Oxygen ordering and superconductivity in $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$

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The observation of superconductivity above 90 K in the Y–Ba–Cu–O system[1,2] has prompted a search for other structures that display high-temperature superconductivity. The discovery of superconductivity above 70 K in $La_{3-x}Ba_{3+x}Cu_6O_{14+y}$[3] raises some questions concerning its relationship to the $YBa_2Cu_3O_{7-\delta}$ structure and the origins of the high-temperature superconductivity. The original X-ray diffraction study of $La_3Ba_3Cu_6O_{14+y}$ indicated a tetragonal structure[4,5], on the basis of which it has been proposed that $La_{3-x}Ba_{3+x}Cu_6O_{14+y}$ is a new class of high-temperature superconductor which, in contrast to $YBa_2Cu_3O_{7-\delta}$, contains no Cu–O chains[3]. More recently, a neutron diffraction study of non-superconducting $La_3Ba_3Cu_6O_{14+y}$[6] has indicated that the correct structure of this compound is simply the tetragonal $YBa_2Cu_3O_{7-\delta}$ structure with partial substitution of lanthanum on the barium site[7–12]. In the present neutron powder diffraction study of a series of $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ compounds, we show that the superconducting phase is a similarly disordered isomorph of the orthorhombic $YBa_2Cu_3O_{7-\delta}$ structure[13–19]. The region of solid solubility for this compound extends from $x = 0.5$ (La:Ba:Cu ratios of 3:3:6) to $x \approx 0.25$ and does not include the stoichiometric compound $x = 0$ ($LaBa_2Cu_3O_{7-\delta}$). The presence of Cu–O chains, and not just a formal copper charge state of >2, is vital for the occurrence of superconductivity.

Five samples in the series $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ were prepared by mixing and grinding La_2O_3, $BaCO_3$ and CuO powders in the correct metal stoichiometries and firing at 975 °C in flowing oxygen. The samples were then reground and refired repeatedly to improve homogeneity. A final annealing of all samples at 600 °C in flowing oxygen was necessary to ensure the presence of superconductivity. Neutron powder diffraction data were obtained using the Special Environment Powder Diffractometer (SEPD) at the Argonne National Laboratory Intense Pulsed Neutron Source (IPNS). Resistivities were measured in a closed-cycle refrigerator from 300 to 8.5 K using silicon-diode thermometry, by the standard four-probe technique. The neutron diffraction data for the five samples indicated that the $x = 0.5$, 0.375 and 0.25 samples were single phase but the two samples with the largest amount of barium, $x = 0.125$ and 0.0, had significant amounts of $BaCuO_2$. Michel *et al.* have reported the synthesis of the stoichiometric $LaBa_2Cu_3O_{7+\delta}$ compound with $T_c = 75$ K (ref. 20), but their preparation technique is somewhat different and they give no details as to sample quality.

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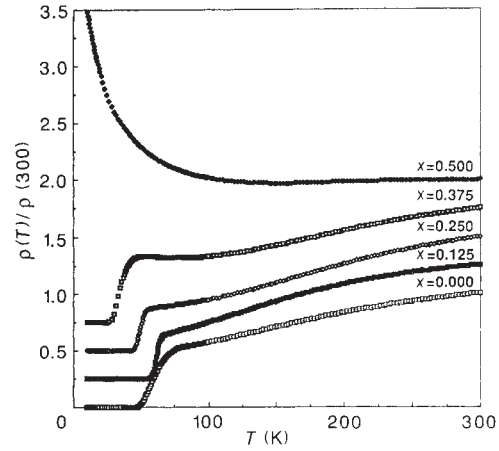

Fig. 1 Relative resistivity versus temperature for the five $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ samples ($x = 0$, 0.125, 0.25, 0.375, 0.5). The curves are displaced in the vertical direction for clarity.

Figure 1 shows the relative resistivities as a function of temperature for the five $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ samples. At $x = 0.5$ the resistivity shows semiconducting behaviour, but as x is decreased, the samples become more metallic and superconductivity appears, with the transition temperature T_c rising to a maximum of ~60 K for the two samples $x = 0.125$ and $x = 0.0$. This behaviour is entirely consistent with previous work[3], and indicates a solid-solution limit between $x = 0.25$ and $x = 0.125$. The broad superconducting transitions of even the single-phase samples are typical of solid solutions, where the stoichiometry is never microscopically identical throughout the sample.

The first-reported $La_3Ba_3Cu_6O_{14+y}$ structure[4,5] is related, as far as metal atoms are concerned, to the tetragonal $YBa_2Cu_3O_{7-\delta}$ structure simply by a doubling of the unit cell along the basal-plane diagonals. To test the recent neutron diffraction result[6], the initial structural refinement of the non-superconducting $x = 0.5$ sample was done using both models (both with space group $P4/mmm$). In agreement with ref. 6, it was discovered that the smaller $YBa_2Cu_3O_{7-\delta}$ tetragonal structure gave a better fit to the data. The remaining samples, all of which are superconducting, were found to be orthorhombic. The two single-phase samples, $x = 0.375$ and 0.25, were fitted by using the orthorhombic $YBa_2Cu_3O_{7-\delta}$ model[13–19]; the remaining two samples, $x = 0.125$ and 0.0, required the inclusion of $BaCuO_2$ as a second phase.

Because of the close relationship between the structure of the orthorhombic superconductor $YBa_2Cu_3O_{7-\delta}$ and the tetragonal but non-superconducting $La(Ba_{1.50}La_{0.50})Cu_3O_{7+\delta}$ compound, both orthorhombic and tetragonal fits were attempted on all of the $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ samples. The $x = 0.50$ sample would only converge for the tetragonal $P4/mmm$ model. For the other four samples, however, both tetragonal and orthorhombic ($Pmmm$) models were found to converge. To determine which of the two models was correct, a statistical analysis of the refined

Table 1 Physical parameters of the $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ samples

x	$7+\delta$	n_{01}	n_{05}	a (Å)	b (Å)	c (Å)	T_c^* (K)	Cu charge
0.5	7.22(3)	0.61(3)		3.9112(1)		11.6975(3)	—	2.31(2)
0.375	7.25(7)	0.74(5)	0.51(5)	3.9090(1)	3.9152(1)	11.7322(3)	27–47	2.38(5)
0.25	7.18(5)	0.76(4)	0.42(3)	3.9112(1)	3.9181(1)	11.7534(3)	44–54	2.37(3)
0.25(0.125)†	7.11(6)	0.85(5)	0.26(3)	3.9085(1)	3.9286(2)	11.7624(5)	57–68	2.32(4)
0.25(0.0)†	7.25(5)	0.86(5)	0.39(3)	3.9137(1)	3.9238(1)	11.7550(4)	47–80	2.42(3)

* T_c data are listed as the interval $T^{R=0}$–T^{onset}.
† Numbers in parentheses refer to the starting compositions, which are also used as sample labels in the text. The first number refers to the stoichiometry actually used in the refinement (see text).
Error in last digit is shown in parentheses.

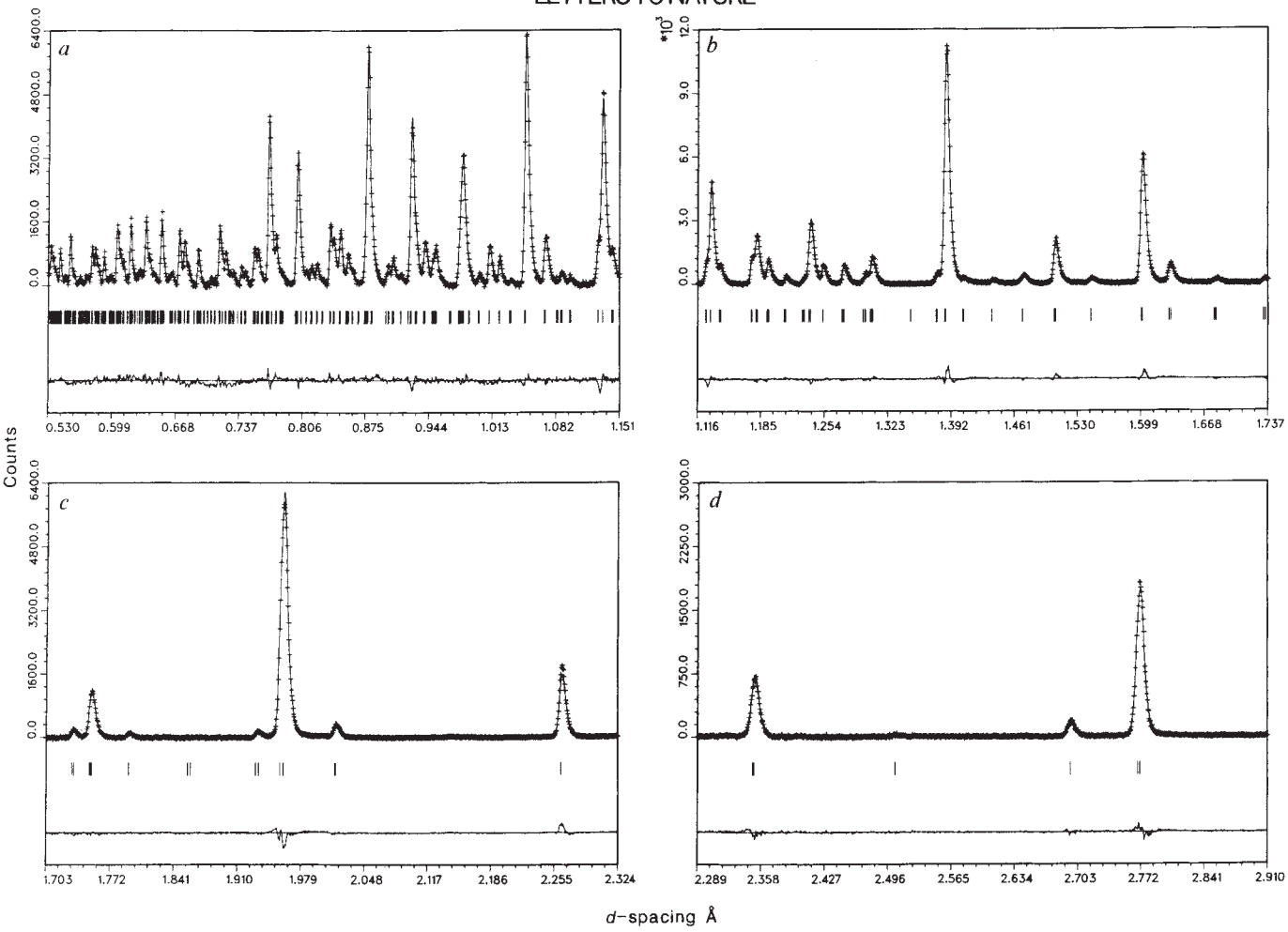

Fig. 2 *a–d*, Neutron diffraction spectrum for $La(Ba_{1.75}La_{0.25})Cu_3O_{7+\delta}$. The refined orthorhombic fit is shown as a line through the data points while the difference plot is shown in the lower portion of each frame.

data was required. First, the orthorhombic model was refined, then a second refinement was performed with constraints imposed to force the model to be tetragonal. The weighted profile R values for the two fits were then compared by the R-factor ratio test[21]. For the $x = 0.25$ sample, the orthorhombic fit had 33 variable parameters and weighted profile $R_0 = 5.527$ while the tetragonally constrained fit had 26 variable parameters and $R_t = 5.910$. The ratio $R_t/R_0 = 1.069$ for the ~3,500 degrees of freedom and order $33 - 26 = 7$ indicates that the tetragonally constrained model can be rejected at the 99.5% confidence level. Figure 2 shows the neutron diffraction spectrum, the refined orthorhombic fit and the difference plot for the $x = 0.25$ sample. It should be noted that the orthorhombic splitting is not visually observable and only the high resolution and the broad range of d-spacings obtainable at IPNS allow us to detect the small orthorhombic distortion.

Figure 3 shows the general structure of the orthorhombic $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ compounds. In all of the orthorhombic samples both the O1 and O5 sites are partially occupied, with more oxygen atoms in the O1 site. The tetragonal sample has essentially the same structure but with the O1 and O5 sites equally occupied. Table 1 shows the refined oxygen stoichiometry, lattice parameters, T_c, formal copper charge state and O1 and O5 site occupancies for each of the samples investigated. The La, Cu1, Cu2, O2, O3 and O4 sites remained fully occupied when permitted to vary, so in the final refinement all atomic sites were held fully occupied except for the O1 and O5 sites in the basal plane. The ratio of barium to lanthanum on the Ba/La site was held fixed because, when allowed to vary, it refined to values not consistent with the starting composition in the single-phase samples. This instability in the Ba/La site occupancy can be accounted for by realizing that when lanthanum, a much smaller atom, substitutes for barium, it is unlikely that it will occupy exactly the same spatial position or surroundings. As a consequence the thermal parameter obtained from the refinements is large and decreases as the site becomes more fully occupied with barium.

As mentioned above, the two samples with the highest superconducting transition temperature contain noticeable amounts of $BaCuO_2$. This indicates that, for our preparation conditions, there is a minimum x for which the structure is stable. Because of the difficulty in refining the occupancy of the Ba/La site, it was not possible to extract the actual value of x for this endpoint. Instead, we chose to fix the composition at the lowest value of x for which we observed a single phase sample, $x = 0.25$. Although this is not the correct composition, changing this number had little effect on the trends observed in the important parameters of the resultant refined structure, that is, the formal charge state of copper and the ordering and occupancies of the O1 and O5 sites.

An important feature of these results is that the formal charge state of copper is always approximately +2.3, even in the non-superconducting sample ($x = 0.5$). This indicates that the copper charge state alone is not sufficient to produce superconductivity. Instead, only those samples that are orthorhombic, owing to a finite amount of oxygen-vacancy ordering, exhibit superconductivity. Figure 4 shows the zero-resistance temperature ($T^{R=0}$) plotted against an order parameter defined as the normalized difference in the O1 and O5 site occupancies, $\xi = (n_{O1} - n_{O5})/(n_{O1} + n_{O5})$. The points plotted in Fig. 4 fall on a smooth, monotonically varying curve and support our original suggestion that T_c is intimately connected to the presence of

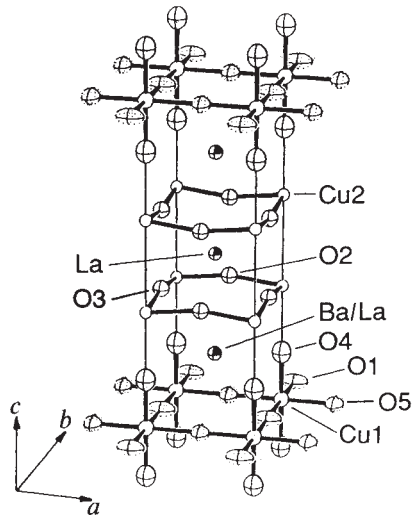

Fig. 3 General structure of the orthorhombic $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ compounds. The O1 and O5 sites are both partially occupied, with higher oxygen content in the O1 site.

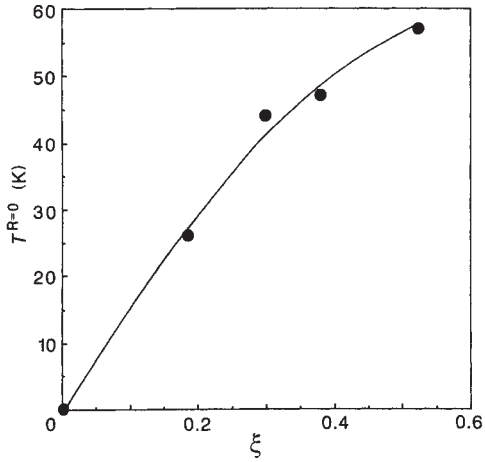

Fig. 4 Zero-resistance temperature ($T^{R=0}$) versus order parameter ($\xi \equiv (n_{O1} - n_{O5})/(n_{O1} + n_{O5})$) for the $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ compounds. The curve is merely a guide to the eye.

ordered Cu-O chains[7]. One would expect that if it were possible to synthesize a perfectly ordered $LaBa_2Cu_3O_{7-\delta}$ compound, it would have $\xi = 1$ and $T_c \approx 90$ K, as in orthorhombic $RBa_2Cu_3O_{7-\delta}$ (R = Y, Sm, Eu, Gd, Dy, Ho, Tm, Yb, Lu; $0 < \delta < 0.2$). Note that the resistivity data shown in Fig. 1 for the two-phase samples are not identical, as would be expected if both samples contained a majority phase with the same stoichiometry. The $x = 0.125$ sample has an appreciably higher $T^{R=0}$ than the $x = 0.0$ sample. The reason for this is that the neutron refinements for these two samples (which are a measure of the structural properties of the majority phase) imply that the $x = 0.125$ sample has a higher value of ξ, and consequently higher $T^{R=0}$ (which is also characteristic of the superconducting properties of the majority phase). Because of their two-phase character, residual inhomogeneities in these two samples could easily account for these effects. This analysis also points out the need for detailed determination of the oxygen stoichiometries and ordering for the understanding of the superconducting behaviour of metal oxides.

We have shown that the superconducting phase in the $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ system is isostructural to the orthorhombic $YBa_2Cu_3O_{7-\delta}$ and contains ordered Cu-O chains. This system is unique in that for a constant copper charge state of >2, T_c is varied merely by changing the degree of order of the Cu-O chains. This contrasts with $YBa_2Cu_3O_{7-\delta}$, in which decreasing T_c is correlated with a decrease in copper oxidation as oxygen is removed (see, for example, ref. 22). Our data show that ordering of the Cu-O chains is essential for superconductivity in the $YBa_2Cu_3O_{7-\delta}$ structure.

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Note added in proof: The authors have recently become aware of the successful synthesis of orthorhombic $LaBa_2Cu_3O_{7+\delta}$ with $T_c \sim 90$ K (ref. 23).

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Microstructure and critical current of superconducting $YBa_2Cu_3O_{7-x}$

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In the few months that have passed since the discovery of high-transition-temperature superconducting oxides[1–3], remarkable progress has been made in identifying the structure of superconducting phases, improving our understanding of factors that control their synthesis, and determining their basic properties. In one area, however, progress has been disappointingly slow; that is, in the control and optimization of the superconducting critical current density, a property vital for effective technological application of these materials. Bulk samples display a critical current that is generally very low and, furthermore, drops steeply in an applied magnetic field. There is persuasive evidence, however, that low critical currents are not an inherent characteristic of the material[4,5], and recent work on thin epitaxial films[6] has indicated that values as high as 10^6 A cm^{-2} can be achieved. It is also generally established that the critical current that can be carried by any superconductor depends predominantly on the local microstructure, its degree of uniformity and the nature of its characteristic defect structures[7]. We present here the main results of a detailed electron microscopical study of sintered $YBa_2Cu_3O_{7-x}$[8], and discuss their relevance to observed critical current and its modification by increased silicon impurity levels[9]. In the light of these results we assess the prospects for controlling microstructure development so as to optimize the critical current for technological application.

The agreed basic structure of the orthorhombic superconducting form of $YBa_2Cu_3O_{7-x}$ is that of an oxygen-deficient perovskite, with Ba and Y in the sequence Ba-Y-Ba on the A sites of the $A_3B_3O_{9-2}$ structure, no oxygen on the Y planes and oxygen vacancies leaving tunnels in the [010] direction on the Cu planes

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