Central-Peak Dynamics at the Ferroelectric Transition in Lead Germanate

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We report spectral line-shape measurements of a singular dynamic central peak associated with a structural phase transition. The quasieleasic light scattering spectra obtained in ferroelectric lead germanate exhibit clear departures from mean-field theory.

The question of critical dynamics near structural phase transitions[1] has become increasingly controversial beginning with the observation by Riste *et al.*[2] of an unresolved diverging quasielastic feature in neutron scattering from $SrTiO_3$. Despite repeated attempts using a variety of techniques, such features associated with structural transitions have thus far defied unambiguous spectral analysis.[3] This has left open the possibility that many, if not all, of these central peaks are due to static, rather than dynamic, phenomena.

In this Letter, we report spectral line-*shape* measurements of a *singular dynamic central peak* associated with a structural phase transition: the displacive ferroelectric transition in lead germanate. In addition to the light scattering from the soft optic mode (polarization fluctuations), for $t < 0.02$ (with $t \equiv |T - T_C|/T_C$) we observe a new quasielastic spectral feature of linewidth ~ 0.13 cm^{-1} whose intensity increases as $t \to 0$.

The ferroelectric transition in lead germanate ($Pb_5Ge_3O_{11}$) is of second order. Direct measurements of the spontaneous polarization P_s, optical rotary power, and dielectric constant, for example,[4] appear to give mean-field critical exponents. Raman spectra[5] well below T_C have shown a well-defined low-frequency optic mode (ω_s) of A symmetry, which softens and becomes overdamped upon approach to T_C. More recently a detailed neutron-scattering[6] study of this transition revealed a quasielastic, but unresolved, central peak whose intensity reached a maximum near T_C. Speculations on the possible dynamic origin of this feature were plagued by the lack of spectral line-shape information.

The frequency range of interest for establishing the dynamic character of this central peak is accessible to study by light scattering. However, as in all quasielastic *light*-scattering studies of solids, the problem of strong elastic scattering is severe in lead germanate. In order to overcome this problem, the spectra were excited by a single-mode 5145-Å Ar^+ laser tuned to the strong absorption frequency of molecular iodine. An iodine filter absorbs all signal within ± 300 MHz of the laser frequency, but it introduces significant distortion of spectral features outside this range. A computer-assisted renormalization technique, described elsewhere,[7] permits quantitative compensation of this distortion and has enabled us to demonstrate clearly the dynamic nature of the quasielastic scattering in this material. Unfiltered spectra are dominated by a strong (500 times the Brillouin intensity) elastic component which also increases near T_C. This feature presumably arises from domain-wall and defect scattering and will not be considered further here. It is completely removed from all spectra discussed here.

Our sample was cut from the same boule as the one used in Ref. 6. The scattering geometry was $X(ZZ)Y$, where Z is parallel to P_s. In order to minimize thermal gradients near T_C due to laser heating (0.06 K/mW), a weakly focused (0.5 mm), low-power (30-mW ± 1%) laser beam (5145 Å) was used. In the region closest to T_C (Fig. 1), the spectral shape showed no change when the laser power was increased to 90 mW and the temperature was corrected accordingly. Temperature variations over the scattering volume (~ 0.05 mm^3) were estimated to be less than ± 0.2 K near T_C. T_C was taken to be the temperature where the anomalous dynamic central-peak intensity was strongest. Extrapolating to zero laser power, this gives a value of 451 K for T_C which agrees well with values given in the literature.[4-6]

Our spectra were analyzed with either a double grating spectrometer [~ 0.2 cm^{-1} instrumental half-width at half-maximum (HWHM)] or a pressure-scanned incommensurate tandem Fabry-Perot interferometer[7] (operated at either 0.04 or 0.08 cm^{-1} instrumental HWHM) with an effective 23-cm^{-1} free spectral range. The former arrangement allowed us to overlap with the earlier Raman data[5] on the soft ferroelectric mode far from T_C. The latter arrangement revealed both

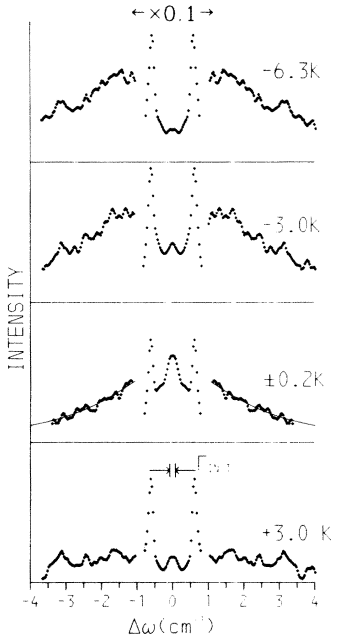

FIG. 1. Quasielastic spectrum of lead germanate near the ferroelectric phase transition. Temperatures are indicated as differences in K from $T_C = 451.0$ K. The sharp peaks at ± 0.6 cm^{-1} are due to the longitudinal Brillouin components. Note the rapid growth of the central peak whose HWHM (~ 0.13 cm^{-1}) is well above the instrumental resolution (HWHM = 0.08 cm^{-1}). The remnant of the overdamped soft optic mode is also visible at 10× higher gain, and, near T_C, may be fitted to a Lorentzian of HWHM = 2.3 cm^{-1} shown by the solid curve.

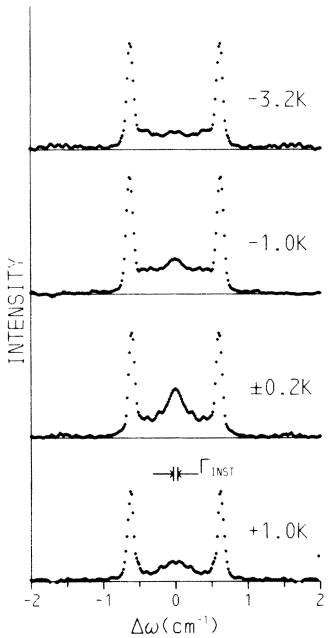

FIG. 2. High resolution spectra (HWHM = 0.04 cm^{-1}) of lead germanate near T_C. Gain is identical for all spectra. Note the highly asymmetric behavior near the Brillouin peaks, the rapid growth of intensity, and the persistence slightly above T_C for the dynamic central peak.

the anomalous ferroelectric mode behavior and the spectral line shape[8] of the central peak, shown in Figs. 1 and 2. The dynamics of the lead germanate ferroelectric transition can be described in three stages: (1) Far from T_C ($T < 395$ K), the soft mode is underdamped and decreases in frequency approximately as $\omega_s^2 \sim (T_C - T)$, while broadening slightly. (2) Between 395 and 440 K, the soft mode is overdamped and the decrease of its half-width $\Gamma = \omega_s^2/\gamma$ is consistent with $\omega_s^2/\gamma \sim (T_C - T)$. In this range, no detectable additional quasielastic scattered intensity is observed. (3) Within ~ 10 K of T_C, the soft mode line shape ceases to change (HWHM ~ 2.3 cm^{-1}) and its intensity begins to decrease, as shown in Fig. 1; at the same time, a much narrower (~ 0.13 cm^{-1}) additional polarized central feature of rather complicated line shape becomes visible, as shown in Fig. 2, between the longitudinal Brillouin peaks and grows rapidly in intensity. Above T_C, all quasielastic scattering decreases rapidly in intensity so that at $(T_C + 5)$ K it is no longer detectable.

The integrated quasielastic intensity of the observed scattering [Fig. 3(b)] represents a departure from mean-field theory (MFT). In general, the refractive-index perturbations causing light scattering are proportional to the square of the total order-parameter displacement $\psi(r,t) = \psi_0 + \delta\psi(r,t)$. Hence near T_C in a pure uniaxial ferroelectric, the total intensity[9] should vary as the specific heat: namely, as $t^{-\alpha}$. In mean-field theory $\alpha = 0$, so the total intensity can provide a particularly sensitive test of MFT. For a pure three-dimensional uniaxial ferroelectric, only logarithmic corrections to MFT are expected,[10] and are exceedingly difficult to observe except in those properties where the power-law singularities either vanish or cancel. The data show clearly that the total intensity *increases* near T_C. We cannot distinguish between a weak power law or a small power of $\ln t$ for this divergence, but we note that a $(\ln t)^{1/3}$ behavior has been predicted[10] for C_P. In view of (i) the persistence of the quasielastic scattering above T_C and (ii) the existence of a strong apparently diverging elastic peak, it is perhaps more likely that our observed departures from MFT are connected with impurity effects on the lead germanate critical behav-

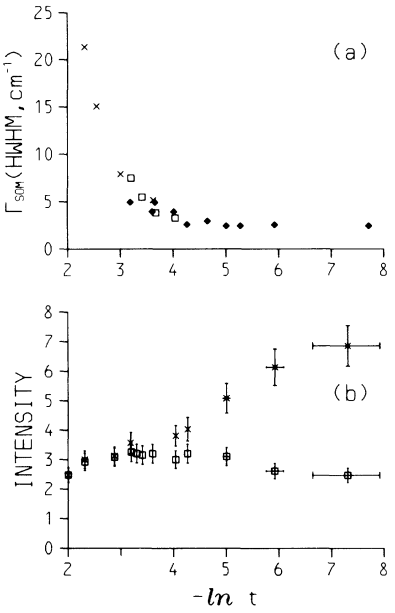

FIG. 3. (a) Temperature dependence of the overdamped soft optic mode width I_{som}. Different symbols refer to different spectral resolutions. The diamonds and squares were obtained with a tandem Fabry-Perot; and the x's, with the double grating spectrometer. $t \equiv (T_C - T)/T_C$. (b) Temperature dependence of the integrated intensity for the quasielastic spectrum. Squares are for the soft mode wing alone; and x's are for the total of soft-mode wing plus the central peak.

ior. As discussed recently from a theoretical viewpoint, the effects of impurities even on systems obeying MFT in their pure form are quite complex and dependent on the nature of the impurity.[11]

We note that, in Fig. 3(a), the range in t over which the overdamped soft-mode linewidth departs from mean-field behavior coincides well with the one where the weak intensity divergence occurs. In the absence of dynamic calculations for corrections to MFT for the uniaxial ferroelectric below T_C, it is difficult to compare or even fully analyze our line-shape data. The high-resolution spectra of Fig. 2 show that the line shape between the Brillouin components is quite unusual. The observed shape suggests rather complicated interactions among the central peak, the soft mode, and the LA phonons (ω_{LA}). We have checked for changes in ω_{LA} near T_C and find none[12] greater than 2%. In the absence of some theoretical guidance, we feel that the temperature dependences of the decidedly nonunique parameters one might extract from fitting our data to coupled-mode expressions would be at best inconclusive, and possibly misleading. We are presently engaged in experiments to uncover possible variations in the central-peak line shape with the electric field, scattering angle, etc. so as to reduce the number of adjustable parameters required to fit the spectral shapes.

Finally, as to the microscopic origin of the central peak, there are at least three mechanisms which might produce a sufficiently narrow response in a crystal: (i) entropy fluctuations for which $\tau^{-1} = Dq^2$, where D is the thermal diffusivity and q the scattering wave vector; (ii) two phonon difference processes determined by the lifetime and dispersion of large wave-vector phonons; and (iii) quasimobile defects or domains whose surrounding deformation field may couple to the order parameter.[11] Quite recently, direct light scattering from processes (i) and (ii) has been observed in $KTaO_3$ and $SrTiO_3$ unrelated to any phase transition.[13] Unfortunately, neither the thermodynamic parameters entering (i), nor the large k phonon behavior determining (ii) are known for lead germanate. However, for typical dielectric solids at these temperatures, entropy-fluctuation scattering exhibits a linewidth of order 0.2 cm^{-1} and appears, perhaps when coupled to (iii), an excellent candidate for the central peak reported here.

In summary, we have presented spectral-line-shape measurements of a singular dynamic central peak associated with a structural phase transition. The line shape is complicated and not yet understood, but the behavior of the scattered intensity shows clear deviations from the one predicted by mean-field theory.

After this work was completed, we received a preprint from Lockwood *et al.*[14] describing a detailed investigation of the unfiltered *elastic* light scattering in single-domain lead germanate. While this component carries no dynamic information, it does exhibit a strong (more than tenfold) intensity increase for $(T_C - T) < 5$ K, which falls off rapidly above T_C. Its relationship to the unresolved central peak observed over a much wider temperature range by neutron scattering[6] and to the weakly diverging *dynamic* central peak we observed remains to be established before a complete understanding of the lead germanate transition can be achieved.

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to H. L. Carter for experimental assistance.

[1]See for example, *Anharmonic Lattice, Structural Transitions and Melting*, edited by T. Riste (Noordhoff, Leiden, 1974).

[2]T. Riste, E. J. Samuelsen, K. Olsen, and J. Feder, Solid State Commun. 9, 1455 (1971).

[3]For example, conflicting values of the central linewidth have been inferred from the $SrTiO_3$ antiferrodistortive transition from ESR [K. A. Muller *et al.*, Phys. Rev. Lett. 32, 160 (1974)], neutron scattering [J. Topler *et al.* Phys. Lett. 51A, 297 (1975)], and γ-ray scattering [C. N. Darlington *et al.* Phys. Lett. 54A, 35 (1975)] experiments.

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[7]P. A. Fleury and K. B. Lyons, Phys. Rev. Lett. 36, 1188 (1976); and K. B. Lyons and P. A. Fleury, to be published.

[8]As noted in Ref. 7, our normalization procedure does not quantitativley reconstitute special features which are much narrower than the instrumental resolution. Therefore, the Brillouin peaks in Figs. 1 and 2 appear 2 to 3 times weaker than they actually are. Also we cannot exclude the possiblity of an *additional* very narrow ($\lesssim$300 MHz) central component in lead germanate. However, our line-shape analysis shows that the dynamic central peak which we do observe (Figs. 1 and 2) cannot merely be the tail of an imperfectly reconstituted much stronger and narrower central peak. If an additional dynamic central peak existed, the quantitative behavior of the integrated intensity shown in Fig. 3 would be modified accordingly.

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Exchange Effects in the Li *K* Edge*

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The Mahan, Nozières, De Dominicis theory of x-ray thresholds is extended to include exchange effects which are found to reduce threshold exponents and increase the orthogonality index. For the lithium *K* edge this represents an important previously neglected feature. Results of detailed numerical calculations of threshold exponents for Li are presented which differ considerably from previous values and which are in better agreement with edge data.

The Mahan, Nozières, and De Dominicis[1,2] (MND) theory of soft x-ray thresholds in metals predicts an absorption shape of the form

$$R(\omega) = \sum_l A_l^2 (\xi/\omega)^{\alpha_l} \theta(\omega), \tag{1}$$

where ω is the energy above threshold, ξ is a range parameter on the order of the Fermi energy, and A_l is the optical matrix element between the core state and the lth conduction band partial wave. The exponent α_l is given by

$$\alpha_l = 2\delta_l/\pi - \Delta, \tag{2}$$

$$\Delta = 2\sum_{l=0}^{\infty} (2l+1)(\delta_l/\pi)^2, \tag{3}$$

where the quantities δ_l are phase shifts at the Fermi surface due to the core hole potential. Equations (2) and (3) are derived assuming no exchange interaction between the conduction electrons and the core hole. We present here a modification of the MND theory which treats the diagonal part of the exchange exactly and includes a lowest-order correction for the nondiagonal part.

In general, the phase shifts, δ_l, may depend not only on l but also on the orientation of the spin and the orbital angular momenta. Examination of the MND derivation shows that Eqs. (2) and (3) are easily extended to include this possibility:

$$\alpha_{lm\sigma} = 2\delta_{lm\sigma} - \Delta, \tag{4}$$

$$\Delta = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{\sigma=\pm 1} (\delta_{lm\sigma}/\pi)^2. \tag{5}$$