Structure of superconducting $Sr_{0.9}La_{0.1}CuO_2$ ($T_c = 42$ K) from neutron powder diffraction

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We have refined the crystal structure of the electron-doped infinite-layer superconducting compound $Sr_{0.9}La_{0.1}CuO_2$ ($T_c = 42$ K) from neutron-powder-diffraction data for an 82-mg sample synthesized at high pressure. The metal- and oxygen-atom lattices are perfectly stoichiometric and there is no excess (interstitial) oxygen in the Sr(La) layer. Thus, neither oxygen vacancies nor interstitial oxygen play a role in the doping of this compound.

INTRODUCTION

The so-called "infinite-layer" compound, based on the $ACuO_2$ structure where A is typically a solid solution (e.g., Sr and La, Sr and Nd, etc.)[1-3] (Fig. 1), is the simplest of the copper-oxide superconductors and, according to recent reports,[4] may display the highest T_c. This structure type was reported by Siegrist *et al.* for the non-superconducting compound $Ca_{0.86}Sr_{0.14}CuO_2$.[1] Superconducting compounds with this structure were synthesized by Takano *et al.*,[5] Smith *et al.*,[6] and Er *et al.*,[7] using high-pressure techniques to achieve partial substitution of Ba, Nd, and La, respectively, on the Sr site. Su-
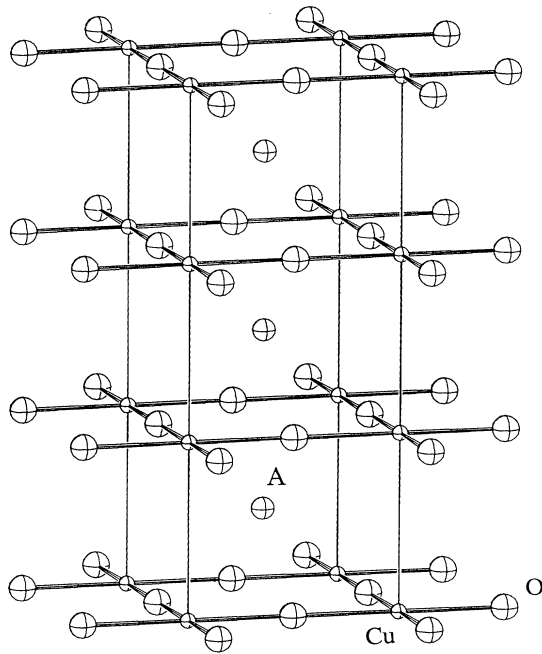

FIG. 1. Structure of the "infinite-layer" compounds $ACuO_2$. Superconducting compounds result from various solid solutions (e.g., Sr and La, Sr and Nd) on the A site.

perconducting critical temperatures in the range 40–90 K were obtained. Er *et al.*[8] confirmed that their samples with composition $Sr_{1-x}La_xCuO_2$ ($x \approx 0.1$) and $T_c \approx 43$ K were electron doped from measurements of the negative thermoelectric power, overall oxygen content, etc. X-ray absorption spectroscopy measurements also support the conclusion that these materials are electron doped.[9] Later, Azuma *et al.*,[10] using a high-pressure synthesis technique, reported T_c's as high as 110 K for an infinite-layer compound with the approximate composition $(Ca_{1-x}Sr_x)_{0.9}CuO_2$ ($0.4 \leq x \leq 0.7$). They speculated that this material was hole doped by vacancies on the Ca (Sr) site. High-resolution electron micrographs revealed defect layers, suggesting that these vacancy defects were ordered leaving other layers intact. Similar materials have recently been synthesized by Li, Kawai, and Kawai[4] by laser ablation in an oxidizing environment. These infinite-layer thin films confirm the existence of T_c's above 100 K and suggest that T_c's in the range of 150–170 K may be present, although the higher T_c's have not been reproduced in other laboratories and are controversial. The requirement for an oxidizing atmosphere, and a comparison of the observed lattice parameters with other infinite-layer compounds, suggest to these authors that the doping mechanism may involve interstitial oxygen in the Ca(Sr) layer (perhaps ordered in layers to leave other layers intact).

Clearly, there is a need to establish the stoichiometry and defect structure of these infinite-layer superconductors in order to understand how the material is doped and to design rational synthesis schemes. In particular, we must learn whether vacancies form on the Ca(Sr) site or the oxygen site in the CuO_2 layers and whether interstitial oxygen is incorporated in the Ca(Sr) layer. Neutron diffraction techniques, which can probe both the metal and oxygen sites, have supplied such information for many other copper-oxide superconductors. However, for these new infinite-layer superconductors, the small sample size (typically less than 100 mg) and the frequent existence of impurity phases resulting from the difficult high-pressure synthesis have hindered such studies. We

report here neutron-powder-diffraction measurements for a superconducting infinite-layer compound.

SYNTHESIS AND CHARACTERIZATION

A powder sample of nominal composition $Sr_{0.9}La_{0.1}CuO_2$ was prepared using a mixture of $SrCO_3$, La_2O_3, and CuO fired at 950 °C for 48 h as described previously.[7] The resulting sample was placed in a boron-nitride capsule and further reacted at a pressure of 5 GPa and temperature of 950 °C for 1 h and then annealed at 500 °C for 20 h at the same pressure. The amount of impurities decreased during the annealing process. Moreover, most of the impurity phases are found on the surfaces of the sample. Thus, the upper and lower sides of the disk-shaped sample were polished with #800 emery paper until only traces of impurity phases were observed by x-ray powder diffraction. The resulting sample was a disk approximately 2 mm in diameter and 1 mm thick with a mass of 82 mg. ac susceptibility measurements for this sample show a well-defined superconducting transition at 42 K and a large diamagnetic signal consistent with bulk superconductivity (Fig. 2).

NEUTRON POWDER DIFFRACTION

Neutron-powder-diffraction data were collected on the Special Environment Powder Diffractometer[11] at Argonne's Intense Pulsed Neutron Source. In order to achieve acceptable statistics for such a small sample, backgrounds were minimized by supporting the sample in the neutron beam with no sample container. Data were collected at room temperature for 12 h.

The structure was refined by the Rietveld technique[12] in the tetragonal $P4/mmm$ space group using only the high-resolution data from the back-scattering ($2\theta = 145°$) detector banks. 144 Bragg peaks with d spacings from 0.53 to 4 Å were included in the refinement. The Rietveld refinement profile is shown in Fig. 3. Refined structural parameters are given in Table I.

Since the difference between neutron scattering lengths for Sr and La is not large [$b(Sr)=0.702$, $b(La)=0.827$] our measurement has rather poor sensitivity for determining
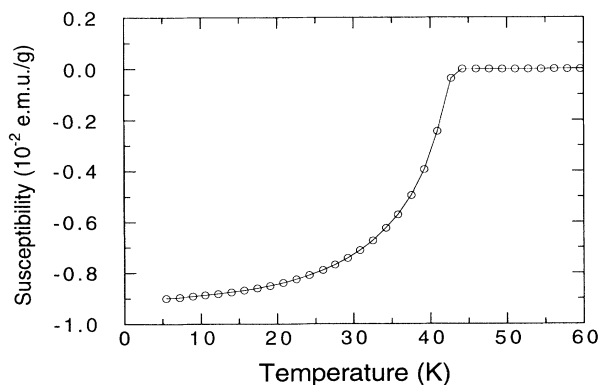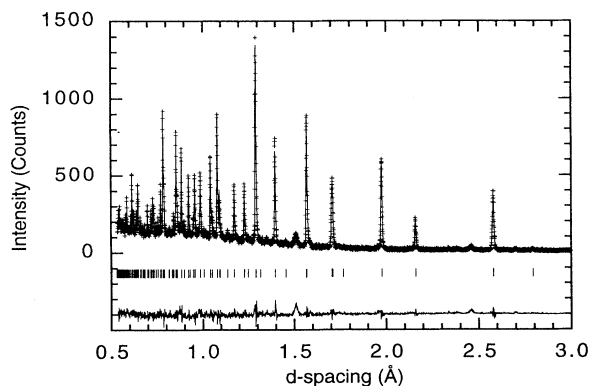

FIG. 3. Portion of the Rietveld refinement profile for $Sr_{0.9}La_{0.1}CuO_2$. Data were collected from an 82-mg sample for 12 h on the Special Environment Powder Diffractometer. Plus marks (+) are the raw time-of-flight diffraction data including background. The solid line is the calculated profile. Tick marks below the profile mark the positions of allowed reflections in the tetragonal $P4/mmm$ space group. A difference curve (observed minus calculated) is plotted at the bottom.

the Sr:La ratio, but has good sensitivity for determining the overall occupancy of the Sr,La site. Strictly speaking, it is not possible to refine both the Sr:La ratio and the overall site occupancy. However, the small contrast between Sr and La allows us to set limits on the vacancy concentration consistent with reasonable assumptions about the Sr:La ratio. If we assume that the Sr:La ratio is the same as the starting composition, 0.9:0.1, the refined occupancy is 1.01(2). This value varies by only

TABLE I. Structural parameters for $Sr_{0.9}La_{0.1}CuO_2$ from Rietveld refinement using neutron-powder-diffraction data. Numbers in parentheses are standard deviations of the last significant digit. Parameters with no standard deviations were not refined. O_i is a possible interstitial oxygen site that was investigated and found to be vacant.

Parameter		Value
$a = b$ (Å)		3.950 68(6)
c (Å)		3.409 02(9)
V (Å^3)		53.21(2)
Sr,La[a]	$x = y = z$	0.5
	n	1.01(2)
	B (Å^2)	0.63(5)
Cu	$x = y = z$	0
	n	1
	B (Å^2)	0.50(3)
O	x	0.5
	$y = z$	0
	n	2.00(3)
	B (Å^2)	0.66(3)
O_i	$x = y$	0
	z	0.5
	n	−0.02(1)
	B (Å^2)	0.7
R_{wp} (%)		16.0
R_{ex} (%)		12.7

[a]Constraint: $n(Sr):n(La)=0.9:0.1$.

FIG. 2. ac susceptibility, taken upon heating in a 1-G field, for $Sr_{0.9}La_{0.1}CuO_2$.

one standard deviation (i.e., 0.02) for assumed ratios of 1.0:0.0 and 0.8:0.2. Previous synthesis studies of the optimum superconducting composition for this compound[7,8] confirm that the Sr:La composition is known well within this level of accuracy. Thus, we conclude that there are no vacancies on the Sr,La site within a 2% experimental uncertainty.

We also find the oxygen site in the CuO_2 layer to be fully occupied within a 1.5% experimental uncertainty [2.00(3) atoms per formula unit]. Since there has been speculation about the incorporation of oxygen on an interstitial site in the Sr(La) layer, we refined the occupancy for an oxygen atom at $(0,0,\frac{1}{2})$ which is the expected site adjacent to Sr(La) and between two Cu atoms. We found this site to be vacant within a 1% experimental uncertainty. Even though interstitial oxygen in this site would imply an unusually short (~ 1.7 Å) Cu-O bond length, we feel that it is logical and necessary to ask whether interstitial oxygen is incorporated. The short bond length implied by such a defect does not preclude its existence. For example, in the two-layer compound, $(La,Sr,Ca)_3Cu_6O_{6+x}$, it has been shown that a small amount of interstitial oxygen can be incorporated in the equivalent site between the CuO_2 planes in structures where the Cu-Cu distance is less than 3.4 Å (although large concentrations of interstitial oxygen are achieved only for a Cu-Cu distance greater than 3.5 Å).[13-19] The short (< 1.7 Å) bond lengths implied by this are perhaps accommodated by local distortion of the host lattice. However, we conclude that this interstitial site is completely vacant in superconducting $La_{0.9}La_{0.1}CuO_2$.

CONCLUSIONS

These results show that the superconducting $Sr_{0.9}La_{0.1}CuO_2$ phase contains no defects (except for the La substitution) on the metal or oxygen sublattices, and that no excess oxygen in the form of an interstitial defect in the Sr(La) layer is present. Thus, the chemical composition and defect structure is consistent with this material being an electron-doped superconductor, as has previously been reported.[8]

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