A 4-unit-cell superstructure in optimally doped YBa$_2$Cu$_3$O$_{6.92}$ superconductor

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Using high-energy x-ray diffraction we show that a 4-unit-cell superstructure, $q_0=(\frac{1}{4}, 0, 0)$, along the shorter Cu-Cu bonds coexists with superconductivity in optimally doped YBCO. A complex set of anisotropic atomic displacements on neighboring CuO chain planes, BaO planes, and CuO$_2$ planes, respectively, correlated over $\sim$3-6 unit cells gives rise to diffuse superlattice peaks. Our observations are consistent with the presence of Ortho-IV nanodomains containing these displacements.

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There have been several experimental indications recently of inhomogeneous phases of various kinds developing in the high-$T_c$ cuprates. These were predicted on purely electronic considerations [1], and were given credibility by the discovery, by neutron scattering, of the so-called “striped phase” in the low-temperature tetragonal La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ [2]. In this phase the magnetic periodicity is equal to twice that of the charge. Later neutron measurements [3] have revealed incommensurate spin density waves with a period close to 8 unit cells along the a axis at optimal doping in the superconducting phases of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) associated with the Cu spins in the CuO$_2$ planes, which are enhanced inside the vortices induced by an applied magnetic field [3]. Recent STM measurements [4] in Bi-2212 reveal a spatial modulation of the local electronic density of states possibly arising from quasiparticle interference between states that are nested across the Fermi surface. Very recent Josephson tunneling work suggests a non-uniform superconducting condensate in LSCO [5]. Inelastic neutron scattering has also revealed the existence of phonon anomalies at a wavevector $q_0=(\frac{1}{4}, 0, 0)$, in reciprocal lattice units, in both YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) and LSCO compounds [6,7]. The role of lattice strains in creating texture has also been discussed recently [8]. In addition, in the YBCO family of compounds, there are O vacancies in the CuO chains (except at stoichiometry, i.e. $x=1.0$, slightly beyond the optimum doping), which order to some degree in well-prepared samples [9]. The phase diagram of the vacancy ordering on the CuO chains has been theoretically discussed by De Fontaine and coworkers [10]. While the exact origin of inhomogeneities is being debated, diffraction studies to understand the nature of such phases are absolutely necessary.

We have used high-energy synchrotron x-ray scattering to look for the occurrence of inhomogeneous phases and lattice modulations in the YBCO family of compounds. In an underdoped YBCO ($x\approx0.63$) compound we previously found modulations with $q_0=(\sim\frac{1}{4}, 0, 0)$ possessing short-range order [11] which coincided with a harmonic of the so-called Ortho-V phase of O-vacancy ordering on the Cu-O chains [10] with a 5-unit-cell repeat along the a axis. However, the intensities of the diffuse satellites clearly showed that displacements of atoms in the CuO chain planes, the CuO$_2$ planes and the BaO planes were involved [11]. This paper describes similar measurements carried out on an optimally doped YBCO crystal, possessing on the average 8% of O vacancies on the chains. We find that a 4-unit cell (Ortho-IV) superstructure, $q_0=(\frac{1}{4}, 0, 0)$, involving correlated displacements of atoms (Fig. 1), indeed coexists with superconductivity.

Note that primary displacements ($\delta u$'s, $\delta v$'s, $\delta w$'s) are along the a axis, i.e. along the shorter Cu-Cu bond direction. $\delta u$'s, $\delta v$'s, and $\delta w$'s, of respective atoms are given in parentheses. $\delta u$'s of all other atoms are related by mirror symmetry.

For this study, a high-quality detwinned crystal ($\sim$1 mm x 1 mm x 130 $\mu$m) of optimally doped YBCO ($T_c = 91.5$ K, $\Delta T_c \approx 1$ K) was chosen. The use of a detwinned crystal allowed us to determine unambiguously the anisotropy of scattering, the direction of modulation, and the polarization of atomic displacements, respec-
tively. The crystal was annealed at 420°C in flowing pure O₂ for about a week and was stress detwinned in flowing O₂ at the same temperature. Polarization-sensitive optical microscopy showed the presence of a single twin domain. The crystal mosaic was ∼ 0.03°. The c axis was perpendicular to the large crystal facet. High-energy (36 keV) x-ray diffraction studies were performed on the 4ID-D beamline at the Advanced Photon Source. Experimental details can be found elsewhere [11].

FIG. 2. (a-d) Raw data showing [H, 0, 0] scans for several integer values of K and L=0. Satellite peaks correspond to \( \mathbf{q}_0 = (\frac{1}{2}, 0, 0) \). Vertical lines (displaced along H for clarity) compare the observed (black) and calculated (red) intensities corrected for geometric factors; (e) [H, 0, 0] scans with high values (odd/even) of K relative to H showing the absence of \( \mathbf{q}_0 \) satellites above background; (f) Contour plot of diffuse intensity at 7 K around (4, 0, 0) Bragg peak; diagonal dashed lines indicate \( [\pm 1, \pm 1, 0] \) directions; (g) Line scans at different \( T \) showing how TDS overwhelms HDS above \( \sim 200 \) K; (h) Contour of diffuse intensity at 300 K. Red line in (f) and (h) indicates where the linescans displayed in (g) were taken.

Figs. 2(a)-(d) show several a-axis [H, 0, 0] scans normal to the Cu-O-Cu chain direction for different integer values of \( K \) taken at \( \sim 7 \) K. Broad satellite peaks corresponding to \( \mathbf{q}_0 = (\frac{1}{2}, 0, 0) \) are clearly visible near Bragg peaks, \( (h, k, 0) \), when \( h \) and \( k \) have mixed parity. When \( h \) and \( k \) have the same parity strong thermal diffuse scattering (TDS), however, overwhelms the superlattice peaks. The intensity of the peak at \( Q = G + q_0 \) (\( G \) is a reciprocal lattice vector) is \( \sim 450 \) photons/second which is some \( \sim 10^9 \) orders-of-magnitude weaker than that of a Bragg peak. The width in the a* direction of \( q_0 \) satellites is much larger than the resolution, indicating a very short correlation range (\( \xi_a \sim 3a \), using Scherrer formula [12]) along the a axis. The use of a detwinned crystal made it unambiguous that the modulation vector is \( q_0 = (\frac{1}{2}, 0, 0) \) and not \( (0, \frac{1}{2}, 0) \). The width in the b-axis direction (Fig 3(b)) corresponds to larger correlation length (\( \xi_b \sim 6b \)), while modulations of the intensity which extend along the c* axis through the satellite peak as shown in Fig. 3(c) indicate correlations only between neighboring Cu-O chain planes, BaO planes, and CuO₂ planes (Fig. 1), respectively, as obtained from Fourier transform (Patterson function) of these intensity patterns (this is very similar to the results found in the underdoped system [11]).

In addition, significant lattice-strain effects are present in this material. A 2-dimensional scan around \( (4, 0, 0) \), as shown in Fig. 2(f), reveals a strongly anisotropic “bowtie”-shape Huang diffuse scattering (HDS) pattern with lobes extending along the four \( [\pm 1, \pm 1, 0] \) directions. The two superlattice peaks at \( (4\pm 1, 0, 0) \) can be discerned, although they are not completely resolved. A set of linescans through the diffuse lobes at several temperatures is shown in Fig. 2(g). Whereas at low temperature two broad peaks corresponding to two lobes are clearly visible, on increasing \( T \) the peaks become indiscernible from the rapidly growing TDS above \( \sim 200 \) K. Room-temperature pattern of diffuse scattering (Fig. 2(h)) is nearly identical to TDS around \( (4, 0, 0) \) calculated using elastic constants of YBCO (not shown). Earlier x-ray studies [13] of tetragonal system \( \text{YBa}_2\text{Cu}_3\text{O}_{6.955}\text{Al}_{0.045}\text{O}_7 \) showed that HDS arises from shear distortions due to long-wave fluctuations of O concentrations in the chains along a and b axes. It is possible that the O stoichiometry in the CuO chains is non-uniform on submicron scales due to the formation of defective short-range O-ordered domains discussed below.

A 4-unit-cell periodic (Ortho-IV) phase is expected near O stoichiometry of 6.75 [10] (i.e. one out of every four CuO chains has no O atoms denoted by \( \langle 1101 \rangle \)) whereas in optimally doped material the stoichiometry is 6.92 (i.e. approximately one out of every ten CuO chains has vacancies). There are two ways to explain the formation of \( \langle 1101 \rangle \) structure near optimum doping. If O concentration is nonuniform within the CuO-chain planes then vacancies tend to phase separate within the formation range of the Ortho-IV phase [10]. Secondly, if the long-range Coulomb interactions among distant-neighbor vacancies are not negligible then the \( \langle 1101 \rangle \) phase can be stable even near the optimal doping with dilute concentration of vacancies. In both cases, however, the ordering will be short ranged and imperfect, leading to significant lattice strains responsible for HDS.

Next, we note some general features of our data which were used to narrow down possible models of atomic displacements (\( \delta \mathbf{u} \)’s). First, a strong intensity asymmetry between the \( +\mathbf{q}_0 \) and \( -\mathbf{q}_0 \) satellites is observed around all Bragg points. A strong asymmetry can occur if \( \delta \mathbf{u} \)’s are large [14], or as a result of destructive interference between diffuse scattering due to disorder and displacive modulation [15] as found in quasi-1D charge density wave systems [16,17]. Secondly, for a given satel-
literate at \((h,k,0)+\mathbf{q}_0\) the intensity is either very strong or weak when \(h\) and \(k\) have the same or mixed parity, respectively. This implies out-of-phase displacements of the dominant scatterers. Thirdly, no second harmonic (2\(\mathbf{q}_0\)) satellites were observed indicating essentially a sinusoidal modulation. Finally, scans (Fig. 2(e)) such as [\(H, -5, 0\]) (\(H \in [0.1 - 0.9]\)) found no superlattice peaks suggesting the absence of any \(\delta\mathbf{u} || \mathbf{b}\) associated with the \(\mathbf{q}_0\) modulation. We performed calculations without assuming any displacements to be small in the presence of an Ortho-IV phase in the CuO-chain plane.

The intensity calculations were performed using

\[
I_{\text{diff}}(\mathbf{Q}) \propto \left| \sum_n f_n(Q)e^{-W_n(Q)}e^{-i\mathbf{Q} \cdot (\mathbf{R}_n + \delta\mathbf{u}_n)} \right|^2
\]

where the displacement relative to an average lattice site \((\mathbf{R}_n)\) of the \(n\)-th atom is \(\delta\mathbf{u}_n\), \(f_n(Q)\) and \(e^{-W_n(Q)}\) are the form factors and Debye-Waller factors (DWFs), respectively. The summation was carried out only over Cu, O, and Ba atoms in the \(4 \times 1 \times 1\) supercell (Fig. 1). The expression above is for integrated intensity of the satellites regardless of peak widths. The extraction of integrated intensity from the experimental data at \(\sim 7\) K, however, was difficult due to the presence of TDS and HDS. Nevertheless, since the satellite peaks are sharper than TDS and HDS, and located away from Bragg peaks, it is possible to model the satellites at the lowest \(T\) using a Gaussian above some monotonic background. We found that extracted intensities for the strong peaks varied \(\sim 15-20\%\) \((\sim 35\%\) for the weak peaks) depending on how the background scattering was modeled. A least-squares procedure was performed taking these errors and the general considerations discussed above into account to fit the intensities of 45 peaks within the \([H, K, 0]\) zone and the intensity modulation of the \((5.25, 0, 0)\) peak along \(\mathbf{c}^*\). We kept the displacements symmetric about the Cu(1)-O(4)-Cu(2) and CuO mirror planes centered on the O-vacancy inside a supercell. Vertical bars in Figs. 2(a)-(d) indicate that there is good agreement between the calculated (red) and observed (black) intensities within experimental uncertainties. The model obtained from fitting is shown in Fig. 1. While the dominant contributions come from displacements of Ba and Cu atoms, both chain (O(1)) and plane oxygen atoms (O(2) and O(3)) are displaced significantly. Note that the displacements are primarily along the \(a\) axis. Although there may be small displacements along the \(c\) axis as well, we are more certain of them in the case of Ba. Our error estimates are \(\sim 10 - 15\%\) for Ba and Cu \(\delta\mathbf{u}\)’s, and \(\sim 15 - 25\%\) for O atoms, respectively. While the model obtained may not be perfect given the difficulty of extracting accurate intensities, it does account for all the systematics of the data. Furthermore, it portrays a pattern of displacements similar to that of Ortho-V phase in an underdoped YBCO obtained from first-principles electronic calculations [18]. In our case, however, the periodicity is \(4a\) (Fig. 1) along the \(a\) axis.

![Fig. 3](image-url)

**FIG. 3.** (a) \([H, 0, 0]\) scans at several temperatures. Lines are fits using a combination of a Lorentzian (TDS), a Gaussian (satellite), and a constant term. (b) \(K\) scans through the \((5.25, 0, 0)\) peak. (c) Intensity modulations along \(\mathbf{c}\) of the same peak. Note that the oscillation amplitude grows on decreasing \(T\). Different \(T\)'s are shown with unique colors (b).

Fig. 3(a) shows \([H, 0, 0]\) scans through a superlattice peak at several temperatures. It is clear from these scans that as \(T\) is increased the intensity of the \(\mathbf{q}_0\) peak decreases relative to the TDS emanating from \((5,0,0)\). In fact, an inspection of the data reveals that the intensity (area under the dome) at \(7\) K is at least twofold larger than that at \(300\) K. Intensity modulation of \((5.25, 0, 0)\) peak presented in Fig. 3(c) shows that while the mean intensity of the oscillations falls with decreasing \(T\) due to the reduction of TDS, the oscillation amplitude about the mean grows. In order to get more quantitative information as a function of temperature we fitted [11] a combination of a Lorentzian (TDS), a Gaussian, and a constant term to the \(H\)-scans (Fig. 3(a)). \(K\)-scans shown in Fig. 3(b) are well represented by a combination of three Gaussian line profiles, one for the central satellite peak and two for the broad lobes, respectively, and a constant term to account for the background which is predominantly made up of TDS. Note that both HDS and TDS contribute to the broad lobes. Since the peak widths and positions do not change with \(T\) only the peak heights and the constant term (i.e. four parameters all together) were needed to fit the entire data. Fig. 4(a) shows the \(T\)-dependence of the fitted intensity for \((5.25, 0, 0)\) peak. Although keeping positions and widths constant may introduce some systematic errors for the central satellite, its integrated intensity (width\(\times\)peak intensity) agrees well with that obtained in fitting the \(H\)-scan as shown in Fig. 4(a). The intensity was also estimated...
via the maximum amplitude of the modulation defined as $I_{(5.25,0,0)} - I_{(5.25,0,1.8)}$. All three cases consistently show that the superlattice peak decreases nearly linearly with increasing $T$ (Fig. 4(a)). If this linear trend continues then the intensity will extrapolate to zero around $\sim 500$ K. Furthermore, Fig. 4(b) shows Fourier amplitudes obtained from intensity modulations (see Fig. 3(c)), which are a measure of displacement-displacement correlations as a function of $T$. It is clear that both amplitudes also grow stronger at lower temperatures.

Although the origin of $q_0$ can be attributed to Ortho-IV phase it is puzzling to observe a large increase of the diffuse peak with decreasing $T$. Using the displacement model presented above and DWFs for the average lattice measured on ceramic samples [19] we estimated a $\delta u$ of $\sim 1.2$ for the intensity of $(5.25,0,0)$ satellite, which is at odds with the observed ratio of at least $\sim 2.2$. Since diffusive motion of chain oxygens (O(1)) practically freezes below $\sim 250$ K, the growth of Ortho-IV patches in size or number seems unlikely. Given that atomic displacements (Fig. 1) are clearly anharmonic in these nanoscale patches it appears that enhanced elastic softening of the lattice takes place within these regions on lowering $T$ which may account for the low-$T$ increase of the intensity.

In conclusion, we have shown that lattice modulations with a 4-unit-cell periodicity exist from above room temperature down to the lowest temperatures in optimally doped YBCO. These correspond to local regions in extent $\sim 3-6$ unit cells in the $ab$ plane and less than one unit cell along the $c$ axis. From the $\delta u$'s (Fig. 1) one may calculate DWFs for the whole crystal and by comparison with the experimental DWFs [19] we estimate roughly $\sim 10$-$20\%$ of the crystal contain these patches at the lowest $T$. At low temperatures clear evidence of anisotropic strain in the lattice is provided by anisotropic patterns of HDS around the Bragg points. This HDS originates with the strain induced by the disorder between $O$ atoms and vacancies along both $a$ and $b$ axes; strains induced by the patches is not assumed. However, the coincidence of the observed periodicity ($q_0=(\frac{1}{2},0,0)$) with values expected for charge instabilities in the CuO$_2$ planes from measurements on other superconducting cuprates is striking. It seems clear that in YBCO the electronic structure and the oxygen vacancies together possess instabilities which can lead to inhomogeneous phases and local softening of the lattice.

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