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BRILLOUIN-SCATTERING DISPERSION IN FERROELECTRIC TRIGLYCINE SULFATE

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Dispersion has been observed in the Brillouin components of the light-scattering spectrum of triglycine sulfate. It is attributed to the Landau-Khalatnikov relaxation of fluctuations in the spontaneous polarization.

We have observed the light-scattering spectrum of triglycine sulfate (TGS) in the temperature range 34-54°C and found an anomalous change in the shifts of both the longitudinal and transverse Brillouin components. TGS is a transparent monoclinic crystal which is ferroelectric at room temperature and undergoes a second-order phase transition to a nonpolar phase at the Curie temperature ($T_c \approx 49°\mathrm{C}$).[1] In the neighborhood of T_c, both the magnitude and the relaxation time of fluctuations in the spontaneous polarization $\vec{\mathrm{P}}$ become very large. According to Landau and Khalatnikov, the relaxation time τ is given by[2]

$$\tau = A(T_c - T)^{-1}\ \mathrm{sec}. \tag{1}$$

Thus, if phonons can couple to polarization, a temperature-dependent relaxation is expected, which will produce a dispersion in the phonon velocity of the form[3]

$$V^2 = V_\infty^{\,2} - (V_\infty^{\,2} - V_0^{\,2})/[1 + (\omega\tau)^2]. \tag{2}$$

The ultrasonic attenuation produced by this relaxation has been studied by O'Brien and Litovitz in the frequency range 15 to 125 MHz.[4] Their measurements give a temperature dependence for the relaxation time which fits Eq. (1) with $A = 2.25 \times 10^{-10}$ sec °C. Since in our experiment the Brillouin shifts are proportional to the phonon velocity, we believe that the changes in the Brillouin shifts which we have observed are due to the L-K relaxation.

Our apparatus, which has been described elsewhere,[5] employs a Spectra-Physics model 125 He-Ne laser (approximately 80 mW at λ6328) as the light source, and a pressure-swept Fabry-Perot interferometer with photoelectric detection for spectral analysis of the scattered light. The sample is placed in a large paraffin-oil bath which acts as the thermostat and also matches the appropriate refractive index of the sample, thus eliminating scattering from the crystal surfaces and refraction of the beam. Silver electrodes painted onto the b faces permit the sample to be electrically polarized between runs.

A typical spectrum is shown in Fig. 1. The measured Brillouin shifts for longitudinal and transverse phonons are shown in Fig. 2 for scattering angles of 90 and 135°, i.e., for two different phonon wavelengths. The orientation in the crystal of the scattering vector $\vec{q}$ was the same for the two scattering angles and is shown in the inset in Fig. 1. The scattering plane was parallel to the crystal (010) plane, and the polarization of the incident and scattered light was perpendicular to this plane. The transverse phonon giving the Brillouin component is polarized in the (010) plane. The refractive

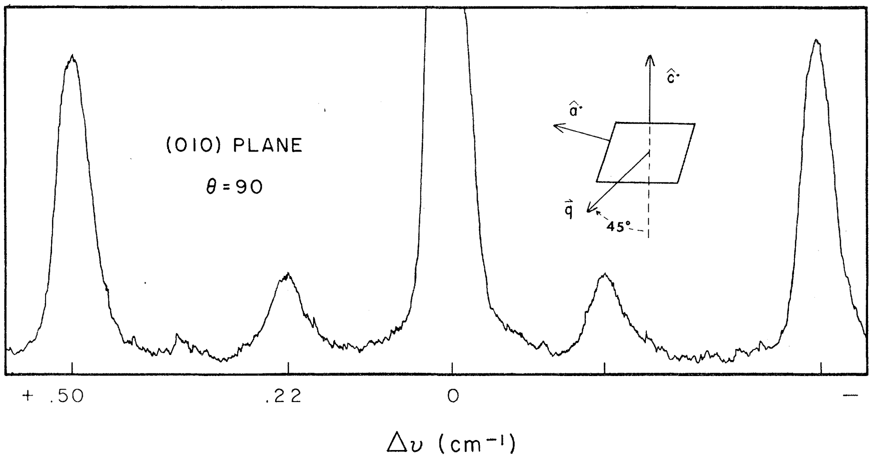

FIG. 1. Typical light-scattering spectrum at $T = 34°\mathrm{C}$ showing transverse ($\Delta\nu = \pm0.22\ \mathrm{cm}^{-1}$) and longitudinal ($\Delta\nu = \pm0.50\ \mathrm{cm}^{-1}$) Brillouin components. Inset, orientation of scattering vector $\vec{q}$ with respect to reciprocal lattice vectors in the (010) plane.

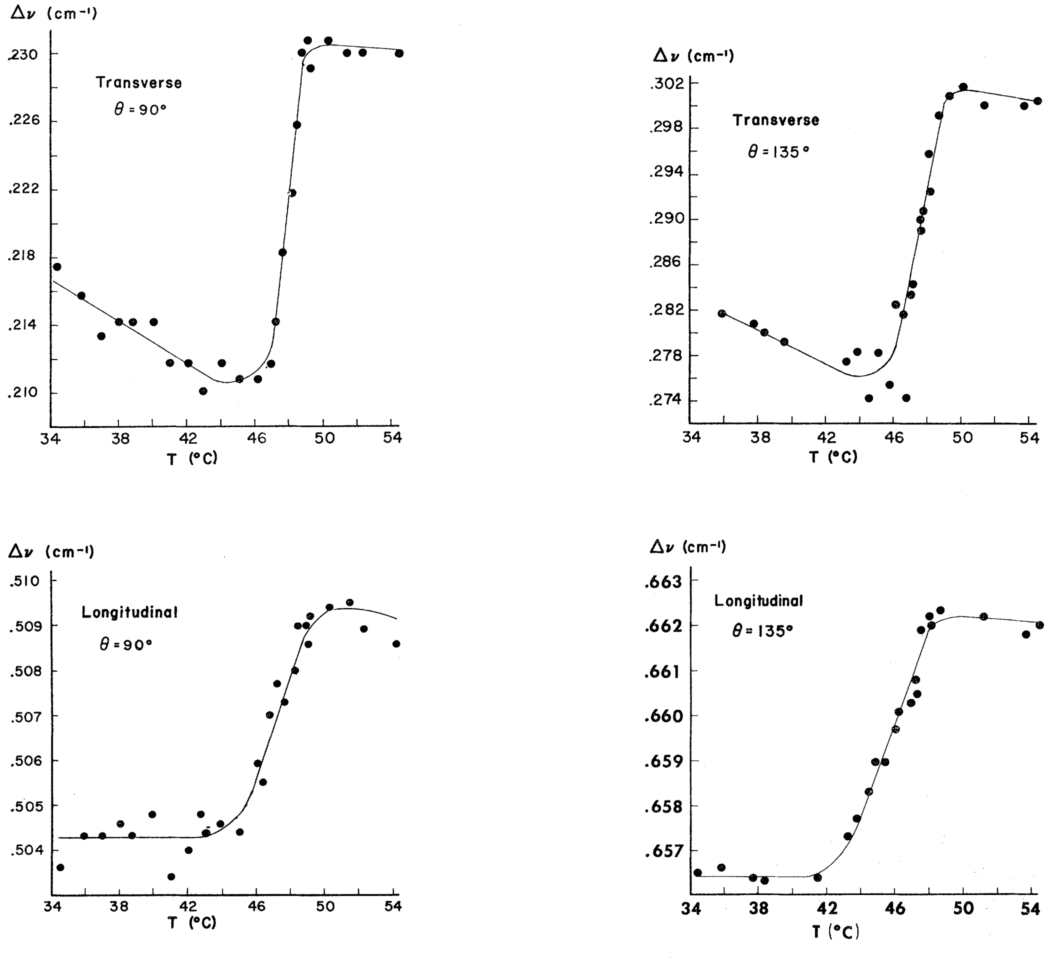

FIG. 2. Brillouin shift versus temperature. Longitudinal and transverse components at scattering angles of 90 and 135°.

index for the incident and scattered light beams was the same, since [010] is a principle axis of the dielectric tensor. The temperature dependence of this index was measured and found to be negligible. Thus the abrupt changes in the observed Brillouin shifts seen in Fig. 2 are apparently produced by the relaxational dispersion of the hypersonic velocity and are found to be describable by a dispersion equation of the form of Eq. (2). Several additional features were observed during the experiment which we mention in passing and which will be described in detail in a future publication: (1) When the crystal was oriented so that the b axis was parallel to the scattering vector $\vec{q}=\vec{K}_S-\vec{K}_0$, no dispersion was observed, in agreement with the conclusion of O'Brien and Litovitz that phonons propagating along the b axis do not couple to polarization. However, for $\vec{q}$ perpendicular to the b axis, the magnitude of the dispersion was found to depend strongly on crystal orientation and actually vanishes for some directions, which indicates a severe anisotropy of the phonon-polarization coupling constant not previously observed. (2) The relaxational dispersion of transverse phonons is approximately 10 times greater than that of longitudinal phonons. Near the center of the resonance, a marked broadening of the transverse components was observed, indicating strong attenuation associated with the large dispersion as is expected. (3) For T slightly above the region of dispersion, application of an electric field across the b faces shifts the Brillouin components back to their low-temperature positions, indicating the equivalence of the dynamic coupling of phonons to spontaneous or field-induced polarization. (4) The slope of the curves away from the dispersion region depends on the orientation of $\vec{q}$ in the crystal and on the phonon polarization, and is presumably due to the temperature dependence of the relevant elastic constants.

The dispersion curves of Fig. 2 may be used to deduce the temperature dependence of the relaxation time τ. Since the dispersion is relatively small (~10% for transverse components and ~1% for longitudinal components), the temperature at which $\omega\tau=1$ is very nearly equal to the temperature at which V (and thus $\Delta\nu$) passes through the midpoint of the dispersion curve. The four points thus deduced from the data fit the L-K equation (1) with $A=(2.9\pm0.3)\times10^{-11}$ sec °C and $T_C=49.2$°C.

Because of the short wavelength of the phonons involved in Brillouin scattering, we modified the L-K equation to include the effects of possible short-range polarization correlations by adding a term proportional to $(\vec{\nabla}P_2)^2$ to the free energy, as first proposed by Landau.[6] The resulting expression for τ is

$$\tau=(a+bq^2)^{-1}(T_C-T)^{-1}. \qquad (3)$$

The correlation term bq^2 leads to a predicted curvature of τ vs $(T_C-T)^{-1}$ which we do not observe, indicating that such correlations are not important for phonon wavelengths as short as 10^{-4} cm, and that the simple L-K Eq. (1) is still valid in this range. In view of this result, the discrepancy of a factor of ten between the ultrasonic results and the present experiment cannot be attributed to correlation effects, and its source remains an open question.

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