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Synthesis, structure, and properties of $Sr_2CuO_2Cl_2$

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Syntheses of single-crystal specimens and single-phase polycrystalline samples of $Sr_2CuO_2Cl_2$ are reported. Differential-thermal-analysis measurements indicate that this compound melts incongruently at 990 °C in air and at 970 °C in helium. Rietveld refinement of powder neutron diffraction data confirms the body-centered-tetragonal ($I4/mmm$) K_2NiF_4-type structure found earlier using x-ray techniques by Grande and Müller-Buschbaum. The CuO_2 planes are the same as in (tetragonal) La_2CuO_4, but the out-of-CuO_2-plane oxygens in the latter are replaced by Cl. The temperature dependences of the lattice parameters and thermal factors are reported; the tetragonal structure is retained from 300 K down to at least 25 K. Electrical-resistivity measurements exhibit essentially insulating behavior near room temperature, with $\rho_{ab} \simeq 3000$ Ω cm and $\rho_c \simeq 6.5 \times 10^5$ Ω cm.

INTRODUCTION

Up to now, out-of-CuO_2-plane oxygen anions have generally been regarded as inert with respect to the magnetic, metallic, and superconducting properties of the high-T_c cuprates. On the other hand, attempts to hole dope the compound $Ca_{0.85}Sr_{0.15}CuO_2$, which contains only CuO_2 layers and no out-of-plane anions, have so far proven unsuccessful,[1] suggesting that out-of-plane oxygens in the cuprates may play a crucial role in the doping mechanism and/or metallic hole conduction. One avenue allowing examination of this issue is to study other similar compounds containing CuO_2 layers and with no out-of-plane oxygens. One such class of materials is typified by the compound $Sr_2CuO_2Cl_2$.[2] From single-crystal x-ray-diffraction studies,[2] it has the tetragonal K_2NiF_4 structure at room temperature. It contains CuO_2 layers as in La_2CuO_4,[3] but with the out-of-plane oxygen ions at the apices of the CuO_6 octahedra replaced by Cl and the La by Sr. The structural similarity to La_2CuO_4 and the fact that the formal valence of the Cu atoms is +2, as in La_2CuO_4, imply that $Sr_2CuO_2Cl_2$ should be an antiferromagnetic insulator at low temperatures.

Herein, we describe the syntheses of single-crystal specimens and polycrystalline samples of $Sr_2CuO_2Cl_2$. A structure determination from Rietveld refinement of neutron diffraction data is presented, in good agreement with that determined earlier[2] using x-ray analysis. Differential thermal analysis (DTA) indicates that the compound decomposes at about 1000 °C. Resistivity measurements that are consistent with semiconducting behavior and a large ($\simeq 0.5$ eV) energy gap are presented. Our studies of the electron- and hole-doping properties[4] of $Sr_2CuO_2Cl_2$ and of the magnetic properties[5] of this compound are planned to be published separately.

SAMPLE PREPARATION

Two methods of sample preparation were employed in making powder samples, both using predried $SrCO_3$ (99.99%), $SrCl_2$, and CuO (99.99%) as starting materials. X-ray powder diffraction (see Fig. 1) was used to follow the progress of the reactions.

In method I, stoichiometric amounts of the precursors were mixed and reacted on gold foil at 700 °C in air with intermediate grindings. After one day it was found that phase segregation occurred in pelletized samples. X-ray analysis revealed that the phases were mainly $SrCuO_2$ and the phases present when the mixture ($SrCl_2 + SrCO_3$) is reacted. The samples were reground and further reacted until x-ray patterns showed the samples to be monophasic $Sr_2CuO_2Cl_2$.

Method II involved the preparation of $SrCuO_2$ by reacting stoichiometric amounts of precursors at 925 °C in air for two days with an intermediate grinding. The x-ray pure $SrCuO_2$ was then mixed with a stoichiometric

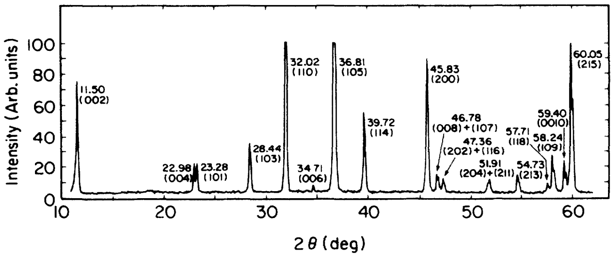

FIG 1. Cu $K\alpha$ x-ray powder diffraction profile for $Sr_2CuO_2Cl_2$.

amount of $SrCl_2$ and reacted for one more day, producing monophasic $Sr_2CuO_2Cl_2$. This method is preferred over the previous method because of the greater ease with which a pure product is obtained.

Single crystals were first grown by melting prereacted $Sr_2CuO_2Cl_2$ at 1125 °C in a cylindrical alumina (Coors) crucible that was in a moderate temperature gradient ($\sim$10 °C/cm). The temperature was decreased slightly to $\simeq$1117 °C at which temperature crystals began to form on the top surface of the melt. After further growth, the resultant "iceberg"-shaped mass of crystals was removed from the liquid. This product contained a large number of small, platelike crystals that were identified as $Sr_2CuO_2Cl_2$ by x-ray precession photographs. Because of thermal instabilities of the crystal growth furnace, larger crystals could not be grown using this apparatus and so an alternate method was sought.

The second method of growing crystals involved melting prereacted $Sr_2CuO_2Cl_2$ in an aluminum boat at 1135 °C in air and cooling at a rate of 3 °C/h. A sheet of $Sr_2CuO_2Cl_2$ crystals was found on the surface of the solidified melt. Below this surface a multiphasic region was found. The black crystals were mechanically removed and found to be micataceous with dimensions $\sim 25 \times 0.3$ mm^3.

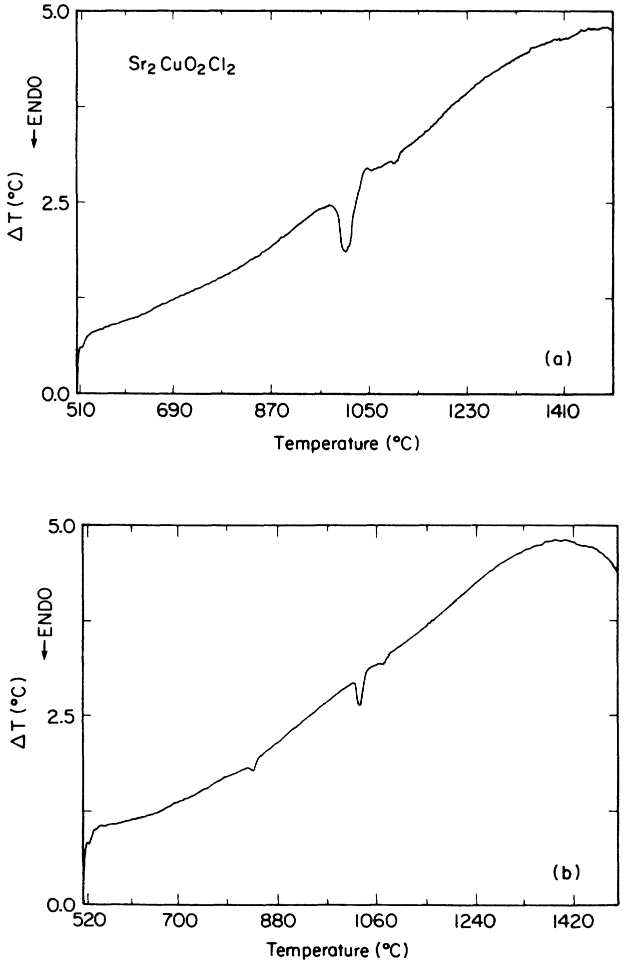

FIG. 2. Differential thermal analysis scans of $Sr_2CuO_2Cl_2$. (a) Data taken over 500–1500 °C range. (b) Data taken after sample had been preheated to 1040 °C.

DTA of single crystals was carried out between 500 and 1500 °C in 20% O_2/80% He at a flow rate of 40 standard cm^3/min using a Perkin Elmer DTA-1700 Differential Thermal Analyzer. The view in Fig. 2(a) shows three peaks at 1015 (onset at 990), 1030, and 1085 °C. In order to elucidate the nature of the peaks, a second run involved heating a sample to 1040 °C, cooling to 500 °C, and subsequently taking data up to 1500 °C. The results, shown in Fig. 2(b), show a new peak at 835 °C, and that the peak at 1015 °C has vanished. The peaks at 1030 and 1085 °C are relatively unchanged and the sample completely evaporated by 1500 °C. In a pure He atmosphere, the lowest temperature peak occurs at 987 °C (onset at 970 °C). Samples placed in ovens at 1050 °C in air or He atmospheres for $\sim$15 min were found to be partially melted, and the x-ray patterns of the products showed many weak unidentified peaks. On the basis of these experiments, we conclude that $Sr_2CuO_2Cl_2$ melts incongruently at 990 °C in air and at 970 °C in pure helium.

DTA of a powder sample of $SrCuO_2$ between 500 and 1500 °C exhibited a transition at 1080 °C, which accounts for the 1085 °C peak in Fig. 2. The peak at 835 °C in Fig. 2(b) may be related to a $SrCl_2$-rich phase, since the melting point of $SrCl_2$ is 870 °C. The 1030 °C peak has not been identified yet but probably arises from a stable phase intermediate in composition between $Sr_2CuO_2Cl_2$ and $SrCuO_2$.

Energy dispersive x-ray analysis of the as-grown surface of the single crystals showed a few small particles of $SrCuO_2$ and a Sr-poor phase. Similar analysis of a freshly cleaved surface showed the crystals to be very clean with no additional elements. The observation of shadowing in scanning electron micrographs indicated that the crystals were essentially insulating; changes in the image with time indicate that the crystals are easily damaged by the electron beam, which we presume is due to loss of chlorine.

NEUTRON DIFFRACTION STRUCTURAL STUDY

Neutron diffraction measurements were performed on 15 g of polycrystalline $Sr_2CuO_2Cl_2$ using a time-of-flight powder diffractometer at the Intense Pulsed Neutron Source of the Argonne National Laboratory. The sample was sealed in a thin-walled vanadium can under 1 atm of He gas at room temperature. Temperatures between 300 and 25 K were achieved using a standard closed-cycle He refrigerator mounted on the sample table of the diffractometer.

Four data sets, at 300, 200, 65, and 25 K, were collected. At each temperature, data were collected by banks of detectors centered at scattering angles of 30°, 60°, 90°, and 150°. The data were analyzed by the Rietveld structure-refinement technique. The results of our analysis are consistent with the room-temperature structure obtained by x-ray measurements: $Sr_2CuO_2Cl_2$ is body-centered-

TABLE I. Temperature dependence of the lattice parameters for $Sr_2CuO_2Cl_2$.

Temperature (K)	Lattice parameters (Å) a	c
25	3.9625	15.5303(2)
65	3.9629	15.5353(2)
200	3.9670	15.5757(2)
300	3.9716	15.6126(2)

tetragonal of K_2NiF_4 type with space group $I4/mmm$.[2] As already noted, the structure is the same as that of (tetragonal) La_2CuO_4, with the oxygens at the apices of the CuO_6 octahedra replaced by Cl atoms. The fitting of the data by this structure is good at all temperatures. In particular, to within experimental resolution, we find no evidence between 25 and 300 K of an orthorhombic distortion from the tetragonal symmetry. The lattice parameters at the four temperatures are listed in Table I.

Since the coherent nuclear scattering amplitudes of Cl and O are considerably different, the neutron diffraction data are very sensitive to position disorder between the Cl and O atoms. Particularly sensitive to disorder of this type are the (202) and (008) reflections. From the refinement of the site occupancies, we find that the position disorder between Cl and O atoms is quite small, (2.0±0.5)%.

From our refinement we also obtained the anisotropic temperature factors U_{ij} of $Sr_2CuO_2Cl_2$. These factors are the elements of a 3×3 matrix $\underline{B}$ defined so that the mean-squared displacement $\langle U_n^2 \rangle$ of an atom along an arbitrary direction defined by the unit vector $\mathbf{n}$ is given by $\langle U_n^2 \rangle = \tilde{\mathbf{n}}\underline{B}\mathbf{n}$, where $\tilde{\mathbf{n}}$ is the transpose of the column vector $\mathbf{n}$. In the case of $Sr_2CuO_2Cl_2$, symmetry requires that for all atoms the matrix $\underline{B}$ is diagonal ($U_{ij}=0$ for $i \neq j$). In addition, for the Sr, Cu, and Cl atoms $U_{11}=U_{22}$.

TABLE II. Structural parameters obtained for polycrystalline $Sr_2CuO_2Cl_2$ ($FW=341.69$ g/mol) from the 90° data set at 300 K. The lattice parameters are $a=3.9716(2)$ Å and $c=15.6126(2)$ Å, $V^{\text{cell}}=246.27$ Å^3, space group $I4/mmm$, $Z=2$, and $\rho^{\text{calc}}=4.606$ g/cm^3. Weighted profile R: 4.07%; expected R: 2.00%.

Atom	Atomic positions x	y	z
Sr (4e)	0	0	0.392 59(7)
Cu (2a)	0	0	0
O (4c)	0	$\frac{1}{2}$	0
Cl (4e)	0	0	0.183 09(6)

Cl-O disorder: (2.0±0.5)%

Atom	Temperature factors (10^{-3} Å^2) U_{11}	U_{22}	U_{33}
Sr	8.7(3)	8.7(3)	12.3(5)
Cu	7.5(4)	7.5(4)	14.5(7)
O	11.4(6)	6.9(6)	14.1(7)
Cl	13.7(3)	13.7(3)	13.9(4)

The structure parameters obtained at 300 K for $Sr_2CuO_2Cl_2$ are listed in Table II; they are in good agreement with those determined by Grande and Müller-Buschbaum.[2] A typical fit of the data obtained at 25 K is shown in Fig. 3. An ORTEP drawing of the structure is shown in Fig. 4. Selected interatomic distances are listed in Table III. The temperature dependences of the thermal factors are shown in Fig. 5. We find that the thermal motion of the Cl atom is isotropic to within the experimental precision. This is to be contrasted with the large anisotropy of the thermal motion of the out-of-plane oxygens in isostructural tetragonal $La_{1.85}Sr_{0.15}CuO_4$.[6] The thermal motion of the in-plane oxygens is anisotropic in both compounds: It is smaller along the Cu-O-Cu chain than in the perpendicular directions. The temperature dependences of the U_{ii} appear normal for the cations, in contrast to the abnormal decrease of some of the cation thermal parameters with increasing temperature found recently in a crystal of $La_{1.92}Sr_{0.08}CuO_{4-\delta}$.[7]

The average interatomic distances within the coordination polyhedra in $Sr_2CuO_2Cl_2$ are within ≃2% of those calculated using the effective ionic radii of Shannon,[8] as shown in Table III. With the exception of the Sr z value, the fractional coordinates of the atoms within the unit cell are essentially the same as in $La_{1.85}Sr_{0.15}CuO_4$. The larger radius of Cl^- relative to O^{-2} causes the Sr atoms to move towards the CuO_2 planes and away from the Cl plane, so that the SrCl "rocksalt layer" is much more puckered than the (La,Sr)O layer in $La_{1.85}Sr_{0.15}CuO_4$. The Sr ions are closer to the Cl ions in their own SrCl layer than to Cl ions in the adjacent SrCl layer, whereas in $La_{1.85}Sr_{0.15}CuO_4$, the rare-earth is closer to the O in the adjacent (La,Sr)O layer rather than to the O in its own layer. Further, the Cl atoms reside inside a much more spherical cation environment, which may account for the isotropic thermal parameters of this atom, in contrast to the anisotropic parameters of the out-of-plane 01 ions in $La_{1.85}Sr_{0.15}CuO_4$. In both compounds, the a-axis

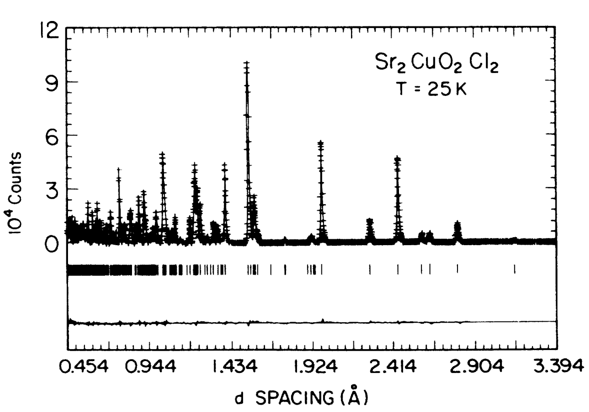

FIG. 3. Fit to the neutron diffraction data at 25 K based on $I4/mmm$ model. The crosses are the experimental data, the solid line is the fit and the difference plot is given at the bottom. The tick marks are the calculated peak positions.

TABLE III. Selected interatomic distances (Å) at room temperature in $Sr_2CuO_2Cl_2$ and in isotypic (Ref. 6) $La_{1.85}Sr_{0.15}CuO_4$. The calculated average values (given in parentheses) were obtained using the effective ionic radii in Ref. 8.

$Sr_2CuO_2Cl_2$		$La_{1.85}Sr_{0.15}CuO_4$	
Cu-O (4×)	1.986	Cu-02 (4×)	1.898
Cu-Cl (2×)	2.859	Cu-01 (2×)	2.406
Average	2.277 (2.27)		2.067 (2.13)
Sr-Cl (4×)	3.047	(La,Sr)-01 (4×)	2.745
Sr-O (4×)	2.599	(La,Sr)-02 (4×)	2.639
Sr-Cl (1×)	3.271	(La,Sr)-01 (1×)	2.353
Average	2.873 (2.94)		2.654 (2.63)
O-Cu (2×)	1.986	02-Cu (2×)	1.898
O-Sr (4×)	2.599	02-(La,Sr) (4×)	2.639
Average	2.395 (2.44)		2.392 (2.46)
Cl-Sr (4×)	3.047	01-(La,Sr) (4×)	2.745
Cl-Sr (1×)	3.271	01-(La,Sr) (1×)	2.353
Cl-Cu (1×)	2.859	01-Cu (1×)	2.406
Average	3.053 (3.02)		2.623 (2.54)

parameter is smaller than expected (4.16 Å) for sixfold-coordinated Cu and O, indicating that the strong Cu—O bonding within the CuO_2 planes primarily determines *a*. In contrast, *c*-axis values of 14.67 and 12.61 Å are calculated for $Sr_2CuO_2Cl_2$ and $La_{1.85}Sr_{0.15}CuO_4$, respectively, using the ionic radii for Cu VI, O VI, Cl VI, La IX, and Sr IX, where the coordination numbers are given by roman numerals; these *c* values are both smaller than the observed values of 15.61 and 13.19 Å, respectively.

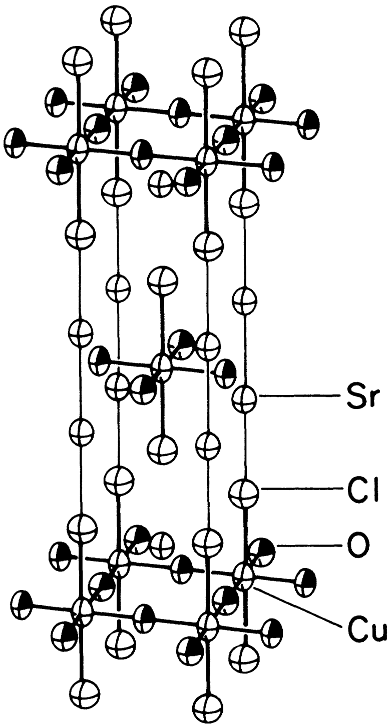

FIG. 4. An ORTEP drawing of the structure of $Sr_2CuO_2Cl_2$. The size of a thermal ellipsoid corresponds to a 99.4% probability of finding the corresponding atom within that ellipsoid.

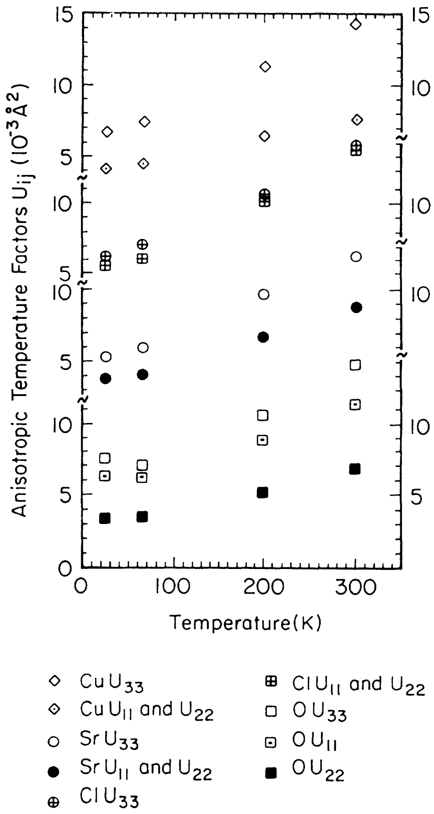

FIG. 5. Temperature dependence of the thermal factors U_{ij}. The sizes of the symbols indicate the precision of the experimental data.

ELECTRICAL RESISTIVITY MEASUREMENTS

Resistivity measurements on a single crystal were made using direct current and the Montgomery technique for anisotropic materials. The influence of thermal emf's was eliminated by averaging voltage readings for plus and minus current directions. Platinum wires were attached to freshly etched surfaces using silver paint. The current-voltage curves were ohmic over the current ranges used here. The resistivity data are shown in Fig. 6 for the temperature range between 293 and 320 K.

As seen in Fig. 6, $Sr_2CuO_2Cl_2$ is highly resistive. The resistivity at 298 K along the crystallographic c axis (ρ_c) is 650 $k\Omega$ cm, whereas in the ab plane (ρ_{ab}) it is 3000 Ω cm, about a factor of 220 smaller. The energy gaps found from the slopes of the $\ln(\rho)$ versus inverse temperature plots in Fig. 6 are very similar: 0.47 eV and 0.52 eV, respectively. Plots of $\ln(\rho)$ versus $T^{-1/4}$ were also almost linear; the differences from linearity were not great enough, however, to conclude whether transport is due to a hopping conduction mechanism or to excitation of carriers across the above energy gaps. The anisotropy ρ_c/ρ_{ab} is similar to that in La_2CuO_4, but the magnitudes of the resistivities are $\sim 10^4$ larger at room temperature than in La_2CuO_4.[9,10] This large difference between the two compounds, which presumably contain similar concentrations of defects, is consistent with the observations that La_2CuO_4 is easily doped with holes to become metallic and superconducting at high temperatures, whereas $Sr_2CuO_2Cl_2$ apparently cannot be doped into the metallic state via substitutions for Sr.[4]

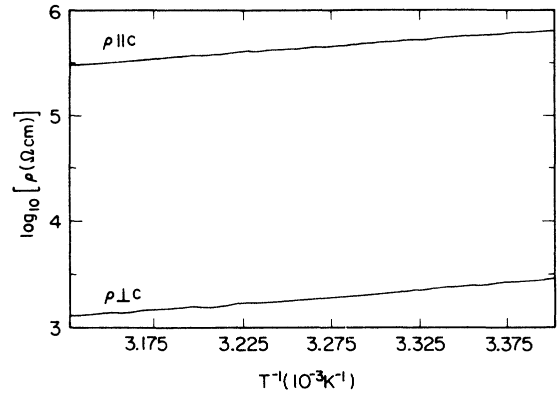

FIG. 6. Log of the resistivity (ρ) versus inverse temperature ($1/T$) for $Sr_2CuO_2Cl_2$. $\rho\perp c$ and $\rho\|c$ were measured using currents of 5 and 2.5 μA, respectively.

CONCLUDING REMARKS

Methods for synthesizing single-phase polycrystalline $Sr_2CuO_2Cl_2$ and single crystals large enough for magnetic neutron diffraction studies[5] have been described. The crystal structure of $Sr_2CuO_2Cl_2$ was determined by Rietveld refinement of neutron diffraction data, and found to be in agreement with that of Ref. 2. Resistivity measurements indicate essentially insulating behavior, with large ($\simeq 0.5$ eV) energy gaps for current flow both parallel (ρ_{ab}) and perpendicular (ρ_c) to the CuO_2 planes. The large resistivity compared to that of La_2CuO_4 suggests that the out-of-CuO_2-plane oxygen anions in the latter compound may be essential to hole doping/metallic hole conduction. Indirect support for this hypothesis is the observation[4] that $Sr_2CuO_2Cl_2$ apparently cannot be doped into the metallic state by substitutions on the Sr sublattice.

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