and V_D and tended toward an insulator behavior.

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Registry No. CdS, 1306-23-6; Ti, 7440-32-6; H_2S, 7783-06-4; NaCl, 7647-14-5; In, 7440-74-6; KCl, 7447-40-7; O_2, 7782-44-7; H_2, 1333-74-0; arachidic acid, 506-30-9; graphite, 7782-42-5; cadmium arachidate, 14923-81-0.

Synthesis and Structure of a New Family of Cuprate Superconductors: $LnSr_2Cu_2GaO_7$

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The synthesis of layered cuprates with nonmagnetic and fixed oxidation state cations separating the Cu–O planes has, until now, led to nonsuperconducting materials. A new series of layered copper oxides with the general formula $LnSr_2Cu_2GaO_7$ (Ln = La–Yb, Y) has been synthesized. The structure has been studied by both powder neutron diffraction and single-crystal X-ray analysis. The typical unit cell is $a \approx 22.8$ Å, $b \approx 5.5$ Å, $c \approx 5.4$ Å, in space group *Ima*2 (No. 46). The structure is closely related to that of $YBa_2Cu_3O_7$ and can be described as replacement of the square-planar copper with a tetrahedral gallium. The larger lanthanides are distributed unevenly over the two A-cation sites, whereas the smaller lanthanides occupy the site between the cuprate planes. We have been able to introduce superconductivity in the Y–Sr–Cu–Ga–O system by appropriate doping with calcium and annealing.

Introduction

The importance of copper–oxygen layers in the high-temperature ($T_c > 35$ K) superconductors was realized in 1986[1] after the report by Bednorz and Müller on their work in the La-Ba-Cu-O system.[2] The conducting planes ($CuO_{4/2}$) of these materials result from the hybridization of the Cu(3d) and O(2p) orbitals, which form closely and symmetrically coordinated copper and oxygen atoms in square nets.[3] Other families of superconductors are $La_{2-x}M_xCuO_4$[1] ($M = Ca^{2+}, Sr^{2+}, Ba^{2+}$), $Nd_{2-x}Ce_xCuO_4$,[4] $YBa_2Cu_3O_{7-\delta}$,[5] $(Tl,Bi)_m(Ba,Sr)_2Ca_{n-1}Cu_nO_{m+2n+2}$[6,7] (*m*, *n* = integers), $Pb_2Sr_2LnCu_3O_{8+\delta}$[8] (Ln = lanthanides), and $La_{2-x}Sr_xCaCu_2O_6$.[9] All of these compounds can be described as an intergrowth of AO rocksalt layers with ABO_{3-x} perovskite units and have the general formula $(AO)_m(ABO_{3-x})_n$, where *m* and *n* are integers and B is copper. Although no theory on the mechanism of high-temperature superconductivity has gained acceptance, the observation of high-temperature superconductivity in this class of layered materials has led to a phenomenological understanding that superconductivity depends on the two-dimensional conducting planes with weak interplane coupling.

The influence of substitutions on superconductivity has been studied in great detail in $YBa_2Cu_3O_{7-\delta}$. All lanthanides have been substituted into the eight-coordinate yttrium position.[10] With the exception of praseodymium,[11] superconductivity is preserved. In contrast, the addition of small amounts of a transition or post-transition metal onto either the square-planar or square-pyramidal copper site generally resulted in the loss of superconductivity.[12]

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Table I. Atomic Positions for $LaSr_2Cu_2GaO_7$[a]

atom	Wyckoff sym	*x*	*y*	*z*	*B*, Å^2	occ
La(1)	4a	0	0	0	0.45 (3)	0.70 (1)
La(2)	8c	0.1510 (1)	0.9859 (3)	0.9985 (7)	0.36 (3)	0.15 (1)
Sr(1)	8c	0.1510 (1)	0.9859 (3)	0.9985 (7)	0.36 (3)	0.85 (1)
Sr(2)	4a	0	0	0	0.45 (3)	0.30 (1)
Cu	8c	0.0779 (1)	0.4992 (3)	0.9965 (7)	0.32 (2)	1.00
Ga	4b	1/4	0.4285 (3)	0.0370 (7)	0.50 (4)	1.00
O(1)	8c	0.0735 (1)	0.2478 (1)	0.2463 (8)	0.53 (4)	1.00
O(2)	8c	0.0700 (1)	0.7513 (7)	0.7492 (9)	0.51 (4)	1.00
O(3)	8c	0.1782 (1)	0.5490 (3)	0.9690 (7)	0.85 (3)	1.00
O(4)	4b	1/4	0.3752 (5)	0.3820 (8)	0.89 (5)	1.00

[a] Space group *Ima*2 (No. 46) with $a = 23.1425$ (9) Å, $b = 5.5662$ (2) Å, $c = 5.4648$ (2) Å.

Incorporation of the trivalent cations aluminum, iron, and cobalt is thought to occur on the square-planar copper site, whereas chromium or zinc is thought to go into the planes.[13,14] When large amounts of gallium or aluminum are incorporated, the new single-layer copper compounds $LaSrCuAlO_5$[15] and $LaSrCuGaO_5$[16] with the brownmillerite (Ca_2FeAlO_5) structure are formed. These structures reflect the preference for tetrahedral coordination by the group 13 elements. In this paper we report on a new series of double-layer copper compounds with the general formula $LnSr_2Cu_2GaO_7$ (Ln = La–Yb, Y), which are structurally similar to $YBa_2Cu_3O_7$. The copper–oxygen layers are separated by chains of $GaO_{4/4}$ tetrahedra instead of square-planar copper chains. The structure of $LaSr_2Cu_2GaO_7$ was determined by Rietveld refinement of powder neutron diffraction data, and the structure of $HoSr_2Cu_2GaO_7$ was solved from single-crystal X-ray data. In these systems, the composition $Y_{1-x}Ca_xSr_2Cu_2GaO_7$ ($x = 0.20$) was found to become superconducting at 30 K when annealed in high-pressure oxygen.

Experimental Section

Neutron Diffraction. A polycrystalline sample of $LaSr_2Cu_2GaO_7$ was prepared by heating stoichiometric amounts of La_2O_3 (Aldrich, 99.99%), $SrCO_3$ (Aldrich, 99.99%), Ga_2O_3 (Aldrich, 99.99%), and CuO (Aldrich, 99.999%). The sample was heated at 980 °C for 2 months with intermittent grindings. A time-of-flight data set was collected at room temperature and ambient pressure at the Intense Pulse Neutron Source (IPNS) facility at Argonne National Laboratory. Approximately 8 g of the sample was contained in a thin-walled vanadium can, and data were collected for 6 h. The data from 0.568 to 2.8931 Å were used to refine the structure. The unit cell was determined by using a nonlinear least-squares Marquet method after Bevington[17] to fit the peaks to an exponential rise and fall convoluted into a Gaussian shape, which is characteristic of the spallation neutron source.[18] The sample was essentially single phase, with a small $LaSrCuGaO_5$ (<5%) impurity.[16] A unit cell was determined from the peak positions by using the program TREOR[19] and refined with the program POLSQ[20] to a 23.160 (2) Å × 5.5706 (6) Å × 5.4682 (8) Å orthorhombic cell. The indexation revealed that body centering was one of the reflection conditions. The structure of $LaSr_2Cu_2GaO_7$ was solved by trial and error using a cell similar to $YBa_2Cu_3O_7$ as a starting model. The space group chosen was the noncentrosymmetric space group *Ima*2 (No. 46), because it allowed all of the atoms to be fully ordered. The structure was refined by the Rietveld method.[21] The scattering lengths used were 8.24, 7.02, 7.718, 7.288, and 5.803 fm, for the lanthanum, strontium, copper, gallium, and oxygen atoms, respectively. Fifty-one parameters were refined. In the final cycle all parameters were allowed to refine undamped, including the scale factor, six peak-shape parameters, five background parameters, the unit-cell parameters, positional, and isotropic thermal factors, the zero-point shift, and the diffractometer constant, as well as the absorption and extinction parameters. The atomic positions are shown in Table I. The final *R* factor was 3.29% ($4.62 R_{wtd}$).[22] The observed and calculated diffraction patterns and difference plot from 0.60 Å ≤ *d* ≤ 2.98 Å are shown in Figure 1.

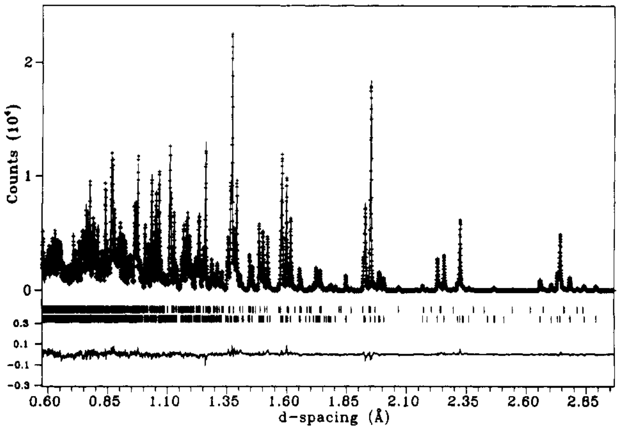

Figure 1. Observed (+), calculated (solid line), and difference (below) neutron diffraction pattern for $LaSr_2Cu_2GaO_7$ at room temperature. The upper tic marks indicate the reflections from impurity phase $LaSrCuGaO_5$, and the lower are $LaSr_2Cu_2GaO_7$.

During the refinement it was observed that the isotopic temperature factors of the lanthanum and strontium sites were very different, suggesting site mixing of the two atoms between the two positions. The occupancies were refined to 30% strontium on the 4a site and conversely 15% lanthanum on the 8c site.

X-ray Diffraction. Single crystals of $HoSr_2Cu_2GaO_7$ were isolated as thin black plates from a flux with the initial composition $HoSr_4Cu_{10}GaO_x$. The mixture was ground thoroughly and heated to 1040 °C in air, allowed to soak for 5 h, and cooled at 6 °C/h until 700 °C, followed by quenching to room temperature. The crystal chosen had the dimensions 0.018 mm × 0.33 mm × 0.18 mm. Diffraction studies were performed on an Enraf-Nonius CAD4 diffractometer with Mo Kα ($\lambda = 0.71069$ Å) radiation. The unit cell was determined from 25 setting reflections to be $a = 22.696$ (4) Å, $b = 5.484$ (4) Å, $c = 5.385$ (4) Å. Data were collected from 2 to 90° 2θ with the conditions $-h,+k,-l$. An additional data set was collected from 2 to 20° 2θ with the conditions $\pm h,\pm k,\pm l$

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(22) $R_{\text{profile}} = 100 \sum[|(Y_{\text{obs}} - Y_{\text{calc}})|]/\Sigma[(Y_{\text{obs}})]$; $R_{\text{weighted profile}} = 100 \times (\sum[W(Y_{\text{obs}} - Y_{\text{calc}})^2])^{1/2}/\sum[W(Y_{\text{obs}})^2]$. Y_{obs} and Y_{calc} are the observed and calculated profile intensities at the particular time-of-flight value, respectively, and *W* is the weight of Y_{obs}.

Table II. Summary of Crystallographic Data

formula	$HoSr_2Cu_2Ga_{0.72}Al_{0.28}O_7$	μ, cm^{-1}	365.91
formula wt	637.010	temp, °C	−120
cryst size	0.018 mm × 0.33 mm × 0.18 mm	scan type	$2\theta/\theta$
space group	*Ima*2 (No. 46)	2θ range, deg	2–90 (2–20)
lattice param, Å		indexes collected	$-h,+k,-l$ ($\pm h,\pm k,\pm l$)
a	22.696 (4)	R (R_{wtd})	0.061 (0.087)
b	5.484 (4)	no. of unique data	1678
c	5.385 (4)	no. of unique data with $I > 3\sigma(I)$	790
vol, Å^3	670.24	no. of variables	30
Z	4	secondary extinction coeff	3.609×10^{-7}
calcd density, g/cm^3	6.43		

Table III. Atomic Positions for $HoSr_2Cu_2GaO_7$

atom	Wyckoff sym	x	y	z	B, Å^2	occ
Ho	4a	0	0	0	0.27 (1)	1.00
Sr	8c	0.8491 (1)	0.0167 (2)	0.085 (7)	0.30 (2)	1.00
Cu	8c	0.9265 (8)	0.5008 (3)	0.997 (1)	0.21 (2)	1.00
Ga	4b	1/4	0.5710 (6)	0.9574 (8)	0.41 (6)	0.72 (1)
Al	4b	1/4	0.5710 (6)	0.9574 (8)	0.41 (6)	0.28 (1)
O(1)	8c	0.9362 (6)	0.762 (2)	0.760 (4)	0.5 (2)	1.00
O(2)	8c	0.9366 (5)	0.263 (3)	0.244 (5)	0.3 (2)	1.00
O(3)	8c	0.8227 (6)	0.450 (2)	0.011 (4)	0.8 (2)	1.00
O(4)	4b	1/4	0.872 (3)	0.105 (3)	0.2 (1)	1.00

[a] The space group is *Ima*2 (No. 46) with the unit cell a = 22.696 (4) Å, b = 5.484 (4) Å, c = 5.385 (4) Å.

to help resolve the centrosymmetric/noncentrosymmetric ambiguity and aid in space group determination. An analytical absorption correction (μ = 365.91 cm^{-1}) based on six indexed crystal faces and accurately measured distances between faces was applied by using the TEXSAN software package.[23] The transmission factors range from 0.022 to 0.510. Reflection conditions of hkl: $h + k + l = 2n$, $0kl$: $k + l = 2n$; $h0l$: $h, l = 2n$; $hk0$: $h + k = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; and $00l$: $l = 2n$, were consistent with the centrosymmetric space group *Imma* (No. 74) and the noncentrosymmetric space group *Ima*2 (No. 46). The data were refined in *Imma* and *Ima*2 using the complete data set consisting of all observed reflections and their Friedel opposites (790 reflections with $I > 3\sigma$). Refinement of the structure in the space group *Imma* (No. 74) with all the significant data resulted in R/R_{wtd} of 13.5%/21.9%. In contrast a refinement of the noncentrosymmetric structure and its inversion were refined to R/R_{wtd} values of the structure reported here of 6.07%/8.57% and for its indistinguishable inversion 6.10%/8.70%.[24] In comparing the centrosymmetric and noncentrosymmetric solutions, the disorder in the gallium and O(4) positions required by the centric structure results in unreasonably large isotropic temperature factors for atoms O(4) and O(3). In contrast reasonable values are obtained in the noncentrosymmetric solution without disorder. The preferred structure is noncentrosymmetric and in the space group *Ima*2 (No. 46).

The gallium metal position revealed a larger than expected temperature factor, indicating the presence of aluminum contamination from the alumina crucible used to grow the crystals. The position was refined with both gallium and aluminum to a more reasonable temperature factor and an aluminum content of approximately 28%, i.e., $HoSr_2Cu_2Ga_{0.72}Al_{0.28}O_7$. Energy-dispersive X-ray analysis (EDX) studies on single crystal from the same batch confirmed aluminum to be present in that approximate amount. In an earlier study of the one-copper-layer brownmillerite type structure $LaSrCuGaO_5$, the maximum aluminum solubility at 980 °C was found to be approximately 20%.[25] The higher percentage of aluminum with the double-layer structure may reflect the higher temperature used for crystal growth. Crystallographic data for this compound are summarized in Tables II and III. Bond lengths and angles are presented in Table IV.

Table IV. Selected Bond Angles (degrees) and Distances (angstroms)

	$LaSr_2Cu_2GaO_7$	$HoSr_2Cu_2GaO_7$
Cu–O1	1.958 (5)	1.94 (2)
	1.941 (5)	1.93 (2)
Cu–O2	1.967 (5)	2.00 (2)
	1.957 (5)	1.88 (2)
Cu–O3	2.342 (2)	2.37 (1)
Ga–O3	1.831 (2) × 2	1.80 (1) × 2
Ga–O4	1.909 (6)	1.92 (1)
	1.891 (4)	1.83 (1)
Ln–O1	2.570 (3) × 2	2.34 (2) × 2
	2.605 (3) × 2	2.47 (2) × 2
Ln–O2	2.533 (3) × 2	2.38 (2) × 2
	2.536 (3) × 2	2.42 (2) × 2
Sr–O1	2.678 (4)	2.87 (2)
	2.705 (4)	2.74 (2)
Sr–O2	2.660 (4)	2.74 (2)
	2.671 (4)	2.70 (2)
Sr–O3	2.517 (2)	2.45 (1)
	2.967 (5)	2.83 (2)
	2.654 (5)	2.70 (2)
Sr–O4	2.500 (2)	2.45 (1)
O1–Cu–O1	89.0 (1)	88.4 (1)
O1–Cu–O2	90.6 (2)	94.3 (9)
	90.9 (2)	86.2 (9)
	171.7 (1)	165.9 (5)
	171.7 (1)	166.3 (5)
O2–Cu–O2	88.3 (1)	88.1 (1)
O3–Ga–O3	130.5 (2)	132.6 (9)
O3–Ga–O4	104.9 (2) × 2	105.2 (5) × 2
	103.7 (1) × 2	102.7 (7) × 2
O4–Ga–O4	107.7 (1)	106.4 (5)

Table V. Lattice Constants for $LnSr_2Cu_2GaO_7$ Compounds

lanthanide (Ln)	a, Å	b, Å	c, Å
lanthanum	23.160 (2)	5.5706 (6)	5.4782 (8)
cerium[a]	22.968 (2)	5.5451 (1)	5.4400 (1)
praseodymium	22.955 (1)	5.5498 (1)	5.4481 (2)
neodymium	22.904 (1)	5.5403 (1)	5.4403 (1)
samarium	22.850 (1)	5.5192 (2)	5.4245 (2)
europium	22.839 (1)	5.5188 (1)	5.4208 (1)
gadolinium	22.825 (1)	5.5121 (2)	5.4167 (2)
terbium	22.827 (7)	5.4975 (2)	5.4057 (2)
dysprosium	22.807 (1)	5.4865 (3)	5.4012 (4)
holmium	22.818 (2)	5.4738 (6)	5.3906 (6)
yttrium	22.815 (1)	5.4800 (3)	5.3928 (3)
erbium	22.802 (1)	5.4701 (1)	5.3804 (1)
thulium	22.806 (2)	5.4911 (3)	5.4035 (4)
ytterbium	22.797 (1)	5.4606 (2)	5.3759 (2)

[a] A small amount of cerium dioxide (CeO_2) was visible in the X-ray powder diffraction pattern.

Polycrystalline Studies. Polycrystalline samples of $LnSr_2Cu_2GaO_7$ (Ln = La–Yb, Y) and "$LuSr_2Cu_2GaO_7$" were synthesized from stoichiometric mixtures of the component oxides and carbonates as above. The components were heated to 980 °C for 3 weeks with frequent grinding. Lattice parameters were determined from an X-ray Rietveld refinement[26] of the structure

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(23) Sweptson, P. N. TEXSAN: Version 5.1; Molecular Structure Corp.: College Station, TX, 1986.

(24) $R = [(\sum F_o - F_{calc})]/(\sum F_o)$; $R_{wtd} = [(\sum w(|F_o| - |F_{calc}|)^2/(\sum w|F_o|^2)]$, $w = 1/\sigma^2(F)$.

(25) Hasty, E. F.; Vaughey, J. T.; Poeppelmeier, K. R., manuscript in preparation.

(26) Wiles, D.; Sakthevel, A.; Young, R. Rietveld Analysis Program—version DBWS-9006; School of Physics, Georgia Institute of Technology, Atlanta, GA, 1990.

with silicon as an internal standard and are summarized in Table V. All samples used for unit-cell determination were quenched to room temperature in air. Lattice constants for the holmium sample (see Table V) are from this study and not from the X-ray single-crystal analysis, where significant incorporation of aluminum during the crystal growth has affected the lattice parameters. The lutetium compound was found not to form after prolonged heating (>3 months). The resulting mixture was found to contain $Lu_2Cu_2O_5$, $Sr_3Ga_2O_6$, $SrCuO_2$, and $CuGa_2O_4$.

Magnetic Susceptibility. Susceptibility measurements were performed on a Quantum Design Corp MPMS Squid Susceptometer between 4 and 300 K. A platinum metal standard was used for instrument calibration. The measurements were done with polycrystalline samples encased in sealed gelatin caps. The data were corrected for the diamagnetism of the sample holder. A 1-kG field was used for all measurements unless otherwise noted.

Chemical Analysis. Scanning electron microscopy (SEM) and EDX were performed on a Hitachi S-570 SEM equipped with a Tracor Northern energy-dispersive X-ray spectrometer. The EDX methods used have been reported elsewhere.[15]

Results

The $LnSr_2Cu_2GaO_7$ (Ln = La–Yb, Y) structure is best described as the replacement of the square-planar copper in the $YBa_2Cu_3O_7$ structure with a tetrahedral gallium. The replacement creates a large supercell of the ideal, cubic perovskite lattice (a_p) where $a \approx 6a_p$, $b \approx \sqrt{2}a_p$, and $c \approx \sqrt{2}a_p$. The Ln^{3+} and Sr^{2+} A cations both occupy eight-coordinate sites. The lanthanide cations preferentially occupy a 4 + 0 + 4 coordination environment between the $CuO_{4/2}$ planes. The strontium is in a more distorted 4 + 3 + 1 environment. The coordination environment of the A cation is described by three numbers: the first denotes the number of oxygen atoms from the $CuO_{4/2}$ layer, the second the number from $AO_{4/4}$ layer, and the third number from either the $GaO_{4/2}$ layer (strontium) or the $CuO_{4/2}$ layer (lanthanide). Because the coordination numbers are the same for both A cations, extensive site mixing between the A cations should be expected for the larger lanthanides, which are similar in size to strontium. Less mixing should be expected for the smaller lanthanides. On the basis of the neutron diffraction study of $LaSr_2Cu_2GaO_7$, lanthanum (La^{3+}, 1.16 Å; Sr^{2+}, 1.26 Å)[27] was found to preferentially occupy site 4a between the copper square pyramids in a 70/30 ratio. The strontium preferentially was on site 8c nearer the $GaO_{4/2}$ tetrahedra. The scattering lengths for lanthanum (8.24 fm) and strontium (7.02 fm) are sufficiently different so that a refinement of possible site mixing can be done confidently. In the X-ray single-crystal structure refinement of $HoSr_2Cu_2GaO_7$, where ordering strongly affects the intensities, the A-cation positions were found not to be disordered, in contrast to the lanthanum compound, but occupy distinct sites. Apparently the holmium atom (1.01 Å) is small enough so that site mixing is not favored. This is consistent with the large (0.25 Å) size difference causing site specificity, although thermodynamic factors including growth temperature, oxygen partial pressure, and sample history probably also affect cation ordering.

The copper coordination for the lanthanum and holmium compounds was found to be square pyramidal with four short in plane distances averaging 1.96 and 1.94 Å and one long apical bond of 2.34 and 2.37 Å, respectively. Figure 2 shows the structure of $LaSr_2Cu_2GaO_7$. Table IV contains bond angles and distances for both compounds. Doping (p-type) studies on a number of these compounds indicate that strontium and calcium but not barium can substitute for the lanthanide on the A site or zinc can substitute on the B site. The oxygen stoichiometry of these compounds has not been thoroughly investigated, but is is clear that oxygen vacancies, if they occur, form in the plane in contrast to $YBa_2Cu_3O_7$.

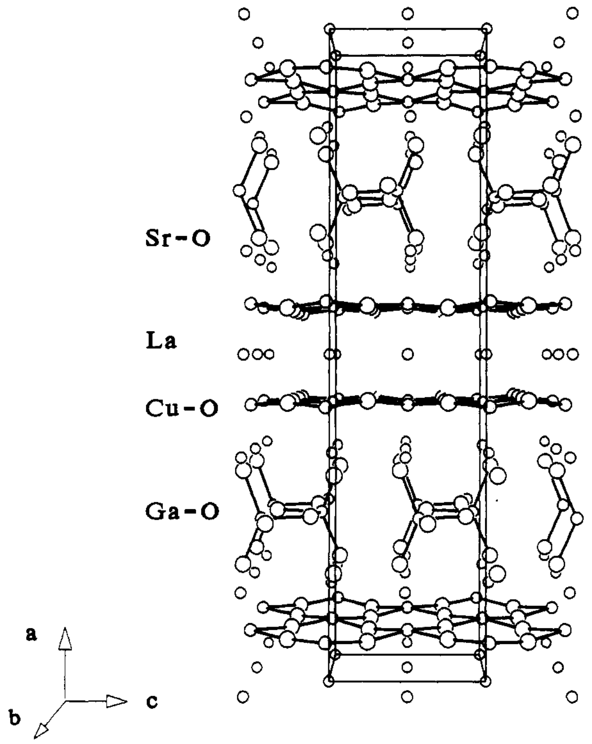

Figure 2. Structure of $LaSr_2Cu_2GaO_7$ as viewed down the *b* axis. Thermal ellipsoids are of arbitrary size.

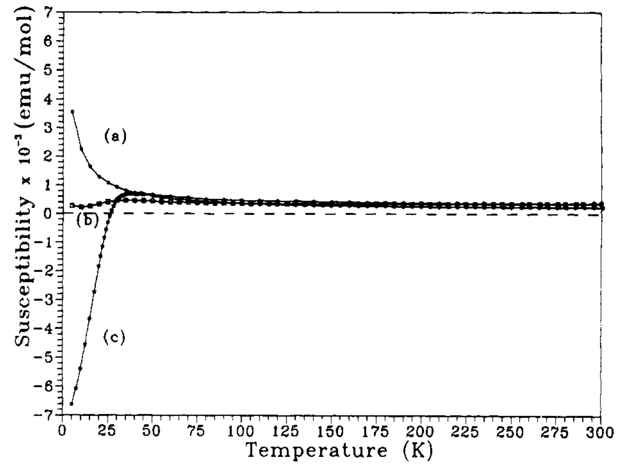

Figure 3. Susceptibility of $Y_{0.80}Ca_{0.20}Sr_2Cu_2GaO_7$ in the range 4–300 K: (a) a quenched sample; (b) the sample slow cooled in air; (c) after high-pressure oxygen annealing.

The system Y–Sr–Cu–Ga–O was chosen for a more intense search for superconductivity because of the shorter Cu–O in-plane distances and the cation ordering observed in the structural (neutron and X-ray) studies. Magnetic susceptibility experiments were performed on all samples. All samples were found to remain paramagnetic down to 4 K when quenched to room temperature in air. It was found that when doped with calcium, i.e., $Y_{1-x}Ca_xSr_2Cu_2GaO_7$ (x = 0.20), a superconducting transition at about 30 K was observed when annealed in high-pressure oxygen at 910 °C (12 h, 200 bar) and cooled to room temperature (2 °C/min). A plot of susceptibility versus temperature is shown in Figure 3. An indexed powder pattern of the sample is reported in Table VI. Excellent agreement between the observed X-ray powder

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(27) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

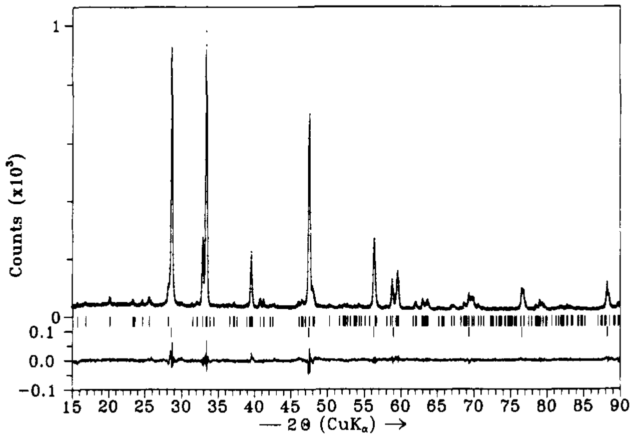

Figure 4. Observed (+), calculated (solid line), and difference (below) X-ray powder diffraction pattern (Rietveld refinement) for $Y_{0.80}Ca_{0.20}Sr_2Cu_2GaO_7$ at room temperature after high-pressure oxygen treatment. The top set of tic marks represents the calculated peak locations for $Y_{0.80}Ca_{0.20}Sr_2Cu_2GaO_7$, and the lower set represents the calculated peak positions for silicon, which was added as an internal standard.

diffraction data and that expected (see Figure 4) based on the orthorhombic *Ima*2 model indicates that the high-pressure oxygen treatment did not cause decomposition.

Table VI. Indexed X-Ray Diffraction Pattern of $Y_{0.80}Ca_{0.20}Sr_2Cu_2GaO_7$[a]

h k l	d_{Riet}	I/I_0[c]	*h k l*	d_{Riet}	I/I_0[c]
2 0 0	7.74	8	10 0 2	1.740	1
4 0 0	5.703	<1	5 3 0	1.694	2
1 1 0	5.323	1	4 1 3	1.634	2
3 1 0	4.442	3	14 0 0	1.629	3
0 1 1	3.838	2	7 3 0	1.592	1
6 0 0	3.802	<1	6 3 1	1.573	14
2 1 1	3.638	3	12 2 0	1.561	4
5 1 0	3.505	3	6 1 3	1.556	16
4 1 1	3.184	5	12 0 2	1.553	4
8 0 0	2.852	<1	14 1 1	1.499	3
7 1 0	2.800	2	8 3 1	1.478	5
0 2 0	2.737	28	10 2 2	1.469	2
6 1 1	2.701	100	8 1 3	1.464	4
0 0 2	2.692	31	5 3 2	1.434	1
2 2 0	2.661	<1	14 2 0	1.400	4
2 0 2	2.620	<1	14 0 2	1.394	3
4 2 0	2.467	<1	0 4 0	1.369	3
4 0 2	2.436	<1	2 4 0	1.359	1
1 2 1	2.426	1	12 2 2	1.351	6
3 2 1	2.323	1	0 0 4	1.346	3
3 1 2	2.302	1	16 1 1	1.336	4
8 1 1	2.289	22	14 2 2	1.242	5
10 0 0	2.281	4	0 4 2	1.219	2
6 2 0	2.221	4	6 3 3	1.213	4
6 0 2	2.197	3	0 2 4	1.208	2
5 1 2	2.135	1	18 1 1	1.203	1
8 2 0	1.975	2	14 3 1	1.186	1
8 0 2	1.958	2	14 1 3	1.178	2
0 2 2	1.919	31	8 3 3	1.167	2
12 0 0	1.901	9	6 4 2	1.161	1
2 2 2	1.893	2	12 0 4	1.099	1
9 2 1	1.757	1	16 1 3	1.094	1
10 2 0	1.752	1	20 1 1	1.093	3

[a] Orthorhombic; a = 22.813 (1) Å, b = 5.474 (1) Å, c = 5.384 (1) Å, *Ima*2 (No. 46). [b] Unobserved reflections ($I/I_0 < 1\%$) after 40° 2θ are not listed. [c] The numbers listed are percentages.

Discussion

The synthesis and characterization of layered materials have been an active pursuit of chemists for many years.[28] Since 1987[5] there has been a worldwide effort centered on the synthesis and characterization of two-dimensional copper oxides directed toward new high-temperature cuprate superconductors. A few similarities exist among the compounds that do superconduct. They include being structurally related to the mineral perovskite as either a perovskite rocksalt or a perovskite-fluorite intergrowth material with copper as the only B cation and the presence of mixed valency on the copper site. An alternative approach to layered cuprates is the synthesis of new phases that contain two different B cations, one of which is copper. The usual stoichiometry of these compounds is $AA'BB'O_{6-x}$ (A, A′ = lanthanides, Y, Ca, Sr, Ba; B′ = post-transition metal or first-row transition metal). Many such mixed-metal perovskite-related oxides are known where the B cations are either random or ordered along the [111] body diagonal to create mixed B–O–B′ layers.[29] A thorough discussion of factors that lead to copper oxygen planes can be found in a recent paper on the structure of La_2CuSnO_6.[30] Two other examples where differences in coordination preference lead to the formation of $CuO_{4/2}$ planes were $LaSrCuAlO_5$[15] and $LaSrCuGaO_5$.[16] Both are structurally related to the brownmillerite structure, although they possess slightly different oxygen vacancy ordering patterns. It was found that doping strontium for lanthanum in the gallium compound leads to much lower resistivity but not superconductivity.[16] These studies also indicated the presence of a strontium-rich phase that was found by EDX to have the approximate stoichiometry $LaSr_2Cu_2GaO_7$, which is the object of this study. Similar phases with nearly the same structure have been found in both the aluminum and iron systems and are presently under investigation.

Tetrahedral coordination is a common structural feature in the perovskite structure and can compensate for oxygen deficiency. Some recent examples include $LaSr_2Fe_3O_8$[31] and $Ca_3Fe_2TiO_8$,[32] where the $FeO_{4/2}$ tetrahedra are separated by two octahedral layers of iron or titanium. The iron–oxygen tetrahedra have the same orientation from layer to layer with no evidence of cell doubling from neutron, X-ray, or electron diffraction. Earlier work on $Ca_3Mn_{1.35}Fe_{1.65}O_{8.02}$[33] found it to have a structure closely related to the iron compounds.[31,32] However, it was found to have excess oxygen in the tetrahedral layer along with a deficiency of oxygen in the octahedral layers. This was attributed to a preference for square-pyramidal coordination over octahedral coordination of the d^4 manganese(III) cations and is consistent with previous studies on manganese perovskites.[34] Recently a new series of compounds with a similar stoichiometry and structure, $LnBa_2Cu_2MO_8$ (Ln = La, Pr; M = Ta, Nb)[35] have been

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(28) (a) Hwu, S.-J.; Poeppelmeier, K. R. *Inorg. Chem.* **1987**, *24*, 3297. (b) Kwon, T.; Pinnavaia, T. *Chem. Mater.* **1989**, *1*, 381. (c) Liimatta, E.; Ibers, J. A. *J. Solid State Chem.* **1987**, *71*, 384.

(29) Goodenough, J. B.; Longo, J. M. *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*; Hellwege, K. H., Ed; Springer-Verlag: Berlin, 1970; Vol. 4a.

(30) Anderson, M. T.; Poeppelmeier, K. R. *Chem. Mater.* **1991**, *3*, 476.

(31) Battle, P. D.; Gibb, T. C.; Lightfoot, P. *J. Solid State Chem.* **1990**, *84*, 237.

(32) Rodriguez-Carvajal, J.; Vallet-Regi, M.; Gonzalez-Calbet, J. M. *Mater. Res. Bull.* **1989**, *24*, 423.

(33) Nguyen, N.; Calage, Y.; Varret, F.; Ferey, G.; Caignaert, V.; Hervieu, M.; Raveau, B. *J. Solid State Chem.* **1984**, *53*, 398.

(34) (a) Poeppelmeier, K. R.; Leonowicz, M. E.; Longo, J. M. *J. Solid State Chem.* **1982**, *44*, 89. (b) Poeppelmeier, K. R.; Leonowicz, M. E.; Scanlon, J. C.; Longo, J. M.; Yelon, W. B. *J. Solid State Chem.* **1982**, *45*, 71. (c) Leonowicz, M. E.; Poeppelmeier, K. R.; Longo, J. M. *J. Soild State Chem.* **1985**, *59*, 71.

(35) (a) Murayam, N.; Sudo, E.; Kani, K.; Tsuzuki, A.; Kawakami, S.; Awano, M.; Torii, Y. *Jpn. J. Appl. Phys.* **1988**, *27*, L1623. (b) Greaves, C.; Slater, P. R. *Physica C* **1989**, *161*, 245. (c) Rey, M.-J.; Dehaudt, P.; Joubert, J.; Hewat, A. H. *Physica C* **1990**, 162.

reported with layers of copper–oxygen square pyramids separated by tantalum (or niobium) oxygen octahedra arranged in a manner similar to $YBa_2Cu_3O_7$.

Various doping studies have been carried out due to the obvious similarity of $LnSr_2Cu_2GaO_7$ and $YBa_2Cu_3O_7$. It was found that in the $La_{1-x}Sr_{2+x}Cu_2GaO_7$ system the solubility of excess strontium in the sample was about 15%, i.e., $La_{0.85}Sr_{2.15}Cu_2GaO_7$. All compositions measured remained semiconductors and paramagnetic down to 4 K. In the series $HoSr_2Cu_2Ga_{1-x}Zn_xO_7$, the samples also remained paramagnetic and semiconducting down to 4 K. A neutron diffraction study[36] on the $x = 0.15$ sample of the later revealed that approximately 50% of the zinc was in the copper planes. Similar results have been observed in other layered cuprate systems when doped with zinc.[13] The highest doping levels attainable were observed in the Y–Sr–Cu–Ga–O system doped with calcium, i.e., $Y_{1-x}Ca_xSr_2Cu_2GaO_7$ ($0 \le x \le 0.30$). The composition $Y_{0.80}Ca_{0.20}Sr_2Cu_2GaO_7$ remained paramagnetic upon quenching to room temperature from 950 °C, but slow cooling at 10 °C/h was found to greatly reduce the susceptibility of the sample. The sample was next heated under high oxygen pressure and temperature (200 bar, 910 °C) and allowed to slow cool at a rate of 2 °C/min. A small but significant fraction of the sample was found to have a superconducting transition near 30 K.[37] The measurement was performed in a 100-G field. Magnetization experiments (field ± 50 000 G) performed at 5 K revealed an H_{c1} of about 400 G and an H_{c2} of about 1800 G. How the high-pressure oxygenation affects only regions of the polycrystalline ceramic is under study. However, in this or any other five-component oxide system, there is always the possibility that a fraction of other phase remains elusive and difficult to detect that could be the superconductor. Nonetheless, we observe (see Tables V and VI) that the lattice constants of the doped, high-pressure annealed sample contract in the plane of the copper oxygen layers (*b*, *c* axes). This is expected when electrons are removed from the antibonding σ^* orbitals increasing the overlap of the in-plane copper oxygen orbitals.

Conclusions

The square-planar copper-oxygen chains in the 93 K superconductor $YBa_2Cu_3O_7$ are an important electronic as well as structural feature. In comparison, the d levels of gallium (d^{10} ion) are much lower in energy than copper and cannot be oxidized, stabilize copper–oxygen acceptor states, or act as a charge reservoir. Further theoretical work is needed to clarify the exact relationship and location of all energy bands and bonding interactions. Nonetheless, considering the similar structural aspects of $LaSrCuAlO_5$, $LaSrCuGaO_5$, and $LnSr_2Cu_2GaO_7$ (Ln = La–Yb, Y), we would expect that when properly doped and annealed, superconductivity should exist in other members of this group that are difficult to dope into the metallic state because of the insulating $Ga(Al)O_{4/2}$ layer.

Acknowledgment. We thank M. Anderson for helpful discussions, as well as F. Rotella, R. Hitterman, and J. Jorgensen for their help at Argonne National Laboratory, and the U.S. DOE/DMS under contract No. W-31-109-Eng-38 for partial support (B.D., D.G.H., and A.W.M.). The neutron diffraction data were collected at the Intense Pulse Neutron Source (IPNS) with support from the Science and Technology Center for Superconductivity (NSF-DMR-8809854). The X-ray diffraction facility is supported by Northwestern's Material Research Center (NSF-DMR-8821571).

Note Added in Proof. A preprint paper by G. Roth et al. on the crystal structure of $RESr_2Cu_2GaO_7$ was brought to our attention by one of the reviewers. The crystallographic results of their paper, to be published in *Journal de Physique*, are in agreement with ours; however, they report no evidence for superconductivity.

Supplementary Material Available: Observed and calculated structure factors for the X-ray structure (7 pages). Ordering information is given on any current masthead page.

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[36] Vaughey, J. T.; Poeppelmeier, K. R., unpublished results.

[37] A similar observation has been made by R. J. Cava, private communication.