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Anisotropy in Anomalies of Hypersound Velocity and Attenuation in Ferroelectric TSCC

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From Brillouin shift and linewidth of longitudinal phonons propagating along the [100] and [001] directions of TSCC, the polarization relaxation time was calculated to be $\tau = 3.1 \times 10^{-12} / (T_c - T)$ sec below the transition temperature T_c . The anomalies in the longitudinal phonons of the [010] propagation were carefully examined using an annealed crystal of excellent quality. No essential difference was observed between the velocities of a normal and high quality crystals. The relaxation time was deduced as a function of temperature from the observed anomalies in the velocity and linewidth. Spectra are observed for nearly forward scattering from the $q//[010]$ phonons.

§1. Introduction

Tris-sarcosine calcium chloride (TSCC), $(\text{CH}_3\text{NHCH}_2\text{COOH})_3 \cdot \text{CaCl}_2$ is a uniaxial ferroelectric¹⁾ whose space group is D_{2h}^{16} (Pnam) in the paraelectric phase (PE) phase²⁾ and C_{2v}^9 (Pn2₁a) in the ferroelectric (FE) phase.³⁾ Courtens *et al.*⁴⁾ reported that the dielectric constant ϵ_b for TSCC exhibits a logarithmic correction to Curie-Weiss behavior, because of the dipole-dipole interaction which is important in the critical region.⁵⁾ Raman scattering studies^{6,7)} show the unusual characteristic that the transverse optic (TO) and longitudinal optic (LO) modes soften in the same way below T_c and have nearly equal frequencies. This indicates that the dipole-dipole interaction is weak,⁸⁾ so short-range interactions must be responsible for the occurrence of transition even though dipole-dipole interaction may be responsible for the reported logarithmic correction.

Brillouin scattering in this crystal is interesting, because we can deduce dynamical behavior of the phase transition in the gigahertz region. Previous Brillouin scattering results have been reported in several papers.^{6,9,10)} The Brillouin shifts and the linewidth of the $q//[100]$ and [001] longitudinal phonons showed large anomalies at the transition temperature. These phonon modes couple piezoelectrically with polarization fluctuations in the FE phase.⁹⁾ From the temperature where the damping constant attains maximum value, the dipolar relaxation time of dipoles can be evaluated.⁹⁾ However, the situation is quite different for the [010] longitudinal phonons. These phonons induces longitudinal polarization waves along the [010] direction. The fluctuations of these polarization waves are suppressed because of the appearance of a depolarization field in the plane waves.¹¹⁾ Thus the [010] longitudinal phonons are presumed to show no anomalies relevant to the polarization fluctuations through piezoelectric coupling.

However, in refs. 9 and 10, relatively large anomalies were observed in the velocity and the damping constant of the $q//[010]$ phonons. Such anomalies are not deduced from the phenomenological theory. So, we should be very careful to assert such anomalies in ferroelectric crystals.

For instance, the anomaly of longitudinal sound velocity of the [001] propagation in TGS in the PE phase was formerly believed to occur from electrostrictive coupling¹²⁾ (fluctuation¹²⁾). However, it was demonstrated that this anomaly is almost completely eliminated by measuring the sound velocity in a very small region of a crystal of very good quality.¹³⁾ Therefore, in this paper, we have grown very good crystals and the sample was annealed to improve the quality.⁴⁾ The Brillouin spectra of the $q//[010]$ phonons were carefully analyzed by a high resolution triple-pass Fabry-Perot interferometer. The temperature dependence of the Brillouin shift and the linewidth was compared with that of the former experiment. To determine the temperature correspondence between this experiment and the former experiment, the dielectric constant ϵ_b was measured simultaneously on the same sample.

To investigate the dispersion of this phonon mode, a small angle scattering¹⁴⁾ ($\theta = 7.6^\circ$) has been performed. This experiment also helps to understand the broadening of Brillouin spectra for right angle scattering. The relaxation time was calculated as a function of temperature from the velocity dispersion and the damping constant. The origin of this relaxation time is discussed.

§2. Experimental Procedure

Single crystals of TSCC were grown from aqueous solutions of sarcosine and calcium chloride by slow cooling. The solution for the sample of precise $q//[010]$ phonon measurement was prepared from chemicals of special quality and was filtered by a $0.2 \mu\text{m}$ pore size membrane filter. This sample was shaped into a form of rectangular parallelepiped and carefully polished. Aluminum was evaporated as electrodes for measurement of the dielectric constant ϵ_b .

This sample was annealed at 140°C for 24 hours in a vacuum glass tube to improve the quality of the crystal as described in ref. 4. No extra mechanical or heat treatment was added to the sample after removal from the vacuum environment. The dielectric constant was measured simultaneously with Brillouin scattering at 10 kHz by the use of a ratio transformer.

For the sample of a small angle scattering, a parallelepiped which is 8 mm long along the c-axis was prepared. This sample was not heat treated.

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The Brillouin scattering equipment and the cryostat are the same as those already described in ref. 9. However, we have used a triplepass Fabry-Perot interferometer, smaller collection angles $\sim 0.5^\circ$ and higher resolution (1.3 GHz $\sim$ 2 GHz Free Spectral Range) in this paper. Therefore, these conditions made us easier to obtain Brillouin shifts and linewidth of much higher accuracy.

§3. Results and Discussion

Figure 1 shows temperature dependence of Brillouin shift and linewidth of longitudinal [100] phonons. The transition temperature is 130 K. A similar result has been obtained for the $q//[001]$ phonons.⁹⁾ The large anomalies in the Brillouin shift and the linewidth arise from the linear coupling of strain and polarization (piezoelectric coupling) in the FE phase. We can evaluate the relaxation time of the electric polarization by comparing the temperature where the linewidth attains a maximum value with the transition temperature.⁹⁾ The transition temperature can be determined either by the ϵ_b measurement or by a knee point in the velocity. The relaxation time was obtained to be $\tau = 3.1 \times 10^{-12}/(T_c - T)$ sec.

The polarization relaxation time measured by the dielectric dispersion measurement¹⁵⁾ gave $\tau = (5.7 \text{ to } 11) \times 10^{-12}/(T_c - T)$ sec. This value is in relatively good agreement with our result. E. Nakamura *et al.*^{3,15)} claim that the TSCC transition has an order-disorder character from the dielectric measurement and X-ray structure analysis. However, even in a displacive ferroelectric, if the soft mode is over-damped, the system shows a character which is quite similar to that of order-disorder transition. In this case, the effective relaxation time is given by γ/ω_0^2 . Here ω_0 is soft mode frequency and γ is damping constant. Recently, very precise Raman spectroscopy⁷⁾ has been done on this crystal by M. Sugo *et al.*, placing special emphasis on the measurement of the

TO and LO soft modes. Their result of temperature dependence of the effective relaxation time gave $3.1 \times 10^{-12}/(T_c - T)$ sec which is identical with our value. The above results suggest that the dielectric relaxation is strongly related to the over-damped TO soft mode.

Slight anomalies in the shift and the linewidth in the PE phase are attributed to quadratic coupling of polarization and strain ($p_y^2 x$). This type of anomaly is referred to as fluctuation damping.¹²⁾ However, as we already mentioned in §1, we should be very careful about assert that this kind of anomaly is really of intrinsic character. Therefore, we measured Brillouin shift and linewidth in an excellent sample. The scattering geometry is $x+y(zz)$ $x-y$ and the dielectric constant ϵ_b was also measured during the Brillouin scattering measurement.

The high contrast of the triple-pass Fabry-Perot interferometer enabled us to determine the linewidth much more accurately than before. The temperature dependence of Brillouin shift of the $q//[010]$ phonons is illustrated in Fig. 2. A comparison of this data with the former result of the shift of the $q//[010]$ phonons leads us to the conclusion that there is no essential difference between these two results. Therefore, we can assert with high probability that this anomaly is intrinsic to the FE phase transition in TSCC.

Fig. 2. Temperature dependence of velocities of the $q//[010]$ phonons measured by right angle Brillouin scattering (●) and by small angle ($\theta = 7.6^\circ$) scattering (○).

Fig. 1. Temperature dependence of Brillouin shift (●) and linewidth (○) (FWHM) of longitudinal phonons in TSCC propagating along the [100] direction. The scattering geometry is $x+y(zz)-x-y$.

Fig. 3. Temperature dependence of Brillouin linewidths of the $q//[010]$ phonons of TSCC at ~ 21 GHz (●) and at ~ 2 GHz (○).

Figure 3 shows the temperature dependence of the linewidth (FWHM) which is expressed as a damping constant (Γ) divided by π in a simple exponential decay process.⁹⁾ The linewidth increases with decreasing temperature and takes a maximum value at 126.5 K which is 3.5 K below the transition temperature.

The temperature dependence of the Brillouin shift and the damping constant is not so simple as that of piezoelectric coupling. For this we calculate the relaxation time at each temperature from the above data. According to the theory of sound attenuation and dispersion,¹⁶⁾ the elastic stiffness $c(\omega)$ and damping constant (Γ) can be expressed as follows using complex elastic stiffness $c^*(\omega)$,

$$c^*(\omega) = c_\infty - \frac{\Delta c}{1 + i\omega\tau} \quad (1)$$

$$c(\omega) = \text{Re } c^*(\omega) = c_\infty - \frac{\Delta c}{1 + \omega^2\tau^2} \quad (2)$$

$$\Gamma(\omega) = \frac{q}{2\pi\rho v} (\text{Im } c^*(\omega)) = \Gamma_\infty + \frac{\Delta c\tau}{1 + \omega^2\tau^2} \frac{q^2}{2\pi\rho}, \quad (3)$$

where Δc is the difference between the high frequency limit elastic stiffness and the low frequency limit elastic stiffness. The other symbols have their usual meanings. From eqs. (2) and (3), the relaxation time is expressed by

$$\tau = \frac{\Gamma}{(c_\infty - c(\omega))} \left[\frac{q^2}{2\pi\rho} \right]^{-1}. \quad (4)$$

Using extrapolated value of the stiffness around 140 K as c_∞ , the relaxation time was calculated as a function temperature. The result is shown in Fig. 4. The relaxation time shows rather unusual behavior which cannot be expressed in a simple power law of $|T_c - T|$.

The phonon velocity and the damping constant of the small angle scattering are also shown in Figs. 2 and 3. Although, the phonon frequency is one order of magnitude smaller than that of right angle scattering, only small dispersion is observed. A large dip-like anomaly is reported in the ultrasonic velocity at 20 MHz.¹⁷⁾ The damping constant at 2 GHz does not show a large anomaly as

Fig. 4. Temperature dependence of relaxation time deduced from the velocity and the damping constant of TSCC propagating in the [010] direction.

at 21 GHz. The anomaly is less than 10 MHz, if it exists. This range is consistent with the calculated Γ at 2 GHz from the velocity at 2 GHz and the relaxation time.

Determination of linewidth around 10 MHz is very difficult, because the accuracy of the measurement is limited not only by the resolution of the Brillouin spectrometer but also by the broadening of the incident laser light. Though we could not determine meaningful temperature dependence of the linewidth in the small angle scattering, the very narrow linewidth might suggest that the line broadening from right angle scattering is not of static origin such as caused by spacial variation of the refractive index, etc.

Considering the complicated feature of the temperature dependence of the relaxation time, the anomaly might not be caused by a single origin such as energy fluctuations which arise from the p^2x coupling term.¹²⁾ Since the dipole-dipole interaction is very small in TSCC, a crossover behavior where the origin of the anomaly changes from dipole-dipole interaction dominant to short-range interaction dominant might be expected. For further investigation, Brillouin scattering of other than these two scattering angles together with precise ultrasonic measurements are strongly recommended.

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