

# Synthesis, structure, and XPS characterization of the stoichiometric phase $\text{Sr}_2\text{CuO}_2\text{F}_2$

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(Received 24 February 1997)

Thermogravimetric analysis has revealed that reduction of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  in 10%  $\text{H}_2/90\% \text{N}_2$ , occurs in two distinct steps on heating up to 930 °C. Whereas reduction to give  $\text{SrF}_2$ ,  $\text{SrO}$ , and  $\text{Cu}$  is complete above 800 °C, a stable intermediate forms in the region between 250 and 450 °C. This has been identified as a new tetragonal ( $I4/mmm$ ) phase,  $\text{Sr}_2\text{CuO}_2\text{F}_2$ , with unit-cell dimensions  $a=3.967(1)$  Å and  $c=12.816(2)$  Å. The structure has been determined from powder x-ray-diffraction data and is related to  $\text{Nd}_2\text{CuO}_4$  ( $T'$ -type). Madelung energy, bond valence sum calculations, and  $F 1s$ -XPS data clearly indicate that the  $\text{F}^-$  ions occupy sites within the fluorite block ( $\text{Sr}_2\text{F}_2$ ) insulating layers. This contrasts with the  $\text{La}_2\text{CuO}_4$  ( $T$ -type) structure which is adopted by  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ . [S0163-1829(97)06629-0]

## I. INTRODUCTION

$\text{Sr}_2\text{CuO}_3$  has a crystal structure<sup>1</sup> which is related to that of  $\text{La}_2\text{CuO}_4$  [ $T$  structure, Fig. 1(a)] but contains channels of oxygen vacancies that transform the sheets of  $\text{CuO}_6$  octahedra in  $\text{La}_2\text{CuO}_4$  into linear chains of corner linked square  $\text{CuO}_4$  units, giving an overall stoichiometry of  $\text{CuO}_3$  [Fig. 1(b)]. Superconductivity has been induced in materials derived from  $\text{Sr}_2\text{CuO}_3$  by the insertion of oxygen and fluorine. Hiroi *et al.*<sup>2</sup> reported that oxygen insertion at high pressure gives  $\text{Sr}_2\text{CuO}_{3+\delta}$ , which is tetragonal and superconducting with  $T_c=70$  K; this can be increased to 92 K by post synthesis annealing in  $\text{N}_2$ .<sup>3</sup> Neutron diffraction has shown<sup>4</sup> that the oxygen vacancies in this phase occur within the  $\text{CuO}_2$  sheets normally associated with superconducting properties, which in this material may therefore originate from impurity phases.<sup>5</sup>

Al-Mamouri *et al.*<sup>6</sup> reported that fluorine insertion into  $\text{Sr}_2\text{CuO}_3$ , using  $\text{F}_2$  gas, occurs at ambient pressure and relatively low temperatures to give the first superconducting oxide fluoride,  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ , with a maximum  $T_c$  of 46 K when  $\delta\approx 0.3$ . This material [Fig. 1(c)] is also structurally related to  $\text{La}_2\text{CuO}_4$ , with  $\text{O}^{2-}$  ions in the equatorial sites and  $\text{F}^-$  ions occupying the apical positions which are filled by  $\text{O}^{2-}$  in  $\text{Sr}_2\text{CuO}_3$ . The excess  $\text{F}^-$  ions ( $\delta$ ) adopt interstitial sites between the  $\text{SrF}$  layers which form the insulating block in this superconductor. This structural rearrangement, which involves an interchange of the  $\text{F}^-$  and  $\text{O}^{2-}$  ions within the lattice to create intact  $\text{CuO}_2$  planes, appears driven by a preference of  $\text{F}^-$  for the apical sites (Madelung energy calculations<sup>6</sup>). The structure has been supported by atomistic calculations.<sup>7,8</sup>

$\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  can also be produced via other fluorination routes involving either  $\text{NH}_4\text{F}$  (Ref. 9) or certain transition-metal difluorides,  $M\text{F}_2$  ( $M=\text{Cu}$ ,  $\text{Ag}$ , or  $\text{Zn}$ ).<sup>10</sup> Substitution

of Ba for Sr in this structure has raised transition temperatures to 64 K in the sample  $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$  which appears to be the highest  $T_c$  for a material with the  $\text{La}_2\text{CuO}_4$  type of structure.<sup>9</sup>  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ , which can be synthesized similarly, is, however, nonsuperconducting and is structurally related<sup>11</sup> to  $\text{Nd}_2\text{CuO}_4$  [ $T'$  structure, Fig. 1(d)] rather than  $\text{La}_2\text{CuO}_4$ , even though  $\text{Sr}_2\text{CuO}_3$  and  $\text{Ca}_2\text{CuO}_3$  are isostructural. This is in accordance with ionic size effects which are generally assumed to determine the relative stability of the  $T$  and  $T'$  structures.<sup>12</sup>  $\text{Ca}^{2+}$  has a smaller ionic radius than  $\text{Sr}^{2+}$  [ $r_{\text{Sr}}=1.31$  Å and  $r_{\text{Ca}}=1.18$  Å for CN=9 (Ref. 13)] and falls below the 1.204 Å limit for the  $T$  structure.

Following these early examples of fluorine playing an essential structural role in the formation of new superconducting phases, subsequent work has led to the synthesis of other important superconducting oxide fluorides. For example, using high pressure, Kawashima, Matsui, and Takayama-Muromachi<sup>14</sup> synthesized  $\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+\delta}\text{F}_{2\pm y}$  with  $n=2$  and  $n=3$ , which have critical temperatures of 99 and 111 K, respectively. These are higher members in the series of which  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  is the first ( $n=1$ ). Chen *et al.*<sup>15,16</sup> have reported a number of  $n$ -type superconductors with the general formula  $L_y\text{Sr}_{2-y}\text{Cu}(\text{O}/\text{F})_{4+\delta}$  where  $L=\text{La}$ ,  $\text{Nd}$ . These materials have  $T_c$  values of 55 and 27 K, respectively, which are very high for  $n$ -type superconductors.

In order to assess the possibility of using other methods of electronic control, e.g., cation substitutions, in the oxide-fluoride  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ , we have investigated further its structural characteristics and in particular explored the possible formation of stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$ . The controlled removal of fluorine from  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  under reducing conditions has been examined, and conditions for the formation of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  have been found. The structure has been determined using powder x-ray diffraction (XRD), and the O/F site distribution deduced from Madelung energy and bond

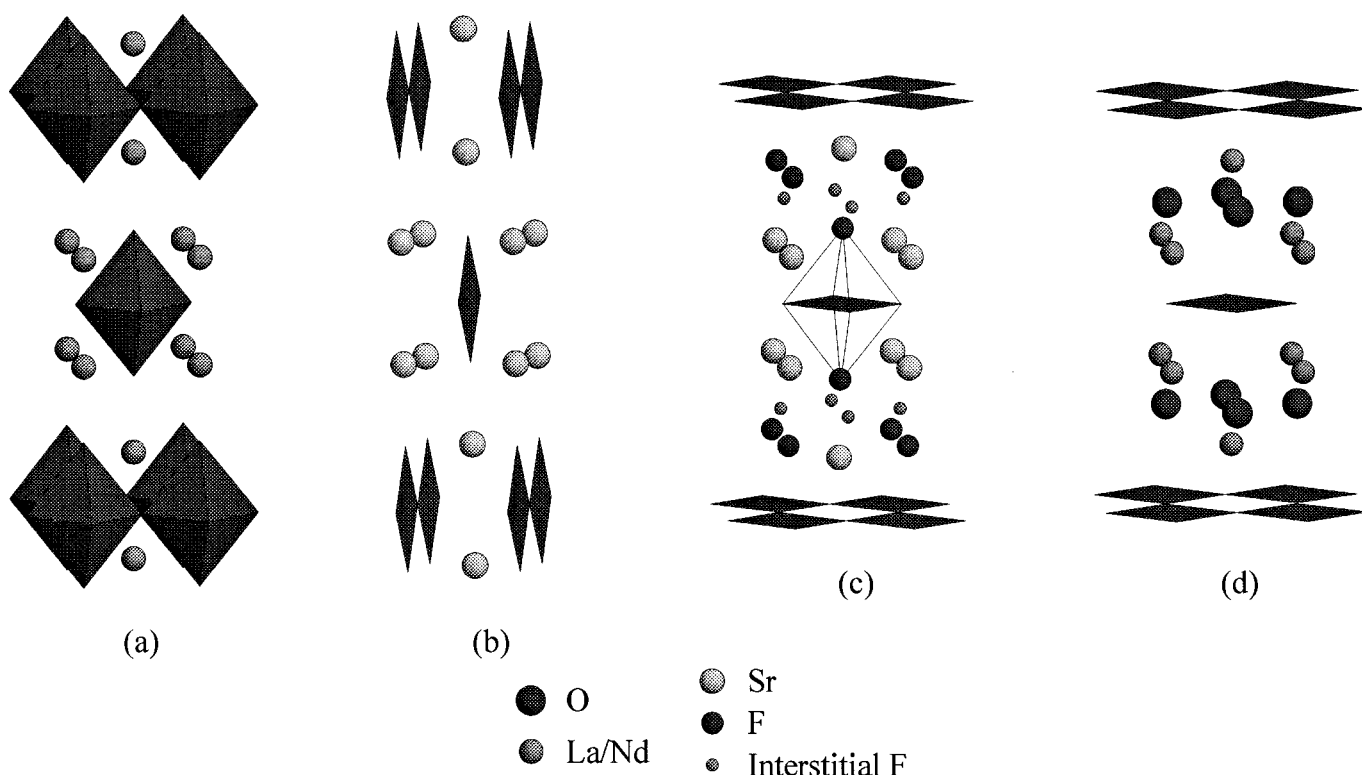


FIG. 1. Crystal structures of (a)  $\text{La}_2\text{CuO}_4$  ( $T$ ), (b)  $\text{Sr}_2\text{CuO}_3$ , (c)  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  (showing the relationship to  $\text{La}_2\text{CuO}_4$ ), and (d)  $\text{Nd}_2\text{CuO}_4$  ( $T'$ ).

valence sum calculations. XPS measurements have been made to compare F  $1s$  and Cu  $2p$  binding energies in  $\text{Sr}_2\text{CuO}_2\text{F}_2$  with those in  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  and  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ .

## II. EXPERIMENTAL

$\text{Sr}_2\text{CuO}_3$  [prepared from stoichiometric amounts of  $\text{SrCO}_3$  (99+%) and  $\text{CuO}$  (98+%) using two heat treatments at 950 °C for 16 h in air] was subjected to heat treatments of 15 min at 215 °C in a flowing 10%  $\text{F}_2$ /90%  $\text{N}_2$  atmosphere (from which traces of HF had been removed by passing over NaF) to give  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ . The thermal stability of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  and its decomposition products were then examined by heating samples to various temperatures under 10%  $\text{H}_2$ /90%  $\text{N}_2$  using a thermal analyzer. Products were characterized using powder XRD (Cu  $K\alpha_1$  radiation, Siemens D-5000 diffractometer) and tested for superconducting properties using a dc superconducting quantum interference device magnetometer (Cryogenics model S100).

XPS measurements were carried out using a Physical Electronics ESCA spectrometer (PHI 5600 ci monochromatic Al  $K\alpha$  radiation) with a full width at half maximum of 0.3 eV. The energy resolution of the analyzer was 1.5% of the pass energy, giving an estimated energy resolution of less than 0.35 eV. Samples in the form of pressed pellets were cleaved in high vacuum in order to produce contaminant-free surfaces. All investigations were performed at room temperature under vacuum at a pressure of less than  $5 \times 10^{-9}$  mbar. The XPS spectra were calibrated using the Au  $4f_{7/2}$  signal from and Au foil [ $E_{b.e.}(\text{Au } 4f_{7/2}) = 84.0$  eV].

## III. RESULTS AND DISCUSSION

Reduction of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  during thermogravimetric analysis (TGA) in 10%  $\text{H}_2$ /90%  $\text{N}_2$  up to 930 °C occurs in

two distinct steps (Fig. 2). Complete reduction to  $\text{SrF}_2$ ,  $\text{SrO}$ , and Cu has occurred by 800 °C but at  $\sim 400$  °C a plateau suggests the formation of some intermediate product. Heating in pure  $\text{N}_2$  was found to give similar two-step behavior, but the final products were  $\text{SrF}_2$  and  $\text{SrCu}_2\text{O}_2$ . No fluorine appears to be lost during the reduction process, and the initial fluorine content of the sample may therefore be determined from the overall weight loss or by determining the copper oxidation state using titration methods,<sup>17</sup> and assuming the composition  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ . The fluorine contents of samples reported in this paper have been estimated using both methods.

As prepared, samples are nonsuperconducting, since  $\delta$  (usually  $\approx 0.5$  or higher) corresponds to a hole density (formal Cu oxidation state) which is too high to support superconductivity. However, as previously reported,<sup>6</sup> superconductivity can be induced by heating at low temperatures under 10%  $\text{H}_2$ /90%  $\text{N}_2$  (TGA, 15 min, temperatures up to 200 °C) or dry  $\text{N}_2$  (furnace, 3 h, temperatures up to 330 °C). In the current study, samples showed a maximum  $T_c$  of approximately 46 K, in agreement with previous measurements.<sup>6</sup>

Further controlled reduction of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  has been attempted in an effort to identify the phase responsible for the apparently stable region in the TGA plot (Fig. 2) and to determine the exact conditions for its formation. Accordingly, samples were heated in 10%  $\text{H}_2$ /90%  $\text{N}_2$  in the thermal analyzer ( $20$  °C  $\text{min}^{-1}$ ) to temperatures between 250 and 450 °C held for 5 min, allowed to cool and then analyzed by powder XRD. For samples heated to 300–340 °C no starting material remained, and decomposition to  $\text{SrF}_2$ , Cu, and a new, unidentified phase was suggested. Similar results were

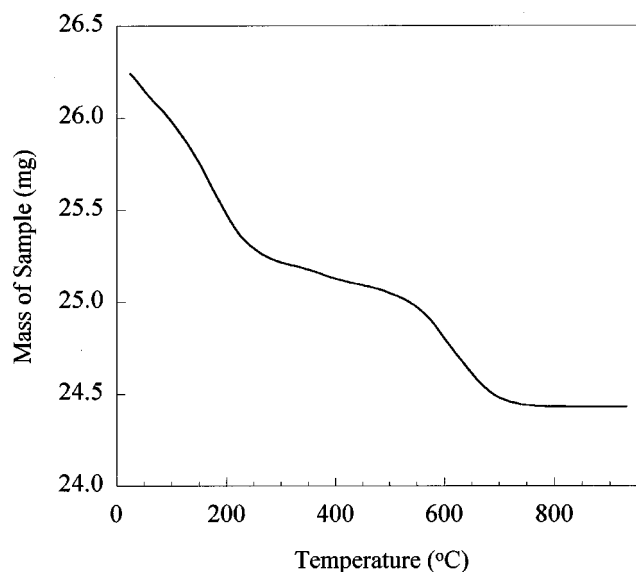


FIG. 2. TGA trace for the decomposition of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  under 10%  $\text{H}_2$ /90%  $\text{N}_2$ .

obtained in  $\text{N}_2$  and a bulk sample was obtained by heating under  $\text{N}_2$  at 350 °C for 14 h. Under these conditions, the unknown phase was mixed with  $\text{SrF}_2$  and  $\text{CuO}$ , and its XRD pattern (Fig. 3) indicated a structural relationship to  $\text{La}_2\text{CuO}_4$  or  $\text{Nd}_2\text{CuO}_4$ . It was tentatively assigned the composition  $\text{Sr}_2\text{Cu}(\text{O}/\text{F})_4$ , and all XRD peaks from this phase could be indexed on a new body-centered-tetragonal unit cell with dimensions  $a = 3.967(1)$  Å and  $c = 12.816(2)$  Å.

Rietveld profile analysis of the XRD data has been used to determine the structure of  $\text{Sr}_2\text{Cu}(\text{O}/\text{F})_4$  using the program FULLPROF.<sup>18</sup> Structural models were based on the  $T$  and  $T'$  structures, which differ only with respect to the location of the anions in the insulating blocks. In order to account for the presence of  $\text{SrF}_2$  and  $\text{CuO}$ , a multiphase refinement was performed. However, since the contribution from  $\text{CuO}$  was restricted to a region which contained only one minor peak (112) from the primary phase, it was preferred to exclude this region ( $32.50 < 2\theta < 41.00$ ) from the refinement to minimize the number of refineable parameters; a two-phase refinement was therefore performed. Refinement based on the  $\text{La}_2\text{CuO}_4$  ( $T$ ) model was unsatisfactory ( $R_{\text{exp}} = 1.24\%$ ,  $R_w$

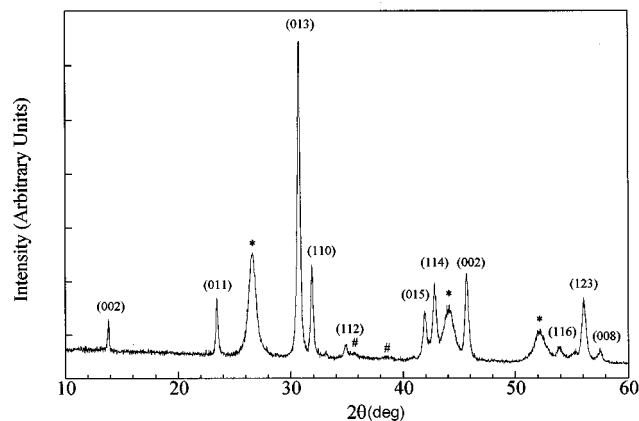


FIG. 3. X-ray-diffraction pattern of  $\text{Sr}_2\text{Cu}(\text{O}/\text{F})_4$  with impurities marked, \* indicates  $\text{SrF}_2$  and # indicates  $\text{CuO}$ .

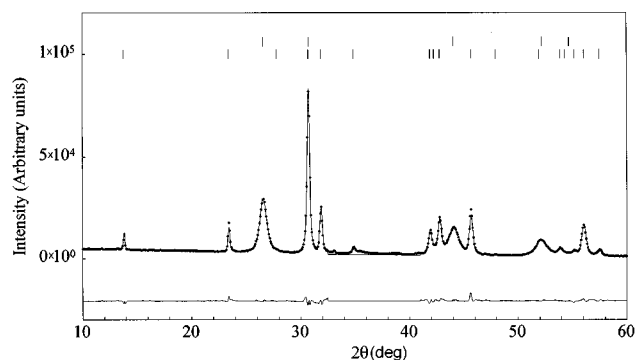
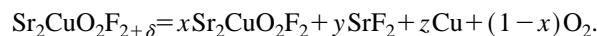


FIG. 4. Observed (dots), calculated (continuous line) and difference Rietveld refinement profiles of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  based on the  $T'$  structure. Reflections from  $\text{SrF}_2$  (upper ticks) and  $\text{Sr}_2\text{CuO}_2\text{F}_2$  (lower ticks) are shown.

$= 22.1\%$ ,  $R_{\text{Bragg}} = 29.4\%$ ). In particular, the apical anion position  $(0,0,z)$  was unstable and varying its occupancy resulted in a value of zero. In contrast, the  $\text{Nd}_2\text{CuO}_4$  ( $T'$ ) model, Fig. 1(d), proved completely successful and the results are presented in Table I with the fitted profiles in Fig. 4. The possibility of a slight fluorine excess was also considered by introducing a small occupancy into the interstitial sites, which are the apical positions for this structure. However, the refined occupancy of this remained zero  $[-0.01(2)]$  confirming the material to be stoichiometric with composition  $\text{Sr}_2\text{Cu}(\text{O}/\text{F})_4$ .

Since O and F are indistinguishable by x rays, the refinement gives no indication of the O/F ratio, and, because of the  $\text{SrF}_2$  impurity phase, use of a fluorine selective electrode is not possible. Copper oxidation state titrations indicated that the oxidation state of Cu in the sample is very close to +2, and since the Cu in  $\text{CuO}$  has an oxidation state of +2,  $\text{Sr}_2\text{Cu}(\text{O}/\text{F})_4$  must also contain  $\text{Cu}^{2+}$ , i.e., it must be  $\text{Sr}_2\text{CuO}_2\text{F}_2$ .

Confirmation of this was obtained by considering the mechanism for the reduction of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  to  $\text{Sr}_2\text{CuO}_2\text{F}_2$  in  $\text{H}_2/\text{N}_2$ :



If  $\delta$  is known,  $x$ ,  $y$ , and  $z$  can be determined (Sr:  $2x + y = 2$ ; Cu:  $x + z = 1$ ; F:  $2x + 2y = 2 + \delta$ ) which then allows the percentage weight loss to be calculated for this reduction. Experimental values determined using a thermal analyzer were found to correlate very well with calculated percentages (e.g., for a sample with  $\delta = 0.72$ ,  $x = 0.64$ , and effectively 0.36  $\text{O}_2$  molecules are lost corresponding to 3.6% mass loss; experimental loss 3.7%) and therefore confirm the phase to be stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$ .

Significant differences between the unit-cell dimensions of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  (Ref. 6) (equivalent to a pseudotetragonal cell with  $a = 3.856$  Å,  $c = 13.468$  Å) and  $\text{Sr}_2\text{CuO}_2\text{F}_2$  are observed, Table I. Contraction of  $c$  to 12.816(2) Å and expansion of  $a$  to 3.967(2) Å are consistent with removal of the  $\text{F}^-$  ions from interstitial positions between the  $\text{SrF}$  "rock-salt" layers in the  $T$ -type structure of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  and transformation to the  $T'$  structure. The corresponding significant increase in Cu-O bond length—from 1.928(1) Å in  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  to 1.984(1) Å in  $\text{Sr}_2\text{CuO}_2\text{F}_2$ —can be attributed

TABLE I. Structural parameters and selected bond lengths of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  based on the  $\text{Nd}_2\text{CuO}_4$  ( $T'$ )-type structure.  $a=3.967(1)$  Å,  $c=12.816(2)$  Å,  $I4/mmm$ ,  $R_{\text{exp}}=1.24\%$ ,  $R_{\text{wp}}=5.93\%$ ,  $R_{\text{Bragg}}=3.68\%$ .

Atom	Pos <sup>n</sup>	x	y	z	$B_{\text{iso}}$ (Å <sup>2</sup> )	Cell occupancy	Bond	Bond length
Sr	4e	0	0	0.365(1)	0.37(8)	4.00	Cu-O(F)1	1.984(1) Å
Cu	2a	0	0	0	1.8(1)	2.00	O(F)2-O(F)2	2.805(1) Å
O(F)1	4c	0	0.5	0	1.00 <sup>a</sup>	4.00	Sr-O(F)2	2.471(7) Å
O(F)2	4d	0	0.5	0.25	1.00 <sup>a</sup>	4.00	Sr-O(F)1	2.632(8) Å

<sup>a</sup>Due to the insensitivity of XRD to O/F in this material, these thermal parameters were constrained to chemically sensible values of 1.0 Å<sup>2</sup>, since attempts to refine them resulted in slightly negative values.

to the decrease in Cu oxidation state and enhancement of the F-F repulsive interactions in the insulating block, as this changes from rocksalt in  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  to “fluorite” in  $\text{Sr}_2\text{CuO}_2\text{F}_2$ .

Bond valence sum calculations<sup>19</sup> for Cu have been performed for  $\text{Sr}_2\text{CuO}_2\text{F}_2$  based on the refined parameters and assuming  $r_0=1.679$  for Cu.<sup>19</sup> Assuming the  $\text{O}^{2-}$  ions occupy the equatorial sites,  $V=1.759$  which is very similar to the value for Cu in the structurally related  $\text{Nd}_2\text{CuO}_4$ , where  $V=1.807$ . On the other hand, occupancy of the equatorial sites by  $\text{F}^-$  ions results in  $V=1.390$ , which is unacceptably low, and these results strongly support the presence of complete  $\text{CuO}_2$  sheets in  $\text{Sr}_2\text{CuO}_2\text{F}_2$ . The  $\text{F}^-$  ions are therefore located between layers of  $\text{Sr}^{2+}$ , to form regions which directly correspond to the  $\text{Nd}_2\text{O}_2$  layers in  $\text{Nd}_2\text{CuO}_4$ , Fig. 1(d). Madelung energy calculations<sup>20</sup> strongly supported this assignment, since the model with equatorial  $\text{O}^{2-}$  ions (and intact  $\text{CuO}_2$  sheets) gives a significantly higher Madelung energy (11 115 kJ mol<sup>-1</sup>) compared with the alternative description containing  $\text{CuF}_2$  layers (9628 kJ mol<sup>-1</sup>). The retention of the  $\text{CuO}_2$  layers in this phase is therefore of potential value for possible electron doping to form *n*-type superconductors.

The structural transition  $T \rightarrow T'$  is normally associated with cation size effects, but in this case only a change in anion stoichiometry is occurring. In order to obtain an indication of the relative stabilities of the  $T$  and  $T'$  structures for anion-excess phases, Madelung energies were calculated for

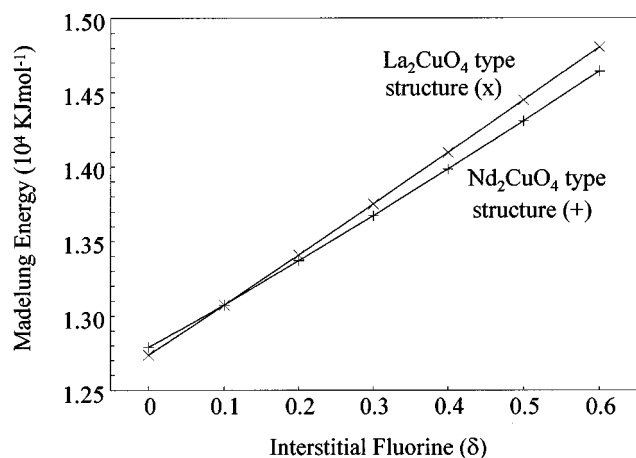


FIG. 5. Plot of Madelung energies against  $\delta$  for  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ , assuming  $\text{Nd}_2\text{CuO}_4$  and  $\text{La}_2\text{CuO}_4$ -type structures.

$\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  as a function of  $\delta$ , and the results are shown in Fig. 5. Madelung energies were calculated assuming structural parameters derived from  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  for the  $T$  structure and  $\text{Sr}_2\text{CuO}_2\text{F}_2$  for  $T'$ . Although such calculations provide only a guide, it is clear that the Madelung energy increases with increasing  $\delta$ , but the rate of increase is different for the two structure types and a crossover in stability occurs at  $\delta \approx 0.1$ . This is in agreement with the observed structural transition but the calculations will be strongly dependent on small structural changes (e.g., cell size, atomic displacements) which are not allowed in this simple approach. Nevertheless, it is instructive that simple electrostatic arguments suggest that as  $\delta$  is decreased, a transition from  $T$  to  $T'$  might be anticipated, although the precise stoichiometry at which this would occur is beyond the accuracy of the calculations.

F 1s and Cu  $2p_{3/2,1/2}$  XPS measurements on  $\text{Sr}_2\text{CuO}_2\text{F}_2$ ,  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  and  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$  have also been performed, and spectra are shown in Fig. 6. Cu  $2p_{3/2,1/2}$  XPS spectra of  $\text{Sr}_2\text{CuO}_2\text{F}_2$ ,  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  and  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$  are practically identical, with main and charge-transfer satellite lines having essentially the same energy and fine structure for all three materials. This implies that the chemical state and immediate environment of the copper atoms is the same for all materials under investigation.

F 1s XPS binding energy of stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$  (684.7 eV) reveals a significant chemical shift with respect to that of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  (683.8 eV). It is, however, found to be very close to that of  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$  (685.1 eV). This chemical shift in the XPS F 1s spectra on reduction of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  to

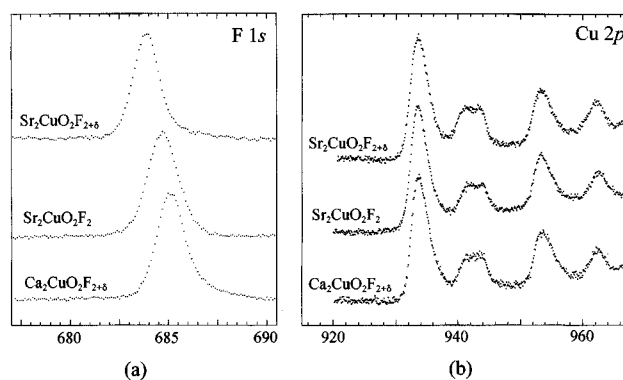


FIG. 6. XPS spectra of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ ,  $\text{Sr}_2\text{CuO}_2\text{F}_2$ , and  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ . (a) F 1s, (22F2), and Cu  $2p_{3/2,1/2}$ .

stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$  can be explained by the change in  $\text{F}^-$  ion site potentials due to the rearrangement of fluorine atoms within the unit cell, from apical sites to interstitial sites. The closeness of the F 1s binding energy for stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$  to that of  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$ , which also has a  $T'$   $\text{Nd}_2\text{CuO}_4$  structure, directly supports this conclusion.

#### IV. CONCLUSIONS

The stable intermediate phase that exists between  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  and its ultimate reduction products has been unambiguously identified as the stoichiometric oxide-fluoride  $\text{Sr}_2\text{CuO}_2\text{F}_2$ , which has a formal copper oxidation state of +2 and is hence nonsuperconducting. The reduction does not simply involve the extraction of excess  $\text{F}^-$  ions

from interstitial sites, but a complicated structural rearrangement occurs, driven by oxygen abstraction and the formation of  $\text{SrF}_2$ . The structure of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  ( $\text{Nd}_2\text{CuO}_4$  or  $T'$  type) is different from that of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  ( $\text{La}_2\text{CuO}_4$  or  $T$  type), which is surprising given their identical cationic size ratios. In  $\text{Sr}_2\text{CuO}_2\text{F}_2$ , the F ions are not bonded to Cu, and occupy sites in the fluorite block ( $\text{Sr}_2\text{F}_2$ ) insulating layers.

#### ACKNOWLEDGMENTS

We would like to thank EPSRC, Air Products (CASE financial support of J.L.K.), the Russian State Program on Superconductivity (Project No. 95026), and the Russian Foundation for Basic Research (Project No. 96-03-32092) for financial support.

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