

X-ray-scattering study of finite-range order in $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$

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We have observed evidence of finite-range order in quenched crystals of nominal composition $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$. X-ray scattering shows diffuse peaks with a reduced wave vector of $(\frac{1}{2}, 0, 0)$ in the oxygen-deficient compound but not in fully oxidized $\text{Ba}_2\text{YCu}_3\text{O}_7$. Although the crystals are twinned, we find that the diffuse satellites occur symmetrically around $(h, 0, 0)$ peaks rather than $(0, k, 0)$ peaks indicating a doubling of the unit cell along the a axis (transverse to the Cu—O chains). The width of the diffuse peaks yields coherence length of 21, 16, and 9 Å for the a_0 , b_0 , and c_0 directions, respectively.

The physical properties of $\text{Ba}_2\text{YCu}_3\text{O}_x$ are intimately connected with oxygen stoichiometry and vacancy ordering. The compound can be synthesized in the range $6 < x < 7$ with superconductivity observed of $x > 6.5$.¹⁻⁵ The $\text{Ba}_2\text{YCu}_3\text{O}_x$ structure is a defect-perovskite structure that is tripled along the c axis due to ordering of yttrium and barium.⁶⁻¹³ For $x = 7$, the oxygen vacancies are ordered such that one has Cu—O chains along the b axis and oxygen vacancies along the a axis, i.e., full occupancy of the O(4) sites¹⁴ and zero occupancy of the O(5) sites. These chains are located between the two Ba—O planes and they are thought to play a pivotal role in the high-temperature superconductivity. As the oxygen stoichiometry is changed from $x = 7$ to $x = 6$, oxygen vacancies are introduced on the Cu—O chains^{5,7-9} resulting in a complete depletion of oxygen from the chains at $x = 6$. The composition $x = 6.7$ corresponds to about a $\frac{1}{3}$ depletion of the oxygen from the Cu—O chains. The effects of vacancy ordering on Cu—O chains has been the subject of structural-stability analyses¹⁵⁻¹⁷ and a study of the relationship between oxygen-vacancy ordering, the electronic properties, and T_c .¹⁸

Recently, the range $6.6 < x < 6.7$ has been identified as a bulk superconducting phase with a transition temperature of 60 K.¹⁹ Electron-diffraction experiments on ceramic samples prepared under varying conditions (but all probably oxygen deficient) show diffuse streaks parallel to the c axis with reduced wave vectors of $(\frac{1}{2}, 0, 0)$ or $(0, \frac{1}{2}, 0)$.²⁰⁻²³ The diffuse streaking has been identified as occurring in samples with the same oxygen stoichiometry associated with the 60-K superconducting phase.¹⁹

The present study is an investigation of finite-range order in $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$ by x-ray scattering. We show that quenched crystals of $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$, prepared by annealing in O_2 at 667°C , have superconducting transitions at 57 K and show diffuse diffraction peaks at room temperature indicating a cell doubling along the a axis. The diffuse scattering yields coherence lengths that are of the order of four to five unit cells in the basal plane and approximately one unit cell along the c axis. This indicates that the Cu—O chains are correlated within the basal plane, but are nearly uncorrelated along the c axis.

Crystals of $\text{Ba}_2\text{YCu}_3\text{O}_x$ were grown as described previously.²⁴ As-grown samples had inhomogeneous oxygen

concentrations with $x < 6.5$ and were subjected to a variety of post-annealing treatments to increase the oxygen content. To obtain the maximum oxygen content, the as-grown crystals were sealed with about 200 mg of $\text{Ba}_2\text{YCu}_3\text{O}_7$ ceramic in a quartz tube (volume equal to 3 cm^3) and approximately 1 atm of oxygen. The ceramic was added to the tube to serve as a buffer for the oxygen and to act as a getter for impurities and water that out-gassed from the quartz. Heating the sealed tubes to 470°C for about two weeks subjected the crystals to an elevated oxygen pressure (about 2 atm). Samples treated in this manner had narrow superconducting transitions with transition temperatures close to 86 K and a flux exclusion as measured in a dc field of better than 75%. We attribute the low transition temperature of the crystals, which is about 6 K lower than the best ceramic samples, to either a slight oxygen deficiency or trace metal-atom impurities. If one assumes that the depression of T_c is due to an oxygen deficiency, comparison with previous measurements¹⁹ indicates that $x > 6.8$ in the "fully oxidized" crystals. Samples were also made with nominal oxygen concentrations of $x = 6.7$ by quenching from 667°C in O_2 . The temperature and oxygen partial pressure was determined from an isocompositional ($x = 6.7$) plot of temperature versus oxygen partial pressure measured with ceramic samples.²⁵ During the annealing, the weight of 10 mg of crystals was monitored in a thermogravimetric (TGA) system. The samples were maintained at the annealing temperature until equilibration of the weight of the crystals occurred, a time period of five days for samples that were 0.5–1 mm in cross section. Measurements of the magnetization of a dc field of 27 Oe on $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$ crystals showed a superconducting transition of 57 K with a dc flux exclusion of about 25%. The temperature dependence of the magnetization of the $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$ crystal used in this study is shown in the inset to Fig. 1.

This experiment was motivated by earlier studies of the superconducting transition temperature and vacancy ordering in oxygen-deficient ceramic samples.^{19,20} In the case of ceramic samples, the oxygen was zirconium gettered at 470°C from $\text{Ba}_2\text{YCu}_3\text{O}_7$ and a plateau near $x = 6.7$ was observed in plots of the superconducting transition temperature versus the oxygen concentration. The

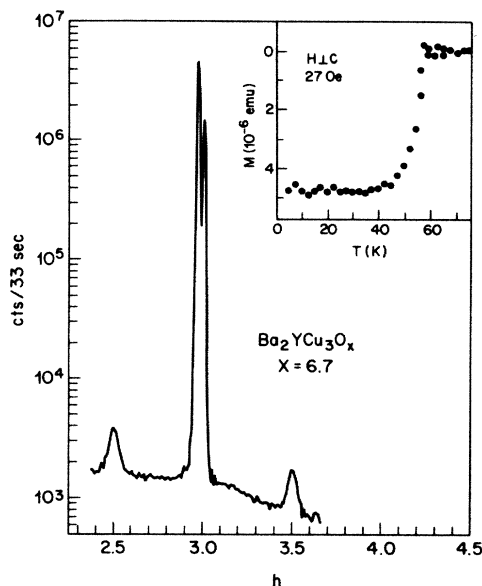


FIG. 1. Scan along $[h00]$ in $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$. The splitting of the Bragg peak at $h=3$ into a $(3,0,0)$ and a $(3,0,0)$ peak indicates that the crystal is twinned. The diffuse satellites are symmetric about $(3,0,0)$ rather than $(0,3,0)$, indicating that the superlattice wave vector is $[\frac{1}{2}, 0, 0]$. The inset shows the magnetization of the crystal cooled in a field of 27 Oe.

low-temperature synthesis was thought to be important to promote sample homogeneity and to reduce thermal disorder by activated occupation of the O(5) sites between the Cu—O chains. Electron diffraction from crystalline grains of the $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$ ceramic showed diffuse streaking with a wave vector of $(\frac{1}{2}, 0, 0)$ or $(0, \frac{1}{2}, 0)$ as well as $(0, \frac{2}{5}, 0)$ in other grains, suggesting finite-range order with multiple wave vectors in the oxygen-deficient material. The diffuse streaking was not present in samples of fully oxidized $\text{Ba}_2\text{YCu}_3\text{O}_7$. The zirconium getter technique is not appropriate for preparing oxygen-deficient crystals because of the slow kinetics of oxygen diffusion in the crystals due to the larger size.

X-ray scattering from $\text{Ba}_2\text{YCu}_3\text{O}_x$ crystals was performed using Cu $K\alpha$ radiation from a rotating anode source, a singly bent pyrolytic graphite monochromator that focused radiation in the vertical plane, and a flat pyrolytic graphite analyzer. In this configuration the instrumental resolution is about 0.024 \AA^{-1} with an angular divergence of the x-ray beam of about 0.5° . Periodic features with coherence lengths less than about 80 \AA will produce diffraction peaks broader than instrumental resolution.

Samples of $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$ and $\text{Ba}_2\text{YCu}_3\text{O}_7$ were mounted in a $(h0l)$ diffraction zone of a four-circle diffractometer with the ϕ axis of the goniometer approximately parallel to $(0k0)$. The sample $\text{O}_{6.7}$ was about $700 \times 1500 \times 12 \mu\text{m}^3$. All samples were twinned so that scans along either $[h00]$ or $[0k0]$ showed both $(h00)$ and $(0k0)$ peaks. A scan along $[h00]$ is shown in Fig. 1 for a sample of $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$. The inset shows a measurement

of the magnetization of the same sample (weight equal to $79 \mu\text{g}$) when cooled in a field of 27 Oe. The magnetic field is oriented transverse to $[00l]$ and the susceptibility corresponds to about 25% of the ideal diamagnetic value. The horizontal axis of Fig. 1 is indexed in h units so that the (300) peak occurs at an integer value. Diffuse satellite peaks can be observed at half-integer values of h . Although the crystals are twinned, the resolution of the scans is sufficient to establish that the diffuse peaks occur symmetrically about the $(h, 0, 0)$ rather than the $(0, k, 0)$ peaks. Note that the intensity of the $(0, 3, 0)$ exceeds that of the $(3, 0, 0)$ by about a factor of 3, indicating that the twinning is not 1:1 in this crystal. If diffuse peaks along $[0k0]$ were present, one would expect that the bulk of the diffuse intensity would be symmetrical about $(0, 3, 0)$, since the b axis twin is dominant along the direction of the scan in Fig. 1. The diffuse peaks were not present in crystals that were fully oxidized.

The coherence length associated with the diffuse peaks can be determined from the peak widths. A scan along $[h00]$ is shown in Fig. 2, showing that the diffuse peak is about four times broader than resolution in that direction. The modulation of the diffuse scattering intensity along the c axis is shown in Fig. 3, where we present a scan along $(2\frac{1}{2}, 1, l)$. Correlations along the c axis produce a modulation of the rodlike scattering that would be present if the ordering was strictly two dimensional. The widths of the peaks along each of the unit-cell directions is presented in Table I together with the instrumental widths obtained from scans through the $(3, 0, 0)$ peak. The diffuse width is much larger than the instrumental resolution in all but the k direction, the direction of poor instrumental resolution (χ scan). We estimated the excess width of the diffuse satellites by subtracting the widths of the satellite from that of the Bragg peak in quadrature. The direct

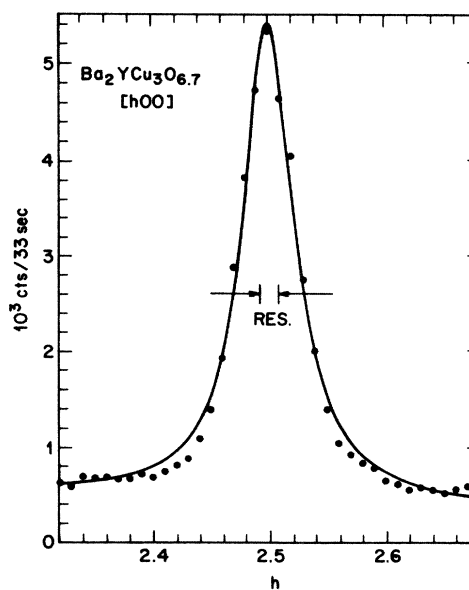


FIG. 2. Scans along $[h00]$ in a crystal of $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$. The solid line is a Lorentzian fit to the data. The instrumental resolution determined from a scan through $(3, 0, 0)$ is indicated.

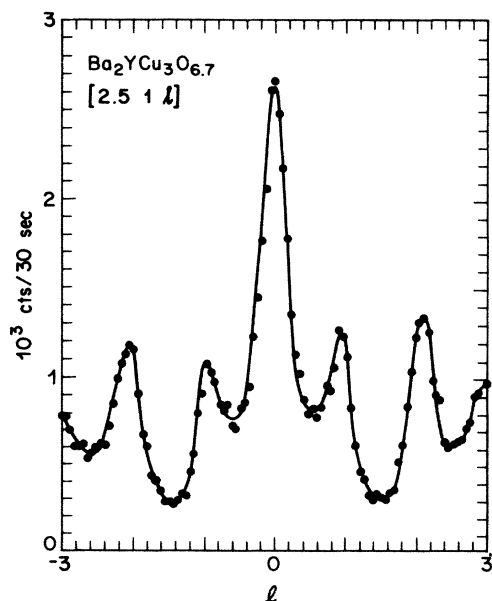


FIG. 3. Scan along $[2\frac{1}{2}, 1, l]$ in $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$ showing the modulation of diffuse intensity along the c axis. The peak widths indicate a coherence length on the order of one unit cell along the c axis. The line is a guide to the eye.

space coherence length is a model-dependent quantity that depends on the type of ordering. All models, however, agree within numerical factors on the order of 2 or 3 and the coherence length is typically defined by assuming that real-space correlations fall as $e^{-r/\xi}/r^{1/2}$ (two-dimensional order-disorder model). This gives a coherence length ξ on the order of $1/\Delta_{\text{FWHM}}$ (full width at half maximum). As seen in Table I, the basal-plane coherence is about four or five unit cells, while along the c axis the coherence is on the order of one unit cell.

This work indicates that for $x=6.7$, the structure orders along the a axis (normal to the Cu—O chains) with a periodicity of two unit cells. We have not determined the relative contribution of oxygen defects versus metal-atom displacements to the scattering; however, by considering pair interaction energies (similar to the approach of de Fontaine, Wille, and Moss¹⁵) one can make plausibility arguments for ordering of oxygen defects transverse to the Cu—O chains. Consider the two vacancy ordering

TABLE I. Diffuse peak widths in $\text{Ba}_2\text{YCu}_3\text{O}_{6.7}$.

	$(2\frac{1}{2}, 0, 0)$ FWHM (\AA^{-1})	$(3, 0, 0)$ FWHM (\AA^{-1})	$(2\frac{1}{2}, 0, 0)$ Excess width ^a (\AA^{-1})	Coherence length ^b (\AA)
h	0.100	0.024	0.097	21
k	0.181	0.128	0.128	16
l	0.213	0.021	0.212	9

$$^a \{ [2\frac{1}{2}, 0, 0] \text{ width} \}^2 - [3, 0, 0] \text{ width} \}^{1/2}.$$

$$^b 2/(\text{excess width}).$$

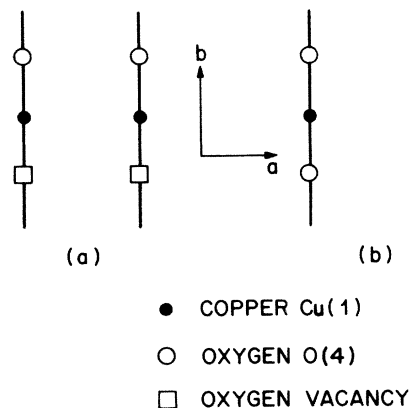


FIG. 4. Schematic illustration of two configurations of oxygen vacancy ordering in $\text{Ba}_2\text{YCu}_3\text{O}_x$ in the Cu—O chains. For $x=7$ the chains are fully occupied; for $x=6$ no oxygen sites are occupied.

schemes in Fig. 4 where we show oxygen-deficient Cu—O chains. We write the configuration energy of Fig. 4(a) as $2E_3$ and that of Fig. 4(b) as $E_2 + E_4$, where the subscripts refer to the copper-oxygen coordination including the oxygen sites above the copper atoms in the chain. If one assumes that the oxygen-oxygen pair interaction energy along the a axis (the direction with no intermediate copper) is negligible, then Fig. 4(b) can be seen to have the lowest energy because threefold coordination of copper is less favorable energetically than either twofold or fourfold coordination. Random vacancies on the chains will not be favored because they produce local threefold coordination. The tendency for oxygen defects to concentrate on a single chain suggests that oxygen-deficient material will order along the a axis with a periodicity determined by the oxygen stoichiometry. For example, at $x=6.5$ one would expect ordering of vacancies on every other chain producing a doubling of the cell along the a axis. Similarly, at $x=6.67$ one would expect an ordering of vacancies on every third chain and superlattice of $(\frac{1}{3}, 0, 0)$. Surprisingly, the experimental results show that a periodicity of $(\frac{1}{2}, 0, 0)$ is strongly preferred even at concentrations different from $x=6.5$. We note that ordering with oxygen vacancies concentrated on every other chain requires the presence of defects and finite-range order to allow the oxygen stoichiometry to be $x=6.7$. This suggests that as the stoichiometry moves toward $x=6.5$ the diffuse peaks should get more sharp as the number of defects decreases. Although the tendency to order with a wave vector of $(\frac{1}{2}, 0, 0)$ is apparently strong, evidence for periodicities other than one-half already exists in electron microscope observations of finite-range ordering at $\frac{2}{5}$ as well as $\frac{1}{2}$ (Ref. 20) and a $2\sqrt{2} \times 2\sqrt{2}$ superstructure at $x=6.85$.²⁶

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