Observation of Two Length Scales for the Critical Fluctuations of $RbCaF_3$

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X-ray scattering measurements of the critical fluctuations in $RbCaF_3$ above T_c have revealed two different length scales. The shorter one arises from the usual critical fluctuations and does not diverge at the transition, which is of first order. The longer one is associated with the presence of defects and appears to diverge at T_c. We suggest that this new feature can be interpreted in terms of large-scale fluctuations into the low-temperature phase, mediated by extended defects such as dislocations.

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The critical fluctuations associated with the cubic-to-tetragonal transition in the perovskite $RbCaF_3$ have been studied by high-resolution x-ray scattering techniques. The transition, at $T_c = 197$ K, is antiferrodistortive and weakly first order.[1] Surprisingly, we find that close to T_c there are two critical length scales; the shorter one results from the usual critical fluctuations, whereas the longer one is associated with the presence of defects and diverges continuously as the temperature approaches T_c. We suggest that this latter length scale characterizes the size of distorted regions forming around defects above T_c, as qualitatively predicted by Imry and Wortis.[2]

The $RbCaF_3$ transition is structurally the same as occurs in $SrTiO_3$: The tetragonal phase is characterized by small rotations of the fluorine octahedra around the cubic ⟨100⟩ directions. But the $RbCaF_3$ transition differs in being first order, and the phonon dispersion relations show[3] that the critical fluctuations are more nearly two dimensional in character than those of $SrTiO_3$. In both $SrTiO_3$[4] and $RbCaF_3$[5] there have been many measurements of the dynamics of the fluctuations showing that there are two *time* scales. One is associated with the soft-mode scattering. The other, the "central peak," is much longer and is generally believed to be due to the presence of defects; but the nature of the defects and their behavior is still not understood in detail.[6] We now report some high-resolution x-ray scattering measurements on $RbCaF_3$ designed to study the *length* scales of the critical fluctuations.

A single-crystal boule of $RbCaF_3$ was grown by Professor J. Nouet of the University of Le Mans, using the Bridgman-Stockbarger technique with highly purified starting materials; the growth axis was along a cubic fourfold axis, here designated [001]. Several plates, about 8 mm across and 2 mm thick, were cut perpendicular to the growth axis, polished, and finally etched in HCl to remove surface damage. These samples were mounted in turn in a closed-cycle cryostat, and oriented with their face normal, [001], and a cubic [110] direction in the (horizontal) scattering plane of our triple-axis x-ray diffractometer. Measurements in this (*hhl*) scattering plane were made in reflection geometry, with Cu $K\alpha_1$ radiation from a rotating-anode source. The temperature stability of the cryostat was ± 0.01 K.

We will present detailed results from just two of the samples examined—crystal I cut from the top of the boule, where the defect and impurity concentration was believed to be at a minimum, and crystal II cut from the middle of the boule. Both crystals were of high and indistinguishable optical quality but, as anticipated, we found crystal II to have a larger mosaic spread [0.012(1)°] than crystal I [0.005(1)°]. It is important to note, though, that a mosaic spread of 0.012° is still *small* by all normal standards of crystal perfection.

Initially, the critical scattering above T_c was measured with a pyrolytic graphite monochromator and analyzer to give a relatively relaxed resolution, FWHH ~ 0.008 Å^{-1}. Scans through the cubic R point at (0.5, 0.5, 3.5) are shown in Fig. 1. Well above T_c, at $T_c + 8$

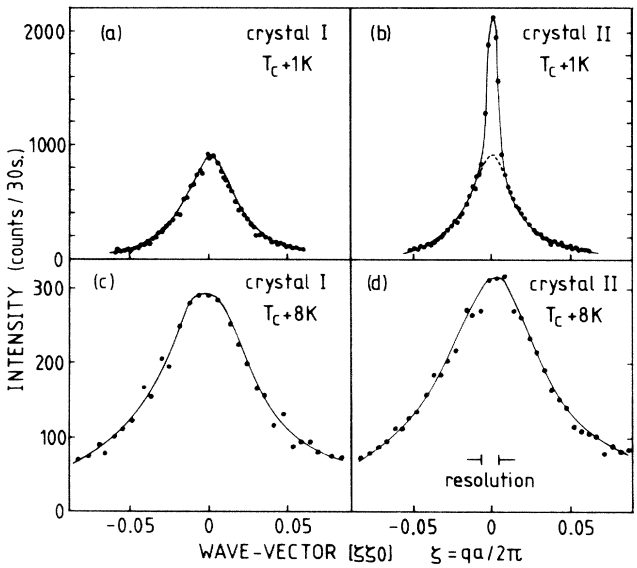

FIG. 1. The intensity observed in [ζζ0] scans through the critical scattering at the (0.5,0.5,3.5) R point, with the relatively relaxed resolution shown, for crystals I and II, at $T_c + 1$ K and at $T_c + 8$ K.

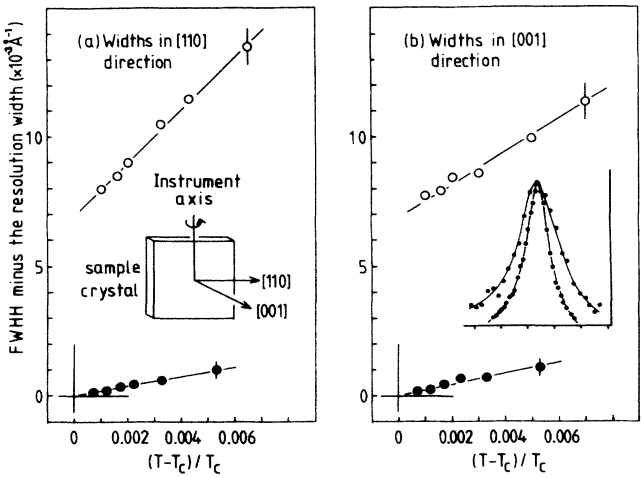

FIG. 2. The temperature dependence of the wave-vector widths for the sharp (filled circles) and broad (open circles) components of the critical scattering at the (0.5,0.5,3.5) R point in crystal II, (a) parallel and (b) perpendicular to the crystal surface. The values plotted are the measured FWHH minus the resolution width. The inset in (a) shows the orientation of the sample on the instrument; that in (b) shows the intensity of the sharp component as a function of wave vector [as in Fig. 3(b)], normalized to the same peak intensity, measured at T_c and at $(T-T_c)/T_c = 0.0032$.

K, the scans from the two crystals are identical within error [Figs. 1(c) and 1(d)]. But closer to T_c a marked difference emerges: While the scattering from crystal I remains a smooth broad curve at T_c+1 K [Fig. 1(a)], that from crystal II has a similar broad component but with an additional, resolution-limited component superimposed on it [Fig. 1(b)]. Other samples yielded similar results except that the intensity of the sharp component varied from crystal to crystal. The open circles in Fig. 2 show the temperature dependence of the observed width of the broad component common to all samples—the width decreases as T_c is approached but is nonzero at T_c, as expected for a first-order transition. A more detailed analysis shows that the line shape is consistent with a Lorentzian form.[7]

The wave-vector dependence of the additional, sharp component in crystal II was then investigated at higher resolution by use of Si(111) monochromator and analyzer crystals to give a resolution of ~ 0.0005 Å^{-1} (FWHH) in the scattering plane and ~ 0.02 Å^{-1} perpendicular to it. At this resolution *only* the sharp component is detected; the broad component becomes simply part of the general background.

A topographic study[7] of the tetragonal-phase domain pattern below T_c showed that the domains were of macroscopic size, and that a large part of crystal II formed only domains with the fluorine octahedra rotated around either the [100] or [010] cubic directions, i.e., *not* around the face normal, [001]. In these (helpful) circumstances each cubic-phase Bragg reflection splits into only two tetragonal-phase reflections, which exactly superimpose in the (hhl) scattering plane, so that in our measurements the cubic-phase reflections appeared simply to shift without splitting at T_c. From this part of crystal II, the scattering around the cubic-phase Bragg reflections (004), (114), and (113), and the critical scattering around (0.5,0.5,3.5), were measured in detail as a function of temperature through T_c. The results are summarized in Figs. 2, 3, and 4.

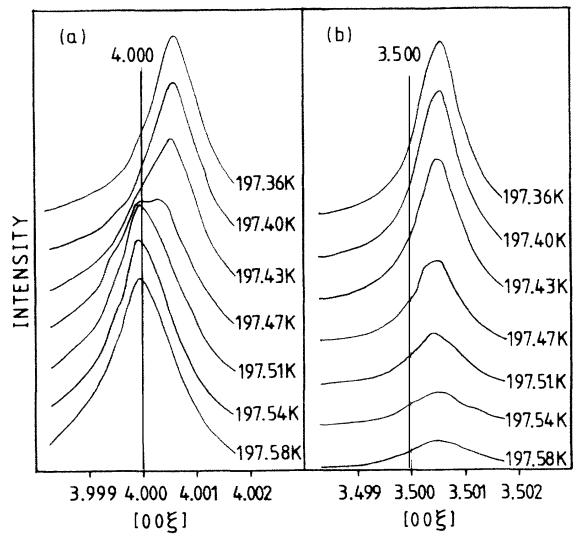

FIG. 3. The intensity observed in [00ξ] scans through (a) the (114) Bragg reflection and (b) the sharp component of the critical scattering at the (0.5,0.5,3.5) R point, as the temperature of crystal II was varied from $T_c+0.1$ K to $T_c-0.1$ K. There was no detectable hysteresis on the time scale of the measurements.

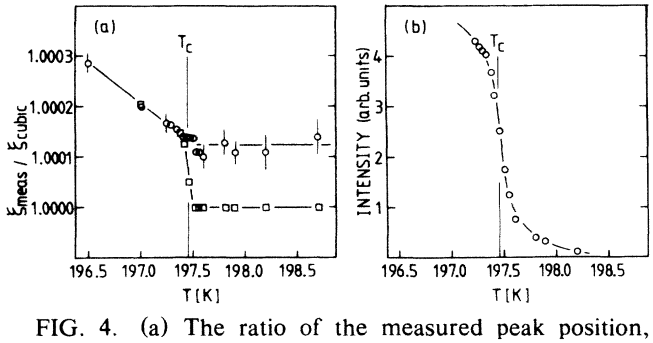

FIG. 4. (a) The ratio of the measured peak position, ξ_{meas}, and its reference location in the cubic-phase reciprocal lattice, ξ_{cu}, for [00ξ] scans, as in Fig. 3, through (squares) the (114) Bragg reflection and (circles) the sharp component of the critical scattering at the (0.5,0.5,3.5) R point, in crystal II, as a function of temperature. (b) The integrated intensity of the sharp component of the critical scattering at the (0.5,0.5,3.5) R point, in crystal II, as a function of temperature.

(i) The cubic-phase Bragg reflections jump abruptly to their tetragonal-phase positions at T_c, as expected for a first-order transition. Figures 3(a) and 4(a) show the measurements for the (114) reflection.

(ii) Figures 3(b) and 4(a) show that the center of the sharp component in the critical scattering is already displaced from the cubic R point *above* T_c, by precisely the magnitude of the discontinuity in the position of the cubic-phase Bragg reflections at T_c. (Above T_c the cubic R point was located by reference to the positions of the three surrounding Bragg reflections. The absence of any relative displacement at and below T_c was established in exactly the same way.)

(iii) The sharp component has a wave-vector width appreciably broader than the instrumental resolution above T_c but decreasing continuously to the resolution limit at T_c (the filled circles in Fig. 2), corresponding to a divergence of the correlation length. This is in contrast to the nondivergent behavior of the broad component (the open circles in Fig. 2). In Fig. 2 we show the measured full width at half height with the resolution width subtracted directly. A more detailed deconvolution of the resolution function gives similar results and, further, suggests that the line shape of the sharp component is Lorentzian squared, rather than Lorentzian.[7]

(iv) The integrated intensity of the sharp component increases smoothly with falling temperature [Fig. 4(b)], with no apparent discontinuity at T_c.

These are surprising results. They suggest that defects can have an important effect on the critical fluctuations within a few degrees of structural phase transitions, even in crystals which are of high quality by the standards of most experimental studies. The effect is to establish a second, much larger length scale in the critical behavior which, as shown in Fig. 2, diverges at T_c while the overall transition remains discontinuous.

The larger length scale cannot be explained as a surface effect. Firstly, the surfaces of crystals I and II were both prepared in an identical manner; and, secondly, the observed widths for the sharp component in Figs. 2(a) and 2(b) show that the correlation lengths are the same parallel and perpendicular to the surface. Rather, the results indicate the formation of large clusters with a tetragonally distorted structure, some 5000 Å across at $T_c + 0.5$ K, embedded in the cubic matrix of the high-temperature phase. Since the tetragonal strain remains constant on approaching T_c [Fig. 4(a)] and this strain is strongly correlated with the rotation of the fluorine octahedra, the increasing intensity as $T \rightarrow T_c$ [Fig. 4(b)] implies an increase in the size, rather than the distortion, of the clusters until they constitute the whole crystal at T_c.

Most theories of the effect of defects on phase transitions have considered point defects and continuous phase transitions. They predict that the range of the distortion around each defect is controlled by the intrinsic correlation length of the fluctuations in the high-temperature phase.[8] One such theory which might have been expected to apply to $RbCaF_3$ is the $n=3$, $d=3$ model with cubic anisotropy and random uniaxial anisotropy. For small cubic anisotropy the random anisotropy is predicted[9] to destroy the long-range order, but for larger cubic anisotropy a first-order transition is predicted. Clearly these predictions are not in accord with our results, and in general such theories cannot explain the occurrence of two length scales.

A possible understanding of our results may be found through the effect of defects on first-order transitions as discussed by Imry and Wortis.[2] They argue that close to a first-order transition there can be two types of fluctuations: the fluctuations about the local minimum of the free-energy function for each phase, and fluctuations from one phase to the other mediated by defects. This type of theory can explain our results, at least qualitatively, if we identify the fluctuations about the cubic minimum of the free-energy function with the phonon normal modes (which do not give rise to a divergent correlation length at T_c), and the second and longer length scale with defect-driven fluctuations into the tetragonal low-temperature phase. The size of the latter fluctuations is then controlled by the free-energy difference between the phases, which decreases continuously as $T \rightarrow T_c$. Imry and Wortis[2] do not discuss in detail the nature of the transition. Our results suggest that the transition changes from first order to continuous, and that the transition is more like a percolation transition when the sizes of the tetragonal-phase clusters become so large that they overlap.

In conclusion, we have shown that the critical fluctuations close to the structural phase transition in $RbCaF_3$ occur on two length scales. The longer length-scale fluctuations are associated with defects, most probably dislocations or stacking faults, and arise from fluctuations into the tetragonal phase while the bulk of the crystal remains in the cubic phase. The size of these fluctuations diverges at T_c. We suggest that this divergent length scale is associated with the phase inhomogeneities discussed by Imry and Wortis,[2] although more work is needed to extend the theory to treat dislocations as the defects and to discuss the transition in detail. A full account of these experimental results and a detailed analysis will be published elsewhere.[7]

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