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Neutron Scattering from the Ferroelectric Fluctuations and Domain Walls of Lead Germanate

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Neutron scattering from the uniaxial ferroelectric $Pb_5Ge_3O_{11}$ shows a quasielastic component in addition to the soft ferroelectric mode. At low temperatures, this scattering increases but can be suppressed by an applied electric field and probably arises from scattering by static domain walls. This scattering also has a maximum near T_c which is largely field independent and which we suggest may arise from scattering by the walls of moving domains or clusters.

The neutron scattering from the fluctuations at several structural phase transitions has been found to consist of two components; one component has a frequency comparable with normal phonon frequencies but the other corresponds to fluctuations which decay on a much longer time scale. In some cases, Nb_3Sn for example,[1] the linear coupling between the order-parameter fluctuations and the phonon-density fluctuations provides a possible mechanism for the very slow fluctuations. In other cases, $SrTiO_3$ for example,[2] it is more difficult to account for the slow fluctuations. It has been proposed that they arise from (a) relaxations of the local order parameter near a defect,[1,3] (b) the motion of large clusters or domain walls (solitons) which are in dynamic equilibrium near T_c,[4] or (c) explicitly nonclassical fluctuation effects.[5] In this Letter we report on neutron-scattering measurements of the quasielastic ferroelectric fluctuations in lead germanate, $Pb_4Ge_3O_{11}$. This material undergoes uniaxial ferroelectric phase transition from a paraelectric phase of symmetry $P\bar{6}$ to a ferroelectric phase of symmetry $P3$.[6] In this case symmetry prohibits a linear coupling between the phonon-density fluctuations and the electric polarization fluctuations in the paraelectric phase. Furthermore, the theory of fluctuations in uniaxial ferroelectrics shows that $d=3$ is the marginal dimension for these materials so that static properties are expected to be described by classical exponents with the possibility of logarithmic correc-

tions.[7] The static dielectric constant of lead germanate is observed[8] to obey a Curie law near the transition in both phases and furthermore the Raman-scattering measurements[9] in the ferroelectric phase show a soft-mode frequency proportional to $(T - T_c)^{1/2}$. In view of these considerations, it seems unlikely that quasielastic scattering in lead germanate could arise from nonclassical behavior of the critical fluctuations.

Measurements were made on crystals grown by Dr. Robertson of the Royal Radar Establishment, Malvern, United Kingdom. Crystal A had a volume of 20 cm^3, while the other crystal, B, which was used for the electric field dependence experiments, was cut in the form of a plate of area 4 cm^2 and thickness 0.3 cm with a [001] axis perpendicular to the plate. Gold electrodes were deposited on the large faces of the plate and platinum leads attached with silver paint. Both crystals were mounted with a [100] axis vertical, on a triple-axis crystal spectrometer. The measurements were made with a fixed incident neutron energy of 5 meV and a cooled beryllium filter placed in the incident beam to suppress beam contamination from higher-order reflections in the pyrolytic graphite monochromator and analyzer. Most of the measurements were made with momentum transfer close to the (004) reciprocal lattice point although qualitatively similar scattering was also observed around certain other lattice points. The temperature of the crystals could be held constant to ± 0.1 K for long periods and measured absolutely to within an accuracy of ± 1.0 K. The ferroelectric transition temperature was found, by measuring the temperature dependence of the (004) Bragg reflection, to be 449.3 K for crystal A and 453.1 K for crystal B.

Energy scans at several temperatures for a constant wave vector transfer of (0.05, 0.05, 4) are shown in Fig. 1, and show an overdamped soft mode whose width decreases as the temperature approaches T_c. (The scattering is asymmetric about $\hbar\omega = 0$ because of the combined effects of thermal population and instrumental resolution.) The behavior of this mode with wave vector and temperature is qualitatively that expected from an anharmonically damped soft mode and its properties together with the effects produced by the interference of this mode with the acoustic modes will be reported in a later publication.

In addition to the phonon mode, Fig. 1 also shows a prominent, narrow, quasielastic peak with an energy width that of the instrumental

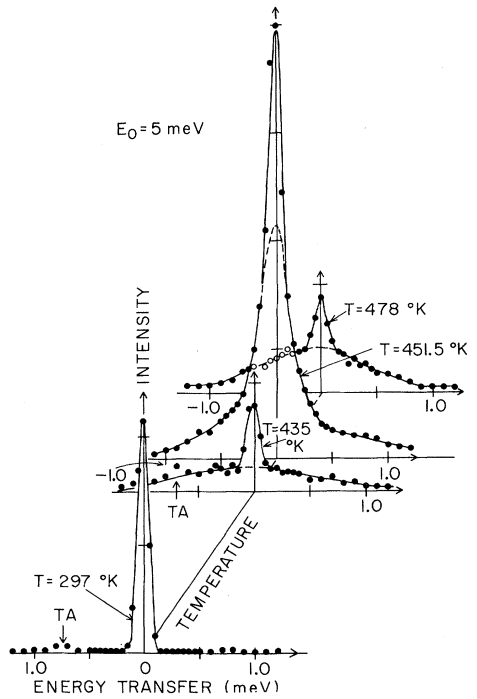

FIG. 1. Energy scans at constant wave vector transfer $\vec{Q} = (0.05, 0.05, 4)$. The solid lines indicate the total scattering after subtraction of the incoherent elastic scattering and the dashed lines the elastic scattering from the overdamped phonon mode.

resolution, 0.11 meV. This scattering increases towards T_c, although close to T_c, it is difficult to separate it unambiguously from the phonon scattering. Below T_c, the scattering initially decreases in intensity but then increases almost linearly with $T_c - T$ reaching a maximum at low temperatures as shown in Fig. 2. Only the intensity of the narrow quasielastic component is plotted, the broader phonon background and a small elastic incoherent contribution having been subtracted. Figure 2 also shows the results of similar measurements on crystal B made after applying an electric field of 1000 V above T_c and subsequently varying the temperature while keeping the field constant. The observations on the two samples were normalized so as to make the $\hbar\omega = 0$, $V = 0$ intensities agree at room temperature. The effect of the applied field was completely reversible, but only after annealing for a long time (~12 h at 650 K) at zero field.

The distribution of the quasielastic scattering in the (100) plane was a ridge along the $[\zeta, \zeta, 0]$ direction whose intensity increased rapidly as $\zeta \to 0$. Measurements in the (110) plane both above and below T_c lead us to believe that this

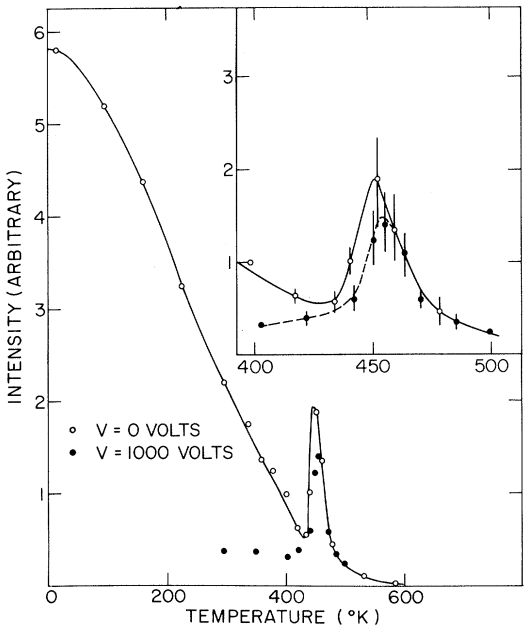

FIG. 2. The temperature dependence of the central component of the scattering for $\vec{Q} = (0.05, 0.05, 4)$. The open points were obtained with crystal A and $V = 0$ while the solid points were obtained for crystal B and $V = 1000$ V.

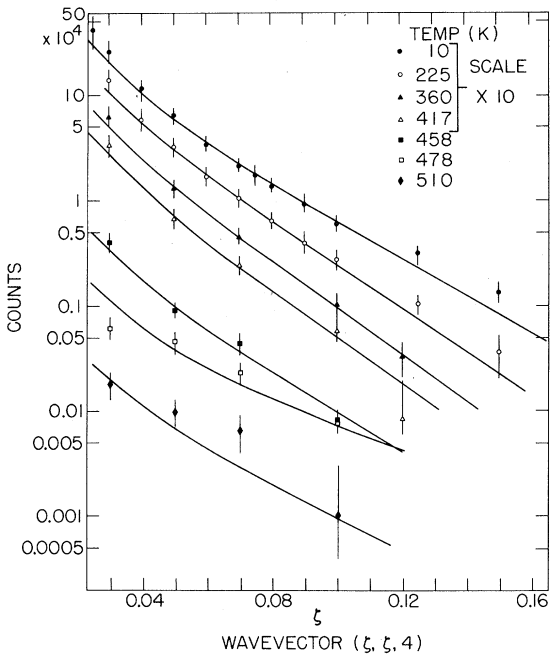

FIG. 3. The wave vector dependence of the quasielastic intensity at several temperatures in crystal A with $V = 0$. The solid lines are the fits obtained with the random-domain-wall model described in the text.

scattering is more or less isotropically distributed in the plane perpendicular to the [001] axis.

These results suggest that the quasielastic scattering consists of two components. One has a maximum at T_c and is largely unaffected by an applied electric field; the other is largely suppressed by an electric field and its intensity increases approximately as $T_c - T$, Fig. 2. This latter behavior suggests that the low-temperature scattering arises from the static ferroelectric domain structure. Cooling in the electric field produces a largely single-domain sample so that the scattering is suppressed.

In order to put this idea to a semiquantitative test, we imagine the sample at $V = 0$ to be composed of randomly distributed domains but with the normals of the domain walls perpendicular to the ferroelectric c axis, which is the energetically favorable orientation in the sample geometry. If the electric polarization near a flat domain wall at $x = 0$ is given by $\vec{P}(x) = \vec{P}_0 \tanh(x/\lambda)$, the scattering from a random distribution of domains in the x direction is given by $I(q_x) = K\lambda^2/\sinh^2(\frac{1}{2}\pi \times q_x \lambda)$ in the limit that q_x is large compared to the inverse width of a typical domain. Here K is a constant which depends on $\vec{P}_0$ and the number of domain walls. In Fig. 3, we show the fits obtained with this function treating K and the domain-wall thickness as parameters. Because of the approximate nature of this calculation and the impossibility of adequately accounting for the influence of instrumental resolution, the agreement shown in Fig. 3 should only be taken to indicate that it is possible to obtain a qualitative description of our results with this functional form. Nevertheless, if our interpretation is correct, the parameter λ should serve as an approximate measure of the width of a domain wall, and this is shown as a function of temperature in Fig. 4. Perhaps the most significant feature is the smooth behavior of λ through T_c, which in turn suggests that something rather akin to dynamic domains or clusters are responsible for the scattering even above T_c.

Finally our results and conclusion may be summarized as follows: (1) The critical scattering in the uniaxial ferroelectric lead germanate has been observed to consist of a broad overdamped "soft mode" and a narrow, quasielastic, "central peak." This scattering is little affected by external electric fields up to 3300 V/cm. (2) There is an additional quasielastic component below T_c which increases roughly as $T_c - T$ and which may be largely eliminated by an applied electric field. (3) This low-temperature scattering is consistent

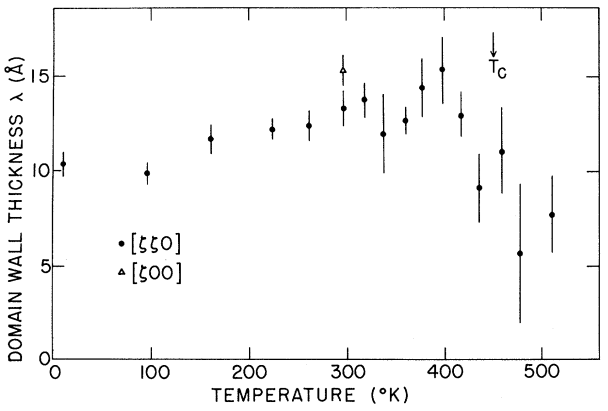

FIG. 4. The domain-wall thickness obtained from the fits shown in Fig. 3. The solid points are taken from measurements along [ζζ0] and the open points from measurements along [ζ00].

with that expected from the polarization reversal which occurs in randomly arranged domain walls. (4) The component of the quasielastic scattering intensity that peaks near T_c may possibly arise from the walls of dynamic domains or large clusters of polarization.

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Critical Behavior at the Metal-Nonmetal Transition in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)*

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We present the results of high-precision electrical resistivity measurements in the vicinity of the metal-nonmetal transition in TTF-TCNQ. We find a sharp negative divergence in the derivative of the resistivity, $R^{-1}dR/dT$, which suggests the existence of a second-order phase transition at about 53 K. A critical-exponent analysis of this divergence implies that the onset of long-range order occurs with a classical exponent (i.e., $\beta=\frac{1}{2}$) within a three-dimensional region which extends to approximately $|T-T_c|/T_c=t=10^{-1}$.

There has been considerable recent interest in the electrical properties of TTF-TCNQ and related highly anisotropic conductors.[1-5] Much of this interest has centered around the possibility of having an electronically driven structural transition, such as a Peierls distortion, or another intrinsically one-dimensional instability. In TTF-TCNQ specifically, recent diffuse x-ray studies[4] as well as elastic neutron scattering experiments[6] have shown that the metal-nonmetal transition is associated with a structural distortion arising from the condensation of a $2k_F$ phonon. On the other hand, there is as yet little specific experimental information about the actual character of the fluctuations associated with this distortion. In this Letter we present the first detailed exami-