Two-length-scale behavior near the ferroelectric phase transition of $Sn_2P_2S_6$

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Synchrotron x-ray diffraction studies of a $Sn_2P_2S_6$ crystal near the continuous ferroelectric phase transition have revealed that the critical scattering contains two independent components. The extraneous narrow component appears to originate from the strained, near-surface parts of the sample. The observed behavior matches the attributes of two-length-scale phenomenon as described previously in crystals with various second-order phase transitions. Identification of the effect in a uniaxial ferroelectric has important consequences for the existing theories describing this phenomenon.

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Most of the current theories of continuous phase transitions assume that the properties close to the critical point are determined by a single-length-scale ξ, which diverges at the phase-transition temperature T_C. Accordingly, the expected wave vector dependence of the x-ray scattering cross section, due to critical fluctuations above T_C, should have a universal form, which becomes critically narrow at T_C. In principle, the available resolution at modern x-ray sources is sufficient for testing this scaling hypothesis, for investigating the temperature dependence of ξ, and even searching for deviations from the approximate Lorentzian line shape of the scattering cross section.

On the other hand, high-resolution x-ray investigations on numerous high-quality single crystals near structural and magnetic phase transitions have revealed that the description of the critical scattering from real systems requires considering a second, so-called sharp component, with a much longer and independently varying length scale ξ'. Recent experiments[1–4] have demonstrated that the sharp component comes from the near-surface region ("skin") of the sample, and that the bulk fluctuations can be described with a single length scale as required by theory. Nevertheless, the presence of the sharp component complicates the experimental investigation of critical fluctuations and clarification of its origin is highly desirable.

A critical comparison of observations of the two-length-scale phenomenon in different compounds and a review of the possible explanations for the sharp component can be found in a recent review paper.[1] Among them, two plausible models have been proposed. The first scenario[5,6] is based on the results of the theory of critical phenomena in the presence of quenched disorder[7] and assumes that the static long-range random strains associated with dislocations or other defects generated near the sample surface, modify the critical exponents in the skin area. The opposing scenario[1] assumes that the properties of the critical fluctuations are modified near the surface because of coupling to the free surface acoustic waves. The theory of this latter mechanism was not worked out in detail, but it was predicted[1] that the effect should be absent for systems with weak order-parameter/strain coupling, for systems near a tricritical point or for systems with mean-field behavior.

Recently, the two-length-scale phenomenon was observed in a rich variety of systems, including, for example, antiferroelectric[3,8–10] or incommensurate insulators,[11] antiferromagnetic metals,[12] spin-Peierls systems,[13,14] disordered invar,[15] etc. This paper describes the existence of the sharp component in a uniaxial ferroelectric system $Sn_2P_2S_6$ (see Fig. 1), and indicates that the two-length-scale phenomenon is also relevant to the ferroelectric phase transitions. In principle, the uniaxial ferroelectrics are of particular interest, because they have mean-field critical behavior, as a consequence of the strong suppression of the longitudinal critical fluctuations by the long-range dipolar interactions.[16–19]

At ambient conditions, the $Sn_2P_2S_6$ compound has a noncentrosymmetric monoclinic structure Pn with two formula units in a pseudo-orthorhombic unit cell[20,21] defined by $a=9.378$ Å, $b=7.488$ Å, $c=6.513$ Å, and $\beta=91.15°$. In this setting, the spontaneous electric polarization is oriented in the ac plane, about 15° from the a axis. The continuous disappearance of the polarization near[24] $T_C \approx 337$ K is associated with the space-group symmetry change from Pn to P$2_1/n$. The order parameter can be understood microscopically as a zone center B_u soft mode involving mainly x, y, and z displacements of Sn^{2+} ions, antisymmetric with respect to the screw axis and symmetric with respect to the glide plane. Therefore, the OKO reciprocal points with $K=2n+1$ offer an excellent opportunity for investigating the order pa-

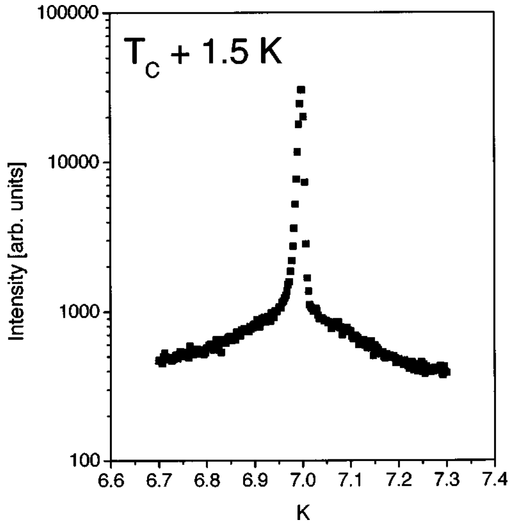

FIG. 1. Typical $\mathbf{Q}=(0,K,0)$ scan showing the coexistence of the broad and the sharp critical scattering components (at $T_C+1.5$ K).

rameter fluctuations above T_C, since both the Bragg and the thermal diffuse scattering by long-wavelength acoustic phonons is absent due to the extinction rule imposed by the screw axis.

The present experiment was carried out at the D2AM beamline[22,23] of the European Synchrotron Radiation Facility in Grenoble, using 12.147 keV x rays. The sample was a 4-mm-thick plate, with polished surfaces parallel to the (ac) plane, cut from an optically transparent single crystal grown by the chemical vapor transfer technique at Uzhgorod University. The sample was glued onto a thick Cu plate placed in a small vacuum chamber with a Be-foil window. The temperature controller allowed us to keep the temperature constant within ±0.05 K over several hours. The diffracted x-ray photons were detected in reflection geometry using a point scintillation counter detector. The typical momentum transfer resolution (in point detector mode) measured on the (080) reference Bragg reflections was $0.0073a^*, 0.0016b^*$, and $0.0007c^*$.

Most of the measurements were performed in the vicinity of the (070) reciprocal point. In the parent high-temperature phase, this point corresponds to an extinct Bragg reflection, but in general, some very weak Bragg contribution is expected due to multiple reflection processes. The importance of this multiple scattering was determined by an auxiliary Φ scan (sample rotation around the [010] direction) at $T>T_C$, which indeed showed a multitude of small sharp peaks. Therefore, special care was taken to select a Φ angle for which the multiple scattering contribution was negligible. Under these conditions we could observe that the scattered intensity near the (070) reciprocal point increased by several orders of magnitude, when the temperature was lowered across the transition point (see Fig. 2). To determine the reference phase-transition temperature T_C, a scan across the (070) reflection was systematically recorded while slowly cooling down the sample ($dT/dt=-0.003$ K/min). Due to an important thermal gradient between the sample holder and the surface of the sample, the reference T_C value of 341.5 K, determined as the position of the inflection point on the peak

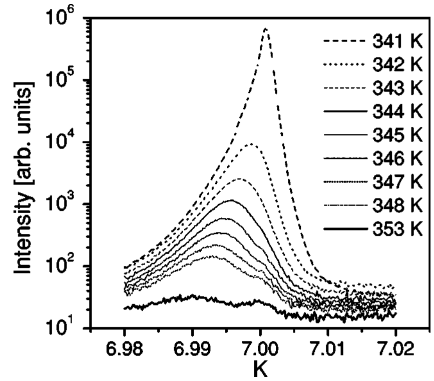

FIG. 2. Set of $\mathbf{Q}=(0,7+\delta,0)$ scans near T_C showing the sharp component of the critical scattering. The sharp component sits on a T-dependent background that corresponds to the broad component.

intensity vs temperature plot, is about 3–4 K higher than the values found in previous experiments.[24] In a subsequent slow-heating run, T_C was found to be about 0.1 K higher. All the further measurements were systematically performed on cooling, after annealing one hour at 373 K.

We remark that for $T>T_C$, the line shapes shown in Fig. 2 are clearly asymmetric and that the position of the intensity maximum does not coincide with the reference (070) reciprocal point, the latter being independently determined by scans across the regular (080) and (060) Bragg reflections. Such a misfit is typical for the sharp component in two-length-scale systems, and it strongly suggests that the observed intensity comes from strained parts of the crystal. This interpretation is further supported by our observation of the same phenomenon near the (030) and (050) reflections, which allowed us to establish that the misfit between the peak position and the reference reciprocal point is directly proportional to the scattering wave vector $\mathbf{Q}$. At about 10 K above the phase transition, the characteristic strain ϵ'_{22} along the b direction (perpendicular to the surface), determined by the ratio of this misfit to the length of $\mathbf{Q}$, reaches values of the order of 10^{-3}. This can be directly read from the lowest curves in Fig. 2, where the reference (070) position is marked by the weak residual multiple scattering peak at $K\approx 7$. Near T_C, ϵ'_{22} vanishes gradually as shown in Fig. 3.

The sharp peak shown in Fig. 2 sits on a temperature-dependent background corresponding to the broad component. Both components are clearly seen in more extended scans along K, as demonstrated in Fig. 1 for $T=T_C+1.5$ K. Two-dimensional intensity maps along the three principal reciprocal planes are shown in Fig. 4. They reveal the typical disk-shape anisotropy expected for ferroelectric order-parameter fluctuations.[18] The direction perpendicular to the disk lies in the ac plane at about 14° from the a axis, which corresponds well to the known direction of the spontaneous polarization, i.e., to the direction where the order-parameter fluctuations are suppressed.

The temperature dependence of the broad component was determined from $\mathbf{Q}=(\delta,7,3\delta)$ scans. In keeping with previous work,[1] we have fitted the data to the sum of a Lorentzian and a squared Lorentzian profile in order to take into account broad and sharp components, respectively. On approaching

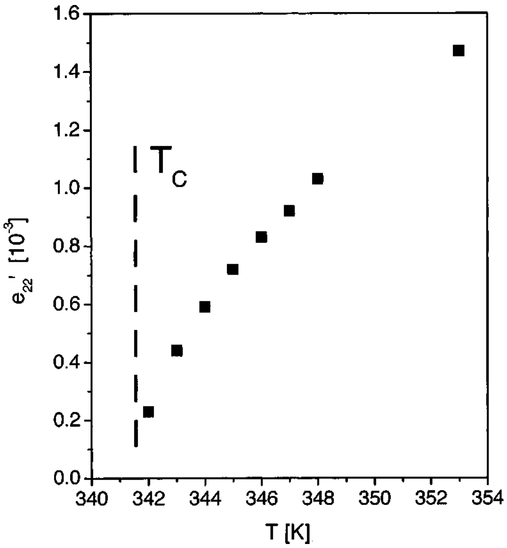

FIG. 3. Relative offset of the sharp component peak position $[0,7*(1-\epsilon_{22}),0]$ from the reference bulk reciprocal point as a function of temperature.

T_C, the maximum intensity and half width at half maximum (proportional to the inverse correlation length) of the broad component shows qualitatively the expected critical behavior (Fig. 5). Unfortunately, the signal and its relative change with temperature is too small for a reliable determination of the critical exponents. We do not display the parameters of the sharp component because they are strongly influenced by offcentering and asymmetry of the sharp component in the b^* direction and thus do not have any straightforward physical interpretation. However, the behavior is qualitatively similar as in the scans shown in Fig. 2, supporting the picture of two critical components with a common critical temperature.

In summary, the critical scattering of $Sn_2P_2S_6$ contains an extraneous sharp component with a behavior matching the essential characteristics of the two-length-scale phenomenon: it is clearly separated from the broad component; it gives appreciable fraction of the diffuse scattering in the vicinity of T_C; it is much more isotropic then the broad component, and it originates from strained parts of the sample. The scenario based on the coupling between the order parameter and surface acoustic waves implies[1] that the two-length-scale phenomenon should be absent in systems with mean-field type critical behavior. Uniaxial ferroelectrics have a one-dimensional order parameter as in the case of anisotropic ferromagnets and the phase transition is thus essentially of the three-dimensional (3D) Ising-type. However, it is known that longitudinal fluctuations in the vicinity of a phase transition are very strongly suppressed by the long-range dipolar interactions.[16–18] Consequently, uniaxial ferroelectrics generally show mean-field critical behavior.[16–18] Therefore, the observation of the two-length-scale phenomenon in $Sn_2P_2S_6$ provides a valid counterexample for such a model. It can be argued, that the critical behavior of our system is not rigorously mean field, e.g., due to logarithmic corrections, or due to the closeness of the system to the tricritical and Lifshitz points. The few reported experimental data on critical exponents in $Sn_2P_2S_6$ indeed indicate[24–27] a crossover to the

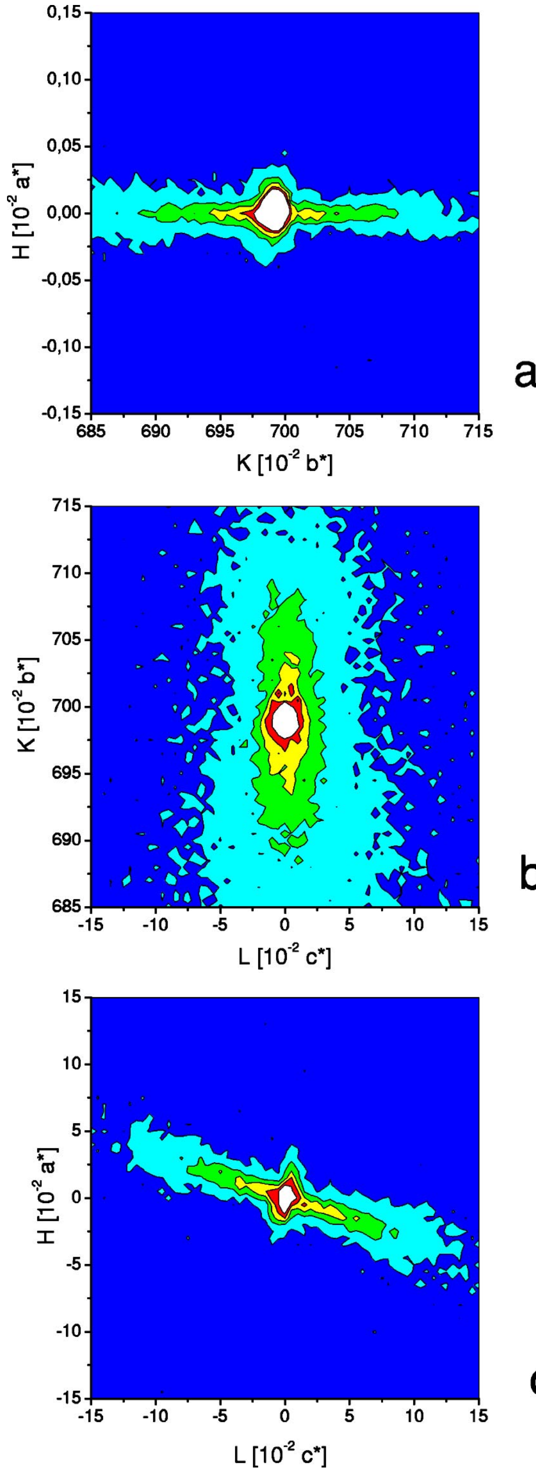

FIG. 4. (Color online) Two-dimensional cuts of the critical diffuse scattering (at T_C+6.5 K) along the principal reciprocal planes [(a) 0*KL* plane, (b) *HK*0 plane, (c) *H*0*L* plane].

uniaxial-tricritical-Lifshitz (UTL) universality class with[18] α=0.5, β=0.25, and γ=1. However, the upper critical dimension d_u for the UTL universality class is d_u=3 as in the case of the ordinary uniaxial ferroelectrics. We thus believe that the observed effect is due to a defective near-surface layer as proposed e.g., in Refs. 5, 6, and10. Nevertheless, the mechanism may not be strictly the same. For example, the

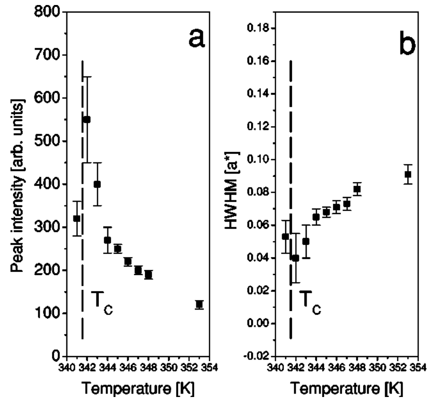

FIG. 5. (a) The temperature dependence of the peak intensity and (b) the half width at half maximum of Lorenzian fits to the broad component.

critical behavior of the characteristic strain shown in Fig. 3 was neither predicted not observed previously.

One of our referees has drawn our attention to the work of Birgeneau *et al.*,[28] which strongly suggests that mean-field critical behavior may occur near spin-Peierls phase transitions. Although the mean-field behavior of spin-Peierls systems is not yet well understood, the cited paper explicitly shows that the magnetic energy gap, specific heat, correlation length, and disconnected staggered susceptibility near the spin-Peierls phase transition of copper germanate ($CuGeO_3$) can be well described by a simple Landau-Ginzburg model exhibiting tricritical to mean-field crossover.[28] At the same time, the two-length-scale effects were clearly observed in this compound.[1,13,14] Therefore, copper germanate, while *a priori* belonging to the 3D Ising universality class,[1] can, in fact, serve as another plausible counterexample for the surface acoustic wave model.

In conclusion, our observations clearly show that the two-length-scale phenomenon can be encountered in uniaxial ferroelectric phase transition. It would be instructive to have evidence for the two-length-scale phenomenon in other "classical" uniaxial ferroelectrics with well-established mean-field critical exponents (like TSCC, KDP, or TGS). However, none of these well-known materials has the fortunate symmetry that allows the observation of the ferroelectric fluctuations near a fully extinct Bragg reflection.

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