Polarization Relaxation and Susceptibility in the Ferroelectric Transition Region of KD_2PO_4†

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Previously published results on the propagation characteristics of sound waves in KD_2PO_4 are analyzed phenomenologically to give the electric susceptibility and the polarization relaxation rate above and below the transition temperature. These results are then compared with the predictions of a modified Slater-Takagi order-disorder model of the phase transition in this crystal. The comparison of susceptibility and relaxation rate as deduced in the sound-propagation experiment with analogous data obtained from direct dielectric and other experiments is moderately good. The comparison with the predictions of the order-disorder model are probably as good as can be expected in view of the simplicity of the model. In particular, the high ratios of slopes in the temperature dependence of the relaxation rate and the reciprocal susceptibility above and below the transition temperature are correctly given using the measured values of certain critical parameters of the order-disorder model and reasonable values of other parameters which are not separately measured.

I. INTRODUCTION

IT is well known that sound waves exhibit anomalous propagation characteristics in the neighborhood of the phase-transition point of ferroelectric crystals. This has been demonstrated[1–12] both for ferroelectrics that are piezoelectric in the paraelectric region and for those which are not, and both for ferroelectrics in which the transition mechanism is believed to be mainly of the order-disorder type and those for which a displacive mechanism is believed to be more nearly valid. In nearly all of these experiments, the principal emphasis has been on obtaining the attenuation and velocity of sound data and then proceeding by a phenomenological interpretation to the electric susceptibility and the polarization relaxation time. It has been regarded as quite satisfying that in most cases the determination of susceptibility and relaxation time by this procedure is in reasonably good agreement with the values and temperature dependence of these quantities as determined by other experiments insofar as reliable data are available. In particular, the experiments have shown that the difference of elastic constants at constant polarization and constant field satisfy a Curie-Weiss law both below and above the transition temperature, and the phenomenological interpretation of the data has led to Curie-Weiss laws for the polarization relaxation rate and for the electric susceptibility with the correct values of the Curie constant in the case of the latter.

The motivation for the experiment[11] that has provided sound-propagation data specifically on KD_2PO_4 has been somewhat different. This crystal in its deuterated form has been studied in some detail by nuclear magnetic resonance methods,[13,14] and it has been established that the deuteron experiences a temperature-dependent jump motion between two equilibrium positions in the hydrogen bond, which becomes a biased motion in the ferroelectric phase when one position has a higher probability of occupation than the other. The temperature-dependent jump time has been measured in the paraelectric phase where its contribution to deuteron spin relaxation is sufficiently large to make such a measurement possible. The activation energy associated with the jump motion in this phase has been identified also as one of the significant energy parameters of the Slater-Takagi[15] order-disorder model of the ferroelectric phase transition, and its measured value was found to be almost precisely that which was required to give the observed shape of the spontaneous polarization curve.[14,16] But the jump time had not been accurately measured in the transition region, and other implications of the order-disorder model based on measured order-disorder parameters had not been fully tested. It is for these reasons that

† Research supported in part by the National Science Foundation.
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[11] E. Litov and E. A. Uehling, Phys. Rev. Letters **21**, 809 (1968).
[12] C. W. Garland and D. B. Novotny, Phys. Rev. **177**, 971 (1969).
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[15] J. C. Slater, J. Chem. Phys. **9**, 16 (1941); Y. Takagi, J. Phys. Soc. Japan **3**, 271 (1948); **3**, 273 (1948).
[16] H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. **133**, A165 (1964). Subsequent references to this paper will employ the designation SUS.

the sound-propagation experiments in KD_2PO_4 were undertaken.

A brief description of the experimental procedure will be given in Sec. II and of the experimental results in Sec. III. This will be followed in Sec. IV by an outline of the procedure used to reduce the data on velocity of sound and attenuation to expressions for the electric susceptibility and the polarization relaxation rate as functions of the temperature. A comparison of these results on susceptibility and relaxation with analogous data obtained in dielectric, Raman, and Brillouin scattering and other experiments will also be given. A microscopic interpretation will be described in Sec. V. This will be based on the order-disorder model of Slater and Takagi,[15] somewhat modified by the inclusion of long-range as well as short-range forces and by the introduction of a basic jump time for the motion of Takagi defects. The comparison of predicted susceptibility and relaxation as a function of temperature above and below the transition temperature with the results deduced from experiment should provide a moderately rigorous test of the model. This comparison is given in some detail. Further discussion of the comparison and the possible role of other models is given in Sec. VI.

II. EXPERIMENTAL METHOD

The pulse-echo method with a single-ended transducer was used to measure relative attenuation and velocity. Optical grade single crystals of KD_2PO_4 with 84% deuteration, Curie temperature $T_c = 205.6°K$, and lateral dimensions of 8 mm and 12 mm along the a and b axes and 12 mm along the c (polarization) axis were used. The electrodes for the E field in the sample were painted on the faces perpendicular to the polarization axis with a thin layer of conducting silver paint. A buffer rod of quartz was inserted between the transducer and the sample in order to ensure that the electric field in the sample would not be distorted by the metallic surfaces of the transducer. Furthermore, in order to keep the electric field uniform inside the crystal and at the edges, as well as to insure good electrical contact with the silver paint electrodes, brass plates slightly larger than the faces perpendicular to the c axis were pressed lightly against them.

The KD_2PO_4 crystal assembly is shown in Fig. 1. The transducer, delay line, and sample were mounted in a brass holder, which in turn was inserted into a narrow copper container. Cooling was provided by cold N_2 gas flowing in copper tubing wound around the copper container. Heating was provided by current in a coil of nichrome wire which was also wound around the copper container. The over-all temperature accuracy was about $\pm 0.015°C$.

Since in KH_2PO_4-type crystals a mechanical shear strain in the a-b plane of the crystal is coupled to polarization along the c axis, a transverse sound wave was used. The wave was propagated along the a (or b) axis and polarized along the b (or a) axis. Measurements were made at four frequencies between 5 MHz and 45 MHz. An electric field of 1.5 kV/cm parallel to the c axis was applied. A field of this magnitude is sufficient to reduce the entire crystal to a single domain in the ferroelectric phase, as verified directly by optical methods. Also it was observed that further increases in the magnitude of the field produced no appreciable change in the measured attenuation in the ferroelectric phase. However, an appreciable reduction in the field below 1.5 kV/cm causes an increase in attenuation, and in zero field below the transition temperature, the crystal is completely opaque to sound waves in the frequency range of interest.

Attenuation and velocity of sound were measured simultaneously as a function of temperature and frequency. Attenuation was measured by observing the height of the first pulse in the train of pulses reflected between opposite faces of the crystal and comparing with the pulse height at a standard reference temperature of 235°K, above which the attenuation remained constant at all frequencies used in this experiment. The velocity was measured by observing the time interval between successively reflected pulses and using the measured thickness of the sample. The time measurement was made using the variable-calibrated trigger delay of the oscilloscope. Some care was required to ensure that temperature equilibrium in the sample had been reached. Below the transition temperature most satisfactory results were obtained by taking data with temperature increasing.

III. EXPERIMENTAL RESULTS

The principal results have been published previously,[11] but will be summarized again for ready reference in the discussion which is to follow.

The attenuation α in dB cm^{-1}, as a function of temperature for several frequencies, is shown in Fig. 2. It is of interest to note the sharp decrease in attenuation with decrease of temperature on the low-temperature side of T_c in comparison with the rate of change on the high-temperature side. This will be reflected in the high rate of change of the polarization relaxation rate in the ferroelectric phase analogous to the high rate of change of the reciprocal susceptibility. It may be noted also that sound-attenuation measurements are not easily used to explore the region very close to T_c. On the high-temperature side the attenuation is simply too large for good measurements within a few degrees of T_c, depending on the frequency, and on the low-temperature side it is difficult to get reproducible results for α within a range of about 0.1°C of the transition. A somewhat better picture of the reliability of data obtained below T_c may be obtained from Fig. 3, which shows α as a function of T on an expanded scale using data from several different samples and, hence, different runs. Each of the curves is terminated within a range of a

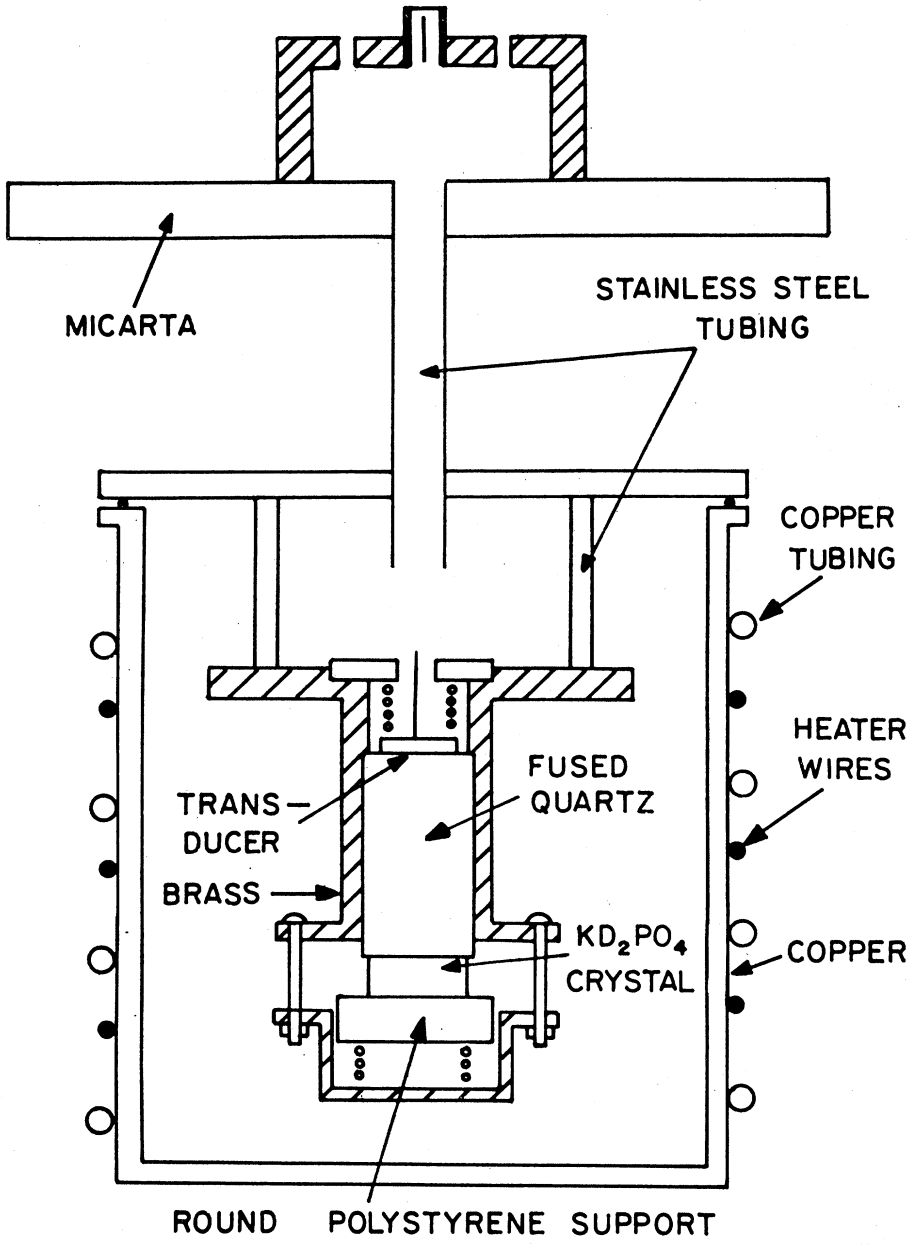

FIG. 1. Crystal assembly.

few tenths of a degree of T_c, within which the attenuation measurement was not strictly reproducible.

The linear dependence of α and ω^2 at all temperatures, except possibly very close to T_c, is shown in Figs. 4 and 5 for temperatures above and below T_c, respectively. The solid lines drawn to represent the best fit to the data to not intersect at the origin of ω^2 and the failure to do so may be outside the experimental error. A reference to this point will be made in Sec. VI, but for the analysis to be presented here it will be ignored. This may be accomplished by taking the slope as a function of ω^2 as the critical experimental value to be used in the evaluation of the polarization relaxation time τ_p. The fact that the curves are linear is then equivalent to the assertion that $\omega\tau_p \ll 1$, as it, in fact, turns out to be when the analysis is made.

The velocity of sound measurements leads immediately to an elastic constant which is to be identified as C_{66}^E, the elastic constant at constant field for shear strain in the *ab* plane. This is the elastic constant which behaves anomalously in the transition region. The elastic constant C_{66}^P that is only slowly varying with temperature is not measured in this experiment but, according to the phenomenological theory, C_{66}^P and C_{66}^E must approach each other at low and high T. Thus, by measuring C_{66}^E and extrapolating to high

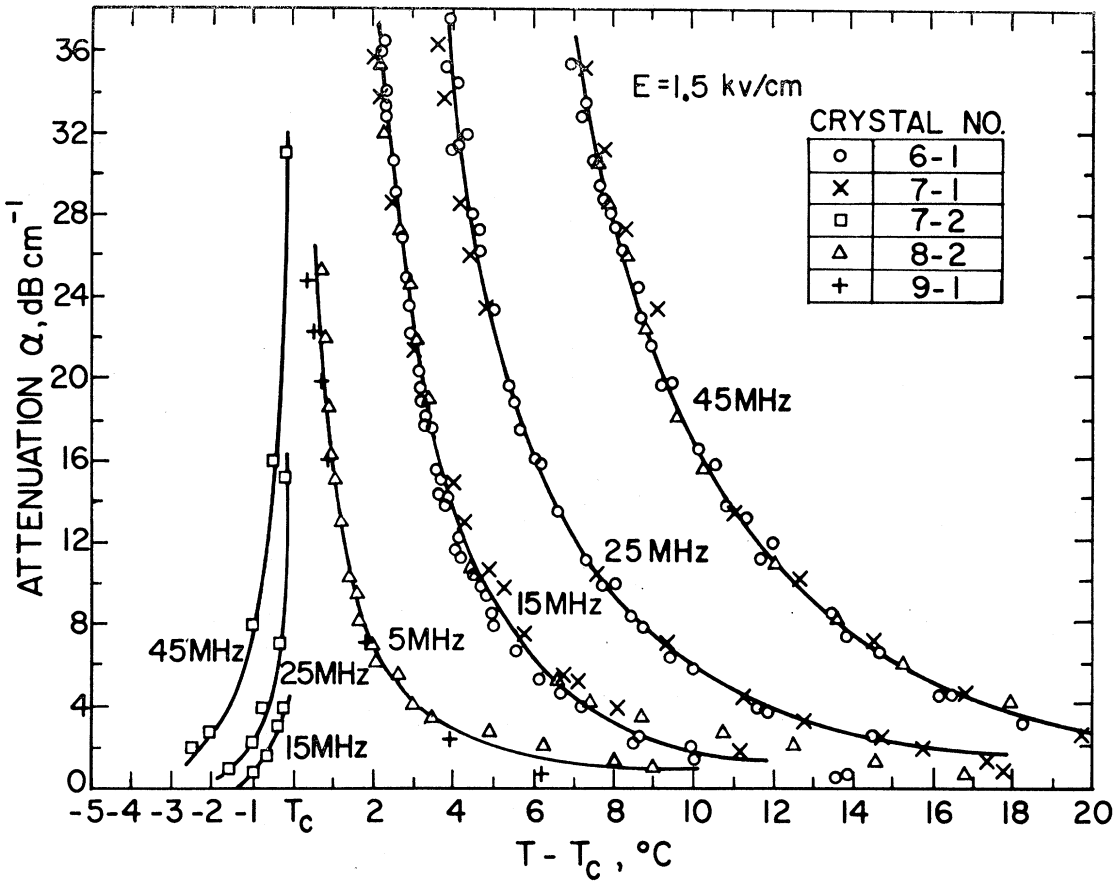

FIG. 2. Acoustic attenuation in the transition region at several frequencies.

and low T, one obtains $C_{66}{}^{P}$. Using $C_{66}{}^{P}=6.4\times10^{10}$ dyn/cm² at 190°K and $C_{66}{}^{P}=5.8\times10^{10}$ dyn/cm² at 280°K, one obtains

$$C_{66}{}^{P}(T)=[5.8+0.0067(280-T)]\times10^{10}\ \text{dyn/cm}^2.$$

A plot of $C_{66}{}^{P}(T)$ and the measured $C_{66}{}^{E}(T)$ is given in Fig. 6. It will be observed that the measured $C_{66}{}^{E}$ is independent of frequency, as it should be if $\omega\tau_p\ll1$. It will also be observed that on the low-temperature side, $C_{66}{}^{E}$ apparently drops discontinuously to zero at T_c. This is suggested in the experiment by a sudden loss of the signal at about $T=T_c-0.050$°K. This behavior suggests a first-order transition in agreement with some other recent observations.[17] The solid line in Fig. 6 represents the best fit to the data.

IV. PHENOMENOLOGICAL INTERPRETATION

In KH_2PO_4-type crystals, a shear strain $\epsilon_{xy}\equiv\epsilon_6$ in the ab plane is coupled to the polarization P_3 along the c axis. Hence a transverse sound wave whose directions of polarization and propagation are in the ab plane is coupled to the polarization along the c axis. The relevant elastic and compliance constants are C_{66} and S_{66}. Since no other components of the stress, strain, and polarization are involved in this experiment, we may drop all tensor indices and denote strain, stress, polarization, elastic, and compliance constants simply by ϵ, σ, P, C, and S. Also the piezoelectric constants which are the coefficients of (ϵP), or $(-\sigma P)$, in the free energy may be denoted by a symbol omitting the tensor subscripts. Then the expression for the free energy in terms of σ and P may be written

$$A_1(\sigma P)=\tfrac{1}{2}\alpha_1P^2+\phi_1(P)+\tfrac{1}{2}S^P\sigma^2-a_1\sigma P, \qquad (1)$$

where the subscript 1 denotes that this is the first of several free-energy expressions. The electrostriction term is omitted since it is always small compared to the piezoelectric term for a system such as KH_2PO_4 which is piezoelectric in both the paraelectric and ferroelectric phases. An unspecified function $\phi_1(P)$ is used instead of the usual power-series development to represent that part of the dependence of A_1 on P at zero stress, which is not contained in the first term. This is necessary because of the steepness of the spontaneous

[17] J. L. Bjorkstam, Phys. Rev. **153**, 599 (1967); W. Reese and L. F. May, *ibid.* **167**, 504 (1968); W. Reese, *ibid.* **181**, 905 (1969); B. A. Strukov, M. Amin, and V. A. Kopchik, Phys. Status Solidi **27**, 741 (1968).

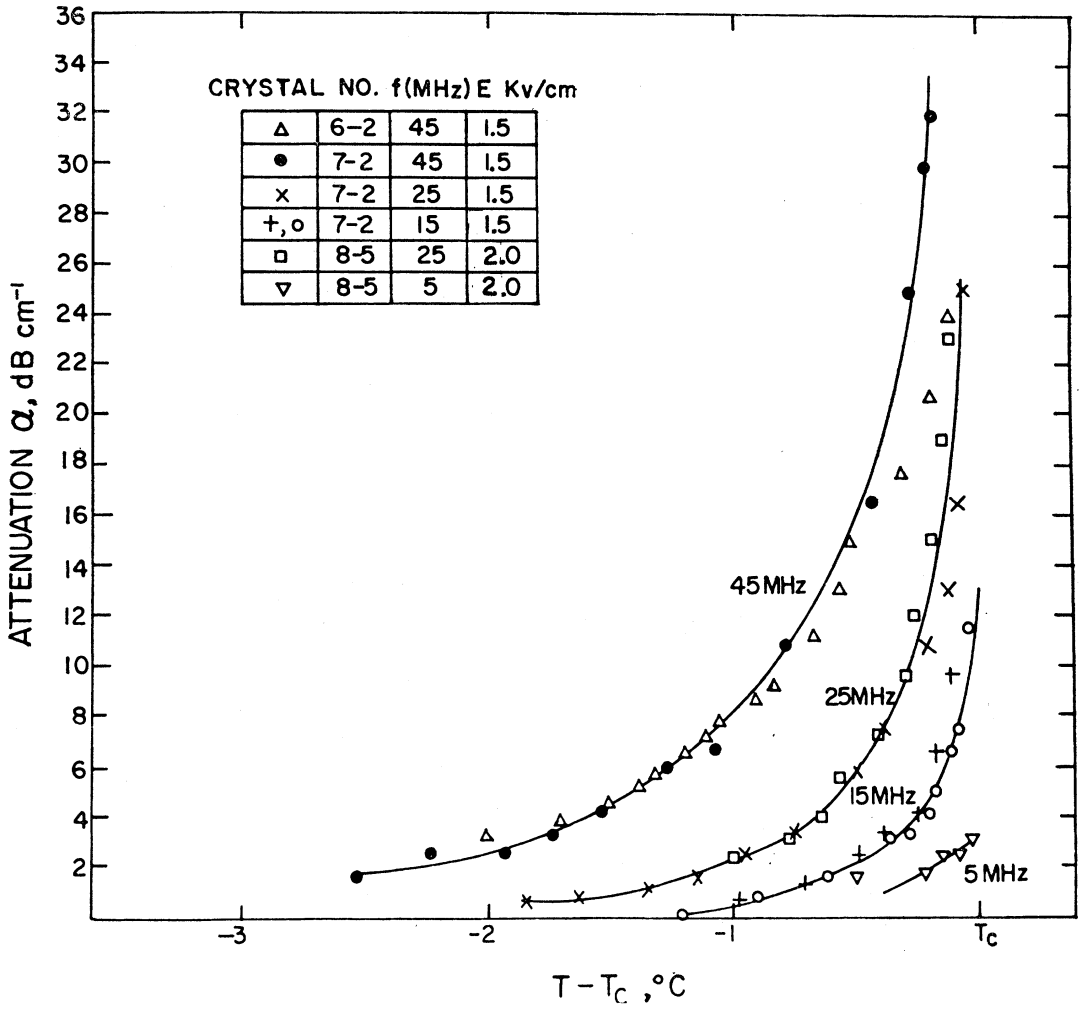

FIG. 3. Acoustic attenuation below the transition temperature on an expanded scale.

polarization curve and the consequent importance of terms involving higher powers of P in such a power-series development.

Analogous expressions for the free energy with different coefficients and other functions $\phi_i(P)$ may be used if other pairs of independent variables such as σ, E, or ϵ, P, or ϵ, E, where E is the applied electric field, are used. From these expressions and the relations

$$\frac{\partial A}{\partial P}=E^*,\quad \frac{\partial A}{\partial \epsilon}=-\sigma^*,\quad \frac{\partial A}{\partial E}=P,\quad \frac{\partial A}{\partial \sigma}=-\epsilon, \tag{2}$$

where E^* and σ^* are the total field and stress, one obtains the piezoelectric equations,[18] as well as certain useful relations among coefficients. In particular, we will wish to refer to the following relations among coefficients which appear in $A_1(\sigma,P)$, $A_2(\epsilon,P)$, $A_3(\sigma,E)$, and $A_4(\epsilon,E)$, and which are derived in this way:

$$\frac{1}{\chi_\sigma}=\left.\frac{\partial E}{\partial P}\right|_\sigma=\alpha_1+\phi_1'', \tag{3a}$$

$$\frac{1}{\chi_\epsilon}=\left.\frac{\partial E}{\partial P}\right|_\epsilon=\alpha_2+\phi_2'', \tag{3b}$$

$$\alpha_1+\phi_1'/P=\alpha_2+\phi_2'/P-a_1a_2, \tag{3c}$$

$$a_1/a_2=S^P=1/C^P, \tag{3d}$$

$$S^E-S^P=1/C^E-1/C^P=a_1^2/(\alpha_1+\phi_1'/P), \tag{3e}$$

$$C^P-C^E=1/S^P-1/S^E=a_2^2/(\alpha_2+\phi_2'/P). \tag{3f}$$

The constants C^E and S^E are to be distinguished from $C_{\text{eff}}{}^E$ and its reciprocal, which are obtained by taking the ratio of the spatial derivatives of σ and ϵ at constant electric field. One obtains

$$S_{\text{eff}}{}^E-S^P=a_1^2/(\alpha_1+\phi_1'')=a_1^2\chi_\sigma, \tag{3g}$$

[18] W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Co., New York, 1946); Werner Känzig, *Ferroelectrics and Antiferroelectrics, Solid State Physics, Advances in Research and Applications* (Academic Press Inc., New York, 1957), Vol. IV, p. 70.

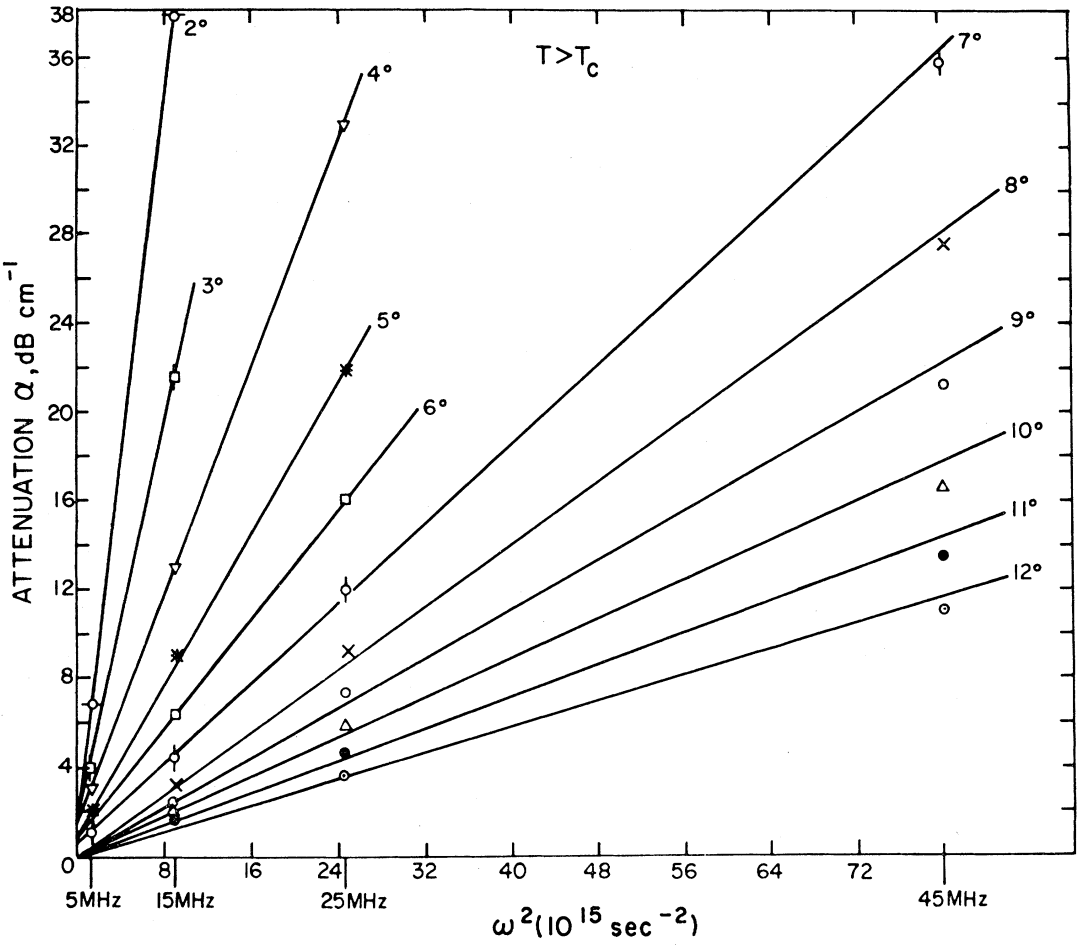

FIG. 4. Linear dependence of the attenuation on the square of the frequency above T_c.

$$C^P-C_{\text{eff}}{}^E=a_2{}^2/(\alpha_2+\phi_2'')=a_2{}^2\chi_\epsilon. \tag{3h}$$

The calculation of the relaxation time associated with a sound wave and due to the coupling between strain and polarization may be based on the Landau-Khalatnikoff kinetic equation[19]

$$\frac{\partial P}{\partial t}=-L\frac{\partial \Psi}{\partial P},$$

where $\Psi=A-E^*P$. Introducing $A_1(\sigma,P)$ or $A_2(\epsilon,P)$ into this equation with σ, ϵ, and P oscillating about their equilibrium values with a time dependence $e^{i\omega t}$, one obtains a relation connecting the amplitudes σ', ϵ', and P'. If $A_1(\sigma,P)$ is used, this relation is

$$P'[i\omega+L(\alpha_1+\phi_1'')]=-La_1\sigma'.$$

Another relation comes from one of the piezoelectric equations:

$$\epsilon'=-S^P\sigma'+a_1P'.$$

Eliminating P' between these equations, one obtains

$$\tilde{C}=-\frac{\sigma'}{\epsilon'}=\left[S^P+\frac{a_1{}^2L\tau}{1+i\omega\tau}\right]^{-1}$$
$$=\left[S_\infty+\frac{S_0-S_\infty}{1+i\omega\tau}\right]^{-1},$$

where

$$1/\tau=L(\alpha_1+\phi_1'')=L/\chi_\sigma, \tag{4}$$

$$S_\infty=S^P, \tag{5a}$$

$$S_0=S^P+a_1{}^2L\tau. \tag{5b}$$

The velocity of sound and the attenuation may be calculated from $\tilde{C}$ using

$$1/v=\text{Re}(\rho/\tilde{C})^{1/2},$$
$$\alpha=-\text{Im}(\rho/\tilde{C})^{1/2}.$$

For $\omega\tau\ll1$, i.e., everywhere except very close to the phase-transition temperature T_c, these expressions

[19] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR 96, 469 (1954) [English transl.: Soviet Phys.—Doklady 96, 469 (1954)].

reduce to

$$\frac{1}{v}=\left(\frac{\rho}{C_0}\right)^{1/2}\left[1+\frac{(\omega\tau)^2}{8}\left(\frac{C_\infty-C_0}{C_\infty}\right)^2\right] \tag{6a}$$

$$\alpha=\frac{1}{2}\left(\frac{\rho}{C_0}\right)^{1/2}\omega^2\tau\frac{C_\infty-C_0}{C_\infty}, \tag{6b}$$

where elastic constants C, rather than compliance constants $S=1/C$, are used.

If the derivation had started with $A_2(\epsilon P)$, rather than $A_1(\sigma P)$, the relaxation time at constant strain, rather than at constant stress, would appear in these relations. But there would also be an additional factor C_∞/C_0 in the expression for α. Since one can show that

$$\tau_\epsilon/\tau_\sigma=S_\infty/S_0=C_0/C_\infty,$$

where subscripts ϵ and σ are used to indicate relaxation times at constant strain and stress, respectively, the two expressions for α are identical.

According to Eq. (5a), the elastic and compliance constants at infinite frequency are identical with these constants at constant polarization. This is reasonable in view of the concept of a finite polarization relaxation time, since for frequencies very much larger than the reciprocal of this time, the polarization cannot change. Similarly, the elastic and compliance constants at zero frequency may be identified as the effective value in a propagating sound wave of these constants at constant electric field. This may be shown as follows.

From Eqs. (3a), (4), and (5b),

$$S_0-S^P=a_1{}^2L\tau=a_1{}^2\chi_\sigma=a_1{}^2/(\alpha_1+\phi_1'').$$

Comparing with Eq. (3g), one obtains $S_0=S_{\rm eff}{}^E$. It is clear that the comparison should be made with Eq. (3g), rather than with Eq. (3e), since the forcing term in a sound wave is the divergence of the stress tensor, and this is related to the Laplacian of the particle displacement by an elastic constant which is here denoted by $C_{\rm eff}{}^E$ for constant field. In the following, we will drop the subscript eff, since there will be no further confusion with C^E and S^E of Eqs. (3e) and (3f). Hence, the final expressions for velocity and attenuation, neglecting the small term in $(\omega\tau)^2$ in the velocity, are

$$1/v=(\rho/C^E)^{1/2}, \tag{7a}$$

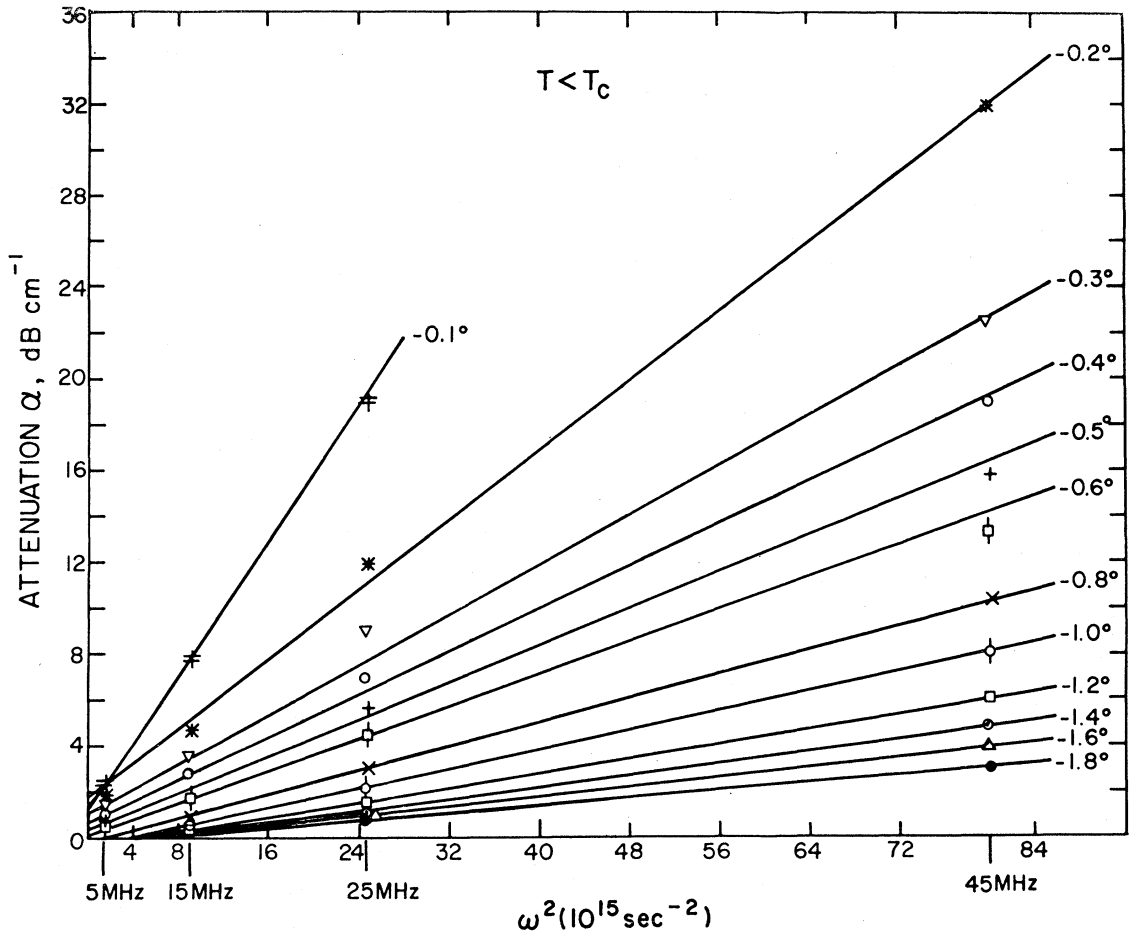

FIG. 5. Linear dependence of the attenuation on the square of the frequency below T_c.

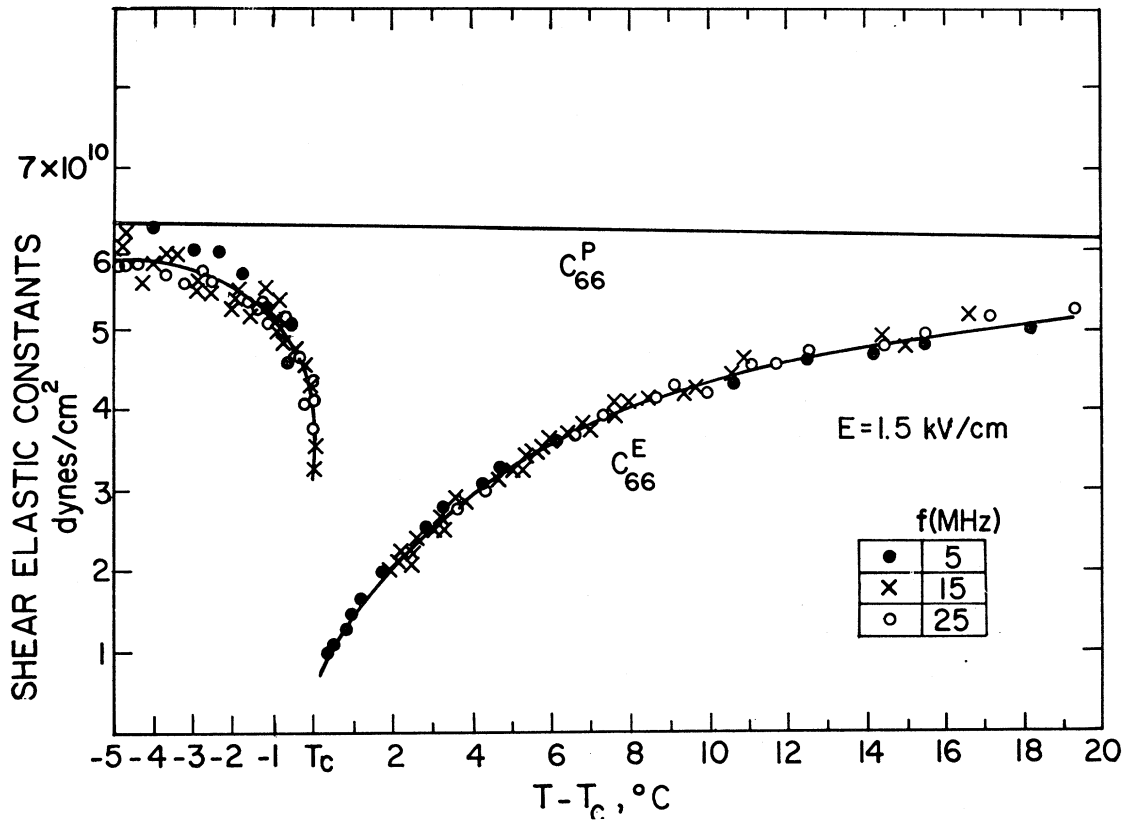

FIG. 6. Elastic constants C^E and C^P as a function of temperature.

$$\alpha=\tfrac{1}{2}(\rho/C^E)^{1/2}\omega^2\tau(C^P-C^E)/C^E, \tag{7b}$$

and the relaxation time at constant stress is meant.

The relaxation time τ appearing in Eq. (7b) is the polarization relaxation time τ_p. This is implied by the derivation given above, but may be demonstrated more concisely as follows:

$$\frac{\partial P}{\partial t}=-L\frac{\partial\Psi}{\partial P}=-L\left[\left(\frac{\partial\Psi}{\partial P}\right)_0+\left(\frac{\partial^2\Psi}{\partial P^2}\right)_0\Delta P+\cdots\right]$$
$$\cong-L\left(\frac{\partial^2\Psi}{\partial P^2}\right)_0\Delta P=-\frac{L}{\chi}\Delta P.$$

Since by definition of polarization relaxation time τ_p

$$\frac{\partial P}{\partial t}=-\frac{\Delta P}{\tau_p},$$

we find

$$1/\tau_p=L/\chi. \tag{8}$$

Identification of τ with τ_p then follows by comparison with Eq. (4). All quantities may be evaluated at constant stress or constant strain. In the following, constant stress will be implied unless otherwise stated.

The determination of $C^E(T)$ is based on velocity of sound measurements and Eq. (7a). Then $C^P(T)$ is obtained as the slowly varying linear function to which $C^E(T)$ is asymptotic at low and high temperatures. The results are shown in Fig. 6 and have been described more fully in Sec. III.

The determination of polarization relaxation time requires both velocity-of-sound and attenuation data. From Figs. 4 and 5 we find the slopes α/ω^2, and from Fig. 6, C^E and C^P. Substitution into Eq. (7b) gives τ_p. The results are shown as plotted experimental points in Fig. 7.

The susceptibility is calculated from the velocity-of-sound measurements. From Eqs. (3g) and (3h), its values at constant stress and strain may be obtained from the measured values of C^E using

$$1/C^E-1/C^P=a_1^2\chi_\sigma, \tag{9a}$$

$$C^P-C^E=a_2^2\chi_\epsilon. \tag{9b}$$

Then from the data shown in Fig. 6 and the known[20] value of $a_1=5.2\times10^{-7}$ cm dyne$^{-1/2}$, one obtains the susceptibility at constant stress. The results are shown as plotted experimental points in Fig. 8.

It is of interest to compare these results with other measurements. The susceptibility may be conveniently

[20] T. R. Sliker and S. R. Burlage, J. Appl. Phys. 34, 1837 (1963).

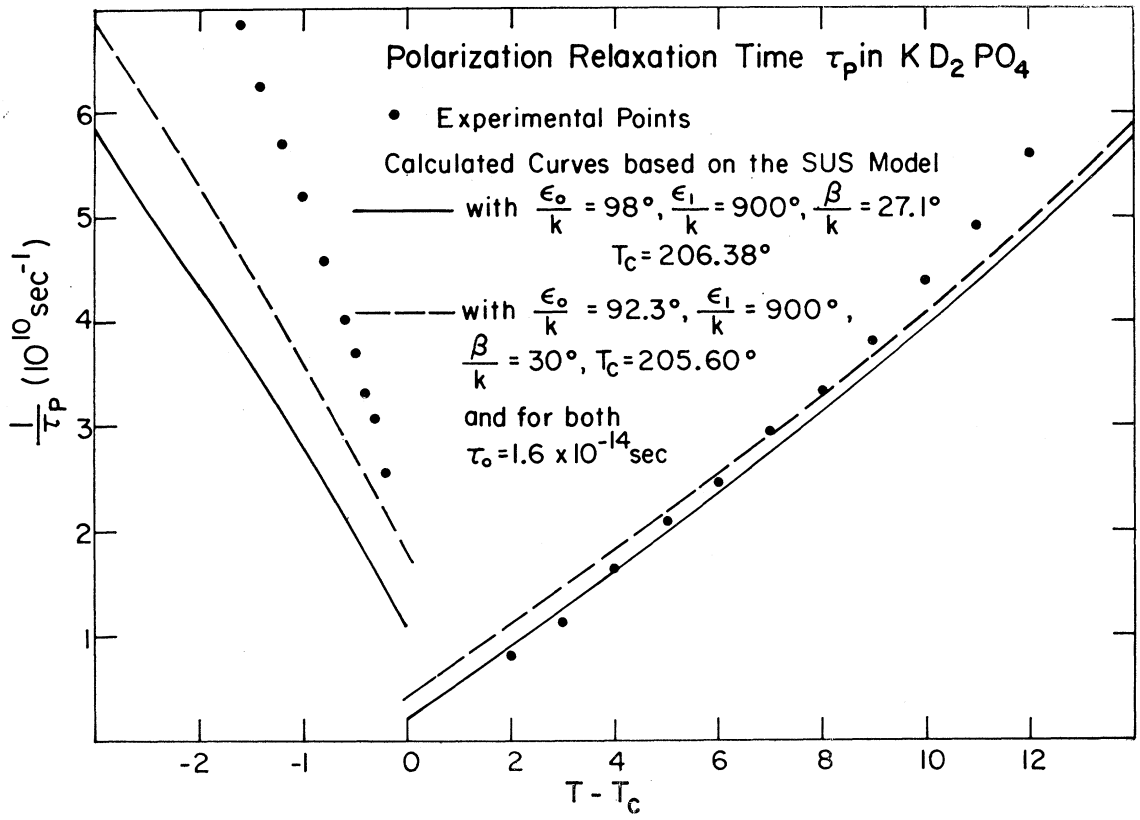

FIG. 7. Experimental and theoretical results for the polarization relaxation rate.

summarized by giving the Curie constant C in

$$\frac{1}{\chi} = \frac{|T-T_c|}{C} + \text{const},$$

valid experimentally over a range of more than 10°K on the high side of T_c and at least 2°K on the low side. According to the data of Fig. 8, C lies between 265°K and 275°K for $T>T_c$, the lower value being appropriate if one draws the best-fit straight line through the origin. For $T<T_c$, C is equal to about 22°K. The result obtained for $T>T_c$ may be compared with two results from dielectric measurements: $C=225$°K by Mayer and Bjorkstam[21] and $C=330$°K by Hill and Ichiki.[22] For additional information we must turn to some measurements on KH_2PO_4, which behaves similarly to KD_2PO_4, at least insofar as saturation polarization and Curie constants are concerned. Thus, for KH_2PO_4, $C=250$°K from Baumgartner's dielectric measurements[23] and $C=255$°K from the sound-velocity measurements of Garland and Novotny.[12] For $T<T_c$ the available data on KH_2PO_4 come from Brillouin scattering and microwave-transmission measurements. Thus, from the measurements of Brody and Cummins,[24] $C=30$°K ($T_c>T>T_c-1$); from Kaminow and Harding,[25] $C=17.5$°K; and from Gauss and Happ,[26] $C=17.0$°K. In all cases the ratio of slopes in the ferroelectric to paraelectric phase is of the order of 10.

The relaxation time is not as well described by a linear relation as the susceptibility. But the initial slope b in

$$1/\tau = b|T-T_c| + \text{const}$$

still provides a simple way of comparing data from various sources. From Fig. 7 we find for KD_2PO_4

$$b = 0.4\times10^{10}, \quad \text{for } T>T_c$$
$$= 3.0\times10^{10}, \quad \text{for } T<T_c.$$

The ratio of these two numbers is 7.5, compared with 12.4 for the Curie constants. The only other measurement on KD_2PO_4 is that of Hill and Ichiki[22] for $T>T_c$. In terms of a damped harmonic-oscillator model with a dominant lowest mode whose frequency is much greater than the excitation frequency, one obtains for

[21] R. J. Mayer and J. L. Bjorkstam, J. Phys. Chem. Solids **23**, 619 (1962).
[22] R. M. Hill and S. K. Ichiki, Phys. Rev. **132**, 1603 (1963); **130**, 150 (1963).
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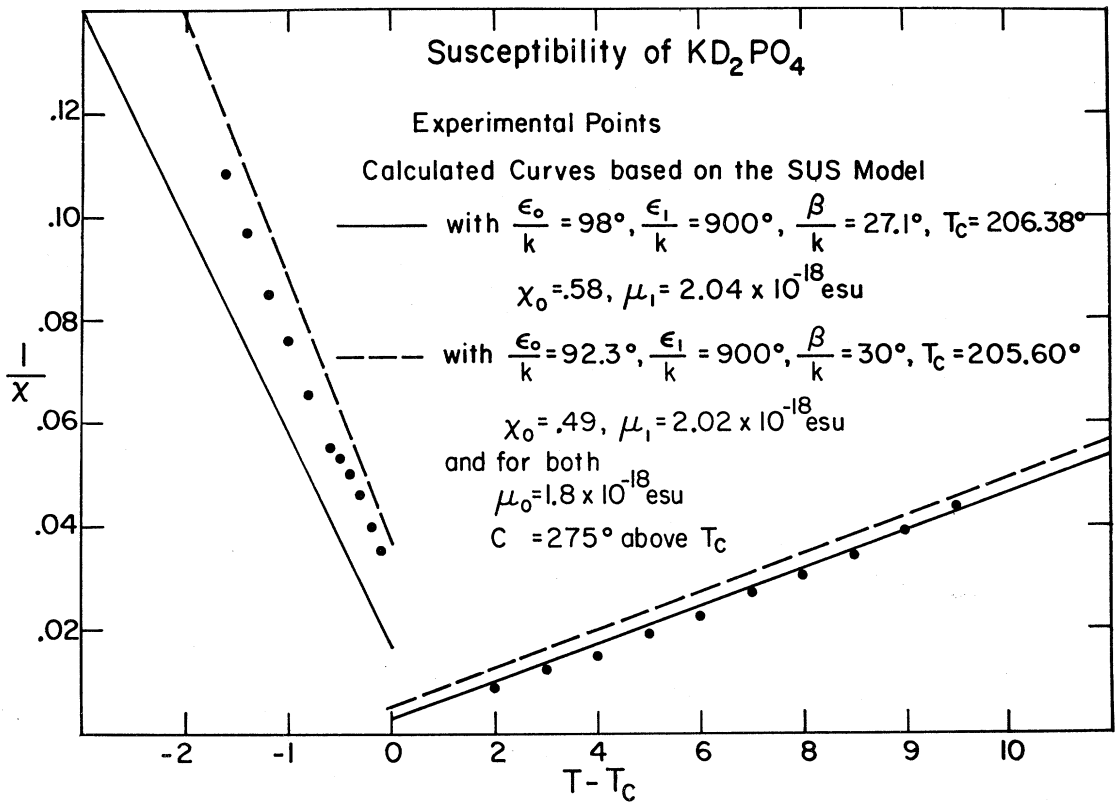

FIG. 8. Experimental and theoretical results for the reciprocal susceptibility.

b the value 0.27×10^{10} which is to be compared with $b=0.4\times10^{10}$ as found in the present experiment. Additional comparisons may be made if we now turn to KH_2PO_4. The most striking result is that b is about the same in the deuterated and nondeuterated crystals for $T<T_c$, but that for $T>T_c$, it is about seven times larger in the normal crystal.[27] The large value of b in KH_2PO_4 for $T>T_c$ has also been found by others. It is about 4.0×10^{10} from the sound attenuation measurements of Garland and Novotny.[12] It is about 1.5×10^{10} from the Raman scattering measurements of Kaminow and Damen,[28] and about 8.5×10^{10} from the microwave transmission measurements of Gauss and Happ,[26] if one calculates τ_p on the basis of a damped harmonic-oscillator model with $\tau_p=2\Gamma/\omega_o^2$.

V. COMPARISON WITH PREDICTIONS OF ORDER-DISORDER MODEL

The model has been described previously,[16] and several of its predictions have been compared with experimental results.[29] In this model, equilibrium properties are determined by the arrangement of protons around PO_4 groups. Normally there are two protons (or deuterons in the case of KD_2PO_4), associated with each PO_4 group and, in the completely ordered phase, the proton arrangement is an ordered one. Deviations from the ordered state occur both because other arrangements of two protons around a PO_4 group are possible, and because the number of associated protons may differ from two. Arrangements in which the number of associated protons is one, three, four, and zero are designated as Takagi groups or Takagi defects. Nonequilibrium properties such as polarization relaxation, domain wall motion, and deuteron spin relaxation are due in this model to the jump motion of these defects.

The expression for the susceptibility has been derived in SUS.[16] We write

$$\chi=\chi'+\chi_0, \tag{10}$$

where χ' is the explicit contribution to susceptibility due to hydrogen and heavy-ion configuration, and χ_0 is an additional induced contribution. From Eq. (9) of SUS

$$\chi'=n^2\mu_0\mu_1\left(\frac{\partial^2 A}{\partial p^2}\right)^{-1},$$

where A is the free energy of the system per unit volume, p is the fractional polarization, μ_0 is the dipole moment associated with heavy-ion polarization, and μ_1 is the

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dipole moment associated with energy change per jump in the presence of an electric field. The two moments differ because of the induced polarization and the presence of long-range forces. In terms of a long-range force parameter β we find

$$\mu_1=\mu_0[1+(2\beta/n\mu_0^2)\chi_0].$$

Then from Eq. (3b) in SUS

$$\frac{n\mu_0\mu_1}{2k}\frac{1}{\chi'}=T\left[\frac{d\lambda}{dp}-\frac{1}{1-p^2}-\frac{\beta}{kT}\right], \tag{11}$$

where λ is a parameter defined in terms of p, T, and the PO_4 group configurational energies ϵ_0, ϵ_1, and ϵ_2.

The right-hand side of Eq. (11) must be evaluated numerically for specified choices of ϵ_0, ϵ_1, ϵ_2, and β. The energy ϵ_2 is so large that it may be set equal to infinity without affecting appreciably any of the conclusions to be drawn in the present context. The energy ϵ_1 has been determined[14] by deuteron spin relaxation measurements. Its value, $\epsilon_1/k=900°\text{K}$, has been inserted into the calculations in all previous applications of the model and will be used again in the present application. This leaves ϵ_0 and β to be determined. Since there is a relation between them involving the Curie temperature and the other energy parameters, there is essentially only one free parameter available for changing the shape and slope of the curve representing the left-hand side of Eq. (11) as a function of T. It is convenient to take β as this free parameter. The associated value of ϵ_0 is then given when T_c is specified. The most important consequence of varying β is that the nature of the transition changes from second order to first order if β is made large enough. For the specified value of ϵ_1, this happens when β/k is equal to about 23°K. In the earlier comparisons of the model with experiment, the strong first-order character of the transition was not fully realized and values of β/k of about 23°K seemed to provide the best fit. But the specific-heat measurements of Reese and May[17] display strong first-order characteristics, and a value of $\beta/k=35.6°\text{K}$ was needed to give a best fit of the model to their data. The present experiment also suggests strong first-order characteristics, and a value of β approaching that used by Reese is required.

But not all features of the experimental data can be reproduced. Hence, we will make the comparison by calculating susceptibility and relaxation rate curves for each of two different sets of parameters. To do this will illustrate, to some extent, the trend in the predictions of the model with changes in numerical values of the parameters, and it will bring out rather well those features which can be reproduced well and those for which this is not the case.

Numerical evaluation of Eq. (11) for each of two selected sets of parameters gives the following results for values of $|T-T_c|$ which are not too large:

For

$$\epsilon_0/k=98°\text{K},\ \epsilon_1/k=900°\text{K},\ \beta/k=27.1°\text{K},\ T_c=206.38°\text{K},$$

$$\frac{n\mu_0\mu_1}{2k}\frac{1}{\chi'}=0.484(T-T_c)+0.339,\quad T>T_c$$

$$=5.45(T_c-T)+2.18,\quad T<T_c.$$

For

$$\epsilon_0/k=92.3°\text{K},\quad \epsilon_1/k=900°\text{K},\quad \beta/k=30.0°\text{K},\quad T_c=205.60°\text{K},$$

$$\frac{n\mu_0\mu_1}{2k}\frac{1}{\chi'}0.480(T-T_c)+0.635,\quad T>T_c$$

$$=6.73(T_c-T)+4.66,\quad T<T_c.$$

The values of T_c correspond to about 83% deuteration, which is that of the samples used in this experiment.

Calculated curves for the susceptibility are now obtained by using Eq. (10) and assigning a value to χ_0, the only additional free parameter. The results are shown in Fig. 8, where in each case the factor $n\mu_0\mu_1/2k$ was chosen so that the Curie constant for $T>T_c$ is $C=275°\text{K}$. The listed value of μ_0 corresponds to a saturation polarization[22,30] $P_s=n\mu_0=6.0\ \mu\text{C/cm}^2$, and the required value of $\chi_0\sim0.5$ is the same as has been estimated[16] for KH_2PO_4, on the assumption that the transition in the latter is second order.

The way in which the polarization relaxation time is to be calculated from the model has been described by Schmidt.[29] Briefly, we note that all configuration changes are a consequence of Takagi group jumps. In the notation of SUS, the fractional numbers of all eight kinds of Takagi groups is $x_T=4(x_1+x_{-1})$. If the mean effective jump frequency of Takagi groups is $1/\tau_0$, then the mean jump frequency of any PO_4 group in the crystal is

$$1/\tau_c=x_T/\tau_0, \tag{12}$$

and the average number of jumps per unit volume is

$$j_T=n/\tau_c.$$

In the presence of an electric field E, the jump motion is biased so as to favor increased polarization along the direction of E. Introducing a Boltzman factor for the relative probability of jumps in the two directions, one can show that the mean polarization change, starting from zero polarization, is

$$\Delta P=\mu_0\mu_1E/2kT.$$

Then

$$\frac{dP}{dt}=j_T\Delta P=\frac{n\mu_0\mu_1E}{2\tau_ckT},\quad \text{for } P=0$$

$$=\frac{n\mu_0\mu_1}{2\tau_ckT}\left(E-\frac{P}{\chi}\right),\quad \text{for } P\neq0,$$

[30] J. L. Bjorkstam (private communication).

from which

$$1/\tau_p = (n\mu_0\mu_1/2\tau_c kT)1/\chi. \quad (13)$$

The factor $n\mu_0\mu_1/2kT$ has been calculated for two sets of parameter values as described above. Expressions for the fractional density x_T of Takagi groups, which appears in Eq. (12) for $1/\tau_c$, are given in SUS, and numerical values for the same values of parameters have been calculated. The only other factor to be specified is τ_0. The results are shown in Fig. 7.

It may be of interest also to note that the Landau-Khalatnikoff coefficient L is given by the model. By comparing Eqs. (8) and (13), we find

$$L = n\mu_0\mu_1/2\tau_c kT = (n\mu_0\mu_1/2\tau_0)x_T/kT.$$

Thus, the temperature dependence is like x_T/T, which exhibits a small positive discontinuity at T_c for our choices of parameters, and is otherwise a slowly increasing function of T. Experimental values of L are obtained simply by dividing the measured susceptibility by the measured relaxation time.

VI. CONCLUSION

With regard to the calculated curves for $1/\chi$ in Fig. 8, it is only the ratio of slopes that is strongly model dependent. It is clear that this ratio is correctly given by some choice of parameter values lying between the two sets which have been chosen. Also, the discontinuity in $1/\chi$ on the low-temperature side of T_c is not very different from the observed discontinuity. But the calculated discontinuity on the high-temperature side is too large by an amount which is probably larger than the experimental error. There is no problem with the absolute slope, which has been easily adjusted to the observed value by introducing a reasonable value for the induced polarization.

On the other hand, both the ratio of slopes and the actual slopes of the calculated $1/\tau_p$ curves in Fig. 7 are too small, and as for $1/\chi$, the calculated discontinuity on the high-temperature side of T_c is too large. Experimentally, there does not appear to be any discontinuity. No reasonable readjustment of parameter values can reduce these discrepancies appreciably. Comparison of these results for χ and τ_p suggests that it is too slow a rate of change of Takagi group density with temperature which is at fault.

The absolute slopes of the $1/\tau_p$ curves can, of course, be increased by making τ_0 smaller. But this would increase the discrepancy in the discontinuity on the high-temperature side of T_c. Also, the value of τ_0 is already smaller than other values which have been specified on the basis of comparisons with other relaxation phenomena. Thus, for example, $\tau_0 \sim 3\times10^{-14}$ sec from dielectric measurements and domain wall motion (in KD_2PO_4 only), and $\tau_0 \sim 8\times10^{-14}$ sec from deuteron spin relaxation measurements have been given.[29] In all of these and in the present application, τ_0 has been regarded as a temperature-independent quantity. But in a less simple model, in which, for example, tunnelling and interactions with the lattice are specifically included, this would not need to be the case. Our failure to obtain a better fit to the data suggests that a pure order-disorder model is not adequate to describe what is happening. There is already some suggestion of this from some recently obtained deuteron spin relaxation measurements in the transition region.[31] But neither does it appear that the model is completely inadequate. Thus, perhaps, the next step may be to combine the order-disorder model with some features of the collective-mode model.

Also, on a different level, it has been noted that there is an unexplained feature of the experimental results on attenuation. The best-fit straight lines drawn through the experimental points shown in Figs. 4 and 5 do not pass through the origin as expected on the basis of the phenomenological analysis leading to Eq. (7b). The discrepancy probably has its origin in the fact that the phenomenological theory is essentially second order, whereas the transition is, in fact, first order. Whatever is the source of this discrepancy, it would most likely be reflected also as a discrepancy in any attempt to make a model interpretation.

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