$\pm 3/2 \leftrightarrow 1/2$:

$$g\beta H = h\nu \pm b_2{}^0 \pm (18/4) b_4{}^0 \mp (7/8)(b_6{}^6 - 5b_6{}^0) + \frac{15[b_2{}^0 + b_4{}^0 + (1/16)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H \pm b_2{}^0 \pm (9/2) b_4{}^0 \mp (7/8)(b_6{}^6 - 5b_6{}^0)} - \frac{15[b_2{}^0 + b_4{}^0 + (1/16)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H \mp b_2{}^0 \mp (9/2) b_4{}^0 \pm (7/8)(b_6{}^6 - 5b_6{}^0)} - \frac{(45/4)[b_2{}^0 - b_4{}^0/6 - (1/8)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H \mp 3b_2{}^0 \mp (33/4) b_4{}^0} + \frac{(21/4)[b_2{}^0 - (5/2) b_4{}^0 + (5/56)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H \mp 5b_2{}^0 \pm (15/4) b_4{}^0 \mp (1/2)(b_6{}^6 - 5b_6{}^0)},$$

$1/2 \to -1/2$:

$$g\beta H = h\nu - \frac{15[b_2{}^0 + b_4{}^0 + (1/16)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H + b_2{}^0 + (9/2) b_4{}^0 - (7/8)(b_6{}^6 - 5b_6{}^0)} - \frac{15[b_2{}^0 + b_4{}^0 + (1/16)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H - [b_2{}^0 + (9/2) b_4{}^0 - (7/8)(b_6{}^6 - 5b_6{}^0)]} + \frac{(45/4)[b_2{}^0 - b_4{}^0/6 - (1/8)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H - 3b_2{}^0 - (33/4) b_4{}^0} + \frac{(45/4)[b_2{}^0 - b_4{}^0/6 - (1/8)(b_6{}^6 + 7b_6{}^0)]^2}{2g\beta H + 3b_2{}^0 + (33/4) b_4{}^0}.$$

For $\alpha = 30$ one has to change the sign of $b_6{}^6$, i.e., $b_6{}^6 \to -b_6{}^6$.

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Paraelectric Response of KD_2PO_4

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The dielectric behavior of KD_2PO_4 in the paraelectric region, i.e., above the Curie temperature, has been measured up to 3.5×10^{10} cps. For frequencies above the crystal resonances, the complex dielectric coefficient exhibits a relaxation behavior very similar to that observed in triglycine sulfate. A model, which assumes a Gaussian distribution of Debye dipoles, fits the data quite well and appears to establish this representation as a valid one for "soft" ferroelectrics.

It was shown recently[1] that the dielectric behavior of triglycine sulfate (TGS), in the paraelectric region above the Curie temperature could be adequately described by assuming a Gaussian distribution of Debye relaxation times among the dipoles of the crystal. To determine whether this type of behavior is a general characteristic of these "soft" ferroelectrics or represented only the behavior of monoclinic TGS, the measurements of clamped, complex dielectric coefficient were extended to deuterated potassium dihydrogen phosphate, KD_2PO_4, which is a tetragonal crystal with a Curie temperature nearly 100°C below that of TGS.

The results reported in this paper show that the model proposed for dipolar relaxation in TGS also gives a good representation of the KD_2PO_4 response.

The complex dielectric coefficient for KD_2PO_4 single crystals were measured from 1 kc/sec through 35 kMc/sec, using measurement techniques essentially identical to those reported previously.[1] Temperature control between -70 and 0°C was provided by circulating an organic fluid, heptane, through the measurement cell. Heptane, which remains liquid to below -70°C, has both a low loss and a low dielectric constant, 1.97, over the frequency range studied. A steady flow rate of 100 cc/min was maintained through the waveguide section and the fluid temperature was controlled by raising or lowering the heptane reservoir in an acetone-dry ice bath. Thin Teflon gaskets sealed heptane off from the rest of the waveguide circuit. This technique provided excellent thermal contact between the crystal and waveguide portions of the measurement cell.

A Curie plot of typical low-frequency data is shown in Fig. 1. The 1000-cps data represent the "free" crystal response, i.e., the contribution of the piezoelectrically coupled, mechanical resonances is present. The 15-Mc/sec data represent the "clamped" crystal response above all significant mechanical resonances. The Curie constants, 4280°C at 15 Mc/sec and 4050°C at 1000 cps, are almost the same but are about 25% higher than the most recently reported value.[2] The transition temperature was about -52.5°C for both cases but the intercept temperature changed from -61.5 to -54.8°C for the clamped and free case, respectively.

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

[2] R. J. Mayer and J. L. Bjorkstam, J. Phys. Chem. Solids **23**, 619 (1962).

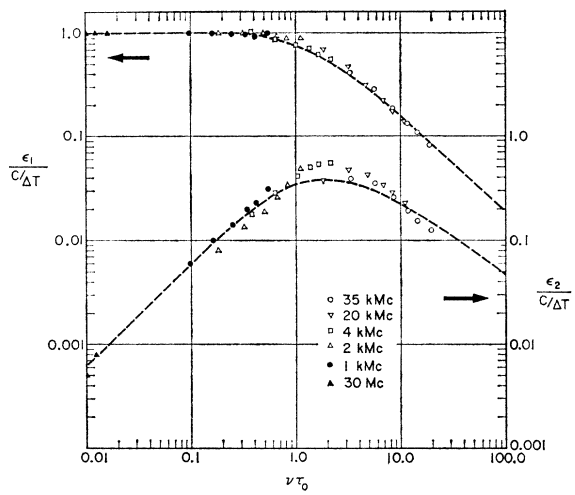

FIG. 1. Curie plot of reciprocal susceptibility vs temperature for KD_2PO_4 at two frequencies. The 1000-cps case represents the nearly free crystal while the data at 15 Mc/sec represent the "clamped" crystal. The Curie constant, C, is given for each frequency.

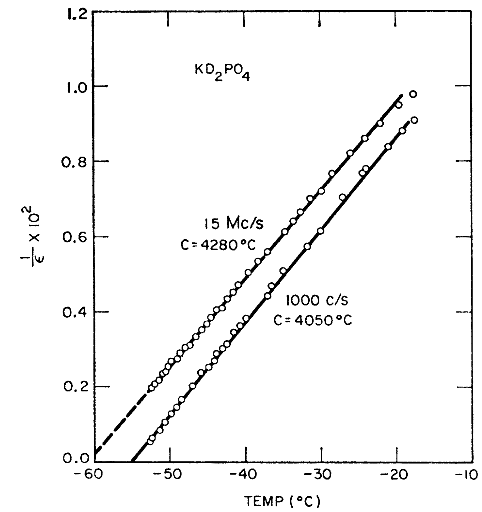

FIG. 2. Real, ϵ_1, and imaginary, ϵ_2, dielectric coefficients normalized by dividing by the low-frequency clamped dielectric coefficient, for KD_2PO_4 as a function of $\nu\tau_0$, the measurement frequency times an empirical relaxation parameter, τ_0, which is inversely proportional to ΔT, the difference between the Curie temperature and the measurement temperature.

Figure 2 shows the normalized real, ϵ_1, and imaginary, ϵ_2, dielectric coefficients as a function of $\nu\tau_0$, where ν is the frequency and τ_0 is an empirically determined relaxation parameter, inversely proportional to ΔT, the separation from the intercept Curie temperature. ϵ_1 and ϵ_2 are normalized by dividing the measured values by the low-frequency, clamped dielectric coefficient, $C/\Delta T$, as given by the 15-Mc/sec data in Fig. 1.

The curves in Fig. 2 are plots of the expression derived previously[1] assuming a Gaussian distribution of Debye relaxation times, i.e.,

$$\epsilon_1=\int_0^\infty \frac{y(\tau)}{1+(\nu\tau)^2}d\tau,\quad \epsilon_2=\int_0^\infty \frac{y(\tau)\nu\tau}{1+(\nu\tau)^2}d\tau,$$

where $y(\tau)=Ae^{-(\tau/\tau_0)^2}$. τ_0 is the half-width of the distribution and is of the form $\tau_0=1/\alpha(T-T_c)$. The proportionality constant α is determined empirically.

The data for ϵ_1 fit the derived curve quite well while ϵ_2 has a region of some deviation around $\nu\tau_0=1$. The scatter in ϵ_2 is larger, partially because it is the more difficult measurement to make accurately. The value of α for a best fit is $\alpha=0.22$ (kMc/sec)/C° which is roughly a factor of 2 smaller than the α for TGS. If we assume that the distribution in relaxation times arises from local ordering or "clustering" of the dipoles,[1] the decrease in α from TGS to KD_2PO_4 could be thought of as a decrease in the dipolar interaction strength. The normalization constant A in the Gaussian distribution is found to be, $A=C\alpha/\sqrt{\pi}$ from the zero-frequency normalization condition and has the units of frequency. A for KD_2PO_4 is 1.27×10^{12} cps which is close to the value, $A=1.77\times10^{12}$ cps, found for TGS.

Känzig[3] has pointed out that the results of Akao and Sasaki[4] on relaxation in Rochelle salt indicate a relaxation time proportional to the susceptibility. We conclude that a Gaussian distribution of relaxation time having a measure, τ_0, proportional to the reciprocal susceptibility gives a good representation of the paraelectric behavior of "soft" ferroelectrics.

[3] W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, pp. 19–20.

[4] H. Akao and T. Sasaki, J. Chem. Phys. **23**, 2210 (1955).