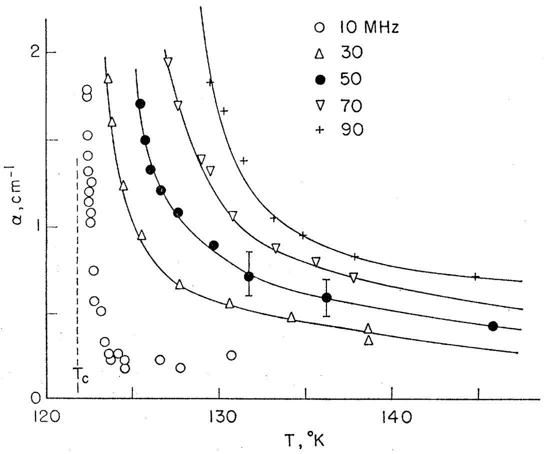

FIG. 2. Attenuation coefficient α, in neper cm^{-1}, at various ultrasonic frequencies. The value of T_C, as determined from the velocity data, is also shown. The smooth curves through the data points at 30, 50, 70, and 90 MHz were drawn independently with no attempt being made to force these curves to conform to a common shape.

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of 0.094×10^{10} dyn cm^{-2} was obtained at 121.88°K, whereas Mason's lowest value was 3×10^{10} at around 125°K). The essentially normal variation of c_{66}^D is also shown in Fig. 1 for comparison; between 122 and 136°K this quantity only varies from 6.955×10^{10} to 6.893×10^{10} dyn cm^{-2}.

Figure 2 shows the attenuation α as a function of temperature for five different frequencies. The overtone measurements at 30–90 MHz were all made at one time on the same KDP crystal, whereas the data at 10 MHz were obtained at a later time on a different crystal. It is clear from Fig. 2 that the background attenuation for the 10-MHz run is lower than that for the other frequencies, and this will have to be taken into account in the analysis of the data.

DISCUSSION

Velocity data. The anomalous temperature dependence of the various equilibrium properties of a ferroelectric crystal can be correlated by a general thermodynamic analysis. In terms of the notation used by Känzig,[1] one finds for KDP that

$$(s_{66}^E-s_{66}^P)^{-1}=\chi_{33}'/b_{36}^2,\quad (c_{66}^P-c_{66}^E)^{-1}=\chi_{33}''/a_{36}^2,\quad (1)$$

where s_{66} is the elastic compliance ($=1/c_{66}$) at constant zero field (s^E) or constant polarization (s^P), χ_{33}' is the reciprocal susceptibility parallel to the z axis in the free crystal, χ_{33}'' is the reciprocal susceptibility in the clamped crystal, a_{36} is the piezoelectric stress constant, and b_{36} is the piezoelectric strain constant. In a high-dielectric-constant material, the elastic properties at constant polarization are essentially identical to those measured at constant dielectric displacement. Thus, no distinction will be made between c^D and c^P.

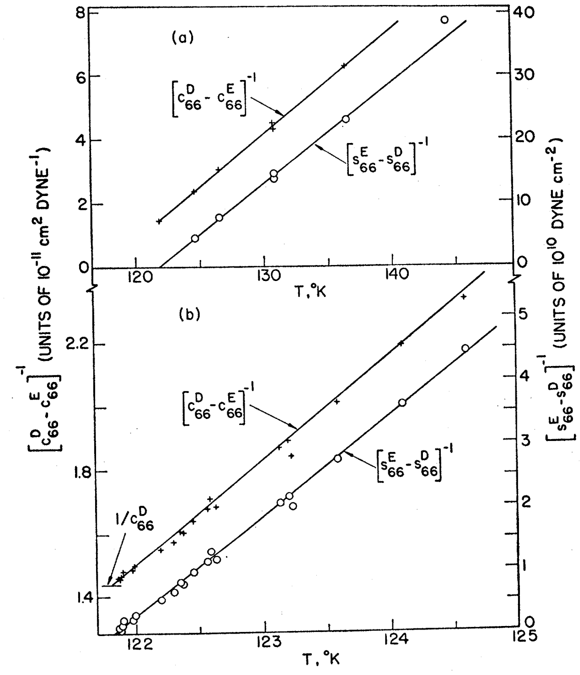

FIG. 3. Elastic Curie-Weiss plots. On the assumption that $c^P(s^P)$ is equal to $c^D(s^D)$, these plots correspond to the two forms of Eq. (3). Data are shown over a wide temperature interval in (a), whereas much more detailed data close to T_C are shown in (b). The corresponding lines in (a) and (b) are identical, i.e., drawn with the same slopes and intercepts.

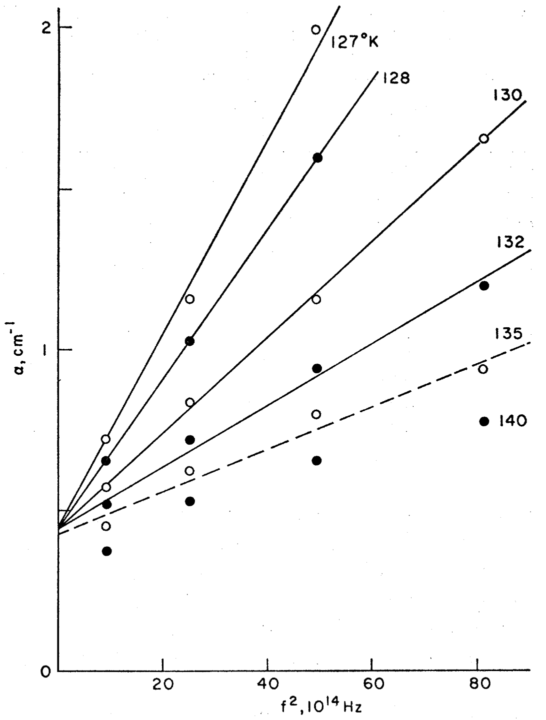

FIG. 4. Plot of α versus f^2 at various constant temperatures. Points were read from the smooth curves in Fig. 2. The dashed line represents a possible linear fit to the 135°K data.

The dielectric susceptibilities are known to follow a Curie-Weiss law

$$\chi_{33}'=(T-T_C)/C,\quad \chi_{33}''=(T-T_0)/C,\quad (2)$$

where the Curie constant $C=259$°K for KDP.[1] In Eq. (2), T_C is the actual temperature at which spontaneous polarization appears, and T_0 is used to denote the lower temperature at which a clamped crystal would become ferroelectric if "spontaneous strain" did not occur at T_C. Combining Eqs. (1) and (2), one obtains

$$\begin{aligned}(s_{66}^E-s_{66}^P)^{-1}&=(T-T_C)/D,\\ (c_{66}^P-c_{66}^E)^{-1}&=(T-T_0)/D_0,\end{aligned}\quad (3)$$

where $D=Cb_{36}^2$ and $D_0=Ca_{36}^2$. Either form of Eq. (3) can be called an elastic Curie-Weiss law, where D or D_0 are the elastic Curie constants.[1,2]

The present ultrasonic velocity data (c^E values) and Mason's data for c^D can be combined to test both forms of Eq. (3). The appropriate plots are shown in Fig. 3, which indicates that the elastic Curie-Weiss law is well

TABLE I. Values of $(\partial\alpha/\partial f^2)_T$ and of $(\alpha-\alpha_0)/f^2$ at 10 MHz, together with values of $C(T)$ calculated from Eq. (6), and the resulting values of the relaxation time τ.

T, °K	$T-T_C$, °K	$(\partial\alpha/\partial f^2)_T$, 10^{-17} cm^{-1} sec^2	$C(T)$, 10^{-7} cm^{-1} sec	τ, 10^{-12} sec
135	13.18	6.55	8.37	1.98
132	10.18	9.72	10.46	2.35
130	8.18	15.0	12.57	3.02
128	6.18	23.5	15.77	3.78
127	5.18	30.4	18.36	4.19
		$(\alpha-\alpha_0)/f^2$		
123.5	1.68	140	39.9	8.9
123.1	1.28	320	47.3	17.1
122.7	0.88	620	59.2	26.5
122.5	0.68	1020	68.8	37.5
122.3	0.48	~1600	83.5	~49

obeyed over a wide temperature interval. The Curie temperature T_C as determined for our sample from the elastic properties is 121.8_2°K, while the value of T_0 is found by extrapolation to be 117.4_5°K. The difference $T_C-T_0=4.37$°K is in good agreement with that obtained from dielectric measurements,[1] and our value for T_C can be compared with the values 121.97 and 121.71_5°K obtained from thermal measurements[17] and 122.0°K obtained from Brillouin scattering.[10] From the slopes of the straight lines drawn in Fig. 3, one obtains $1/D=1.585\times10^{10}$ dyn cm^{-2} deg^{-1} and $1/D_0=3.30\times10^{-12}$ cm^2 dyn^{-1} deg^{-1}. Thus, $D=6.31\times10^{-11}$ dyn^{-1} cm^2 deg and $D_0=3.03\times10^{11}$ dyn cm^{-2} deg. It can easily be shown that $D/D_0\equiv(s_{66}{}^P)^2$. Since $s_{66}{}^P(=s_{66}{}^D)$ varies by only 0.6% over 10 deg, the $s_{66}{}^D$ value at 123°K can be used to test the internal consistency of the two straight lines shown in Fig. 3. One finds that $D/D_0=2.08\times10^{-22}$, in good agreement with $(s_{66}{}^P)^2=(1.438\times10^{-11})^2=2.067\times10^{-22}$. Another check on the data involves comparing the experimental value of D with the value calculated from $D=Cb_{36}{}^2$. According to data cited by Känzig,[1] the piezoelectric constant b_{36} varies from 5×10^{-7} at 122°K to 4.9×10^{-7} at 127°K. On the assumption that $b=4.95\times10^{-7}$ and $C=259$ the calculated value of D is 6.35×10^{-11}, and this value is probably uncertain by ±3%. In any case, the present elastic results are in much better agreement with the dielectric and piezoelectric data than the earlier data of Mason, which indicated that D was 4.6×10^{-11} dyn^{-1} cm^2 deg.[12]

The analysis by Geguzina and Krivoglaz[15] of the velocity of ultrasonic shear waves in a ferroelectric crystal having one polar axis indicates that at acoustic frequencies

$$\rho U^2=\rho U_\infty{}^2(\chi'/\chi'')=\rho U_\infty{}^2-a^2/\chi''. \tag{4}$$

This is identical with the static thermodynamic result given in Eq. (3) if ρU^2 is equated to c^E and $\rho U_\infty{}^2$ is equated to c^P. We have already used the relation $\rho U^2=c^E$ in calculating our c^E values, and the relation $\rho U_\infty{}^2=c^P(=c^D)$ will be used below in analyzing the attenuation data. This latter relation is clearly valid since at infinite frequency the polarization would not be able to follow the applied stress and the effective (or "frozen") elastic constant would correspond to a constant polarization.

Evidence that our velocity data at 10 MHz were obtained at a sufficiently low frequency to correspond to static $c_{66}{}^E$ values is provided by the relaxation times obtained below. These τ values indicate that velocity dispersion should be negligible at 10^7 Hz and very small (<1%) even at 5×10^9 Hz. This is confirmed by very good agreement between our velocity data and Brillouin data obtained at frequencies ranging from 0.5×10^9 to 5×10^9 Hz.[10] Thus dispersion measurements at frequencies below 10^{10} Hz are not very suitable for determining the relaxation times in KDP, and we must turn to an analysis of ultrasonic losses.

Attenuation data. Landau's theory of the relaxation of a long-range order parameter near a critical point was first applied to ferroelectric crystals by Yakovlev and Velichkina[18] and more recently by Geguzina and Krivoglaz[15] (see also Refs. 14 and 16). For a mechanism involving a single relaxation time associated with the polarization, one finds that the low-frequency ultrasonic attenuation in KDP can be written in the form[15]

$$\alpha=\alpha_0+C(T)\omega^2\tau, \tag{5}$$

where α_0 is a largely instrumental background attenuation and $C(T)$ is a function of the shear velocities which is highly temperature-dependent. With

$$C(T)=(U_\infty{}^2-U_0{}^2)/2UU_\infty{}^2, \tag{6}$$

the corresponding relaxation time is τ_X, the relaxation time at constant (zero) stress. It is also possible to choose $C(T)=(U_\infty{}^2-U_0{}^2)/2UU_0{}^2\simeq(U_\infty{}^2-U_0{}^2)/2U_0{}^3$ and thus obtain τ_x, the relaxation time at constant strain.[19] These two relaxation times are simply related by

$$\tau_X/\tau_x=c_{66}{}^P/c_{66}{}^E=\chi_{33}{}''/\chi_{33}{}'. \tag{7}$$

We shall consider only τ_X. (For convenience, the subscript X will be dropped from τ_X in the subsequent discussion.) For this case, $C(T)$ in Eq. (6) can be expressed in terms of the elastic constants by $C(T)=\rho^{1/2}(c_{66}{}^P-c_{66}{}^E)/2c_{66}{}^P(c_{66}{}^E)^{1/2}$, which can be calculated directly from the data shown in Fig. 1. According to Geguzina and Krivoglaz,[15]

$$\tau=\gamma^{-1}/\chi'=A/(T-T_C), \tag{8}$$

where γ is a temperature-independent rate constant describing the time variation of the polarization and

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$A=C\gamma^{-1}$. Thus, we can analyze the attenuation data in Fig. 2, obtain experimental values of $\tau(T)$, and compare these results with Eq. (8).

As long as $\omega^2\tau^2\ll 1$, Eq. (5) indicates that the excess attenuation $\alpha-\alpha_0$ at any given temperature should increase as f^2. Figure 4 shows a plot of α versus f^2 for each of six different temperatures between 127 and 140°K. The points shown in this figure were read directly from the smooth curves in Fig. 2; no 10-MHz data have been used since there is practically no overlap in temperature between the excess attenuation at 10 MHz and the data obtained at higher frequencies and since the background α_0 value is also different. The data shown in Fig. 4 are quite consistent with a f^2 dependence at 127, 128, 130, and 132°K. At 135°K the data show appreciable curvature, and the dashed line drawn at that temperature represents a reasonable linear fit which is consistent with the other lines. No attempt has been made to fit the 140°K points, which correspond to readings quite far out in the tail of the curves of Fig. 2. It would appear from Fig. 4 that α_0 has a constant value (0.45 cm^{-1}) over the small range 127–135°K. The slopes $(\partial\alpha/\partial f^2)_T$ obtained from Fig. 4 are given in Table I along with the appropriate values of $C(T)$. Since $(\partial\alpha/\partial f^2)_T=4\pi^2C(T)\tau$, one can immediately obtain the value of τ at each temperature.

The 10-MHz attenuation data were treated separately to obtain values of τ very close to the Curie point. For this purpose, α_0 was assigned the constant value 0.18 cm^{-1} (which is the experimental 10-MHz value of α at 125°K and above). The resulting values of $(\alpha-\alpha_0)/f^2$ and $C(T)$ are listed in Table I for five temperatures in the range 122.3–123.5°K.

The reciprocals of the τ values in Table I are plotted against temperature in Fig. 5. On the basis of Eq. (8), one would expect τ^{-1} to be linear in T and to vanish at $T=T_C$, and the data certainly seem to be consistent with that conclusion.[20] The straight line shown in Fig. 5 is given by

$$\tau=24\times10^{-12}/(T-T_C)\text{sec},\tag{9}$$

and this provides a reasonable fit to the two somewhat scattered groups of data points. In retrospect, it might be desirable to have more data in the temperature range 123–128°K, and this could be obtained best by working at the odd harmonics of a 5-MHz transducer. However, it is worthwhile to mention that such short relaxation times (2–50×10^{-12} sec) can only be determined from acoustic measurements at 10^7–10^8 Hz because of the unusually large values of $C(T)$ near T_C. In contrast to the $C(T)$ values given for KDP in Table I (8–80×10^{-7}), the corresponding C values in NH_4Cl near its λ point[16] are only ~0.3×10^{-7}. In view of the very rapid temperature variation in both α and $C(T)$ for KDP, it is not surprising that the temperature dependence of τ is somewhat difficult to determine.

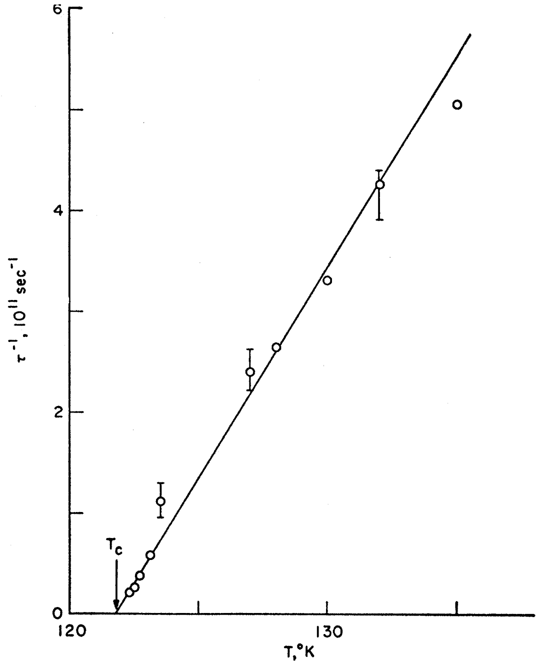

FIG. 5. Plot of τ^{-1} versus T.

The above results for KH_2PO_4 can be compared with those of a recent ultrasonic investigation[11] of KD_2PO_4, in which it was found that $\tau=24.4\times10^{-11}/(T-T_C)$, where $T_C=205.6$°K for the incompletely deuterated sample studied. This tenfold increase in the relaxation time on deuteration seems quite reasonable in view of the proton tunneling which is an intrinsic feature of this ferroelectric transition.[7]

Both the Brillouin work[10] on KH_2PO_4 and the ultrasonic work[11] on KD_2PO_4 show interesting features in the region below T_C. Therefore, it would be of interest to improve our technique for poling KDP crystals and investigate the ferroelectric phase at ultrasonic frequencies. Such an investigation is now in progress.

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[20] It should be noted that τ_x, the relaxation time at constant strain, is given by $\tau_x=A/(T-T_0)$. Thus τ_x will have the finite value $A/(T_C-T_0)$ at the Curie point in contrast to τ, which diverges.