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Frequency Dependence of the Damping Function of the Soft E-Symmetry Phonon in $PbTiO_3$

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(Received 30 December 1974)

We have measured, by means of Raman scattering from phonon polaritons, the frequency dependence of the damping function $\gamma(\omega, T_{\rm rm})$ of the soft E-symmetry phonon in $PbTiO_3$ at room temperature. Our result shows that the divergence of $\gamma(\omega,T)$ for $T \to T_c$ arises mainly from the frequency dependence of $\gamma(\omega,T)$ and that $\gamma(\omega,T)$ for a fixed frequency ω is simply proportional to the temperature. The apparent divergence of $\gamma(\omega,T)$ for $T \to T_c$ observed by Burns and Scott results from the temperature dependence of the soft-mode frequency.

It is generally recognized that in order to understand the behavior of soft modes[1] occurring in displacive phase transitions one should study the soft-phonon self-energy $\Sigma = \Delta + i\Gamma$.[2,3] The temperature dependence of the real part Δ causes the softening, and the imaginary part Γ determines the soft-phonon lifetime. Thus, there has been considerable interest in the temperature dependence of the imaginary part Γ which is related to the damping function $\gamma(\omega,T)$ by $\Gamma = \omega\gamma/2\omega_0$.[4,5]

Recently, Burns and Scott[6] reported the first observation of the divergence of $\gamma(T)$ for the underdamped soft mode in the perovskite ferroelectric $PbTiO_3$ as the transition temperature $T_c = 493°\mathrm{C}$ is approached from below. They related the temperature dependence of $\gamma(T)$ to an empirical relation similar to that obtained for the dielectric constant $\epsilon_c(T)$ along the ferroelectric axis which also diverges as T approaches T_c. Theoretically, the observed divergence of $\gamma(T)$ was not expected for a three-dimension system.[4] Subsequently, Silverman[5] proposed a theory which explained the anomalous divergence of $\gamma(T)$.

In this Letter we report the results of the measurement of the soft E-mode damping function in $PbTiO_3$ as a function of the mode frequency at a constant temperature, $\gamma(\omega, T_{\rm rm})$. All measurements were made at room temperature $T_{\rm rm}$, and the frequency dependence was measured by a polariton method described in detail previously.[7,8] Our result shows that the divergent behavior of γ arises solely from a linear temperature dependence and from the dependence of γ on the soft-mode frequency $\omega_0(T)$, which in turn varies with temperature. The damping function, γ, as a function of T at constant frequency was found to be simply proportional to T and has no anomalous temperature dependence.

The Raman-scattering cross section for polaritons can be calculated either from the Green's-function method of Benson and Mills[9] or from the fluctuation-dissipation theorem as reviewed by Barker and Loudon.[10] Their result for the Stokes-scattering function from a polariton of wave vector q and frequency ω can be written as[11]

$$S(q,\omega) = S_0[n(\omega)+1]\left(1+\frac{B}{c^2q^2/\omega^2-\epsilon_\infty}\right)^2 \frac{\omega_0^2\omega\gamma(\omega)}{(\omega_0^2\{1-[\epsilon(0)-\epsilon_\infty](c^2q^2/\omega^2-\epsilon_\infty)^{-1}\}-\omega^2)^2+\omega^2\gamma^2(\omega)}, \tag{1}$$

where S_0 is a frequency-independent constant of scattering efficiency; $n(\omega)$ is the Bose-Einstein thermal population factor; $B = 4\pi ne^*b/a$ is the ratio of the electro-optic and the displacive contributions to the scattering[12]; c is the velocity of light in vacuum; ω_0 is the transverse-optical-phonon frequency (soft E mode in the present case); $\epsilon(0)$ and ϵ_∞ are the static and optical dielectric constants, respectively; and $\gamma(\omega)$ is the phonon damping function which may depend on frequency. A result similar to this was obtained by Laughman, Davis, and Nakamura[13] in the ferroelectric case where $\epsilon(0) \gg \epsilon_\infty$. The important feature of Eq. (1) will become apparent if we write it in a slightly different form as

$$S(\omega_-,\omega) = S_0[n(\omega)+1]\left(1+\frac{B(\omega_0^2-\omega^2)}{\omega_0^2[\epsilon(0)-\epsilon_\infty]}\right)^2 \frac{\omega_-^2\omega\bar{\gamma}}{(\omega_-^2-\omega^2)^2+\omega^2\bar{\gamma}^2}, \tag{2}$$

where

$$\omega_-^2 \equiv \omega_0^2\left[1+\omega_0^2\left(\frac{\epsilon(0)-\epsilon_\infty}{c^2q^2-\omega^2}\right)\right]^{-1} \tag{3}$$

and

$$\bar{\gamma} = (\omega_-^2/\omega_0^2)\gamma(\omega). \tag{4}$$

Here, ω_- is the lower-polariton-mode frequency satisfying the dispersion relation in the absence of damping:

$$c^2q^2/\omega^2 = \epsilon(\omega) = \epsilon_\infty + [\epsilon(0)-\epsilon_\infty]\omega_0^2/(\omega_0^2-\omega^2), \tag{5}$$

and $\bar{\gamma}$ is the *polariton* damping function, which is related to the *phonon* damping function $\gamma(\omega)$ by Eq. (4). This simple connection was also demonstrated by Loudon[14] for the case of small damping $\gamma \ll \omega_0$ and large oscillator strength $\epsilon(0) \gg \epsilon_\infty$. Equation (5) is valid in the present case at low frequencies where the phonon contribution to $\epsilon(0)$ is dominated by the soft mode.

Next, it is necessary to relate the scattering angle to the polariton wave vector. From the conservation of energy and crystal momentum, one obtains[12]

$$c^2q^2 = \{\omega_i(n_o-n_e)+\omega[n_e+\omega_i(\partial n_e/\partial\omega)]\}^2 + \omega_i^2 n_e n_o \theta^2 \tag{6}$$

for the geometry used in the present experiment, where ω_i is the incident laser frequency, n_o and n_e are the ordinary and extraordinary indices of refraction, respectively, and θ is the scattering angle as measured from the incident direction inside the crystal. The optical constants that were used in Eq. (6) are given by Singh, Remeika, and Polopowicz[15] for crystals similar to ours.

The sample was a single crystal of $PbTiO_3$ approximately 5 mm×1 mm×1 mm in size.[16] The scattering geometry employed was $y(xz)y+\Delta z$ so that only the pure E-symmetry polariton was observed.[12]

The crystal was cut and polished on faces perpendicular to the [010] axis to permit forward scattering. It was found to be single crystal in nature when observed through crossed polarizers and by strict compliance with Raman selection rules.[17] The Raman-scattering experiment was performed on the sample at room temperature using a 50-mW He-Ne laser operating at 6328 Å. The laser light was focused into the sample using a 100-cm-focal-length lens. The light scattered in the near-forward direction was collected by a 20-cm-focal-length lens. The collection optics had an adjustable stop aperture to limit the acceptance angle before it was spectrally analyzed by a Spex Model-1400 double-grating spectrometer. The analyzed light was then detected by a cooled ITT model-FW130 photomultiplier with S-20 cathode. The spectrometer was controlled by a PDP-11 minicomputer which made it possible to measure weak scattered signals by using very long integration times.[18] The digitally stored data were then easily transferred to a large-memory computer where extensive analysis could take place.

Since the polariton frequency ω_- depends on the scattering wave vector q, and q in turn depends on the scattering angle θ through Eq. (6), the observed polariton linewidth in the Raman spectrum depends on the acceptance angle $\Delta\theta$ of the spectrometer entrance optics. Thus, the observed polariton linewidth contains the broadening due to finite acceptance angle $\Delta\theta$ (or finite q resolution) and the broadening due to finite resolving width W of the spectrometer slits in addition to the intrinsic polariton linewidth $\bar{\gamma}$ which we wish to obtain. In order to extract γ from the experimental polariton spectra, we used the numerical analysis procedure described in detail in Refs. 7 and 8. In the work described in these references, the polariton line shape at a fixed q was assumed to be Lorentzian and integration of $S(q,\omega)$ over a finite range of q values was performed analytically. However, in the present work, Eq. (1) was numerically integrated over q values corresponding to θ and $\Delta\theta$.

The results of the soft-phonon damping function $\gamma(\omega)$ as a function of frequency at room temperature are plotted in Fig. 1. $\gamma(\omega)$ increases slowly with decreasing ω, and then increases rapidly below ~55 cm^{-1}. Also plotted in Fig. 1 are the results of Burns and Scott[6] which contain both temperature dependence and frequency dependence through the variation of the soft-mode frequency $\omega_0(T)$ with temperature. The decrease in $\omega_0(T)$ corresponds to higher temperatures close to T_c. We see in Fig. 1 that the apparent divergence of γ for T approaching T_c is caused by the fact that $\omega_0(T)$ moves into the region of high damping as T_c is approached.

Since $kT_{rm} \cong 208$ cm^{-1}, the high-temperature approximation for the Bose-Einstein factor is valid. Then we expect that $\gamma(\omega,T)$ is proportional to T at fixed ω if the dominant damping mechanism of the soft mode is due to the third-order anharmonicity of the crystal potential.[2,3] If this is the case and no temperature-dependent anomaly exists, then we should have

$$\gamma(\omega,T_{rm}) = (T_{rm}/T)\gamma(\omega_0(T)) \tag{7}$$

for $\omega = \omega_0(T)$, where $\gamma(\omega_0(T))$ is the value measured by Burns and Scott at temperature T, and the left-hand side (LHS) is the value measured in the present work at T_{rm}. Figure 2 shows the comparison of the LHS and the RHS of Eq. (7). We see that Eq. (7) holds exactly without any adjustable parameter for all ω and T measured.

Several important conclusions can be drawn concerning the nature of the soft-mode damping function $\gamma(\omega,T)$ and consequently the imaginary part of the self-energy $\Gamma(\omega,T)$. The apparent divergence of the damping function γ for T approaching T_c is caused by two factors: (a) For $T \to T_c$ from below the soft-mode frequency $\omega_0(T)$ decreases and moves into the frequency region where Γ is large; (b) at a fixed frequency Γ is proportional to the absolute temperature T as expected for damping due to cubic anharmonicity. There is no anomalous behavior of Γ directly dependent on T. Since the anharmonic matrix elements that enter the real part Δ and the imaginary part Γ of the self-energy are identical,[3] we conclude that the dominant mechanisms responsible for softening of the mode are also three-phonon processes caused by cubic anharmonicity.

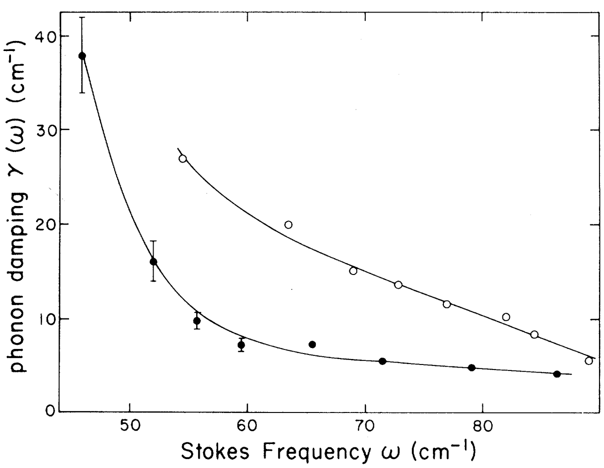

FIG. 1. Frequency ω versus phonon-damping function $\gamma(\omega,T_{rm})$ for the soft E-symmetry mode in $PbTiO_3$. The solid circles represent the polariton data measured at room temperature in the present experiment. The open circles represent the data of Burns and Scott $\gamma(\omega_0(T))$ taken between room temperature and $T_c = 493°C$. The solid lines are drawn to aid the eye.

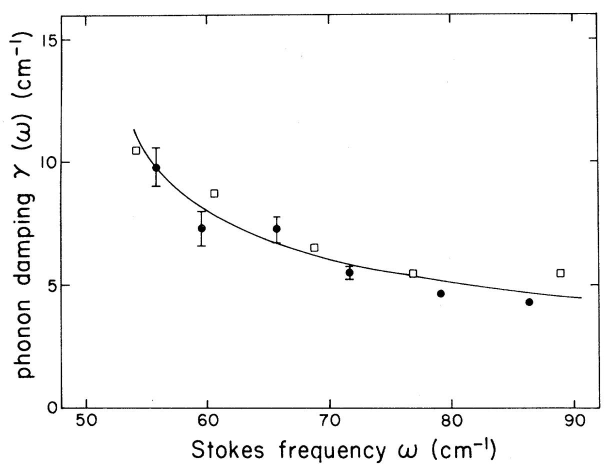

FIG. 2. Frequency ω versus phonon-damping function $\gamma(\omega,T_{rm})$ for the soft E-symmetry mode in $PbTiO_3$. The open squares represent the temperature-dependent data of Burns and Scott scaled by assuming damping proportional to the absolute temperature $\gamma(\omega_0(T))T_{rm}/T$. The solid circles represent the constant-temperature data of the present experiment. The solid curve is drawn to aid the eye.

Now let us consider why $\gamma(\omega)$ and similarly $\Gamma(\omega)$ rise rapidly below 55 cm^{-1}. If damping is mainly due to three-phonon processes (cubic anharmonicity), the frequency dependence of $\Gamma(\omega)$ closely follows the two-phonon density of states.[3,8] By inspecting the inelastic-neutron-scattering data,[19] one sees that a peak in the two-phonon density of states may be expected at ~32 cm^{-1}. This peak arises from two zone-boundary phonons TA and LA at $(\pi/2a, 0, 0)$ with frequencies 73 and 105 cm^{-1}, respectively. The damping process that corresponds to this peak in the two-phonon density of states is the scattering of the soft phonon by a TA phonon (73 cm^{-1}) into an LA phonon (105 cm^{-1}). The rapid rise in $\Gamma(\omega)$ below 55 cm^{-1} observed in this work is probably the high-frequency tail of this peak in $\Gamma(\omega)$ at ~32 cm^{-1}.

In the case of a closely related perovskite $BaTiO_3$, $\Gamma(\omega)$ of the soft E mode decreases with frequency below $\omega_0 = 33$ cm^{-1},[12,13] and this mode is heavily overdamped at 33 cm^{-1}. Inelastic-neutron-scattering data[20] show that it is underdamped for $\omega_0(q) > 33$ cm^{-1} corresponding to finite q values. Thus, it appears that both in $BaTiO_3$ and in $PbTiO_3$ there is a peak in the damping function $\Gamma(\omega)$ near 30 cm^{-1}. The soft-mode frequency in $PbTiO_3$ lies above this peak and it lies very near or below the peak in $BaTiO_3$. This may be the reason why the soft mode is overdamped in $BaTiO_3$ and underdamped in $PbTiO_3$. A similar peak in the damping function may explain the divergence of γ for soft modes in other systems such as $BaMnF_4$.[21]

The lowest frequency ($\omega \approx 45$ cm^{-1}) at which we can measure $\Gamma(\omega, T_{rm})$ is determined by the polariton frequency for the smallest scattering angle that can be attained experimentally. Since the soft-mode frequency decreases considerably as T_c is approached, this lower limit can be reduced by raising the temperature toward $T_c = 493$ °C. Further work is being carried out at elevated temperatures, in order to see if $\Gamma(\omega)$ decreases below 32 cm^{-1} as predicted by the proposed damping mechanism. We also expect that $\Gamma(T)$ will decrease rapdily for $kT < \hbar\omega_{TA}$ ($\cong 73$ cm^{-1}). Work at low temperature to check this prediction is also planned.

It is a pleasure to acknowledge many helpful and stimulating discussions with D. L. Mills and A. A. Maradudin.

*Research supported by a grant from the National Science Foundation, No. GH-42408.

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