

Superconductivity in the Sr-Ca-Cu-O system and the phase with infinite-layer structure

H. Shaked,* Y. Shimakawa,† B. A. Hunter,‡ R. L. Hitterman, and J. D. Jorgensen

Materials Science Division and Science and Technology Center for Superconductivity, Argonne National Laboratory, Argonne, Illinois 60439

P. D. Han and D. A. Payne

Materials Science and Engineering Department, University of Illinois, Urbana, Illinois 61801

(Received 25 August 1994; revised manuscript received 27 December 1994)

Superconductivity and structure in samples of (Sr,Ca)CuO₂ with the infinite-layer structure, prepared by high-pressure synthesis, have been studied using magnetic susceptibility measurements, small angle x-ray diffraction, and neutron diffraction. It is found that the superconducting ($T_c \sim 100$ K) samples in this system are phase impure and contain, in addition to the infinite-layer phase, members of the two homologous series Sr_{*n*-1}Cu_{*n*+1}O_{2*n*} ($n=3,5,\dots$; orthorhombic), and Sr_{*n*+1}Cu_{*n*}O_{2*n*+1+ δ} ($n=1,2,\dots$; tetragonal), as minor phases. Samples with larger phase fractions of the Sr_{*n*+1}Cu_{*n*}O_{2*n*+1+ δ} compounds showed higher superconducting fractions. Phase-pure infinite-layer samples are not superconducting. Based on these results, and results previously published in the literature, it is proposed that the superconductivity in these infinite-layer samples comes from the tetragonal Sr_{*n*+1}Cu_{*n*}O_{2*n*+1+ δ} compounds, not from the phase with the infinite-layer structure.

I. INTRODUCTION

The cuprate $ACuO_2$ (A =alkaline earth) with the infinite layer (IL) structure was first synthesized in 1988.¹ This layered structure, which is the simplest among all superconducting cuprates, is tetragonal and consists of CuO₂ planes and cationic A planes, alternately stacked along the c axis (see Fig. 1, where A =Sr,Ca). At ambient pressure, Sr_{1- x} Ca _{x} CuO₂ can be stabilized in the IL structure only near the composition $x \sim 0.92$ – 0.82 , which is not superconducting.¹⁻³ However, when synthesis is done at high oxygen pressure (~ 4 – 6 GPa) and high temperature ($\sim 1050^\circ\text{C}$) the composition range can

be extended and small fractions of superconductivity are observed (as described below). Using high-pressure synthesis, samples of Sr_{1- x} M _{x} CuO₂ with the IL structure have been obtained for divalent M =Ba with $0 < x < 1/3$,⁴ Ca (Refs. 2, 3, and 5–10) with $0 < x < 0.7$, and for trivalent M =Nd (Refs. 11 and 12), Pr (Ref. 11), La (Refs. 12–14), Sm (Ref. 12), Gd (Ref. 12), and Y (Ref. 15) with $0 < x < 0.16$.

Cuprates of the IL structure with trivalent M are electron-doped superconductors with a maximum T_c of about 40 K, and have been obtained phase pure with large superconducting fractions.¹¹⁻¹⁴ Upon substitution of the small M^{3+} ion for the larger Sr²⁺ ion, these superconductors show an *increase* in the Cu-O bond length, as expected if electrons were added to the CuO₂ plane.¹⁶⁻²⁰

Superconducting cuprates were also obtained with divalent M for various ratios, $y = (\text{alkaline earth})/\text{Cu}$, in the starting mixture. Samples of starting composition (Ba_{0.2}Sr_{0.8}) _{y} CuO₂ with $y \sim 0.8$ – 1.0 (Ref. 4) and (Sr_{0.7}Ca_{0.3}) _{y} CuO₂ with $y \sim 0.9$ (Ref. 6) and $y = 1.1$ (Refs. 21 and 22) exhibited $T_c \sim 90$, 110, and 110 K, respectively. These samples are thought to be hole-doped superconductors because they do not show the increase in the Cu-O bond-length characteristic of electron doping. However, these “hole-doped” samples are invariably phase impure,^{4,6,10,21-23} exhibit small superconducting volume fractions ($< 10\%$), can incorporate a high concentration of structural planar defects,^{4,6,8,22,24} and do not show the decrease in Cu-O bond length expected of hole doping.¹⁶⁻²⁰ Phase-pure samples of (Sr_{0.7}Ca_{0.3}) _{y} CuO₂ were obtained with $y = 1$ but were not superconducting.^{22,23} Moreover, since the substitution (Ca and Sr on the A site) is divalent, the source of doping is not understood. One proposal is that the planar defects act as the doping mechanism.^{6,10,24} Phase-pure samples of Sr_{0.14}Ca_{0.86}CuO₂ (prepared in ambient pres-

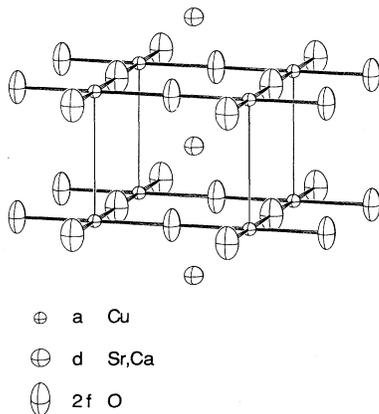


FIG. 1. Crystal structure of the infinite-layer phase of (Sr,Ca)CuO₂. The Wyckoff site designation (Ref. 39) is given. The anisotropic thermal factors found in the Rietveld refinement (Table I) are represented by the anisotropic shape of the oxygen atoms.

sure¹) and a single crystal of $\text{Sr}_{0.74}\text{Ca}_{0.26}\text{CuO}_2$ (Ref. 25) could not be made superconducting. Thin films that are phase pure and defect free can be made superconducting when electron doped.²⁶ No superconductivity has been found in many studies of films that are intended to be hole doped.^{27–30} However, in a recent study of thin films of $(\text{Sr,Ca})\text{CuO}_2$ and $(\text{Sr,Ca})_{0.8}\text{Na}_{0.2}\text{CuO}_2$ superconductivity with $T_c \sim 90, 125, 130$ K was reported, but the superconducting phases were not identified.^{31,32}

The IL structure and the T' structure,³³ where electron-doped superconductivity is found, bear a close resemblance. Both structures contain square CuO_2 planes with no apical oxygen. To the best of our knowledge, no hole-doped superconductivity has been found in layered cuprates without apical oxygen atoms³⁴ except for the claims of hole-doped superconductivity in the IL compound (also, no electron-doped superconductivity was found in layered cuprates with apical oxygen atoms). Furthermore, as the number of adjacent CuO_2 layers in the superconducting layered cuprates is increased, T_c reaches a maximum at 3 or 4 layers; upon further increase (as the structure converges towards the IL structure, i.e., the nonapical oxygen structure), T_c monotonically decreases, as was recently shown in $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ ($n=1, 2, \dots, 8$).³⁵ In view of these considerations it is widely accepted that the source of the (90–130)-K (which will be referred to as 100 K below) superconductivity in these samples is not understood and requires explanation.

In the present paper, we report results obtained in our study of samples of $(\text{Sr}_{0.7}\text{Ca}_{0.3})_y\text{CuO}_2$ by magnetic susceptibility, x-ray diffraction, and neutron powder diffraction, and of a sample of $\text{Sr}_2\text{CuO}_{3+\delta}$ by magnetic susceptibility and x-ray diffraction. On the basis of these results and the wide variety of results published in the literature, we present a reasonable explanation for the source of the 100-K superconductivity in samples of $(\text{Sr,Ca})_y\text{CuO}_2$ with the IL structure.

II. EXPERIMENT AND ANALYSIS

Samples of $(\text{Sr}_{0.7}\text{Ca}_{0.3})_y\text{CuO}_2$ with a metal ratio of $y=1.1$ in the starting mixture were prepared using the methods described previously.²¹ The synthesis was done at a pressure of 5.7 GPa and a temperature of 1050°C in an opposed-anvil belt press. An important difference between our synthesis procedure and those used previously is the large sample volume we can achieve. Pressed pellets of starting materials of roughly 3-g mass were loaded into a gold capsule sandwiched between two flat pellets (~ 0.3 g) of KClO_4 as shown in Fig. 2. Pressure is applied first, and then the temperature is raised. Upon heating, the KClO_4 decomposes to provide a source of high-pressure oxygen that is contained within the gold capsule during the synthesis. Using this method, it is speculated that oxygen pressures as high as the sample pressure (5.7 GPa in this case) can be achieved; however, the actual oxygen pressure is not known.

The product of the high-pressure synthesis was a sintered cylindrical pellet. We found that properties were

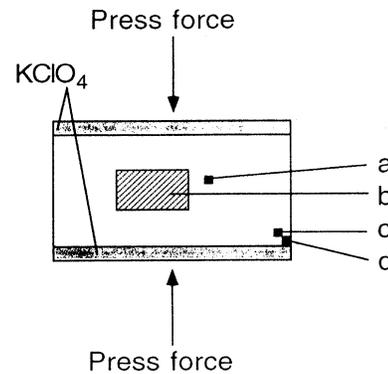


FIG. 2. Configuration of the sample starting materials and KClO_4 oxygen source used for high-pressure synthesis. Letters *a*, *b*, *c*, and *d* mark the positions of individual small samples investigated in the present study.

not homogeneous across this pellet. This allowed us to correlate superconducting phase fraction with other properties by comparing small samples extracted from different positions in the pellet. Four specimens were extracted from different positions as shown schematically in Fig. 2. Magnetic susceptibility measurements showed that specimen *a* was not superconducting and specimens *b*, *c*, and *d* were superconducting with a T_c of about 100 K (Fig. 3). The diamagnetic signals correspond to superconducting volume fractions of 0, 4, 10, and 20 % for *a*, *b*, *c*, and *d*, respectively. X-ray powder diffraction (XRD) showed that a phase with the IL structure was the major phase in all four specimens. The XRD data of the superconducting specimens (*b, c, d*) also showed contributions from other phases, but the XRD data of the nonsuperconducting specimen (*a*) showed no additional phases. The Bragg reflections from the additional phases are most easily seen in small-angle XRD data, where there are no reflections from the IL phase, as shown in Fig. 4. These high- d reflections were indexed using $00l$ ($l=\text{even}$) reflections of two phases with $c=27.8$, and 20.4 Å.

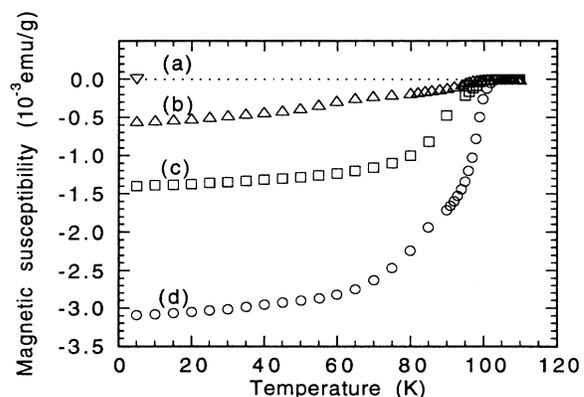


FIG. 3. Field-cooled (10-G) dc magnetic susceptibilities as a function of temperature for the four specimens *a*, *b*, *c*, and *d*. Specimen *a* was measured only at 4.2 K, and the dotted line is a guide to the eye.

These values correspond to the c parameters of tetragonal $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ and $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$,^{7,9,36} leading us to conclude that these phases, which are known to form under similar high-pressure synthesis conditions, are present as minor phases.

Neutron-powder-diffraction data were collected for specimens b and d on the Special Environment Powder Diffractometer³⁷ at Argonne's Intense Pulsed Source. The data collection times were 8 and 45 h for specimen b (400 mg) and d (17.7 mg), respectively. In order to minimize the background, the specimens were mounted on a thin boron-coated tungsten wire with no sample container. The structures were refined by the Rietveld technique³⁸ using the high-resolution data from the back-scattering (145°) detector banks. The tetragonal space-group $P4/mmm$ was used for the IL structure (major phase). The minor phases included in the analyses were $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ [space-group $Cmmm$ (Refs. 39 and 40)], which was identified in the XRD data (full pattern not shown) for sample b , and $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ [space-group $I4/mmm$

(Refs. 39 and 36)], which as identified in the small-angle XRD data [3 L, Fig. 4(d)] for sample d . Refined structural parameters are given in Tables I and II, and the Rietveld refinement profiles are shown in Fig. 5. Three-phase refinements where the third phase was $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$ or $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ for specimen b , and $\text{Sr}_3\text{Cu}_2\text{O}_5$ for specimen d , did not improve the fit to the observed patterns. These results are consistent with the low-angle XRD data (Fig. 4), which show only a small contribution from $\text{Sr}_3\text{Cu}_2\text{O}_5$ in specimen b and a dominant contribution from $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ in specimen d . These refinements served to confirm the identify of the minor phases and provide a quantitative measure of the phase fractions (as given in Tables I and II).

We note that our diffraction experiments yield an explanation for the sample inhomogeneity that is consistent with the synthesis process. Specimens c and d , which were extracted from a location near the source of oxygen (KClO_4) contain $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$ and $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$, whereas, specimen b , located further from the oxygen source, was

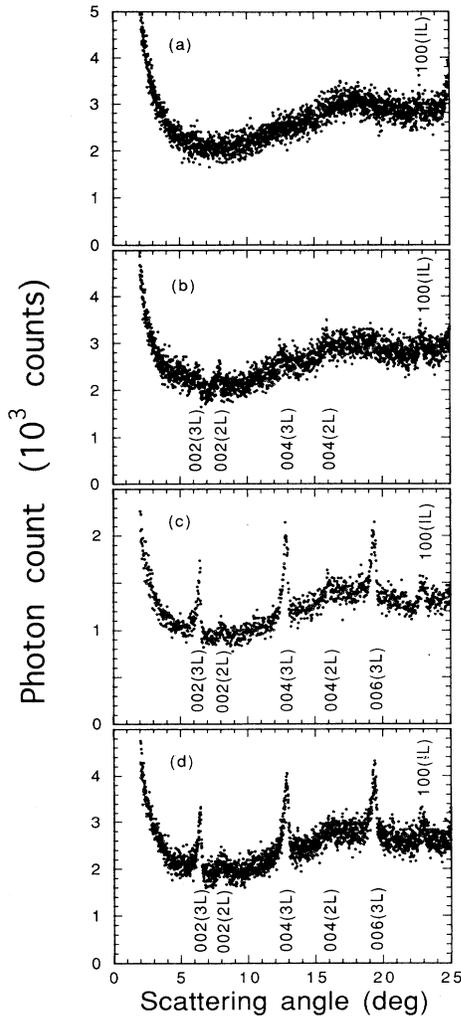


FIG. 4. Small-angle x-ray-diffraction data for the four specimens a , b , c , and d . Contributions from $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ (3 L), $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$ (2 L), and $(\text{Sr,Ca})\text{CuO}_2$ (IL) are observed.

TABLE I. Structural parameters for the two phases obtained from the Rietveld refinements of the neutron diffraction data of specimen b . Numbers in parentheses are standard deviations of the last significant digit. Parameters with no standard deviations were not refined. Scattering amplitudes (10^{-12} cm): 0.702, 0.490, 0.7719, and 0.5803 were used for Sr, Ca, Cu, and O, respectively (Ref. 41).

Parameter		Value
First phase: $(\text{Sr,Ca})\text{CuO}_2$; Space group: $P4/mmm$		
$a = b$ (\AA)		3.9035(1)
c (\AA)		3.3452(1)
V (\AA^3)		50.972(4)
Sr,Ca	$x = y = z$	0.5
	$n(\text{Sr}) = 1 - n(\text{Ca})$	0.62(3)
	B (\AA^2)	0.50(3)
Cu	$x = y = z$	0
	n	1
	B (\AA^2)	0.46(3)
O	x	0.5
	$y = z$	0
	n	0.97(1)
	U_{11} (\AA^2)	0.0047(5)
	U_{22} (\AA^2)	0.0083(5)
	U_{33} (\AA^2)	0.0126(6)
R_F^2 (%)		6.63
Volume fraction (%)		87(2)
Second phase: $\text{Sr}_4\text{Cu}_6\text{O}_{10}$; Space group: $Cmmm$		
a (\AA)		3.9192(4)
b (\AA)		19.345(2)
c (\AA)		3.4063(4)
V (\AA^3)		258.26(4)
R_F^2 (%)		11.92
Volume fraction (%)		13(2)
Overall agreement factors		
R_{wp} (%)		8.354
R_{ex} (%)		7.168

TABLE II. Structural parameters for the two phases obtained from the Rietveld refinements of the neutron diffraction data of specimen *d*. Numbers in parenthesis are standard deviations of the last significant digit. Parameters with no standard deviations were not refined. Scattering amplitudes (10^{-12} cm): 0.702, 0.490, 0.7719, and 0.5803 were used for Sr, Ca, Cu, and O, respectively (Ref. 41).

Parameter	Value
First phase: (Sr,Ca)CuO ₂ ; Space group: <i>P4/mmm</i>	
$a=b$ (Å)	3.9046(1)
c (Å)	3.3460(1)
V (Å ³)	51.014(6)
R_F^2 (%)	10.73
Volume fraction (%)	73(6)
Second phase: Sr ₄ Cu ₃ O ₈ ; Space group: <i>I4/mmm</i>	
$a=b$ (Å)	3.8730(5)
c (Å)	27.39(2)
V (Å ³)	410.8(3)
R_F^2 (%)	11.59
Volume fraction (%)	27(6)
Overall agreement factors	
R_{wp} (%)	13.86
R_{ex} (%)	11.66

found to contain Sr₄Cu₆O₁₀. This is consistent with the results of a detailed study of the pressure synthesis of small samples, which showed that Sr_{*n*+1}Cu_{*n*}O_{2*n*+1+δ} forms under high pressure when a source of oxygen (such as KClO₄) is present and Sr_{*n*-1}Cu_{*n*+1}O_{2*n*} forms under normal high-pressure conditions.¹⁰ A pressure gradient across the sample during synthesis could also contribute to the compositional inhomogeneity.

III. DISCUSSION

The correlation between the superconducting phase fraction and the abundance of Sr_{*n*+1}Cu_{*n*}O_{2*n*+1+δ} phases leads us to conclude that the latter phases, which are reported to be superconducting with maximum T_c 's in the range of 100 K,^{7,9,36} are responsible for superconductivity in our "infinite-layer" samples. In further support of this conclusion, we argue (as follows) that the lattice parameters of the infinite layer phases in our samples are not consistent with what one would expect if they were doped with holes. As Sr²⁺ is replaced by the smaller Ca²⁺ ion (isoelectronic replacement) in the IL structure, the lattice parameters a and c decrease because of the size effect⁴³ with a linear relation between a and c . With nonisoelectronic replacement, e.g., as Sr²⁺ is replaced by the smaller La³⁺ ion, the c parameter decreases because of the size effect,⁸ whereas, the a parameter expands due to the addition of electrons to the Cu—O bond.¹⁶⁻²⁰ This behavior is delineated in Fig. 6 for samples of (Sr,*M*)CuO₂ with $M=Ca$ (insulating^{1,2,21,25} and superconducting^{6,8,21} samples) and for $M=La$ (Ref. 13) and Nd (Ref. 11) (superconducting samples). The expected increase in a due to the electron doping of the CuO₂ planes in the $M=La,Nd$

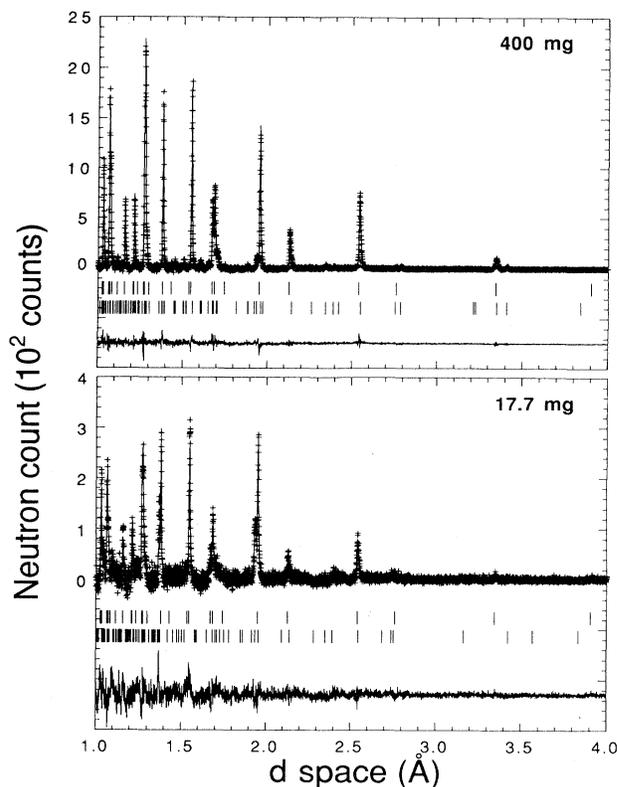


FIG. 5. Portions of the neutron-powder-diffraction data and Rietveld refinement profiles for specimens *b* and *d*. The + signs represent the raw time-of-flight neutron-powder-diffraction data. The solid line represents the calculated profile. Tick marks represent the positions of the allowed Bragg reflections (two phases for each specimen, see Tables I and II). The background was fit as a part of the refinement but has been subtracted prior to plotting. A difference curve (observed minus calculated) is plotted at the bottom for each profile. Small-angle XRD and magnetic susceptibility were measured on a specimen broken off the neutron diffraction *b* specimen (400 mg) prior to the neutron diffraction.

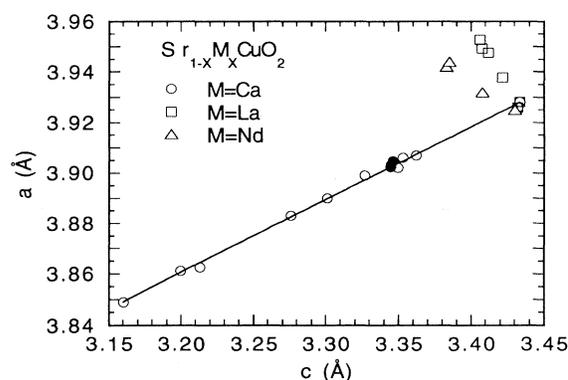


FIG. 6. Relation between the lattice constants a and c , of Sr_{1-*x*}M_{*x*}CuO₂, for various substitutions $M=Ca$ (Refs. 1, 2, 6, 8, 21, and 25), and La (Ref. 13), Nd (Ref. 11), and values of x . The solid line was obtained by a linear fit to the $M=Ca$ data and represents the size effect. The neutron-diffraction results for specimens *b* and *d* (Tables I and II) are represented by the closed circles.

samples is clearly observed. The addition of holes to the Cu—O bonds should cause an opposite effect (i.e., decrease) of similar magnitude on the a parameter.^{16–20} The values for a for a hole-doped IL lattice would, therefore, be expected to appear below the “size effect” line of a vs c that applies to insulating compounds. The IL lattice parameters for the superconducting specimens of the present work (closed circles, Fig. 6), as well as other hole-doped superconducting^{6,8,21} and nonsuperconducting^{1,2,21,25} samples fit a single size effect line. The deviation from this line, which is clearly observed in the case of electron doping, is not observed in the hole-doped superconducting samples. This result strongly suggests that this IL material is not hole doped and, thus, implies that it is not superconducting.

An alternative explanation that must be considered is that only a fraction of the IL material is hole doped (and superconducting). Such a situation could occur if only part of the material had a high enough density of planar defects to provide the required doping. We used the neutron diffraction data for sample *d* (20% superconducting fraction) to explore the possibility of two phases with the IL structure, but with slightly different lattice parameters resulting from one phase being hole doped (and therefore superconducting) and the other not. Such a model could explain the small superconducting phase fractions. We estimate that the lattice parameters of a hole-doped IL lattice should map a point onto the a -vs- c plane that should deviate by 0.01–0.02 Å from the size effect line of Fig. 6. If 20% or more of the sample (corresponding to the 20% superconducting fraction of sample *d*) displayed these lattice parameters, it should be possible to model the resulting distinctive line broadening with a two-phase Rietveld refinement. It was not possible to achieve convergence using such models, leading us to conclude that specimen *d* does not contain a hole-doped fraction with the IL structure that is responsible for the 20% superconducting volume fraction observed in this specimen. Moreover, we do not see any significant difference in line broadening between the various samples, as would be expected if there were substantial differences in the density of planar defects.

The small-angle XRD data (Fig. 4) show significant contributions from $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ in the specimens with the largest superconducting fractions (*c, d*), a small contribution from $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ in the specimen with smaller superconducting fraction (*b*), and no contribution in the nonsuperconducting specimen (*a*). The volume fraction of $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ in specimen *d*, as estimated from the refinement of the neutron data, is about 30%. These results show that the superconducting volume fraction scales with the volume fraction of $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ and suggest that the source of superconductivity is this phase with the likelihood that other phases of the homologous series $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ also contribute. This conclusion is consistent with several previous studies of superconducting samples of $(\text{Sr},\text{Ca})\text{CuO}_2$, where these same minor phases were found.^{7,9,23,44}

There are several unresolved questions concerning superconductivity in the $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ series of compounds. The structures of these compounds, and their re-

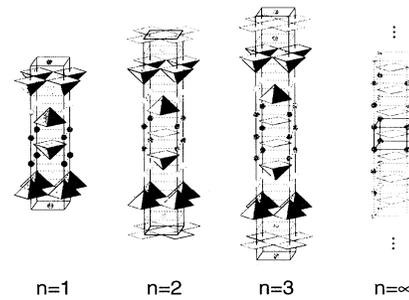


FIG. 7. Structures of the $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ compounds for $n=1, 2,$ and 3 and the infinite layer compound, $n=\infty$. Tetrahedra and square sheets represent five- and four-coordinated copper atoms with their associated oxygen atoms, respectively. Circles represent Sr atoms.

lationship to the IL structure, are illustrated in Fig. 7. The cuprate $\text{Sr}_2\text{CuO}_{3+\delta}$, the first member of this series, which was synthesized under high pressure, was reported to be superconducting with $T_c \sim 70$ K and a superconducting volume fraction of 22%.³⁶ However, the sample contained some $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$ as a second phase. A neutron diffraction study of the structure of this cuprate revealed that its CuO_2 planes are highly (nearly half) oxygen deficient,⁴⁵ raising serious doubts about whether these planes can support superconductivity. As part of the present study, we investigated the minor phases present in a superconducting sample of $\text{Sr}_2\text{CuO}_{3+\delta}$. The sample was prepared at 5-GPa pressure and 930°C as described previously.⁴² The magnetic susceptibility of a small specimen of the sample measured as a function of temperature showed $T_c \sim 70$ K with a superconducting fraction of $\sim 5\%$, as shown in Fig. 8. Small-angle XRD of the same specimen showed contributions from $\text{Sr}_2\text{CuO}_{3+\delta}$ (1 L, major phase), $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$ (2 L), and $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ (3 L) as shown in Fig. 8. A conclusion consistent with all of our results is that the members of the homologous series $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ are superconducting as was previously reported,^{7,9,36} except for the first member, $\text{Sr}_2\text{CuO}_{3+\delta}$, which is *not* superconducting. This conclusion is consistent with the fact that phase-pure samples of $\text{Sr}_2\text{CuO}_{3+\delta}$ prepared by a low-temperature synthesis technique⁴⁶ and having a structure *identical* to that of “superconducting” samples obtained by high-pressure synthesis,⁴⁵ are *not* superconducting.

We have attempted to assign specific transition temperatures, T_c , to the $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ phases ($n=2,3,4$), as identified in the present work and in the literature, in a consistent way. This attempt proved unsuccessful. We believe that this difficulty arises because the T_c for each phase can vary depending on oxygen content (which is controlled by preparation conditions). Such a variation has been reported for material of nominal composition $\text{Sr}_2\text{CuO}_{3+\delta}$, where T_c was changed from 70 K in an as-made sample to 94 K by N_2 heat treatment at 310°C for 1 h.⁴² (Note that we would propose that it is actually a 2-L or 3-L minor phase in this sample, not the dominant 1-L phase, whose T_c is changing.) Because of this difficulty, the assignment of specific T_c 's to the members of the

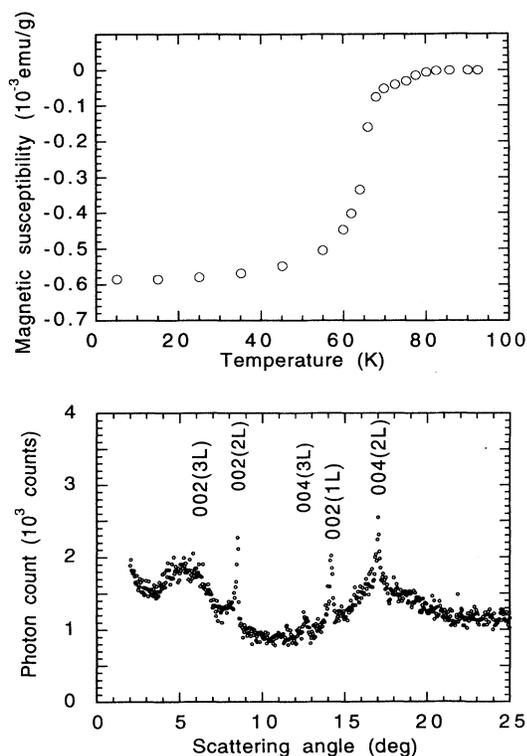


FIG. 8. Field-cooled (10-G) dc magnetic susceptibilities as a function of temperature (top), and small-angle x-ray diffraction of a specimen of tetragonal $\text{Sr}_2\text{CuO}_{3+\delta}$ (1 L). Contributions from $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$ (2 L) and $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$ (3 L, very small) are observed.

series $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1+\delta}$ will probably not be possible until single-phase samples of the members of the series are available.

With this conclusion, superconductivity in the cuprates of the IL structure conforms with the empirical rule that CuO_2 layers with no apical oxygen support electron superconductivity but not hole superconductivity.¹⁶⁻¹⁹ However, it is possible that an appropriate way to hole dope the IL structure has simply not yet been found. Thus, the search for hole-doped superconducting IL phases should continue. The choice of the appropriate Cu-O bond length for hole-doping is essential. The bond length to an oxygen atom for a (pure $3d^9$) Cu^{2+} ion is nominally 1.95 Å,⁴³ which corresponds to $a=3.90$ Å in the cuprates with the IL structure. To be susceptible to electron-doping ($3d^9, 3d^{10}$) the bond length should be longer (under tension).^{17,19} Successful electron doping

(by La or Nd substitution) was indeed achieved with SrCuO_2 , for which $a=3.918$ Å prior to doping (Fig. 6). To be susceptible to hole-doping ($3d^9, 3d^8$) the bond length should be shorter (under compression).^{17,19} Taking a lattice change of the same magnitude as in the case of electron-doping (but an opposite sign), one might predict $a=3.882$ Å as the expected a lattice parameter appropriate for hole doping. Hence, following the above considerations, the IL phase $\text{Sr}_{0.4}\text{Ca}_{0.6}\text{CuO}_2$, having $a=3.882$ Å (see the references associated with Fig. 6), may be the most susceptible to hole doping.

IV. CONCLUSIONS

Cuprates of the IL structure have CuO_2 layers with no apical oxygen. These materials can be electron doped and exhibit bulk superconductivity with $T_c \sim 40$ K. Superconductivity with $T_c \sim 90-130$ K has been reported in many samples of the IL structure claimed to be hole doped. However, these samples are invariably phase impure and exhibit small superconducting fractions. We conclude that the superconductivity in these samples can be attributed to the phases $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$, $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$, and $\text{Sr}_5\text{Cu}_4\text{O}_{9+\delta}$ and not the major phase with the IL structure. Hence, for presently known materials, superconductivity in the cuprates with the IL structure is consistent with the empirical rule that CuO_2 layers with no apical oxygen support only electron superconductivity.

The preparation of single-phase samples of $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$, $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$, and $\text{Sr}_5\text{Cu}_4\text{O}_{9+\delta}$ for the purpose of characterization and optimization of their superconducting properties is a primary future goal. Attempts to hole-dope the IL phase should also continue.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Division of Basic Energy Sciences—Material Science, under Contract No. W-31-19-ENG-38 (J.D.J. and R.L.H.), the National Science Foundation, Science and Technology Center for Superconductivity under Grant No. DMR 91-20000 (H.S., B.A.H., P.D.H., and D.A.P.), the Nuclear Research Center—Negev and Ben Gurion University in the Negev (H.S.), and the NEC Corporation, Japan (Y.S.). The Intense Pulsed Neutron Source is operated as a user facility by the U.S. Department of Energy, Division of Basic Energy Sciences—Material Science, under Contract No. W-31-109-ENG-38.

*Permanent address: Department of Physics, Nuclear Research Center-Negev, P.O.B. 9001, Beer Sheva, Israel 84190 and Department of Physics, Ben-Gurion University of the Negev, P.O.B. 653, Beer Sheva, Israel 84105.

†Permanent address: Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305, Japan.

‡Permanent address: Australian Nuclear Science and Technolo-

gy Organization, Private Mail Bag 1, Menai, N.S.W. 2234, Australia.

¹T. Siegrist, S. M. Zahurak, D. W. Murphy, and R. S. Roth, *Nature* (London) **334**, 231 (1988).

²M. Takano, Y. Takeda, H. Okada, M. Miyamoto, and T. Kusaka, *Physica C* **159**, 375 (1989).

³C.-J. Liu, S. Koriyama, and H. Yamauchi, *Physica C* **215**, 395

- (1993).
- ⁴M. Takano, M. Azuma, Z. Hiroi, Y. Bando, and Y. Takeda, *Physica C* **176**, 441 (1991).
 - ⁵Z. Hiroi, M. Takano, M. Azuma, Y. Takeda, and Y. Bando, *Physica C* **185-189**, 523 (1991).
 - ⁶M. Azuma, Z. Hiroi, M. Takano, Y. Bando, and Y. Takeda, *Nature (London)* **356**, 775 (1992).
 - ⁷S. Adachi, H. Yamauchi, S. Tanaka, and N. Mori, *Physica C* **208**, 226 (1993).
 - ⁸Z. Hiroi, M. Azuma, M. Takano, and Y. Takeda, *Physica C* **208**, 286 (1993).
 - ⁹S. Adachi, H. Yamauchi, S. Tanaka, and N. Mori, *Physica C* **212**, 164 (1993).
 - ¹⁰M. Takano, *J. Supercond.* **7**, 49 (1994).
 - ¹¹M. G. Smith, A. Manthiram, J. Zhou, J. B. Goodenough, and J. T. Markert, *Nature (London)* **351**, 549 (1991).
 - ¹²N. Ikeda, Z. Hiroi, M. Azuma, M. Takano, Y. Bando, and Y. Takeda, *Physica C* **210**, 367 (1993).
 - ¹³G. Er, Y. Miyamoto, F. Kanamaru, and S. Kikkawa, *Physica C* **181**, 206 (1991).
 - ¹⁴J. D. Jorgensen, P. G. Radaelli, D. G. Hinks, J. L. Wagner, S. Kikkawa, G. Er, and F. Kanamaru, *Phys. Rev. B* **47**, 14 654 (1993).
 - ¹⁵X. Zhou, Y. Yao, C. Dong, J. Li, S. Jia, and Z. Zhao, *Physica C* **219**, 123 (1994).
 - ¹⁶A. W. Sleight, *Science* **24**, 1519 (1988).
 - ¹⁷J. B. Goodenough, *Supercond. Sci. Technol.* **3**, 26 (1990).
 - ¹⁸M. Brian, *MRS Bull.* **XV**, 60 (1990).
 - ¹⁹Y. Tokura, *Comments Condens. Mater. Phys.* **16**, 69 (1992).
 - ²⁰J. K. Burdett, *Physica C* **191**, 282 (1992).
 - ²¹H. Shaked, Y. Shimakawa, B. A. Hunter, P. G. Radaelli, B. Dabrowski, R. L. Hitterman, J. D. Jorgensen, P. D. Han, D. A. Payne, S. Kikkawa, G. Er, and F. Kanamaru, *Phys. Rev. B* **50**, 12 752 (1994).
 - ²²P. D. Han (unpublished).
 - ²³C. Prouteau, P. Strobel, J. J. Capponi, C. Chaillout, and J. L. Tholence, *Physica C* **228**, 63 (1994).
 - ²⁴H. Zhang, Y. Y. Wang, H. Zhang, V. P. Dravid, L. D. Marks, P. Han, D. A. Payne, P. G. Radaelli, and J. D. Jorgensen, *Nature (London)* **370**, 352 (1994).
 - ²⁵G. Berghöfer, W. Pietzuch, and D. Reinen, *J. Solid State Chem.* **108**, 395 (1994).
 - ²⁶E. C. Jones, D. P. Norton, D. K. Christen, and D. H. Lowndes, *Phys. Rev. Lett.* **73**, 166 (1994).
 - ²⁷H.-S. Wang, W. Dietsche, and X.-Q. Pan, *Z. Phys. B* (to be published).
 - ²⁸D. P. Norton, B. C. Chakoumakos, E. C. Jones, D. K. Christen, and D. H. Lowndes, *Physica C* **217**, 146 (1993).
 - ²⁹K. Kubo, M. Ichikawa, N. Sugii, K. Yamamoto, and H. Yamauchi, *Phys. Rev. B* **49**, 6919 (1994).
 - ³⁰R. Feenstra, X. Li, M. Kanai, T. Kawai, S. Kawai, J. D. Budai, E. C. Jones, Y. R. Sun, J. R. Thompson, S. J. Pennycook, and D. K. Christen, *Physica C* **224**, 300 (1994).
 - ³¹X. Li, T. Kawai, and S. Kawai, *Jpn. J. Appl. Phys.* **31**, 934 (1992).
 - ³²X. Li and T. Kawai, *Physica C* **229**, 251 (1994).
 - ³³Y. Tokura, H. Takagi, and S. Uchida, *Nature (London)* **337**, 345 (1989).
 - ³⁴Y. Tokura and T. Arima, *Jpn. J. Appl. Phys.* **29**, 2388 (1990).
 - ³⁵B. A. Scott, E. Y. Suard, C. C. Tsuei, D. B. Mitzi, T. R. McGuire, B.-H. Chen, and D. Walker, *Physica C* **320**, 239 (1994).
 - ³⁶Z. Hiroi, M. Takano, M. Azuma, and Y. Takeda, *Nature (London)* **364**, 315 (1993).
 - ³⁷J. D. Jorgensen, J. Faber, Jr., J. M. Carpenter, R. K. Crawford, J. R. Haumann, R. L. Hitterman, R. Kleb, G. E. Ostrowski, F. J. Rotella, and T. G. Worlton, *J. Appl. Crystallogr.* **22**, 321 (1989).
 - ³⁸F. J. Rotella, *Users Manual for Rietveld Analysis of Time of Flight Neutron Diffraction Data at IPNS, Argonne National Laboratory, IPNS report, 1988* (unpublished); R. B. Von Dreele, J. D. Jorgensen, and C. G. Windsor, *J. Appl. Crystallogr.* **15**, 581 (1982).
 - ³⁹*International Tables for Crystallography, Volume A, Space-Group Symmetry*, edited by T. Hahn (Reidel, Dordrecht, 1987), p. 468.
 - ⁴⁰Z. Hiroi, M. Azuma, M. Takano, and Y. Bando, *J. Solid State Chem.* **95**, 230 (1991).
 - ⁴¹*International Tables for Crystallography, Volume C, Mathematical, Physical and Chemical Tables*, edited by A. J. C. Wilson (Reidel, Dordrecht, 1983), p. 384.
 - ⁴²P. D. Han, L. Chang, and D. A. Payne, *Physica C* **228**, 129 (1994).
 - ⁴³R. D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).
 - ⁴⁴S. Adachi, H. Yamauchi, S. Tanaka, and N. Mori, *J. Supercond.* **7**, 55 (1994).
 - ⁴⁵Y. Shimakawa, J. D. Jorgensen, J. F. Mitchell, B. A. Hunter, H. Shaked, D. G. Hinks, and R. L. Hitterman, *Physica C* **228**, 73 (1994).
 - ⁴⁶J. F. Mitchell, D. G. Hinks, and J. L. Wagner, *Physica C* **227**, 279 (1994).