

High-Frequency Behavior of Hydrogen-Bonded Ferroelectrics : Triglycine Sulphate and KD_2PO_4 †

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(Received 27 June 1963)

The small signal dielectric coefficient of triglycine sulfate (TGS) and KD_2PO_4 has been determined as a function of frequency, temperature, and dc bias field in both the ferro- and paraelectric regions. The data for TGS are found to agree with a heuristic model involving a Gaussian distribution of relaxation times when the spontaneous and induced polarization are properly taken into account. It is suggested that the clamping out of the electrostrictive contribution to the polarization is a non-negligible factor. For KD_2PO_4 a large domain-associated loss is found in the ferroelectric region. This loss persists up to 2 kMc/sec indicating piezoelectric coupling to very small domains. The data for KD_2PO_4 suggest that the usual designation of first- or second-order transition is not sufficient.

INTRODUCTION

RECENT measurements of the paraelectric behavior of triglycine sulfate (TGS), its deuterated isomorph DTGS,¹ and potassium dideuterium phosphate,² KD_2PO_4 , have shown a temperature-dependent relaxation of the dielectric coefficient for these hydrogen-bonded materials. The characteristic relaxation time τ was found to be proportional to the susceptibility, i.e., $\tau \sim 1/T - T_c$ where T_c is Curie temperature. At high frequencies the dielectric coefficient was found to be inversely proportional to ν , the measuring frequency indicating that there was a distribution of relaxation times. A Gaussian distribution of relaxation times was found to provide a good fit to the data for all three materials.

Additional measurements are reported here for TGS and KD_2PO_4 which extend the temperature range into the ferroelectric region, $T < T_c$, and include a bias field for both ferroelectric and paraelectric regions.

The data for TGS are shown to agree with the paraelectric results if the macroscopic spontaneous and induced polarization is included properly. In particular, the effects due to electrostriction are considered.

For KD_2PO_4 a simple extension of the prior model is not feasible. In the ferroelectric region a large domain-dependent loss is found extending up to 2kMc/sec. These data, plus the effect of a bias field on the clamped dielectric constant, indicate that the transition has some aspects of both first- and second-order types.

TRIGLYCINE SULFATE: FERROELECTRIC REGION

For TGS in the paraelectric state above T_c we have previously found that a distribution of simply relaxing dipoles gave a good representation of the observed behavior.¹ If each dipole is assumed to behave as an overdamped oscillator, its response is proportional to $1/(1 + i\nu\tau)$, where ν is the measuring frequency and τ

the relaxation time for the particular dipole. If $y(\tau)$ is the distribution function for the relaxation times of the dipoles, the dielectric response of the medium as a whole is given by

$$\epsilon_1 - \epsilon_\infty = \int_0^\infty \frac{y(\tau)}{1 + (\nu\tau)^2} d\tau, \quad (1)$$

$$\epsilon_2 = \int_0^\infty \frac{\nu\tau y(\tau)}{1 + (\nu\tau)^2} d\tau, \quad (2)$$

where ϵ_1 and ϵ_2 are the real and imaginary components of the dielectric coefficient, respectively, and ϵ_∞ is the optical dielectric constant. $y(\tau)$ is normalized by the zero frequency condition,

$$\int_0^\infty y(\tau) d\tau = \frac{C}{T - T_c}, \quad (3)$$

where C is the Curie constant of the material and ϵ_1 is assumed very large compared to ϵ_∞ .

For both TGS and KD_2PO_4 in the paraelectric state, the assumption of a Gaussian distribution with a temperature-dependent width for $y(\tau)$ agreed with the results. If we set $y(\tau) = A e^{-(\tau/\tau_0)^2}$, where $\tau_0 = 1/\alpha(T - T_c)$ and $A = 2C\alpha/\sqrt{\pi}$ from (3), Eqs. (1) and (2) are integrable and give

$$\epsilon_1 = B\pi^{1/2} \operatorname{erfc}(1/\nu\tau_0), \quad (4)$$

$$\epsilon_2 = B\pi^{-1/2} [-\operatorname{Ei}(1/\nu\tau_0^2)], \quad (5)$$

where

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = 1 - 2\pi^{-1/2} \int_0^x e^{-t^2} dt,$$

$$-\operatorname{Ei}(-x) = \operatorname{Ei}(x) = \int_x^\infty \frac{e^{-t}}{t} dt,$$

and

$$B = \frac{C}{T - T_c} 1/\nu\tau_0 e^{1/(\nu\tau_0)^2}.$$

The parameter τ_0 gives the temperature dependence of the distribution. It is proportional to the dc suscepti-

† Part of this work was performed while the authors were at the former General Telephone and Electronics Laboratories, Palo Alto, California. That part performed at Lockheed was sponsored by the Lockheed Independent Research Fund.

¹ R. M. Hill and S. K. Ichiki, Phys. Rev. **128**, 1140 (1962).

² R. M. Hill and S. K. Ichiki, Phys. Rev. **130**, 150 (1963).

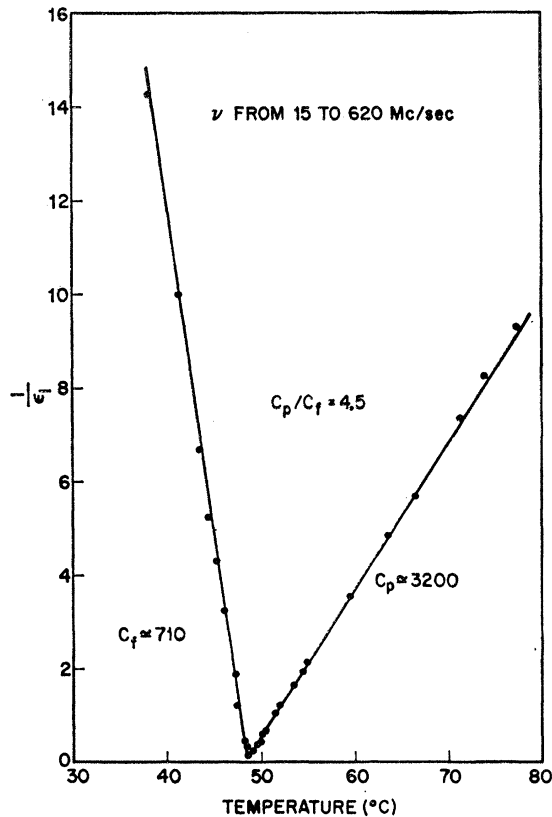


FIG. 1. Curie plot, $1/\epsilon_1 (\times 10^3)$ versus T_c , for TGS. This plot represents the data between 15 Mc/sec and 620 Mc/sec.

bility and the constant α is determined empirically. The normalization constant A is seen to have the dimensions of a frequency. Values of α , C , A , and T_c for TGS, DTGS, and KD_2PO_4 are given in Table I. The data were obtained by three related techniques, each pertinent to one frequency, which were discussed earlier.¹ The data taken in the ferroelectric region were taken in the same manner as before,¹ but with a slower rate of temperature variation, since the rate of change of ϵ with T is so much greater.

Figure 1 is a Curie plot of the inverse dielectric coefficient versus temperature for several different frequencies. The slope of the resulting straight lines is the Curie constant C . The existence of a Curie constant on the ferroelectric side of T_c implies that a modified Curie-Weiss relation describes the behavior for this region as well as the paraelectric one. This is expected for a ferroelectric material.

TABLE I. Parameters for hydrogen-bonded crystals.

	TGS	Deuterated TGS	KD_2PO_4
C	3300	4000	4200
T_c	48.3°C	60.5°C	-52°C
α	0.48 (kMc/sec)/°C	0.38 (kMc/sec)/°C	0.22 (kMc/sec)/°C
A	1.77×10^{12} /sec	1.70×10^{12} /sec	1.27×10^{12} /sec

This is seen most simply by considering Devonshire's³ thermodynamic theory of ferroelectrics. The free energy of the crystal is expanded in even powers of the polarization as

$$G = G_0 + A'P^2 + DP^4 + FP^6 + \dots \quad (6)$$

A' is assumed to depend linearly on temperature and will be written $A' = A(T - T_c)$, and G_0 is the polarization independent part of G . If we assume the contribution from the P^6 term to be negligible and $\epsilon \gg 1$ we have

$$\partial G / \partial P = E = 2A(T - T_c)P + 4DP^3, \quad (7)$$

which leads to

$$P^2 = -A(T - T_c) / 2D \quad (8)$$

in the ferroelectric region when the applied electric field E is zero. The dielectric coefficient ϵ_1 is given by

$$\partial^2 G / \partial P^2 = \partial E / \partial P = 4\pi / \epsilon_1 = 2A(T - T_c) + 12DP^2 \quad (9)$$

which reduces to the Curie-Weiss law with a Curie constant, $C = 4\pi / 2A$, in the paraelectric region where $P = 0$. For $T < T_c$, substitution of (8) into (9) gives

$$4\pi / \epsilon_1 = 4A(T_c - T). \quad (10)$$

We expect, therefore, that the ratio (for the para and ferro cases) $C_p / C_f = 2$. The results shown in Fig. 1 and for measurement at other frequencies where a Curie constant can be defined give $C_p / C_f = 4.5$. Triebwasser⁴ has pointed out that there is a correction to the thermodynamic expression which is an isothermal relation because the measurement is made adiabatically. He estimates this correction at no more than 20%, which is insufficient to explain the observed ratio.

It appears possible to explain this ratio if electrostriction makes a significant contribution to the spontaneous polarization. This contribution would not appear in the high-frequency clamped dielectric response, and the value of C_p / C_f should be larger than for the free crystal. We can estimate this effect by re-writing the free energy as

$$G(X, P) = A(T - T_c)P^2 + DP^4 - S_{ij}X_iX_j + Q_{1kj}X_jP_1P_k, \quad (11)$$

where S_{ij} is the elastic compliance tensor, the X 's are the stresses, Q_{1kj} is the electrostrictive coefficient tensor, and the Voigt notation is used.

For TGS, only P_2 is finite; therefore, the Q_{1kj} reduce to Q_{2j} . The strain x_i is found from

$$(\partial G / \partial X_j)_P = x_j = -S_{ij}P^2X_i + Q_{2j}P^2. \quad (12)$$

Therefore,

$$X_i = (S_{ij})^{-1}(Q_{2j}P^2 - x_j) = C_{ij}(Q_{2j}P^2 - x_j), \quad (13)$$

since $(S_{ij})^{-1} = C_{ij}$ the elastic constant tensor. Now from (11)

$$(\partial G / \partial P)_X = E = 2AP + 4DP^3 + 2Q_{2j}X_jP. \quad (14)$$

³ A. F. Devonshire, Suppl. Phil. Mag. **3**, 85 (1954).

⁴ S. Triebwasser, IBM J. Res. and Develop. **2**, 212 (1958).

Substituting (13) into (14) and differentiating with respect to P holding the strain, x , constant gives the high-frequency dielectric constant as

$$\begin{aligned} (\partial E/\partial P)_x &= 4\pi/\epsilon_x = 2A(T-T_c) + 12DP^2 \\ &\quad + 6C_{ij}Q_{2j}Q_{2i}P^2 - 2C_{ij}Q_{2i}x_i \quad (15) \\ &= 2A(T-T_c) + 12DP^2 \\ &\quad + 4C_{ij}Q_{2j}Q_{2i}P^2 + 2Q_{2j}X_j. \end{aligned}$$

Now since the stress $X=0$ we find that the ratio C_P/C_f is given by

$$C_P/C_f = (3\delta - 1), \quad (16)$$

where $\delta = 1 + C_{ij}Q_{2i}Q_{2j}/3D$.

Konstantinova *et al.*⁵ have measured the C_{ij} and Ikeda *et al.*⁶ have measured the electrostrictive co-

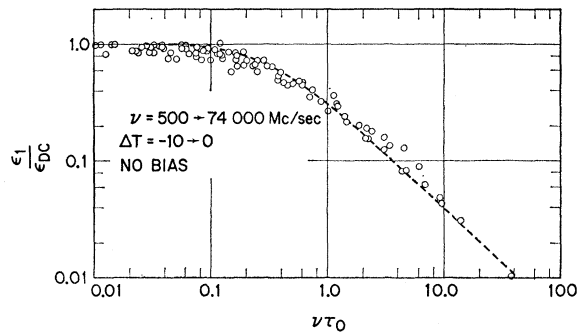


FIG. 2. Normalized ϵ_1 versus $\nu\tau_0$ for TGS in the ferroelectric region, $T < T_c$. τ_0 includes a term accounting for the spontaneous polarization. Solid curve is a plot of Eq. (4) in text taking polarization into account.

efficients. Using their values and Triebwasser's⁴ value for D , ($D = 2 \times 10^{-10}$ cm²/dyn) we find $\delta = 1 + 0.35 = 1.35$ and $(3\delta - 1) = 3.02$ indicating that electrostriction does make a significant contribution to the observed ratio, 4.5. We suggest that more accurate values of the various C 's would show that the electrostriction can account for the observed ratio. Jona and Shirane⁷ have measured the shift in T_c with hydrostatic pressure. They obtain a value of 0.5×10^{-11} cm²/dyn for a coefficient which is equal to $(Q_{21} + Q_{22} + Q_{23})$. Ikeda's⁶ values for the Q 's give 0.4×10^{-11} cm²/dyn for this sum indicating that these values are reasonably correct. There is, however, almost a factor of 2 variation in some of the reported elastic coefficients.

In any event, the data in the ferroelectric region can be fitted by the same model used in the paraelectric region with one minor change. The low-frequency clamped dielectric coefficient is now given by

$$\epsilon_1(\nu=0) = \frac{C_p}{(3\delta - 1)(T_c - T)} = \frac{C_f}{(T_c - T)}, \quad (17)$$

where δ is the experimental value, 1.8.

⁵ V. P. Konstantinova, I. M. Silvestrova, and K. S. Aleksandrov, *Kristallografiya* 4, 70 (1960) [translation: *Soviet Phys.—Cryst.* 4, 63 (1960)].

⁶ T. Ikeda, Y. Tanaka, and H. Toyoda, *J. Appl. Phys. Japan* 1, 13 (1962).

⁷ F. Jona and G. Shirane, *Phys. Rev.* 117, 139 (1960).

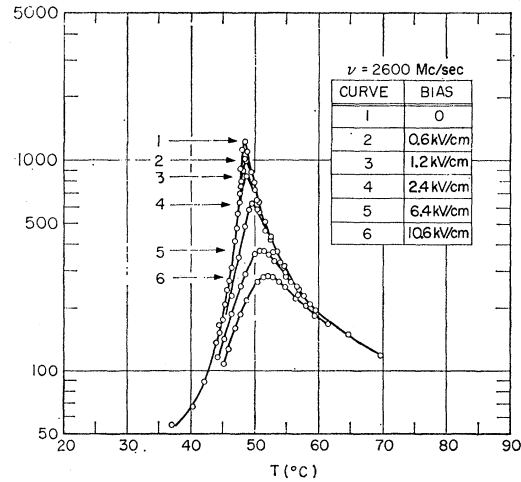


FIG. 3. Real dielectric coefficient ϵ_1 versus temperature T for TGS at 2600 Mc/sec at various values of dc bias field.

To describe the frequency dependence of ϵ_1 a similar change is made in the relaxation parameter τ_0

$$\tau_0 = \frac{1}{\alpha(3\delta - 1)(T_c - T)}, \quad (18)$$

where δ is obtained from the low-frequency case above and $\alpha = 4.8 \times 10^8$ cps/ $^{\circ}$ C. which was obtained from the paraelectric data.¹ Figure 2 shows the data and a plot of Eq. (4) with these modifications. The agreement is seen to be excellent showing that the relaxation behavior is directly proportional to the low-frequency susceptibility. The imaginary term ϵ_2 can be treated in a like manner.

TGS: WITH BIAS FIELD

With a dc bias field applied to the crystal, the distinction between ferroelectric and paraelectric regions is lost. For all temperatures there is now some polarization and the second-order transition temperature no longer exists. The dielectric coefficient exhibits a broad maximum which shifts to higher temperatures and

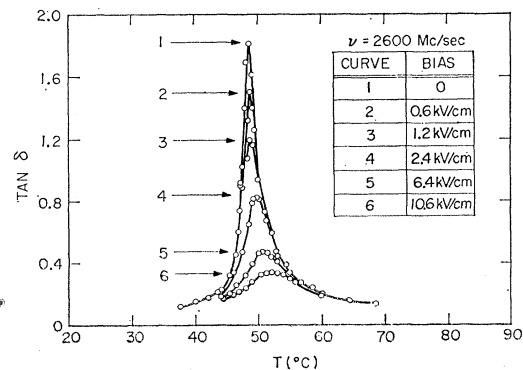


FIG. 4. Loss tangent ϵ_2/ϵ_1 versus temperature T for TGS at various values of dc bias field.

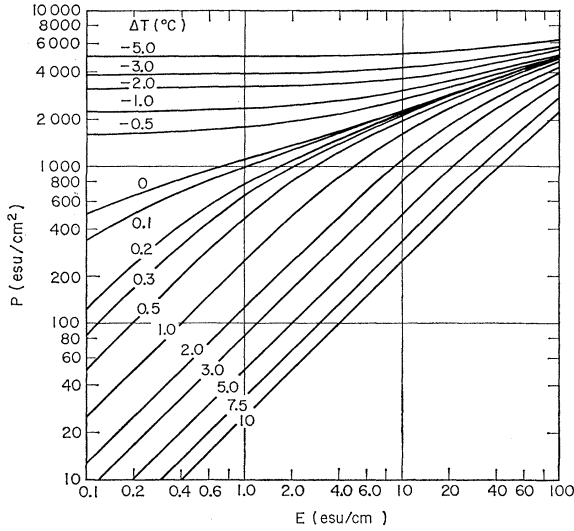


FIG. 5. Spontaneous and induced polarization P versus dc bias field E at various values of $\Delta T = (T - T_c)$.

lower maxima as a function of the applied field. The low-frequency dielectric coefficient is again given by Eq. (9) but the polarization P now includes both spontaneous and induced contributions. The behavior of ϵ_1 at 2600 Mc/sec as a function of bias field is shown in Fig. 3. The loss tangent for the same conditions is given in Fig. 4. These and similar data taken at other frequencies will also fit properly modified expressions of the form of (4) and (5). This consists of using the proper expression for the low-frequency dielectric coefficient, $\epsilon_1(\nu=0)$ and for the relaxation parameter τ_0 ,

$$\epsilon_1(\nu=0) = \frac{C}{(T - T_c) + 3\delta CDP^2/4\pi}, \quad (19)$$

$$\tau_0 = \frac{1}{\alpha[(T - T_c) + 3\delta CDP^2/4\pi]}, \quad (20)$$

with the proper choice of P . P as a function of the temperature and the bias field, E , is given by Eq. (7).

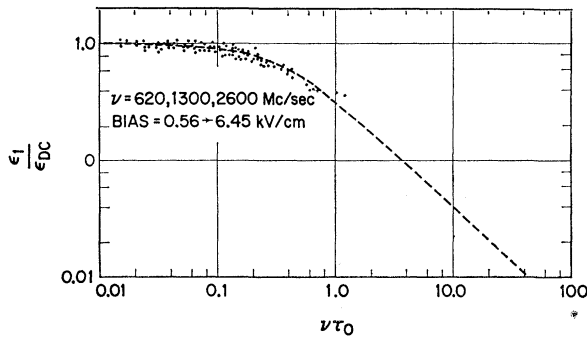


FIG. 6. Normalized ϵ_1 versus $\nu\tau_0$ for TGS at various bias fields. τ_0 has been adjusted for presence of spontaneous and induced polarization. Dashed curve is a plot of Eq. (4) in text taking polarization into account.

Figure 5 is a plot of (7) for P versus E with $\Delta T = T - T_c$ as a parameter. Figure 6 shows the data taken at various field strengths, temperatures and frequencies with a plot of (4) using (20) to determine the proper τ_0 . Again the agreement is quite good but the data do not extend to very high $\nu\tau_0$. This results from our having no experimental arrangement for frequencies above 4 kMc/sec, which allowed us to apply a bias field.

KD₂PO₄: FERROELECTRIC REGION

The data for KD₂PO₄ in the ferroelectric region or in both ferroelectric and paraelectric regions with a bias field are quite different from similar data for TGS, whereas the data are remarkably similar in the paraelectric region. In TGS, immediately above the fundamental crystal resonances, the ferroelectric dielectric

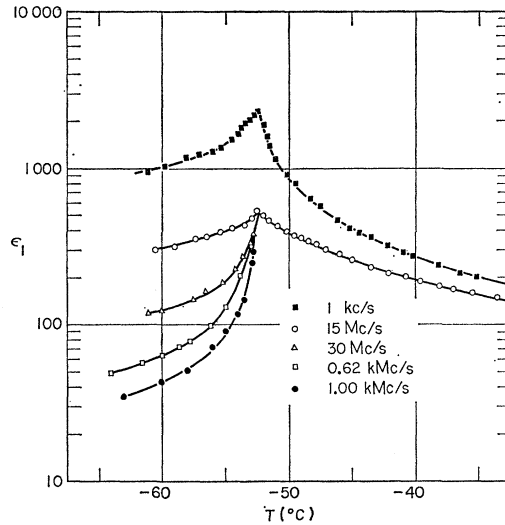


FIG. 7. Real dielectric coefficient ϵ_1 versus temperature for KD₂PO₄ at several frequencies. Main crystal resonances are clamped out between 1 kc/sec and 15 Mc/sec as shown but for $T < T_c$ (-52°C) there is a considerable anomalous response up to 1 kMc/sec.

coefficient obeys a Curie law with a Curie constant lower by a factor of 4.5 than the Curie constant in the paraelectric region (Fig. 1). As discussed above, the C_p/C_f ratio holds to very high frequencies for this material. One finds, however, that in KD₂PO₄ the ferroelectric dielectric coefficient continues to show a relaxation behavior into the kilomegacycle frequency range. These data are shown in Figs. 7 and 8. The real part ϵ_1 continues to decrease up to 2 kMc/sec and the loss tangent ϵ_2/ϵ_1 , which is very large at low frequencies, does not attain its expected value until approximately 2 kMc/sec.

This large anomalous response in the ferroelectric region is apparently associated with the domains in the material. When a biasing field is applied, the anomalous response decreases as the biasing field is increased,

indicating that the response is suppressed as the crystal tends toward a single domain. This behavior is shown in Fig. 9, which shows the decrease in $\tan\delta = \epsilon_2/\epsilon_1$ ($T < T_c$) at 620 Mc/sec as a function of the applied dc field. One sees that even at fairly high field strengths there remains an anomalous response for temperatures five or more degrees lower than the transition point. Since the field required to reorient a domain increases with ΔT , the temperature difference from the transition temperature, more domains remain at larger ΔT to contribute to ϵ_1 .

If the domains in KD_2PO_4 are very narrow then the high piezoelectric coefficient will allow strong coupling to higher order, mechanical modes of the crystal. This coupling will continue up to frequencies such that the wavelength of the mechanical resonance is of the same order as the domain dimension. To estimate the size of the domains we note that Mason⁸ found that a KDP

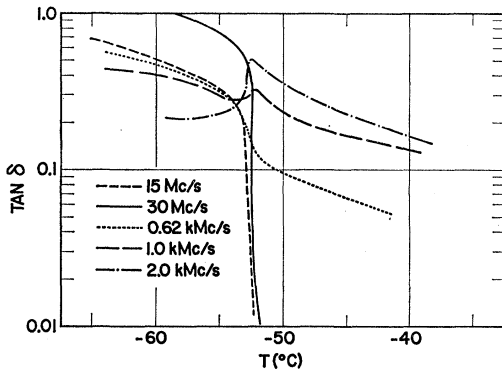


FIG. 8. Loss tangent ϵ_2/ϵ_1 versus temperature T for KD_2PO_4 at several frequencies. The large anomalous loss for $T < T_c$ ($-52^\circ C$) up to 2 kMc/sec is discussed in text.

crystal 1 cm long resonated at nearly 10^5 cps. Let us estimate, on the basis of Fig. 7, that the fundamental domain resonances are near $5 \times 10^8 \text{ sec}^{-1}$. This leads to a value of 2×10^{-4} cm for the significant domain dimension. We can also estimate domain sizes from a knowledge of the spontaneous polarization P_s which gives us an estimate of the depolarizing energy available to form domain walls and of the energy required to form a domain wall. Measurements were made of P_s using the usual hysteresis curve technique, which led to the results shown in Fig. 10. We can make use of the calculations of Kinase and Takahashi⁹ who show that the domain dimensions are inversely proportional to P_s and proportional to the square root of the wall energy. For $BaTiO_3$ they calculated a domain thickness of 0.19×10^{-4} cm using a $P_s = 2.2 \times 10^{-5}$ C/cm² and a wall

⁸ W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. Van Nostrand Company, Inc., New York, 1950), p. 150.

⁹ W. Kinase and H. Takahashi, *J. Phys. Soc. Japan* **12**, 464 (1957).

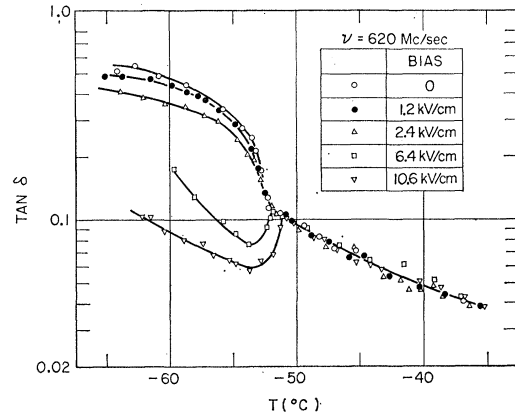


FIG. 9. Loss tangent ϵ_2/ϵ_1 versus temperature T for KD_2PO_4 at 620 Mc/sec for several values of dc bias field. The anomalous loss for $T < T_c$ ($-52^\circ C$) is seen to be decreased at large values of bias field.

energy of 1.5 ergs/cm². If we use the same equation but substitute $P_s = 5 \times 10^{-6}$ C/cm² and a wall energy of 50 ergs/cm²,¹⁰ the domain thickness becomes 4×10^{-4} cm in reasonable agreement with the result deduced from the high-frequency behavior. There is no direct experimental evidence concerning domains in KD_2PO_4 to support or contest the existence of domains of this size¹¹ but the high-frequency behavior strongly suggests it.

Above 2 kMc/sec the domain effects are essentially damped out. In general the dielectric behavior does not exhibit Curie behavior below T_c but for a small temperature range, $\Delta T < 4^\circ C$, a Curie constant can be de-

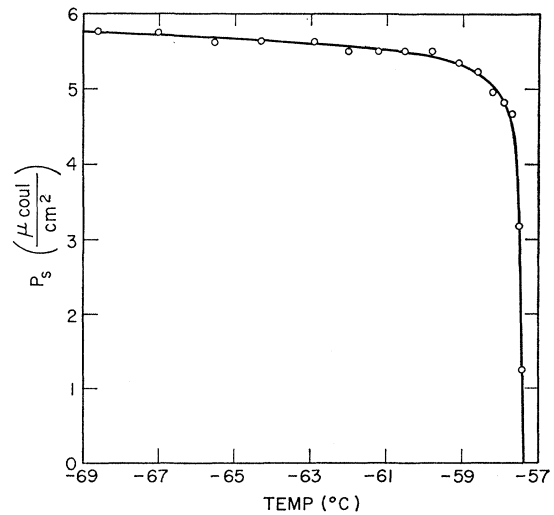


FIG. 10. Spontaneous polarization P_s versus temperature T for KD_2PO_4 measured by hysteresis loop. The level of deuteration is not quite the same as for sample shown in Figs. 8 and 9 leading to slightly lower T_c .

¹⁰ W. Kanzig and R. Sommerhalder, *Helv. Phys. Acta.* **26**, 603 (1953).

¹¹ F. Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Company, New York, 1962), p. 103.

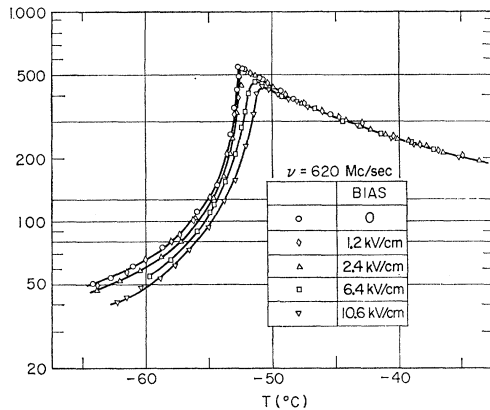


FIG. 11. Real dielectric coefficient ϵ_1 versus temperature T for KD_2PO_4 at 620 Mc/sec and various dc bias fields. Contrast with similar measurements for TGS (Fig. 3).

terminated which leads to a ratio $C_p/C_f \sim 16$ far in excess of the expected value of 2. A rough estimate of the electrostrictive contribution based on the "quadratic strain coefficients," gives a value of δ an order of magnitude too small to account for the observed ratio. It is difficult to see how a second-order or "blurred" second-order transition would lead to behavior of this kind.

In addition, the dependence of T_c on an applied electric bias field E has been measured. The results are shown in Figs. 11 and 12. The data show clearly that the net effect is to preserve the transition temperature T_c but shift it to higher temperatures directly proportional to the bias field strength. For a material undergoing a second-order ferroelectric transition, one can define a

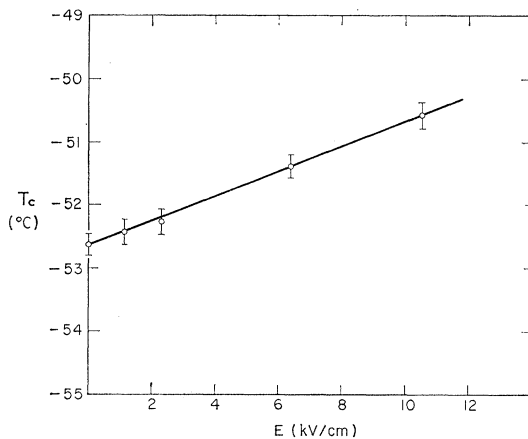


FIG. 12. Value of transition temperature T_c versus dc bias field E .

$\epsilon_1(\text{max})$ which shifts to higher temperature proportional to $E^{2/3}$ (TGS exhibits this behavior). However, Devonshire⁹ has shown that $\partial T_c/\partial E$ for a first-order transition is given by

$$\partial T_c/\partial E = \Delta P/\Delta S, \quad (21)$$

where ΔP and ΔS are the change in polarization P and entropy S across the transition. Experimentally, $\partial T_c/\partial E = 1.9 \times 10^{-4} \text{C/V/cm}$ (Fig. 12). Taking $\Delta S = 0.47 \times (\text{cal/mole})/^\circ\text{C}$,¹² we obtain a value $\Delta P = 6 \times 10^{-6} \text{C/cm}^2$ for the discontinuous change in polarization at T_c . This is in fair agreement with the saturation value, $P = 5.5 \times 10^{-6} \text{C/cm}^2$, which we measured (Fig. 10).

From these data, it appears that neither the usual first- or second-order designation³ is adequate to describe the behavior of KD_2PO_4 .

SUMMARY

It has been shown that for triglycine sulfate the high-frequency dielectric behavior in the para- and ferroelectric regions, with and without an applied bias field, can be adequately described by a model involving a Gaussian distribution of relaxation times among the dipoles of the system. The half-width of the distribution is found to be proportional to the low-frequency susceptibility. It is found necessary to introduce an empirical correction to the low-frequency susceptibility to account for the observed C_p/C_f ratio. This correction amounts to a change in the coefficient of the P^4 term in the expansion of the free energy, and it is suggested that it arises from the damping out of the electrostrictive contribution to this term at the measuring frequencies.

The dielectric behavior of KD_2PO_4 at high frequency is not that characteristic of a second-order ferroelectric transition. There is a large loss term between 10 Mc/sec and 2 kMc/sec in the ferroelectric region attributed to many small domains (10^{-4}cm). Above 2 kMc/sec $C_p/C_f \approx 16$, and the transition temperature varies linearly with applied bias field. These observations are taken to indicate that KD_2PO_4 does not fit the usual designation of first- or second-order transition.

ACKNOWLEDGMENTS

We would like to express our appreciation to Dr. G. F. Herrmann for many stimulating discussions and to J. Little for assistance with the measurements.

¹² Reference 11, p. 69.