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BRILLOUIN SCATTERING NEAR THE FERROELECTRIC PHASE TRANSITION IN TSCC

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Abstract Brillouin spectra from longitudinal phonons in ferroelectric tris-sarcosine calcium chloride (TSCC) propagating along [100], [010) and [001] have been measured as functions of temperature. Large anomalies were found in the Brillouin shift and linewidth in the [100] and [001] phonons. These anomalies are interpreted as arising from the linear coupling of the polarization and phonons. From the the temperature where the linewidth is maximum, the relaxation time of the polarization fluctuations is estimated to be $\tau=3.1\times10^{-12}/(T_c-T)$ sec, where T_c is the ferroelectric transition temperature. We also observed anomalies in Brillouin shift and linewidth of the [010] phonons which propagate along the ferroelectric axis. These anomalies are interpreted as coming from electrostrictive coupling. The energy relaxation time was estimated to be $\tau_E=2.5\times10^{-10}/(T-T_c)$ sec in the paraelectric (PE) phase and $\tau_E=1.0\times10^{-9}/(T-T_c)$ sec in the ferroelectric (FE) phase, by comparing our Brillouin results with those f the ultrasonic measurements.

INTRODUCTION

Tris-sarcosine calcium chloride (TSCC) is a uniaxial ferroelectric, with a Curie temperature near 130 K.[1] At room temperature it has orthorhombic symmetry characterized by space group D_{2h}^{16}-Pnma with four formula units per unit cell.[2] In the FE phase this crystal remains orthorhombic with spase group C_{2v}^{9}-Pna2_1.

There are disputes concerning whether the FE transition of this crystal is order-disorder or displacive. Soft modes have been found in TSCC both in the PE and FE phases.[3-5] Scott's group claims that this crystal is a textbook example of a displacive type ferroelectric from their analysis of the results of millimeter wavelength spec-

troscopy.[5] They could satisfactorily explain the temperature dependence of the dielectric constant in the above frequency region by a simple oscillator model. However, Chen and Schaack recently showed that their Raman and infrared spectra can be much better explained by the pseudospin-phonon coupling theory.[6,7] They concluded that TSCC and partially brominated TSCC (i.e. $TSCC_{1-x}B_x$) undergo phase transitions which are mostly of the order-disorder type.[6,7] Furthermore, Schmidt showed that the pressure-temperature phase diagram[8] of TSCC can be interpreted by a cluster model,[9] which indicates that this phase transition is partly of the order-disorder type. Since Brillouin scattering measures the velocity and attenuation of acoustic phonons in the GHz region, its use in TSCC helps to understand the dynamical behavior in this frequency region.

EXPERIMENTAL

Single crystals of TSCC were grown from an aqueous solution of pure sarcsine and reagent grade $CaCl_2$. Since this crystal has ferroelastic domains at room temperature, single domain portions were carefully examined with a polarizing microscope. Exceptionally clear parts were chosen from these crystals and two samples which have the form of a rectangular parallelepiped 3x3x2 mm^3 were prepared. One sample was cut so that the longitudinal phonons $q \parallel [100]$ and $q \parallel [010]$ could be measured by right angle scattering and the other was cut so that longitudinal phonons $q \parallel [001]$ and $q \parallel [010]$ could be measured. The two samples were polished and then masked together by a blackened coper foil with pinholes for the incident and the scattered light beams. The masked sample pair was placed in a high pressure optical cell described previously.[10] The cell was filled with isopentane for index matching. The optical cell temperature could be controlled within 3 mK during the measurement.

A Lexel Model 95-2 argon laser operating in a single mode at a wavelength of 514.5 nm and a power level of 200 to 300 mW was used as a light source. The scattered light was collected in a cone of

1^{o} and analyzed by a piezoelectrically scanned Burleigh Model 140 Fabry-Perot interferometer. Finesse optimization and drift control were achieved by a home-made control system using an AIM-65 microcomputer.

RESULTS AND DISCUSSION

Figures 1-3 show the temperature dependence of the Brllouin shift and linewidth for longitudinal phonons propagating along [100], [010] and [001]. The temperature dependence of the Brillouin shift and the decay rate of the [100] phonons is quite similar to that of the [001] phonons though the anomlies are smaller for the latter case. In the above two cases, the polarization and the strain couple bilinearly in the FE phase.[11] For these two phonon propagations, the velocity v and the attenuation in the FE phase are given by[12-14]

$$v^2 = v_\infty^2 - [(v_\infty^2 - v_o^2)/(1+\omega^2\tau_o^2 t^{-2})], \qquad (2)$$

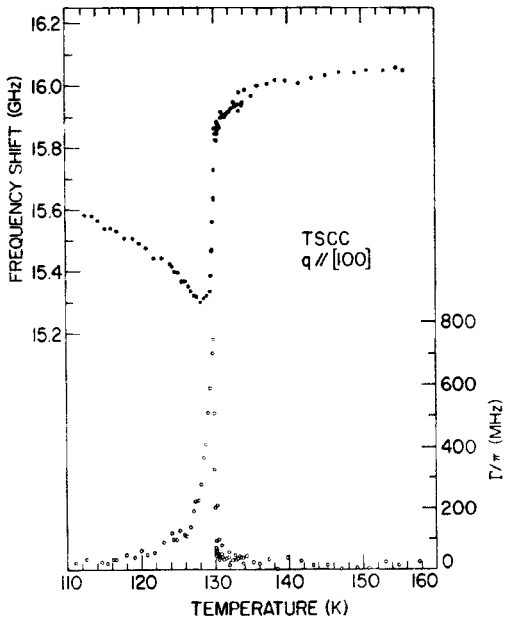

Figure 1 Temperature dependence of Brillouin shift (●) and linewidth (○) (FWHM) of longitudinal phonons in TSCC propagating along the [100] direction. The scattering geometry is x+y(zz)-x+y.

$$\alpha = [(v_\infty^2 - v_o^2)/2v_\infty^3][\omega^2\tau_o t^{-1}/(1+\omega^2\tau_o^2 t^{-2})] . \qquad (3)$$

where t is the reduced temperature $(T_c-T)/T_c$, τ_o is the individual dipole relaxation time in the expression $\tau=\tau_o t^{-1}$ for the relaxaion time τ. From Eq. (2) we notice that the phase transition is marked by a quick drop in the velocity with decreasing temperature. However, experimentally the [100] and [001] phonon velocities do not exhibit

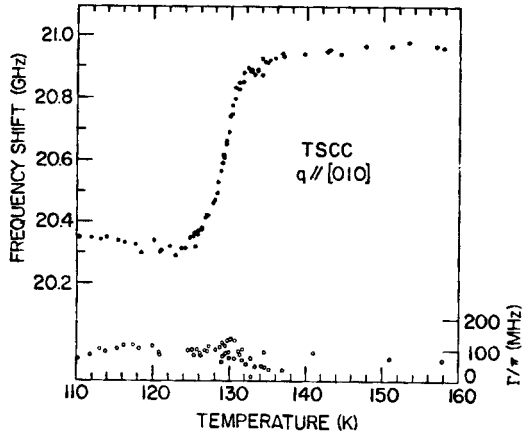

Figure 2 Temperature dependence of Brillouin shift (●) and linewidth (○) (FWHM) of longitudinal phonons in TSCC propagating along the [010] direction. The scattering geometry is x+y(zz)x-y.

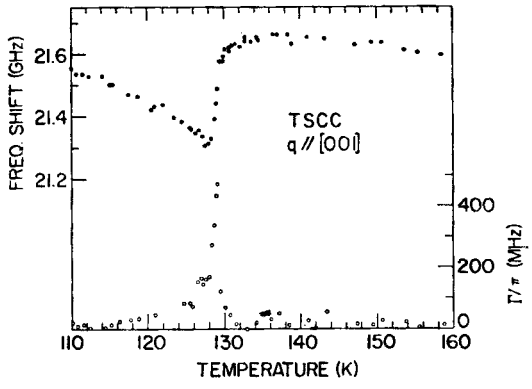

Figure 3 Temperature dependence of Brillouin shift (●) and linewidth (○) (FWHM) of longitudinal phonons in TSCC propagating along the [001] direction. The scattering geometry is x+y(xx)y-z.

such sharp drops at T_c, but rather slow rounding. These anomlies are attributed to the quadratic coupling of the polarization and the strain or in other words, electrostrictive coupling.[11,15] Such contributions to the anomalies of the velocity and the attenuation are schematically illustrated in Fig. 4. As we see from Fig.4, the temperature T_m at which the attenuation coefficient is maximum does not equal T_c, but occurs somewhat below T_c. From Eqs. (2) and (3) we obtain the relation $(T_c-T_m)/T_c=\omega\tau_o$. By this relation we can calculate the elementary relaxation time. Though the clear indication of T_c is blurred by the additional small anomaly from the electrostrictive contributions, we can use the steepest dropping point of the velocity as T_c. From the velocity and attenuation for the above two cases, we obtain the following results: For the $q \| [100]$ phonons, $\tau_o = 2.4\times10^{-14}$ sec, and for the $q \| [001]$ phonons, $\tau_o=2.3\times10^{-14}$ sec. These two results agrees well. we will use their average, $\tau_o=2.4\times10^{-14}$ sec.

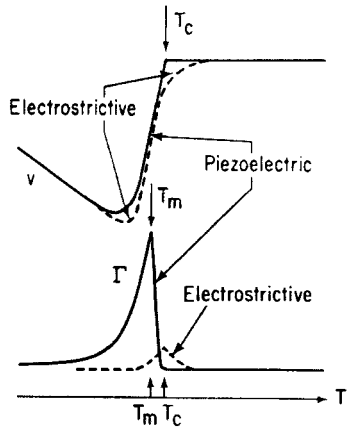

Figure 4 Anomalies in the velocity and the attenuation caused by piezoelectric coupling and electrostrictive coupling for longitudinal phonons propergating perpendicular to the polarization axis.

We next consider the temperature dependence of the Brillouin shift and the phonon decay rate for the longitudinal phonons parallel to the spontaneous polarizaion. In this case, polarization fluctuations do not couple bilinearly to the strain, because of the appearance of the depolarization field in the longitudinal polarizaion wave.[15,16] Therefore, the anomalies in the velocity and attenuation of these phonons should be expained by quadratic coupling of the polarization to the strain in both PE and FE

phases.

We now compare the velocity and attenuation of the acoustic waves in the GHz and MHz regions. Ultrasonic velocity and attenuation measurements have been performed on this crystal by Sorge and Straube.[17] Their results are reproduced in Figs. 5 and 6, together with our Brillouin results which are converted to the velocity and attenuation scale.

We use the velocities obtained by Brillouin scattering and ultrasonic measurements for v_∞ and v_o, respectively. We assume the simplest form for the relaxation time to be $\tau_E=\tau_o^E t^{-1}$, where τ_o^E is the elementary relaxation time. The E designates that these relaxation times are related to energy rather than polarization fluctuations. By putting into Eq. (3) the values of the attenuation coefficient of the ultrasonic measurements at the temperature $T-T_c=$ $=0.9K$ and -1.3 K (2.7 db/cm and 11.1 db/cm, respectively), we obtain the following values of the relaxation time: $\tau_o^E=1.9\times10^{-12}$ sec for $T>T_c$ and $\tau_o^E=7.7\times10^{-12}$ sec for $T<T_c$.

Chen and Schaack[6,7] obtaied $\tau_o=2.7\times10^{-13}$ sec from their analysis of the pseudospin-phonon coupling of Raman and infrared spectra. This value is one order of magnitude larger than ours. Deguchi et al.[18] showed that the relaxation time in TSCC is expressed by $\tau=3.8\times10^{-13}(\epsilon_s-\epsilon_\infty)$ sec from their dielectric dispersion measurements. If we use the values $C^+=30$ to 50 K for the Curie constant[19,20] and the relation $C^+/C^-=2$, we obtain the values $\tau_o=4.4$ to 8.5×10^{-14} sec for the elementary relaxation time which is in relatively good agreement with our values. Though we can obtain an order-parameter relaxation time from the Brillouin scattering experiment, this does not necessarily mean that TSCC undergoes an order-disorder phase transitions. It is also possible to adopt the interpretation that soft mode frequency ω_o decreases and the damping constant γ diverges as T_c is approached. In such an extremely damped case, the system has the same correlation function as that of the relaxational mode where the effective relaxation time is given by γ/ω_o^2. Recently, Sugo et al.[21] performed an precise Raman measurements in the ferroelectric

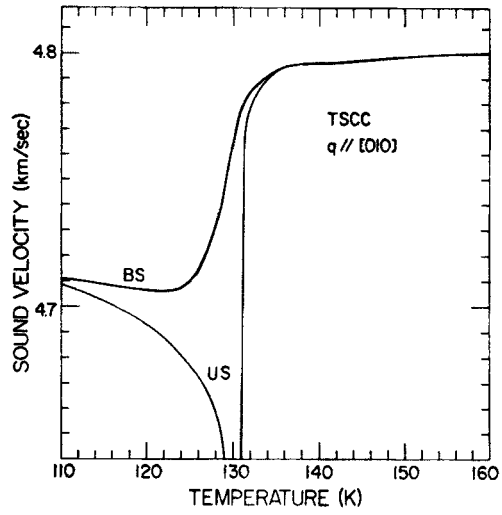

Figure 5 Temperature dependence of sound velocity in TSCC for Brillouin (BS) at 16 GHz and for ultrasonic (US) measurements at 20 MHz. The velocity scale for the Brillouin scattering was adjusted to that of the ultrasonic measurements.

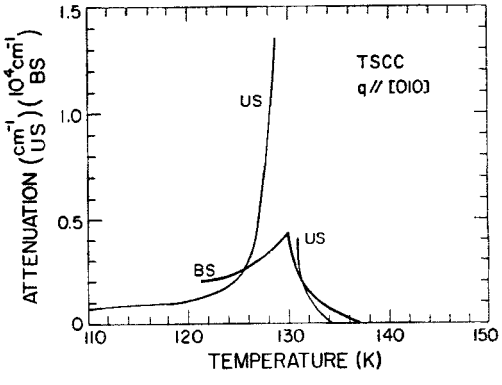

Figure 6 Temperature dependence of the attenuation in TSCC for Brillouin scattering (BS) at 16 GHz and for ultrasonic (US) measurements at 20 MHz.

phase of TSCC up to T_c. They showed that ω_o^2/γ is nearly proportional to T_c-T near T_c (within about 10 K) and $\tau = 5.9 \times 10^{-11}$ sec at T_c-0.05 K. Our result gives $\tau = 6.3 \times 10^{-11}$ sec at the same temperature.

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