

Random-Field Structural Transition in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$?

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Synchrotron x-ray diffraction measurements on a high purity single crystal reveal that the absence of long-range ortho-II order in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is most likely due to random-field effects. The ortho-II superstructure peaks show three qualitative features consistent with random-field behavior: First, instead of the development of a sharp Bragg peak at the transition $T_{\text{OII}} = 125(5)^\circ\text{C}$ (for $x = 0.5$), the initial diffuse anisotropic Lorentzian (critical scattering) above T_{OII} transforms to a Lorentzian-squared form below T_{OII} . Second, the equilibration time increases dramatically at the onset of ordering. And third, the domain growth is logarithmic in time below T_{OII} .

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The structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ has been a continuously popular subject ever since the discovery of high temperature superconductivity. From a practical point of view, detailed structural knowledge is important, since it is closely linked to the occurrence of antiferromagnetism and superconductivity. More fundamentally, the oxygen ordering and Cu-O chain formation in the basal plane is quite intricate, with the underlying mechanisms rooted in the strongly correlated nature of the electrons themselves [1], and is an interesting topic in its own right.

One particularly intriguing subject concerns the nature of the ortho-II phase [2]. It is characterized by alternating full and empty Cu-O chains in the basal plane running along the b axis (see Fig. 1), doubling the unit cell along the a axis, and thus giving rise to superstructure diffraction peaks at half-integer values of h . Its appearance has a significant influence on the electronic properties. Most notably, it is thought to be responsible for the "60 K plateau" in the x dependence of the superconducting critical temperature [3]. Despite playing such a prominent role, not much is actually known about the boundary between the ortho-II and other phases (tetragonal, ortho-I, ortho-III, and possibly $2\sqrt{2}a_0 \times 2\sqrt{2}a_0$). One has only recently been able to estimate the ortho-I to ortho-II transition temperature [4,5]. More importantly, however, there has been no observation of sharp, resolution limited Bragg peaks emerging at the superstructure positions which would indicate long-range order (LRO). This is in contradiction to what many oxygen ordering models would predict [6], and the reason for the absence of LRO has never been addressed in the literature, neither experimentally, nor theoretically.

Experimentally, it has proven difficult to obtain clear enough ortho-II signatures to allow a quantitative and systematic study of its dependence upon temperature (T)

and time (t). By using high purity single crystals and the novel technique of hard x-ray scattering, we provide the first detailed information about the nature of the ortho-II transition and shed some light on the issue of why no LRO develops. In the process, the oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ reveals itself as an interesting example of a structural random-field system.

Single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ were grown by a flux method in yttria stabilized zirconia crucibles and exhibit exceptionally good physical qualities and purity [7]. After growth, an 18 mg crystal was placed in a volumetric titration system [8] and slowly cooled from 650 to 150°C at constant oxygen stoichiometry [8], $x = 0.5$, over a period of five weeks, then cooled to room temperature overnight. The crystallographic parameters [$a = 3.831(5) \text{ \AA}$, $b = 3.887(5) \text{ \AA}$, and $c = 11.75(1) \text{ \AA}$] and the oxygen content

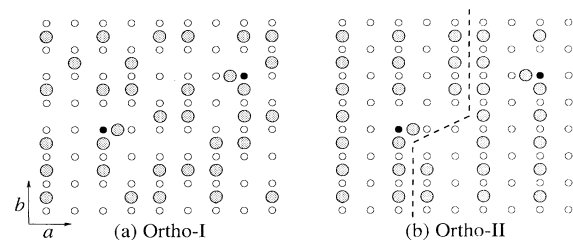


FIG. 1. Schematic of the Cu-O basal plane in the (a) ortho-I and (b) ortho-II phase at $x = 0.5$. The small open circles are Cu(1) site atoms. The larger grey circles are oxygens on the O(1) site. In the ortho-I phase at $x = 0.5$, oxygen atoms form short chains running along b . In the ortho-II phase, full and empty chains alternate, increasing the average chain length. Impurities on the Cu(1) site (small solid circles) within a twin domain, depicted here in a tetrahedral coordination, can act as pinning centers for chains, which create antiphase domain boundaries (dashed line) inhibiting the LRO development.

$x = 0.51(1)$ of the $Pmmm$ ortho-I subcell were determined from the integrated intensities of 700 integer Bragg reflections measured by neutron diffraction on the four-circle diffractometer at Risø National Laboratory. The midpoint of the superconducting critical temperature, from ac susceptibility, was 59 K with a 3 K transition width. From inductively coupled plasma chemical analysis, we estimate the level of Cu-site impurities at 0.1 at. % (Zn, Mg, Fe, Al, Ti). The impurity concentration on the Y and Ba sites is also about 0.1 at. % (K, Na, Ca). Such low impurity levels have a very minor effect upon the transport and superconducting properties, but might actually be responsible for the inhibition of long-range ortho-II order, as we will see later.

The ortho-II superstructure reflections were measured using 95 keV x-ray diffraction on the newly developed, dedicated hard x-ray beam line BW5 at HASYLAB, described in detail in Ref. [9]. The penetration depth of the x rays at this energy is of the order of millimeters, enabling one to study the bulk properties of large single crystals. The setup consisted of a triple crystal diffractometer in (horizontal) dispersive Laue scattering geometry with the sample mounted in a standard Huber four-circle diffractometer. We used the (200) reflection of SrTiO₃ single crystals with 12 mdeg mosaicities as the monochromator and analyzer. The longitudinal resolution was about 0.018 Å⁻¹. The transverse, or Ω resolution was significantly better, about 6 mdeg [$\approx 4 \times 10^{-4}$ Å⁻¹ at the (5/2,0,0)]. The sample mosaicity, however, effectively reduced this to about 0.1–0.16°, depending upon the crystal orientation. The signal was measured using an energy sensitive solid state Ge detector where a very small contamination from higher order reflections was removed electronically through the use of a discriminator.

Figure 2 plots the superstructure peak shape along h , k , and l at room temperature. It is not possible to reasonably fit simple Lorentzians by these curves, which has been typically used in the past [2]. More generally, one can propose an anisotropic Lorentzian raised to some power, $S(\vec{q}) = A(1 + \vec{q}^2)^{-y/2}$, convoluted with the three-dimensional resolution function. Here, \vec{q} is the deviation from the ortho-II reciprocal lattice position, rescaled by the anisotropic correlations, i.e., $\vec{q} = 2\pi(\xi_a h, \xi_b k, \xi_c l)$, where ξ_a , ξ_b , and ξ_c are the correlation lengths (in number of unit cells), respectively, along the a , b , and c axes. We find that the power law exponent $y = 3.5(2)$ at room temperature, where the error bar is estimated from fits using different simplifying assumptions for the detailed form of the mosaicity and resolution function.

One possible interpretation of such a value would be to propose a weighted sum of two contributions to the scattering [10,11]: a Lorentzian ($y = 2$) coming from remnant critical scattering and a Lorentzian squared ($y = 4$) due to scattering from domain walls. More generally, power law tails can arise from the presence of topological order parameter defects [12], with an exponent depending on the dimensionality of the predominant defect type. In

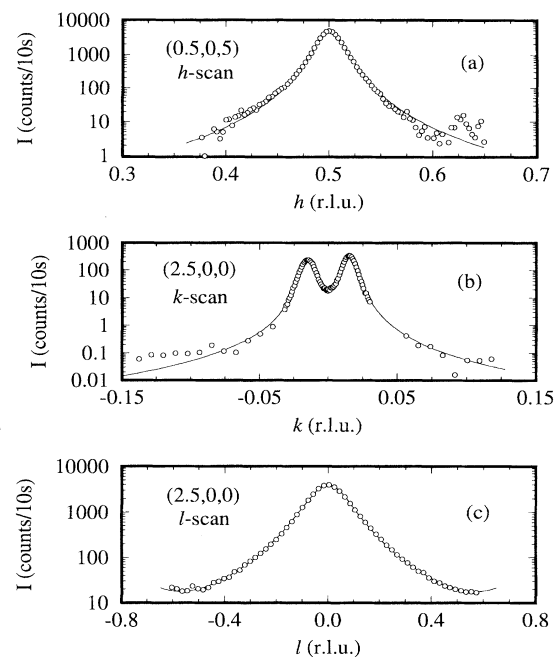


FIG. 2. Ortho-II superstructure reflections measured along h , k , and l at room temperature. The solid lines are fits using a Lorentzian to variable power, as described in the text, plus a linear background which has been subtracted. The data are plotted as open circles and is the result of about one dozen repeated scans measuring 10 s/point. The split peaks along k are due to the twinning in the a - b plane.

a 3D system, a Lorentzian squared is consistent with the presence of 2D domain boundaries, i.e., domain walls. The deviation from $y = 4$ might, therefore, be due to the layered nature of YBa₂Cu₃O_{6+x}, making the system somewhat two dimensional. The quasi-2D nature of the ordering and the strong tendency for chain formation is reflected in the anisotropic correlation lengths; from the room temperature fits we obtain the correlation lengths in a number of unit cells: $\xi_a = 10.2(1)$ (39.1 Å), $\xi_b = 45(1)$ (175 Å), and $\xi_c = 1.66(2)$ (19.5 Å). These correspond to half-width-at-half-maximum (HWHM) peak widths, respectively, along h , k , and l of $\Delta h = 0.0107$, $\Delta k = 0.00274$, and $\Delta l = 0.0674$ [in r.l.u. (reciprocal lattice units)], and are the narrowest peak widths published so far [2]. In any case, the point is that a dominant Lorentzian squared, i.e., $y = 4$, component has developed at room temperature. The implication is that the entire system has local ortho-II order, but that it is broken up into domains separated by sharp antiphase domain walls.

The temperature dependence of the ortho-II superstructure is shown in Fig. 3 [13]. The peak widths remain virtually constant until 120°C [Fig. 3(b)], whereupon the width along k , i.e., along the chains, begins to broaden relatively more than along h or l . This is not surprising, since the process of going from ortho II to ortho I must break up the chains (Fig. 1). Concurrent with the broadening of the peak, the power law exponent has

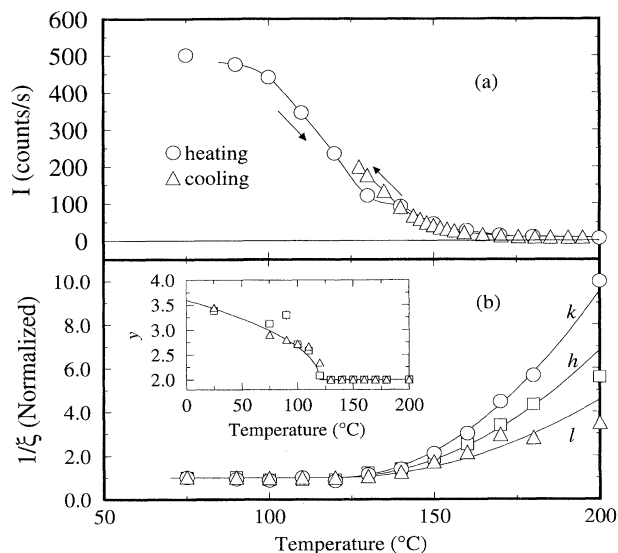


FIG. 3. The fitted (5/2,0,0) peak intensity vs T upon heating (\circ) and subsequent cooling (\triangle) (top figure). The bottom figure plots the fitted inverse correlation lengths, $1/\xi_a$ (\square), $1/\xi_b$ (\circ), and $1/\xi_c$ (\triangle), vs T , normalized to their room temperature values. The inset shows the fitted Lorentzian power law exponent γ vs T for the h (\square) and l scans (\triangle). The k -scan values have been omitted: they have a large uncertainty due to the overlapping twin peaks and significant mosaicity corrections. All lines shown are guides for the eye.

converged to a simple Lorentzian [$\gamma = 2$, see inset of Fig. 3(b)]. We define this point as the transition temperature $T_{\text{OII}} = 125(5)^\circ\text{C}$, since a crossover to a Lorentzian form is typically indicative of critical scattering above a phase transition [14]. Below T_{OII} , the *integrated* intensity is not constant in T , presumably caused by the atomic displacements of primarily the Ba, apical oxygen, and Cu(2) sites associated with the appearance of ortho-II correlations [2], resulting in a transfer of intensity between reflections [15].

The crossover from a Lorentzian to a Lorentzian squared is very reminiscent of the random-field Ising system [10,11], where the disordering field does not destroy LRO in an *equilibrium* system (i.e., the lower critical dimension is thought to be $d_l = 2$ [16–18]), but instead gives rise to *metastability* at the onset of ordering [17,19,20] due to growing energy barriers against domain wall movement. The system rapidly falls out of equilibrium and the characteristic separation between domain boundaries is expected to increase logarithmically in time, i.e., the measured correlation lengths should scale as $\xi(t) = \ln t$ [12,17,21–23].

To investigate this possibility further, we conducted quench experiments from above the onset of ordering to temperatures near the transition. The quenching process from 200°C took about 1 min, and the qualitative behavior is as follows: When quenched to 150°C , the intensity followed the instantaneous sample temperature with no measurable delay. For progressively lower T , the inten-

sity development slowed exponentially, as shown in the inset of Fig. 4. Experimental time constraints did not allow us to directly measure $\xi(t)$ vs time with sufficient accuracy. Nevertheless, it is possible to estimate $\xi(t)$ from a measurement of the peak intensity. To see this, one notes that the integrated intensity goes as $A(\xi_a\xi_b\xi_c)^{-1}$. The peak intensity measured with the a and c axes in the scattering plane, owing to the poor vertical and excellent in-plane resolution, measures $A\xi_b^{-1}$. If we *assume* that the scaling hypothesis holds [24], implying that the integrated intensity is invariant in time, then $\xi_a\xi_c \approx CI(t)$. From Fig. 3 we obtain the necessary T -dependent scale factor C . Figure 4 plots the estimated $\xi_{\text{eff}} = \sqrt{\xi_a\xi_c}$ vs t for three quenches below T_{OII} . At 120 and 110°C the growth is clearly logarithmic in time, as expected for a random-field system. Quenching to lower T , we see an initial period where the data are consistent with the Allen-Cahn growth law for pure systems, $\xi(t) \sim \sqrt{t}$, which should also hold in the early stages of growth of a random-field system [23,25].

The random fields might come from Cu(1) (chain) site substitutional impurities which can pin the Cu-O chains (Fig. 1), or strain fields interfering with the coupling between the oxygen order and atomic displacements. The strain could arise, for example, from twin domain boundaries, dislocations, or cation substitutional impurities. Since the transition from ortho I to ortho II involves oxygen rearrangements into long Cu-O chains, the transition should be quite sensitive to such random fields. The quasi-2D character of the ordering should further increase the sensitivity to random-field induced disorder (the 2D random-field Ising system has no LRO [16–18]). If indeed it is the small amount of impurities which are responsible, one would expect a crossover from Allen-Cahn to logarithmic growth when the characteristic separation

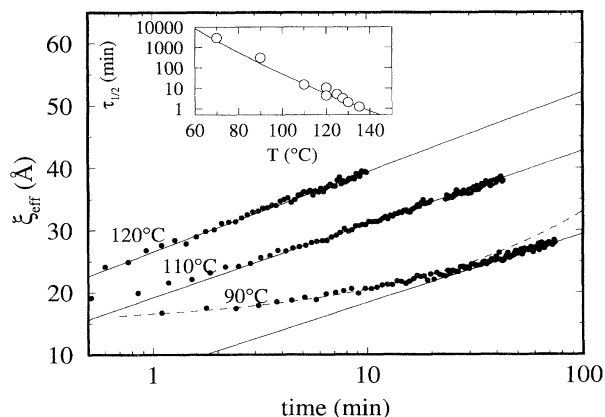


FIG. 4. Plot of $\xi_{\text{eff}} (= \sqrt{\xi_a\xi_c})$ vs the time elapsed after commencing a quench to 90 , 110 , and 120°C . The straight lines correspond to $\xi_{\text{eff}} = AT \ln(t/t_0)$, with $A \approx 0.024 \text{ \AA/K}$, and t_0 is T dependent. The dashed curve corresponds to Allen-Cahn growth, $\xi \sim \sqrt{t}$. The inset shows the estimated time $\tau_{1/2}$ required for a quench to reach one-half the intensity obtained upon slow cooling vs T . The line is an Arrhenius fit with an activation energy of 1.4 eV .

between domain boundaries surpasses the typical distance between defects. In this case, the effective correlation length at the crossover point ξ_{eff}^c is a measure of the defect concentration. From Fig. 4 we see that $\xi_{\text{eff}}^c \approx 25 \text{ \AA}$, which corresponds to an impurity level of the order of 0.2 at. %. This is consistent with the estimated amount of impurities for our crystals.

Another possible scenario is that the oxygen atoms themselves give rise to anisotropic (long-range) strain fields which could generate frustrated effective oxygen interactions. The transition to ortho-II order would then be preempted by a glass transition driven *intrinsically* by the interaction between oxygens.

The following physical picture of the transition thus emerges: At an oxygen content of $x = 0.5$, the lattice is optimally filled for the ortho-II phase and should exhibit extremely long Cu-O chains. Upon passing the transition to ortho II, a prominent feature of the ordering process is the lengthening of these chains. The doubling of the unit cell along the a axis in the ortho-II phase allows for antiphase domains, which initially coarsen consistent with Allen-Cahn growth. However, the nature of the transition is fundamentally changed, perhaps due to the presence of Cu(1) site impurities, to that of a random-field system, and remains in a metastable state with only diffuse Lorentzian-squared peak shapes and a logarithmic growth of domains. The observation of critical scattering suggests that the underlying transition near $T_{\text{OII}} = 125^\circ\text{C}$ is either second order or weakly first order.

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