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Neutron and Raman scattering at structural phase transitions

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Neutron scattering measurements have been made of the soft mode in the uniaxial ferroelectric lead germanate for which the transition temperature is 450 K. The results are consistent with the simple soft-mode picture of the soft mode. A comparison with the results of Raman scattering measurements suggests that the latter measurements do not provide information about the one-phonon spectral function for temperatures greater than $(T_c - 10)$ K.

I. INTRODUCTION

Structural phase transitions are known to be associated, in many systems, with an instability of the crystal against a particular normal mode of vibration, which is known as a soft mode. Experimental studies of the temperature dependence of this mode have frequently been made using neutron scattering techniques for temperatures above the transition temperature, T_c, but Raman scattering techniques at temperatures below T_c. The experimental results are then usually analyzed by assuming that the incident radiation, light or neutrons, couples linearly to the soft-mode displacements and that the spectral response of the soft mode can be described by a classically damped harmonic oscillator. When this procedure is applied to the Raman scattering measurements the results show a number of unexpected and unsatisfactory features close to T_c: the frequency does not decrease to zero at T_c,[1-3] the damping constant becomes large close to T_c,[1-4] and the fits give only a very unsatisfactory description of the experimental spectra.[2,3]

Two different mechanisms for this behavior have been suggested.[5] In one of these the difficulties result from the failure of the simple classically damped oscillatro model close to T_c—the dynamics of the soft mode are more complicated. The other mechanism is that the Raman scattering does not measure the one-phonon response function close to T_c, because the light couples quadratically to the soft-mode coordinate.[6] The Raman scattering then gives an excellent measure of the one-phonon response function well below T_c, but close to T_c the one-phonon contribution is only of the same size as the two-phonon contribution.

The experiment described in this paper was designed to distinguish between these two possibilities by performing measurements of the one-phonon scattering below T_c with neutron scattering techniques and comparing the results with those obtained using Raman scattering techniques. If the same spectra are obtained using both techniques, this would be a strong indication that the Raman scattering can be described as one-phonon scattering, but if a different result is obtained then the indications are that the Raman scattering cannot be described as a solely one-phonon process.

Lead germanate $Pb_5Ge_3O_{11}$ was chosen as a suitable material for this study. It has favorable properties for both Raman and neutron scattering studies and is a uniaxial ferroelectric with a transition temperature $T_c \approx 450$ K, when the crystal changes from a high-temperature phase of $p\bar{6}$ symmetry to a ferroelectric phase of symmetry $p3$.[7] It therefore is an example of the universality class of uniaxial dipolar systems for which $d = 3$ is the marginal dimension, and is therefore expected to show only small logarithmic corrections to mean-field theory.[8] (No experimental evidence has yet been found for these logarithmic corrections in lead germanate.)

There have been several studies of the Raman scattering from the soft mode for $T < T_c$. Ryan and Hisano[9] showed that there was a mode whose frequency varied approximately as $(T_c - T)^{1/2}$ and which became overdamped close to T_c. Hosea *et al.*[3] did more careful measurements and concluded that none of the current models of the one-phonon response give a good account of their results close to T_c. At much lower frequencies, quasielastic scattering of both static and dynamic origin has been observed using light scattering techniques[10] and using neutron scattering techniques close to T_c.[11] The origin of these different quasielastic scattering processes is still uncertain,[5] but may arise from defects, moving domain walls, or nonlinear phonon relaxation.

In Sec. II we report on measurements of the soft mode in lead germanate using neturon scattering techniques. The results are fitted to a classically damped harmonic-oscillator response and compared with those found from Raman scattering techniques. The results suggest that this model is adequate to describe the inelastic neutron scattering in contrast to the Raman scattering result close to T_c. We therefore suggest that for temperatures $T > (T_c - 10)$ K, Raman scattering results do not provide an adequate representation of the inelastic part of the one-phonon spectral function, so frequencies and linewidths derived from the analysis of such measurements must not be treated as one-phonon frequencies and linewidths.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The experiments were performed on a triple-axis crystal spectrometer at the high-flux beam reactor of Brookhaven National Laboratory. The incident energy of the neutrons was either 13.5 or 5.0 meV. A pyrolytic graphite filter (13.5 meV) or a cooled beryllium filter (5 meV) was used in the incident beam to remove neutrons reflected from the higher-order reflections of the pyrolytic graphite monochromator. The sample used was a large single crystal of volume 10 cm^3. The temperature of the sample, in the furnace, could be controlled to an accuracy of ±0.5 K. The temperature dependence of the (0 0 4) Bragg reflection, both while cooling and heating the sample, was measured to obtain the ferroelectric phase transition temperature. The temperature T_c thus obtained was 449.5 ± 1 K. The inelastic scattering was measured in the energy gain mode. First, a series of runs were made with $E_i = 13.5$ meV with wave-vector transfers $\vec{Q}$, equal to several different Bragg points, to determine the wave-vector transfer where the structure factor for the soft optic phonon is most favorable in comparison with the other optic phonons. A few of these spectra, at $T = 383$ K, are shown in Fig. 1(a). The peak at ~2.5 meV arises from scattering by the soft mode and, that at ~4.5 meV, from another optic mode which is largely suppressed in the scan with $\vec{Q} = (0, 0, 5)2\pi/c$.

One of the difficulties with the experiment arises because of the appreciable extent of the resolution function in wave-vector space in a neutron scattering experiment. The rapidly increasing intensity for energy transfers below 2.0 meV [Fig. 1(a)] arises from scattering by the low-frequency acoustic modes. This scattering essentially prohibited the collection of useful data for energy transfers below ~1.5 meV with 13.5-meV incident neutrons.

Figure 1(b) shows two scans for a wave-vector transfer, $\vec{Q} = (0, 0, 5)2\pi/c$, with slightly better resolution. There is a fairly well-defined inelastic peak in the scattering from the soft mode at 383 K, but at higher temperatures this scattering is at lower energies and is characteristic of an overdamped mode.

In order to examine the behavior of this mode at energy transfers below 1.5 meV and hence closer to T_c, experiments were also performed with 5.0-meV incident neutrons. It was then not possible to perform experiments with $\vec{Q} = (0, 0, 5)2\pi/c$, but measurements could be performed with $\vec{Q} = (0, 0, 4)2\pi/c$, as shown in Fig. 2. Under these conditions the scattering from the acoustic modes was negligible at energy transfers larger than 1.0 meV, and by careful subtraction reliable data for the optic-mode scattering could be obtained for $|\hbar\omega| > 0.4$ meV. In this manner the scattering from the soft mode was measured at 13 different temperatures between 400 and 500 K. The solid lines shown in Fig. 2 are the results of fitting these spectra to the models described below.

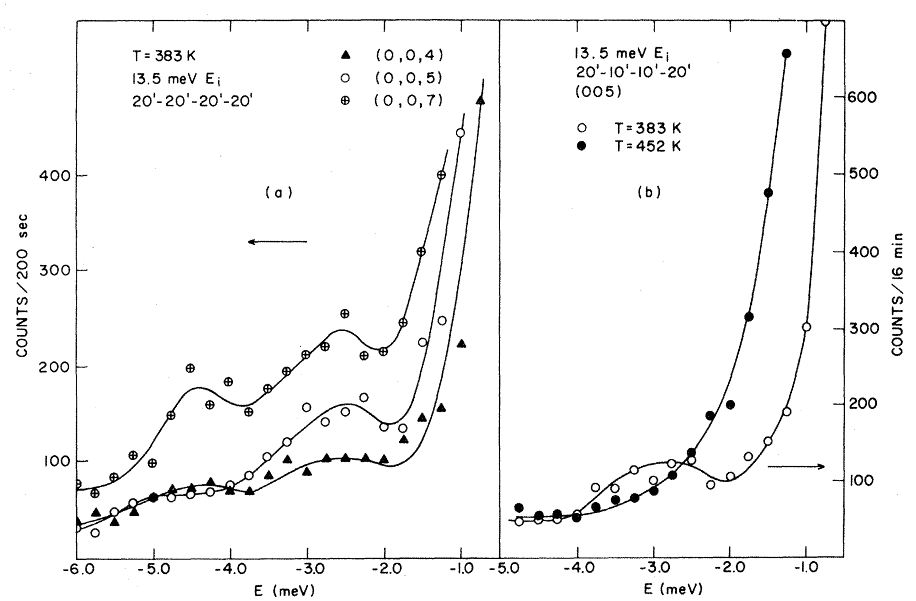

FIG. 1. Neutron scattering spectra from the soft mode in lead germanate using incident neutrons with an energy of 13.5 meV. The lines in part (b) are fits to the data as described in the text.

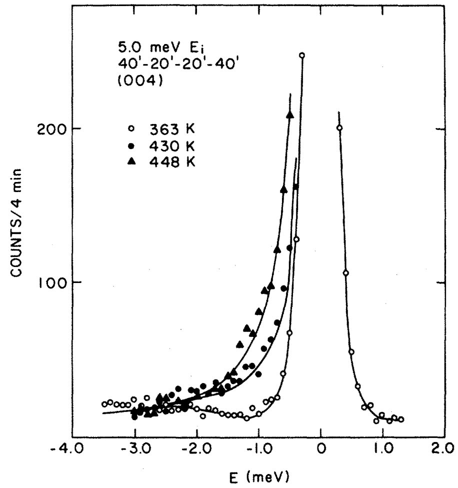

FIG. 2. Neutron scattering spectra from the ferroelectric soft mode in lead germanate using incident neutrons with an energy of 5.0 meV. The solid lines are fits as described in the text.

The simplest theory of the scattering from a soft mode[12] describes the cross section as the scattering by a classically damped harmonic oscillator

$$S(\vec{Q},\omega)=\frac{1}{\pi}\frac{k_F}{k_I}|F(\vec{Q})|^2[n(\omega)+1]\frac{\omega\Gamma}{(\omega_0^2-\omega^2)^2+\Gamma^2}\ , \quad (1)$$

where k_F and k_I are the wave vectors of the scattered and incident neutrons, $F(\vec{Q})$ is the inelastic structure factor of the soft mode, $n(\omega)$ is the Bose-Einstein occupation number, Γ is the width of the soft mode, and ω_0 is its frequency. Γ is expected, on the basis of low-order anharmonic perturbation theory, to be only weakly dependent on temperature, while the simplest mean-field theory of structural phase transitions gives

$$\omega_0^2=\begin{cases}2a(T_c-T), & T<T_c\\ a(T-T_c), & T>T_c\ .\end{cases} \quad (2)$$

It is well known[3] that it is difficult to extract the parameters ω_0 and Γ by fitting Eq. (1) to the experimental results, particularly when the mode becomes overdamped. In the overdamped regime the scattering was fitted to the Debye form

$$S(\vec{Q},\omega)=\frac{k_F}{k_I}[n(\omega)+1]\frac{\omega P_0}{\omega^2+\gamma^2}\ , \quad (3)$$

where in terms of the notation of Eq. (1) $P_0=(1/\pi)|F(\vec{Q})|^2/\Gamma$ and $\gamma^2=\omega_0^2/\Gamma$. In the temperature range $366<T<425$ K, where the mode is heavily damped but not overdamped, the scattering was taken to have the form

$$S(\vec{Q},\omega)=\frac{k_F}{k_I}[n(\omega)+1]\frac{\omega P_0}{\left(\gamma^2-\omega^2/\Gamma\right)^2+\omega^2}\ , \quad (4)$$

which when $\omega^2/\Gamma << \gamma^2$ reduces to the Debye form of Eq. (3). The effect of the instrumental resolution was included by convoluting the forms given in Eqs. (3) and (4) with a Gaussian (full width at half maximum = 0.12 meV) and allowing for the varying efficiency of the analyzing spectrometer as the scattered energy varied during the scan.

Initially least-squares fits were performed for $T>414$ K with the Debye model, Eq. (3), and the parameters P_0 and γ were allowed to vary freely while the background was held fixed at a reasonable value. The fits were quite satisfactory with χ^2 varying between 1.0 and 1.6. The parameter γ showed a monotonic decrease as $T\rightarrow T_c$ and, although there was some scatter in the values of P_0, they were essentially constant (1.05–1.75) throughout this temperature range.

Since the least-squares fits showed that the values of the parameters γ and P_0 were strongly correlated, the next set of fits were performed with P_0 held fixed

TABLE I. The soft-mode parameters.

a. Debye model

T (K)	p_0	γ(meV)	χ^2
415	1.15	1.20(±0.1)	2.1
424	1.15	0.95(±0.1)	2.0
430	1.15	0.82(±0.14)	1.6
433.5	1.15	0.68(±0.1)	1.7
438.5	1.15	0.60(±0.1)	1.6
444	1.15	0.38(±0.07)	1.3
448.5	1.15	0.28(±0.08)	1.3
454	1.15	0.27(±0.07)	1.4
456	1.15	0.30(±0.1)	2.1
462	1.15	0.32(±0.08)	1.7
476	1.15	0.40(±0.07)	1.4
494.5	1.15	0.60(±0.14)	2.2

b. Damped simple harmonic oscillator

T (K)	p_0	γ (meV)	$\frac{1}{\Gamma}$ (meV^{-1})	χ^2
363.5	1.15	2.8	0.30	1.1
385	1.15	2.65	0.50	2.2
404	1.15	1.25	0.13	1.0
414	1.15	1.36	0.20	1.14
424	1.15	0.69	0.09	1.0

at its average value of 1.15. The fits were in general poorer, but not very significantly so: χ^2 varied between 1.3 and 2.2. Two of these fits at 430 and 448 K are shown in Fig. 2.

In the temperature region between 363 and 424 K another set of fits were performed fitting Eq. (4) to the scattering. The parameter P_0 was held fixed at 1.15 and γ and $1/\Gamma$ varied. The quality of the fits was similar to that obtained for the Debye model for $T > 414$ K, and one such fit is shown in Fig. 1 for 363 K. The results for the fitting of γ and $1/\Gamma$ are listed in Table I.

III. DISCUSSION AND CONCLUSIONS

The experimental values for the damping parameter, γ, shown in Fig. 3 and Table I, decrease to a minimum value close to T_c and increase almost linearly with $|T - T_c|$ both above and below T_c. There are several reasons why the damping constant does not decrease to zero at T_c. Firstly, it is known[10,11] that, very close to T_c, the response is dominated by the quasielastic or central peak scattering, which could not be observed in this experiment. More seriously, the finite wave-vector resolution of the experiment means that scattering is observed from modes which do not have wave-vector $q = 0$. These modes will have a large γ than that for the $q = 0$ mode, and so lead to an overestimate in the value of γ produced by the fitting. (It is not possible to do a detailed correction for this effect in lead germanate as the details of the Coulomb singularity in the modes as $\vec{q} \to 0$ have not been determined.) Making an *ad hoc* allowance for this overestimate in the value of γ at T_c (solid lines in Fig. 3), the results for γ can be written as $\gamma = A\,|T - T_c|$, where for $T < T_c$, $A^- = 0.033 \pm 0.004$ meV/K and for $T > T_c$, $A^+ = 0.015 \pm 0.007$ meV/K. The ratio A^-/A^+ is within error close to the value 2 predicted by mean-field theory.

Besides the results of the neutron scattering experiments, Fig. 3 also shows the width deduced from Raman scattering measurements.[3] The Raman scattering measurements give values of γ which are higher than the neutron scattering results for $T > (T_c - 7)$ K and also higher at low temperatures. The reason for the discrepancy at low temperatures is probably because the effect of other optic modes is more pronounced in the Raman scattering than in the neutron scattering experiment.

Close to T_c there is clear evidence that the neutron scattering gives a narrower linewidth than the Raman scattering, as shown also in Fig. 4, where the neutron and Raman scattering data are directly compared. Since the wave-vector resolution in the neutron scattering case is much larger than in the Raman scattering case, the difference in width cannot be of experimental origin. We believe it is a clear indication that the Raman scattering spectra do not give the one-phonon spectral function for temperatures close to and above T_c.

The critical behavior of the ratio of the widths of the one-phonon and two-phonon spectral functions above T_c have been discussed by Bruce and Bruce[13] for systems with short-range interactions. These calculations have been extended by them as detailed in the Appendix, to apply to uniaxial dipolar systems. The results show that the width of the one-phonon spectral function, γ, decreases as $r = t\,|\ln t|^{-1/3}$ where

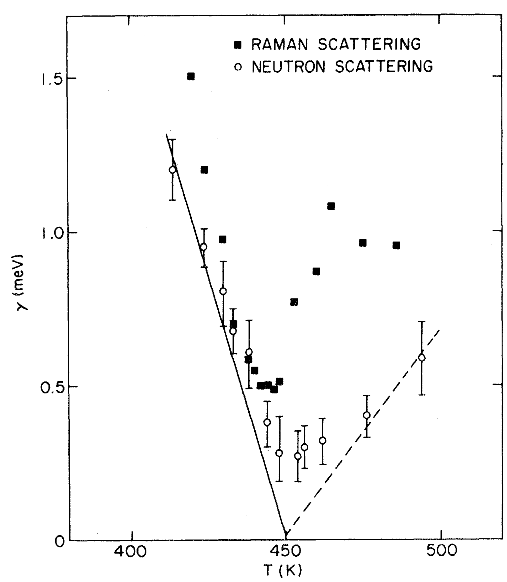

FIG. 3. The widths of the scattering from the soft mode in lead germanate as measured with neutron and Raman scattering techniques.

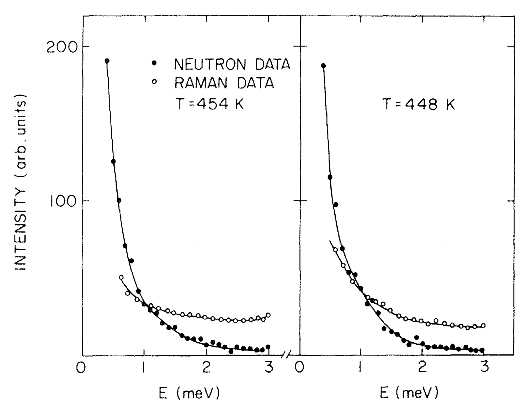

FIG. 4. Neutron and Raman scattering spectra from the soft mode in lead germanate. The spectra were normalized to have the same intensity at 1.0 meV and have had the background subtracted.

$t = a(T - T_c)$, while the width of the two-phonon response γ_2 varies as $r|\ln r|$. The ratio $\gamma_2/\gamma = 12|\ln t|$. This is different from the result for systems with short-range interactions in that the ratio is not constant but diverges as $T \to T_c$. Nevertheless, these results are not readily compared with the measurements because the two-phonon width does not decrease to zero at T_c, possibly because all the weight of the strictly critical fluctuations is contained in the central peak part of the spectral function[10] which we have not considered.

In conclusion, we have shown that the classically damped simple harmonic-oscillator model can be used to describe the inelastic neutron scattering from the soft mode in lead germanate. The results for the linewidth are within experimental error consistent with the simplest predictions of the theory. The results are in agreement with those found from Raman scattering results for $T < (T_c - 10)$ K, but at higher temperatures there are significant discrepancies, which suggest that it is unsatisfactory to deduce one-phonon frequencies and widths from Raman scattering measurements close to T_c. Possibly many of the results from Raman scattering, which have been interpreted as indicating a failure of the soft-mode picture of structural phase transitions, arise because of the failure to consider two-phonon and one- and two-phonon interference terms in the scattering cross section.

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APPENDIX: RATIO OF THE WIDTHS OF THE ONE- AND TWO-PHONON SPECTRAL FUNCTIONS IN $d = 4$

This appendix is an extension of the work by Bruce and Bruce[13] to $d = 4$ and was performed by them. The notation is the same as in their earlier work.

The two-phonon correlation function for the thermodynamic fluctuations $\Gamma_T(k=0,\omega)$ can be obtained from Table I of Ref. 13 as

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\Gamma_T(k=0,\omega)\,d\omega = -nK_d[2+\ln r + 2(n+2)\bar{u}\ln^2 r + 4(n+4)(n+2)\bar{u}^2\ln^3 r + \dots]\ , \tag{A1}$$

where $\bar{u}$ is the dimensionless coupling constant and r is the exact inverse susceptibility, and only the lowest terms in $\ln r$ have been kept in the expansion in powers of $\bar{u}$. Equation (A1) is consistent with an expansion of the form

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\Gamma_T(k=0,\omega)\,d\omega = \frac{nK_d}{2(4-n)\bar{u}}[1+2(n+8)\bar{u}|\ln r|]^{4-n/n+8} \approx \frac{nK_d}{2(4-n)\bar{n}}[2(n+8)\bar{u}|\ln r|]^{(4-n)/n+8}\ , \tag{A2}$$

which, furthermore, is consistent with the known behavior of the specific heat.[14] Repeating the analysis for the two-phonon correlation function at zero frequency gives

$$\Gamma_T(k=0,\omega=0) \approx \frac{nK_d\gamma_0}{2r}[2(n+8)\bar{u} \times |\ln r|]^{-2(n+2)/(n+8)}\ . \tag{A3}$$

Hence the two-phonon width is given for $n = 1$ by

$$\omega_T^{(2)} = \gamma_2 = \frac{\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\,\Gamma_T(k=0,\omega)}{\Gamma_T(k=0,\omega=0)} = \frac{\Gamma}{3\bar{u}\gamma_0}(18\bar{u}|\ln r|)\ .$$

The one-phonon width behaves[15] as

$$\omega_T^{(1)} = \gamma = \frac{r}{2\gamma_0}\ ,$$

so that the ratio of the widths

$$\frac{\omega_T^{(2)}}{\omega_T^{(1)}} = \frac{\gamma_2}{\gamma} = 12|\ln r|\ ,$$

which since

$$r \approx a(T - T_c)|\ln[a(T-T_c)]|^{-1/3}$$

gives

$$\frac{\omega_T^{(2)}}{\omega_T^{(1)}} \approx 12|\ln[a(T-T_c)]|\ .$$

It is unfortunately very difficult to estimate the range of temperature within which the logarithmic corrections to scaling are important, and hence we do not attempt to estimate the constant a. Outside the critical region the ratio of the one- and two-phonon widths are not simply related to one another.

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