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Structural Study of $\text{Sr}_2\text{CuO}_{3+\delta}$ by Neutron Powder Diffraction

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Structural study of $\text{Sr}_2\text{CuO}_{3+\delta}$ by neutron powder diffraction

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ABSTRACT

Average crystal structures of superconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized under high pressure and nonsuperconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized at ambient pressure from a hydroxometallate precursor were refined from neutron powder diffraction data. A simplified model was used to fit the modulated superstructures. Both compounds have an oxygen deficient La_2CuO_4 -type tetragonal T structure with oxygen vacancies located in the CuO_2 planes, not in the Sr_2O_2 layers. This result raises important questions regarding the nature of superconductivity in $\text{Sr}_2\text{CuO}_{3+\delta}$ reported to be a 70 K superconductor.

INTRODUCTION

The recently discovered $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ superconductors are unique materials in that they contain only two metallic elements, strontium and copper, and yet display superconducting transition temperatures (T_c) over 70 K. Hiroi *et al.* [1] reported a homologous series of compounds, $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ made by a high-pressure synthesis technique, and found $T_c=70$ K for the $n=1$ compound ($\text{Sr}_2\text{CuO}_{3+\delta}$) and $T_c=100$ K for the $n=2$ compound ($\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$). Adachi *et al.* [2] also observed the same superconducting phases in the mixed-phase samples while studying the Sr-Ca-Cu-O system.

At ambient pressure, Sr_2CuO_3 forms as an orthorhombic structure with CuO chains along the a -axis [3]. Lobo *et al.* [4] reported that oxidation under 16 MPa of oxygen at about 400 °C converts this compound to a K_2NiF_4 -type tetragonal structure with approximate composition $\text{Sr}_2\text{CuO}_{3.9}$. Their material was not superconducting and they speculated that the oxygen deficient $\text{CuO}_{1.9}$ layer and the implied high oxidation state of Cu (~ 3.8) prevent this material from being superconducting. Hiroi *et al.* [1], on the other hand, synthesized a tetragonal form of $\text{Sr}_2\text{CuO}_{3+\delta}$ under oxidizing conditions by using KClO_4 as an oxygen source at 800-900 °C and 6 GPa pressure in a cubic anvil apparatus and found a superconducting material. They measured a T_c of 70 K and a Meissner volume fraction of about 22%, suggesting bulk superconductivity. The oxygen content of their superconducting sample was estimated to be 3.1 atoms per formula unit by iodometric titration. The nominal Cu valence of 2.2 implied by this oxygen content seems to be consistent with the doping level observed in other copper-oxide superconductors. A superstructure of $4\sqrt{2}a \times 4\sqrt{2}a \times c$, which is seen in both x-ray and electron diffraction data, has made it difficult to determine the detailed structure of this compound.

Recently, Mitchell *et al.* [5] have reported the synthesis of a tetragonal form of $\text{Sr}_2\text{CuO}_{3+\delta}$ at ambient pressure by using a hydroxometallate precursor. The x-ray diffraction pattern of their sample is nominally the same as that of the superconducting compound prepared at high pressure, including the $4\sqrt{2}a \times 4\sqrt{2}a \times c$ superstructure, suggesting that the two

compounds are isostructural. In spite of the similarity of the crystal structures, the sample made by Mitchell *et al.* does not show superconductivity. The oxygen content of this nonsuperconducting material is estimated to be 3.29 by thermogravimetric analysis. Assuming stoichiometric cation compositions, this oxygen content implies a formal Cu oxidation state of 2.58. Because of the small particle size of the powder, transport measurements are somewhat difficult. However, initial measurements indicate that this compound is insulating.

The most important questions about the tetragonal $\text{Sr}_2\text{CuO}_{3+\delta}$ structure concern the oxygen atom locations and site occupancies. The metal sublattice of this compound is the same as for the T (tetragonal La_2CuO_4 -type), T' (Nd_2CuO_4 -type), and T* ($(\text{Nd,Ce,Sr})_2\text{CuO}_4$ -type) structures [6], as confirmed by both x-ray and electron diffraction [1, 2]. The measured oxygen content near 3 atoms per formula unit means that nearly one fourth of the oxygen atoms that would be present in the ideal structures are missing. If one assumes the existence of an undefected CuO_2 plane, which is believed to be a common feature in the high- T_c cuprates, nearly half of the oxygen sites in the Sr_2O_2 layer are required to be vacant in the superconducting material. In the case of the T structure, this means that the half of the apical oxygen atoms are missing. Such a structure has been proposed by both Hiroi *et al.* [1] and Adachi *et al.* [2].

This paper reports the results of neutron powder diffraction studies of superconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized under high pressure and nonsuperconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized at ambient pressure from a hydroxometallate precursor. Because the neutron scattering length for oxygen is nominally as large as that for the metal atoms, neutron diffraction is the best technique for investigating the oxygen defect structures. The goal of this work is to determine the oxygen atoms positions and site occupancies and to learn what differentiates the superconducting from the nonsuperconducting materials. Although the full details of the $4\sqrt{2}a \times 4\sqrt{2}a \times c$ superstructure cannot be uniquely refined, a simplified model of the supercell allows the essential features of the structures to be obtained. Remarkably, for both compounds the oxygen vacancies appear to be located entirely in the CuO_2 planes, not in the Sr_2O_2 layers.

SYNTHESIS AND DATA COLLECTION

A 0.11 g "high pressure tetragonal" sample of superconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ was synthesized using the high-pressure technique described previously [1]. Orthorhombic Sr_2CuO_3 was annealed at 850 °C and 6 GPa for 2 hours with KClO_4 as a source of oxygen. The sample was superconducting with a sharp diamagnetic transition at about 65 K, as shown in Fig. 1. The superconducting fraction was 5.6% as determined by cooling the as-made sintered sample in a dc magnetic field in a SQUID and 7.1% as determined by ac susceptibility after grinding the sample to powder (following the neutron diffraction experiment). Both x-ray and electron diffraction patterns of this sample show essentially the same features as previously reported for other superconducting samples made by Hiroi *et al.* (some of which had larger superconducting fractions) [1]. Scanning electron microscopy and electron-probe microanalysis showed a small amount of KCl on the surface of the sample (apparently too small in quantity to be seen in x-ray or neutron diffraction) but did not show any phases with a Sr:Cu ratio other than 2:1.

A 2.23 g "low-pressure tetragonal" sample was synthesized at 370 °C in 1 atm oxygen from a copper hydroxometallate precursor, $\text{Sr}_2\text{Cu}(\text{OH})_6$. The details of the synthesis procedure are described elsewhere [5]. This sample does not show superconductivity above 4 K.

Time-of-flight (TOF) neutron powder diffraction data were collected at room temperature on the Special Environment Powder Diffractometer (SEPD) and the General Purpose Powder Diffractometer (GPPD) at Argonne's Intense Pulsed Neutron Source (IPNS) [7]. For the small superconducting sample, data were collected for 24 hours with the sintered sample suspended in the neutron beam on an amorphous boron fiber to minimize background. The larger nonsuperconducting sample was contained in a thin-walled vanadium can and data were collected for 19 hours. The crystal structures were refined by the Rietveld technique [8] using only the high-resolution data from the back-scattering ($2\theta = 145^\circ$) detector banks.

STRUCTURE REFINEMENT

The average structure (ignoring the modulation) was investigated by first assuming the three possible tetragonal structures; T, T' and T*. R factors of the refinements for the superconducting sample were 13.07%, 15.54% and 15.62%, respectively. From these initial refinements it was concluded that the T structure (La_2CuO_4 -type, tetragonal space group $I4/mmm$) best represents the average structure for this compound.

The data for the superconducting sample included peaks from the untransformed low-pressure orthorhombic form as a minor phase. The data for the nonsuperconducting sample included peaks from a small amount of SrO. Thus, these impurity phases were included in the subsequent refinements. Figures 2(a) and 3(a) show the results of the Rietveld refinements for the two samples. The refined structural parameters are listed in Tables I (a) and II (a). The most surprising results are the refined occupancies for the oxygen sites. Although the results for refinements based only on the average structure are subject to systematic errors, as evidenced by the unphysically large site occupancies for Sr and O(2) (outside the statistical uncertainties), it is evident that nominally the expected amount of oxygen is found and that the oxygen vacancies are on the O(1) site in the CuO_2 plane for both samples. We observe a slight difference in the lattice parameters for the two samples; the unit cell of the superconducting sample has a shorter a -axis and a longer c -axis.

For both samples, most of the major peaks can be assigned to the basic T structure (Fig. 2(a) and 3(a)). However, some fairly large peaks, for example, those with d -spacings of 1.45 Å, 1.77 Å, 2.01 Å, and 2.64 Å, are not consistent with the T structure or known impurity phases. These peaks are associated with a commensurate modulation of the structure leading to a $4\sqrt{2}a \times 4\sqrt{2}a \times c$ supercell as was seen by electron diffraction [1]. With the present data, we were not able to perform a full refinement of the supercell. However, we were able to refine a simplified model for the supercell that resulted in a significant improvement in the fit. Our model assumes that the major contribution to the modulation is from atom displacements. This

assumption was based on the observation, in high-resolution electron microscope lattice images as shown in Fig.4, of atomic displacements forming two sinusoidal waves in the a - b plane. From the unusually large thermal parameters obtained in our initial refinements of the average structure, we concluded that the Cu, Sr, and O(2) atoms are displaced from their ideal sites and participate in this modulation.

In our refinements of the modulated structure we assumed a two-dimensional commensurate modulation as shown in Fig. 5, leading to a $4\sqrt{2}a \times 4\sqrt{2}a \times c$ supercell and belonging to the tetragonal space group $P4/mbm$. In reciprocal space the superstructure wave vectors are denoted as

$$q^{\pm*} = \left(\frac{1}{8}a_p^* \pm \frac{1}{8}b_p^* \right), \quad (1)$$

where a_p^* and b_p^* are the unit vectors reciprocal to the basic lattice vectors a_p and b_p , respectively. Thus, the reciprocal lattice vector for the modulated structure can be expressed as

$$h = ha_p^* + kb_p^* + lc_p^* + m_1q_+^* + m_2q_-^*, \quad (2)$$

by using integers h, k, l, m_1 , and m_2 . All observed supercell reflections can be refined with this latter vector. In this model, the atomic positions for the Sr, Cu and O(2) sites in fraction of lattice constants of the supercell are defined as

$$x = x_p - s \sin(2\pi y_p) \quad y = y_p + s \sin(2\pi x_p), \quad (3)$$

for each atom, where (x_p, y_p) is a nonmodulated position of each atom, which coincides with the atomic position of the basic T structure, and s is an amplitude of sinusoidal atomic displacement. The same phases of the sinusoidal waves along the c -axis are assumed. The displacement amplitudes, s , for Sr, Cu, and O(2) are refined. Figures 2(b) and 3(b) show the results of these refinements for both samples. Refined structural data are also listed in Tables I (b) and II (b).

Agreement between the observed and calculated intensities is significantly improved compared with the previous refinements based only on the nonmodulated structure. In particular, the peaks that could not be assigned to the basic T structure are consistent with the superstructure model. All superstructure peaks visible in the neutron diffraction data are first order ($m_1, m_2 = 0$ or ± 1) satellite reflections associated with the modulated structure, as indexed in the Figures 2(b) and 3(b).

The refined amplitudes of the sinusoidal atomic displacements for Sr, Cu and O(2) are 0.24 Å, 0.23 Å and 0.31 Å for the superconducting sample, and 0.23 Å, 0.18 Å and 0.27 Å for the nonsuperconducting sample, respectively. When this simple model for the superstructure is used, the refined thermal parameters decrease to more reasonable values. More importantly, the unphysically large occupancies for the Sr and O(2) sites fall within one or two standard deviations of unity. Thus, this model gives the same conclusion as for the refinement of the average structure. The apical oxygen site, O(2) is fully occupied and the oxygen vacancies are located entirely in the CuO₂ planes. The total oxygen contents from the refinements (assuming O(2) to be fully occupied) are 3.14 for the superconducting sample and 3.26 for the nonsuperconducting sample, in good agreement with the iodometric titration (3.1) [1] and TGA (3.29) [5] estimates of the oxygen contents, respectively.

An obvious improvement in our refinement model would be to attempt to refine the site occupancies of inequivalent O(1) oxygen sites in the CuO₂ plane. Several such refinements were attempted. Unfortunately, none of these converged in a convincing way, although some models did suggest clustering of occupied sites. This failure to learn how the site occupancies are modulated (as would certainly be expected) may indicate that our assumed space group for the supercell is wrong or that some other aspect of our simplified model for the modulated structure is incorrect. Thus, the model we used should be properly viewed as allowing us to improve our fit to the data, and, thus, our knowledge of the average structure, but may not give a correct view of the details of the modulation.

The average structure can best be understood by comparing the orthorhombic and tetragonal $\text{Sr}_2\text{CuO}_{3+\delta}$ structures shown in Fig. 6. Since nearly half of the oxygen sites in the CuO_2 plane are vacant in the tetragonal structure, it should be viewed as a disordered form of the orthorhombic structure [3]. The a -axis lattice parameter for the tetragonal compound, ~ 3.76 Å, is near the average of the a and b lattice parameters for the orthorhombic compound, 3.50 Å and 3.92 Å. Refined z positions of Sr (~ 0.15) and O(2) (~ 0.16) are almost identical to those of the orthorhombic compound and suggest that the rock-salt-type SrO layer is almost flat, which results from an alternation of neutral layers of $-\text{CuO}-\text{SrO}-\text{SrO}-\text{CuO}-$. These observations indirectly confirm that the oxygen vacancies have not moved to the apical site.

DISCUSSION

Our results raise important questions regarding the nature of superconductivity in $\text{Sr}_2\text{CuO}_{3+\delta}$. If this compound is accepted to be a bulk superconductor, it is the first copper-oxide superconductor with large (approaching 50%) oxygen vacancy concentrations in the CuO_2 planes. Such a finding is in serious conflict with the commonly held belief that these planes must be intact to support superconductivity. We offer no explanation for why the high-pressure synthesized sample is superconducting while the sample made by decomposition at low temperature is not. There is no significant difference in the average structures except for a difference in the total oxygen contents, which would change the number of carriers. However, the small superconducting fraction, 7% for our sample and a maximum of about 20% reported in the literature [1, 2, 9], suggests that other explanations must be considered.

One interesting possibility is that oxygen clustering within the CuO_2 planes creates islands of superconducting material where the CuO_2 planes are intact. Such clustering would not be detected in our neutron diffraction measurements, although diffraction line broadening resulting from the strain fields around such clusters would be expected. We do, in fact, see a small amount of isotropic strain broadening for the superconducting sample, and an even larger

amount of line broadening (which could also result from the small particle size) for the nonsuperconducting sample. Since clusters would require a larger a -axis lattice parameter, we would see them as a discrete phase in the diffraction data if their size was more than several hundred Angstroms.

A second possible explanation could involve a favorable ordered arrangement of oxygen vacancies in the CuO_2 planes that preserves a connected network of Cu atoms with the oxygen coordination required for superconductivity. No copper-oxide superconductors with such a structure have been reported. If the full details of the superstructure can be determined in subsequent experiments, it will be known whether such a structure exists. We are not hopeful about refining the full superstructure from the present data.

The third, and perhaps least interesting, explanation is that superconductivity in samples of $\text{Sr}_2\text{CuO}_{3+\delta}$ made at high pressure comes from a phase that has not yet been correctly identified. Due to the complications of the modulated structure, we are not able to completely rule out the possibility of an additional phase in our data at the 5-10% level. However, scanning electron microscopy and electron-probe microanalysis did not show any phases with a Sr:Cu ratio other than 2:1. In particular, we do not see any evidence for the infinite-layer phase with the nominal formula SrCuO_2 [10, 11] which would be readily identified in the neutron diffraction data. Moreover, if another phase exists, it has not been seen by x-ray or electron diffraction in samples that showed 20% superconducting fractions [1]. Clearly, this possibility should be explored further by working to raise the superconducting fraction of this system and by careful analytical measurements. If the superconductivity arises from another phase, it is nevertheless a compound with only two metallic elements, Sr and Cu, and is clearly of great interest whatever its structure.

Although our work cannot give definitive answers, it provides important new information about the $\text{Sr}_2\text{CuO}_{3+\delta}$ phase reported to be a 70 K superconductor; namely, that the oxygen sites in the CuO_2 planes of this compound are, in an average sense, nearly half empty. This result

emphasizes the importance of further work aimed at clarifying the nature of superconductivity in this system.

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Table I Refined structural parameters for the superconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized under high pressure based on (a) the average T structure, and (b) a simplified modulated supercell. In the superstructure model Sr, Cu and O(2) atoms are displaced from their ideal positions in the a - b plane. s is an amplitude of sinusoidal atomic displacements. Numbers in parentheses are standard deviations of the last significant digit. Parameters with no standard deviations were not refined.

(a)

Space group, $I4/mmm$			$a=3.7631(1) \text{ \AA}$	$c=12.5601(9) \text{ \AA}$	
atom	x	y	z	$B (\text{\AA}^2)$	g
Sr	0.5	0.5	0.1483(6)	2.5(2)	1.13(4)
Cu	0.0	0.0	0.0	3.1(2)	1.0
O(1)	0.0	0.5	0.0	1.0(2)	0.45(2)
O(2)	0.0	0.0	0.1538(4)	4.0(3)	1.16(4)
$R_{wp}=10.450\%$			$R_{exp}=5.909\%$ (2 phase analysis		22 variables)

(b)

Space group, $P4/mbm$			$a=21.2900(6) \text{ \AA}$	$c=12.5611(6) \text{ \AA}$	
			$a/4\sqrt{2}=3.7636 \text{ \AA}$		
atom	x	y	z	$B (\text{\AA}^2)$	g
Sr	0.5 ^a	0.5 ^a	0.1474(4)	1.1(2)	1.05(3)
Cu	0.0 ^b	0.0 ^b	0.0	1.3(0)	1.0
O(1)	0.0	0.5	0.0	1.3(3)	0.57(2)
O(2)	0.0 ^c	0.0 ^c	0.1578(4)	0.9(2)	1.00(3)
^a s (Sr) = 0.0112(3)			^b s (Cu) = 0.0110(5)		^c s (O(2)) = 0.0147(4)
$R_{wp}=9.412\%$			$R_{exp}=6.775\%$ (2 phase analysis		28 variables)

Table II Refined structural parameters for the nonsuperconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized at ambient pressure from a hydroxometallate precursor based on (a) the average T structure, and (b) a simplified modulated supercell. Format is the same as Table I.

(a)

Space group, $I4/mmm$			$a=3.7696(1) \text{ \AA}$	$c=12.5412(7) \text{ \AA}$	
atom	x	y	z	$B (\text{\AA}^2)$	g
Sr	0.5	0.5	0.1489(4)	1.8(1)	1.04(4)
Cu	0.0	0.0	0.0	1.8(2)	1.0
O(1)	0.0	0.5	0.0	0.9(2)	0.64(2)
O(2)	0.0	0.0	0.1563(5)	3.6(2)	1.20(3)
$R_{wp}=9.730\%$			$R_{exp.}=2.569\%$ (2 phase analysis		22 variables)

(b)

Space group, $P4/mbm$			$a=21.3290(5) \text{ \AA}$	$c=12.5411(5) \text{ \AA}$	
			$a/4\sqrt{2}=3.7705 \text{ \AA}$		
atom	x	y	z	$B (\text{\AA}^2)$	g
Sr	0.5 ^a	0.5 ^a	0.1477(3)	0.8(1)	0.93(3)
Cu	0.0 ^b	0.0 ^b	0.0	1.9(1)	1.0
O(1)	0.0	0.5	0.0	1.8(2)	0.63(1)
O(2)	0.0 ^c	0.0 ^c	0.1558(3)	1.4(2)	1.05(2)
$a_S (\text{Sr}) = 0.0107(3)$			$b_S (\text{Cu}) = 0.0083(3)$		$c_S (\text{O(2)}) = 0.0126(3)$
$R_{wp}=7.487\%$			$R_{exp.}=2.568\%$ (2 phase analysis		25 variables)

Figure Captions

Figure 1. Temperature dependence of ac susceptibility for $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized under high pressure.

Figure 2. Neutron powder diffraction data and the Rietveld refinement profiles for superconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized under high pressure. Refinements were performed based on (a) the average T structure, and (b) a simplified modulated supercell. The raw time-of-flight diffraction data are shown as plus marks; the calculated profile is shown as a solid line. Tick marks below the profile mark the positions of allowed reflections. The differences between the observed and the calculated intensities are shown at the bottom. The sample contains untransformed orthorhombic Sr_2CuO_3 as an impurity phase.

Figure 3. Neutron powder diffraction data and the Rietveld refinement profiles for nonsuperconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized at ambient pressure from a hydroxometallate precursor. Refinements were performed based on (a) the average T structure, and (b) a simplified modulated supercell. Format is the same as Fig. 2. The sample contains SrO as an impurity phase.

Figure 4. Electron microscopy image of superconducting $\text{Sr}_2\text{CuO}_{3+\delta}$ synthesized under high pressure. The inset is an electron diffraction pattern for this sample taken with the incident electron beam along the c -axis.

Figure 5. Schematic drawing of SrO plane in the simplified modulated superstructure with a $4\sqrt{2}a \times 4\sqrt{2}a \times c$ unit cell. Closed circles represent Sr atoms and open circles represent O(2) atoms. a_p is the lattice parameter of the average T structure.

Figure 6. Structures of (a) orthorhombic Sr_2CuO_3 and (b) "average" tetragonal $\text{Sr}_2\text{CuO}_{3+\delta}$. The oxygen sites in the CuO_2 plane of the tetragonal compound are nearly half empty.

Fig. 1. Y. Shimakawa et al.

Fig. 2(b). Y. Shimakawa et al.

Fig. 3(a). Y. Shimakawa et al.

Fig. 3(b). Y. Shimakawa et al.

Fig. 4. Y. Shimakawa et al.

Fig.5 Y. Shimakawa et al.

Fig. 6 Y. Shimakawa et al.