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Structure and superconductivity without apical oxygens in $(Ca,Na)_2CuO_2Cl_2$

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Recently superconductivity has been reported in $(Ca,Na)_2CuO_2Cl_2$ in which the apical anion position was proposed to be occupied by Cl [Hiroi *et al.*, Nature **371**, 139 (1994)]. In this paper we report a neutron-powder-diffraction investigation of nonsuperconducting $Ca_2CuO_2Cl_2$ and superconducting $(Ca,Na)_2CuO_2Cl_2$ ($T_c = 26$ K). We confirm that in both compounds the apical anion position is fully occupied by Cl. Unlike the recently reported superconductor $Sr_2CuO_2F_{2+\delta}$, in $(Ca,Na)_2CuO_2Cl_2$ we find little evidence for the presence of interstitial atoms. In our structural data the substitution of Na^+ for Ca^{2+} is evidenced by a shortening of the Cu-O bond and lengthening of the Cu-Cl bond. The bond valence of the Cu atom increases, consistent with holes being created by the Na substitution.

I. INTRODUCTION

Recently two new superconducting cuprates have been reported in which the apical position, above and below the CuO_2 planes, is occupied by an anion other than oxygen.[1,2] Al-Mamouri *et al.*[1] reported superconductivity in $Sr_2CuO_2F_{2+\delta}$ fabricated by fluoridation of Sr_2CuO_3 which was prepared under ambient pressure. This material, which has a T_c of 46 K, crystallizes in an orthorhombic structure (space group *Fmmm*) and is structurally similar to La_2CuO_4. A neutron-powder-diffraction investigation has indicated that the apical site is occupied by F and that significant amounts of F^- anions reside on interstitial positions between apical anions and Sr layers.[1] Very recently, Hiroi, Kobayashi, and Takano[2] reported superconductivity in $(Ca,Na)_2CuO_2Cl_2$ fabricated at 6 GPa and at a temperature of 1173 K. This material, which has a T_c of 26 K, also crystallizes with the La_2CuO_4 structure (space group *I4/mmmm*). Preliminary x-ray analysis indicates that Cl resides on the apical position.[2] These two materials are of interest because they exhibit *p*-type superconductivity in an environment where the Cu atom is not coordinated entirely by O atoms. This provides a new opportunity to investigate the role of the apical anion in the superconducting properties of layered cuprate materials.

The most important questions regarding the crystal chemistry of $(Ca,Na)_2CuO_2Cl_2$ are the extent of the substitution of Na into the Ca site and the location of the anions and their site occupancies. In this paper we report a neutron-powder-diffraction study of nonsuperconducting $Ca_2CuO_2Cl_2$ made under ambient pressure and superconducting $(Ca,Na)_2CuO_2Cl_2$ made under high pressure. We confirm that the apical position is occupied by Cl in both materials. Unlike $Sr_2CuO_2F_{2+\delta}$, in $(Ca,Na)_2CuO_2Cl_2$ we find little evidence for the presence of interstitial anions.

II. SAMPLE PREPARATION AND DATA COLLECTION

These samples were prepared following the method described by Hiroi, Kobayashi, and Takano.[2] The nonsuperconducting compound, $Ca_2CuO_2Cl_2$, was prepared under ambient pressure. The superconductor with nominal composition, $Ca_{1.88}Na_{0.12}CuO_2Cl_2$, was prepared under a pressure of 6 GPa and at a temperature of 1173 K in the presence of both Na_2O_2 and $NaClO_4$. The inclusion of Na_2O_2 in the high-pressure synthesis has recently been found to increase the Meissner fraction of this material from ~10% (as initially reported[2]) to ~50%.[3] For the latter sample, characterization by x-ray diffraction revealed the presence of two impurity phases, CuO and $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$. Superconductivity in the $(Ca,Na)_2CuO_2Cl_2$ sample was confirmed by measuring the ac susceptibility as a function of temperature; Fig. 1 displays a sharp diamagnetic transition at a temperature (T_c) of 26 K. The Meissner fraction for the sample was estimated to be ~43% at 5 K, while Hiroi, Kobayashi, and Takano[2] report a value of 10% at 5 K from previous samples. The sample was not pulverized because for the neutron-diffraction experiments with such small samples a pellet sample is required to minimize background scattering as described below.

Neutron-powder-diffraction patterns were measured from these samples at room temperature using the Special Environment Powder Diffractometer operating at Argonne's Intense Pulsed Neutron Source.[4] For the measurement of $Ca_2CuO_2Cl_2$, a 5 gm pellet was ground and placed into a thin-walled vanadium can. Data from $(Ca,Na)_2CuO_2Cl_2$ were measured from a small cylindrical sintered pellet (mass 72 mg) suspended in the neutron beam on a tungsten fiber coated with amorphous boron. This technique has the advantage of providing a measurement from samples with a much lower background than would be observed if a sample container was used. The

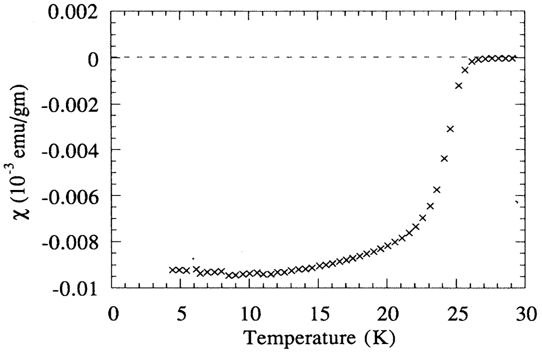

FIG. 1. Temperature dependence of the ac susceptibility for $(Ca,Na)_2CuO_2Cl_2$ synthesized under a pressure of 6 GPa and 1173 K.

neutron-scattering lengths for Cl and O are relatively higher than for x rays and show significant contrast between the two anions ($b_{Cl}=0.958$ $b_O=0.58$). Thus the use of neutron diffraction provides a greater sensitivity to the position and occupancy of these anions than would be obtained by x-ray diffraction.

Neutron-diffraction patterns were analyzed using the well-known general structure analysis system (GSAS) suite of programs.[5] In these refinements, the background was modeled using a cosine Fourier series with eight terms. Peak shape profiles were modeled using a two-sided exponential convoluted with a Gaussian to describe the instrument contribution[6] and a Lorentzian to account for the sample contribution to the peak profile.[5] Preferred orientation was modeled using the Dollase and March model.[7,8]

The $(Ca,Na)_2CuO_2Cl_2$ sample was first mounted with the axis of the cylindrical pellet parallel to the incident neutron beam. Subsequent Rietveld analysis of the pattern suggested that crystallites in the sample were preferentially oriented with the *c* axis in the plane of the incident beam. To overcome the effects of the preferred orientation, a second measurement was made with the sample mounted with the axis of the cylindrical pellet perpendicular to the incident beam. Diffraction data from this sample were analyzed from both measurements simultaneously. In this refinement, structural parameters were obtained from both measurements while refining an individual preferred orientation parameter for each data set. This allowed us to minimize the effects of preferred orientation on the refined parameters. For both samples only data from the backscattering bank were analyzed over the *d*-spacing range of 0.5–4 Å.

Data from the $Ca_2CuO_2Cl_2$ sample were analyzed as a single phase, while the CuO impurity phase was included in the analysis of the $(Ca,Na)_2CuO_2Cl_2$ sample. The structure of the $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$ impurity is not known and could not be included in the refinement. Fortunately the diffraction peaks from this latter phase are weak and have little effect on the refinement. Somewhat higher than normal backgrounds were observed in the superconducting sample due to the incoherent scattering of neutrons by H atoms.

III. RESULTS AND DISCUSSION

Refinement of the neutron-diffraction data from both samples was carried out assuming the tetragonal structure of La_2CuO_4 (space group $I4/mmm$). There was no visible indication of an orthorhombic splitting and attempts to refine with orthorhombic cells, such as *Fmmm*, were not stable.

At first, analysis of the $Ca_2CuO_2Cl_2$ diffraction data was carried out by fixing occupancies to the nominal composition and placing the Cl atom at the apical position above and below the Cu atom. Subsequent refinement of occupancies (except for that of Cu) indicated that the apical position was fully occupied by Cl, while the anion position in the CuO_2 planes was occupied by O. The final refined parameters are listed in Table I and the resulting fit to the data is illustrated in Fig. 2. There is no evidence for substitution of Cl in the plane anion position (O1). For comparison with the superconducting $(Ca,Na)_2CuO_2Cl_2$ compound, a Ca/Na ratio was also refined for this sample producing a full occupancy of Ca at the cation site.

TABLE I. Refined structural parameters and occupancies for $Ca_2CuO_2Cl_2$ and $(Ca,Na)_2CuO_2Cl_2$. The neutron data were modeled on the tetragonal space group $I4/mmm$ with Ca and/or Na placed at $(0,0,z)$, Cu at (0,0,0), O at (0,1/2,0), and Cl at $(0,0,z)$. The interstitial oxygen (O_{int}) was placed at (1/2,0,1/4).

		$Ca_2CuO_2Cl_2$	$(Ca,Na)_2CuO_2Cl_2$
Ca[a]	n	2.04(6)	1.90(13)
Na	n	−0.04(6)	0.10(13)
	z	0.3958(1)	0.3959(3)
	U_{11}	0.0096(4)	0.011(1)
	U_{33}	0.014(1)	0.022(2)
Cu	n	1.0	1.0
	U_{11}	0.0037(3)	0.0031(9)
	U_{33}	0.0085(6)	0.012(1)
O	n	1.97(1)	1.96(3)
	U_{11}	0.0104(6)	0.009(2)
	U_{22}	0.0037(5)	0.002(2)
	U_{33}	0.0118(7)	0.016(2)
Cl	n	2.01(1)	2.02(3)
	z	0.18298(6)	0.1820(1)
	U_{11}	0.0135(3)	0.014(8)
	U_{33}	0.0107(5)	0.013(1)
O_{int}	n	−0.05(3)	0.02(2)
a (Å)		3.8688(1)	3.8495(1)
c (Å)		15.0501(2)	15.1729(5)
R_{wp} (%)		5.0	8.5
GoF		1.6	1.2
$R(F^2)$ (%)		4.0	10

[a] In the analysis of both samples the following constraints were used: $n(Ca)+n(Na)=2$, $z(Ca)=z(Na)$, $U_{11}(Ca)=U_{11}(Na)$, and $U_{33}(Ca)=U_{33}(Na)$.

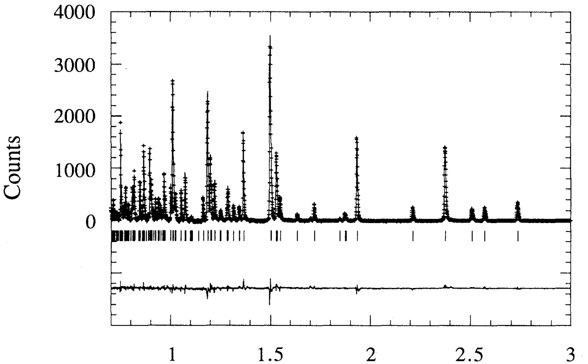

FIG. 2. Observed (shown as +) and fitted (shown as a continuous line) neutron-diffraction pattern for $Ca_2CuO_2Cl_2$ at room temperature. The difference between the observed and fitted patterns is displayed at the bottom of the figure. The expected reflection positions are marked underneath the diffraction pattern. The background has been subtracted.

Analysis of the $(Ca,Na)_2CuO_2Cl_2$ data proceeded in a similar fashion. For the refinement of the Ca and Na occupancies the constraint $n(Ca)+n(Na)=2$ was imposed. Refinement of the O and Cl occupancies shows again that the apical position is entirely occupied by Cl and the plane anion position is fully occupied by O. The results of this analysis are shown in Table I and the fitting to the second measurement of this sample is illustrated in Fig. 3. Although neutron-scattering lengths provide a significant contrast between Na and Ca ($b_{Na}=0.363$, $b_{Ca}=0.490$) our analysis, as seen in Table I, is rather insensitive to the Ca/Na ratio. Albeit our refined parameters are in reasonable agreement with the nominal composition. This result suggests that there is Na on the Ca site although the amount is uncertain. Further support for the presence of Na is given by the change in lattice parameters between the two samples, which is consistent with the results of Hiroi, Kobayashi, and Takano.[2] The a-lattice parameter of $(Ca,Na)_2CuO_2Cl_2$ is smaller than that of nonsuperconducting $Ca_2CuO_2Cl_2$ resulting in a ~ 0.01 Å decrease of the Cu-O bond length (see Table II). For the c axis the result is opposite resulting in a similar increase of the Cu-Cl bond length. Table III compares the Cu-O and Cu-Cl bond lengths with those found in other compounds with similar structures. It is interesting to note that $(Ca,Na)_2CuO_2Cl_2$ exhibits a significantly larger Cu-apical anion bond than that found in similar materials. The Cu-O in-plane bond on the other hand is similar to that in $Sr_2CuO_2F_{2+\delta}$ but, again, somewhat larger than that in $La_{1.85}Sr_{0.15}CuO_4$.

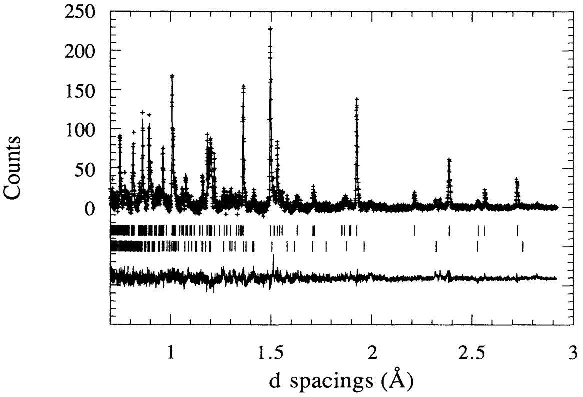

FIG. 3. Observed (shown as +) and fitted (shown as a continuous line) neutron-diffraction pattern measured from $(Ca,Na)_2CuO_2Cl_2$ at room temperature. The difference between the observed and fitted patterns is displayed at the bottom of the figure. The expected reflection positions for $(Ca,Na)_2CuO_2Cl_2$ (top row of markers) and CuO (bottom row) are marked underneath the diffraction pattern. The background has been subtracted.

The presence of interstitial anions in the $A_{2-x}B_xCuO_{4+\delta}$ family of superconductors can be an important contribution to the doping of these materials. For example interstitial anion defects have been reported for $La_2CuO_{4+\delta}$,[9] $La_{1.25}Dy_{0.75}CuO_{3.75}F_{0.5}$,[10] and more recently, $Sr_2CuO_2F_{2+\delta}$.[1] Static displacements of the near-neighbor atoms are associated with these defects. In this work we find little evidence to support the presence of interstitial anions in $(Ca,Na)_2CuO_2Cl_2$. Refinement of the occupancy of an O atom at the interstitial position (1/2,0,1/4) produces an occupancy of 0.02(2) oxygens per formula unit. This result is consistent with the absence of any static displacements. Further, the Goldsmidt tolerance factor[11] for this material is $t=1.05$ which would indicate that the $(Ca,Na)_2O_2$ layer is under compression and has no capacity to accommodate interstitial atoms. By comparison La_2CuO_4 has a tolerance factor of 0.88 which indicates that the La_2O_2 layer is under tension and can readily form interstitial defects within this layer.[8]

The possible doping mechanisms for this material have been discussed by Hiroi, Kobayashi, and Takano.[2] Attempts to optimize the doping for the solid solution $Ca_{2-x}Na_xCuO_2Cl_2$ (by varying $NaClO_4$ during fabrication) have indicated that a maximum T_c of 26 K is obtained at $x\sim 0.08$.[2] The Na content is estimated from the starting composition, not directly measured, and is not accurately known. However, this value is lower than the accepted optimum doping typically found in superconductors with this structure. For example, in $La_{2-x}Sr_xCuO_4$ an optimum T_c of 38 K is obtained at $x=0.15$.[9] To account for the smaller amounts of dopant for which the maximum T_c occurs Hiroi, Kobayashi, and Takano[2] considered additional doping mechanisms such

TABLE II. Selected bond lengths (in Å) for $Ca_2CuO_2Cl_2$ and $(Ca,Na)_2CuO_2Cl_2$.

Bond	$Ca_2CuO_2Cl_2$	$(Ca,Na)_2CuO_2Cl_2$
Cu-O (×4)	1.9344(1)	1.9248(1)
Cu-Cl (×2)	2.7539(1)	2.7615(3)
Ca-O (×4)	2.4902(2)	2.4899(5)
Ca-Cl (×4)	1.1856(1)	1.1820(1)

TABLE III. Comparison of selected bond lengths of superconductors with the tetragonal La_2CuO_4 structure.

	$La_{1.85}Sr_{0.15}CuO_4$ (Ref. 9)	$Sr_2CuO_2F_{2+\delta}$ (Ref. 1)	$(Ca,Na)_2CuO_2Cl_2$
Cu-apical anion	2.5959	2.45(1)	2.7615(3)
Cu-O_{plane}	1.8880	1.9228(1)	1.9248(1)

as doping via interstitial anions and the partial (rather than full) substitution of Cl^- for O^{2-} at the apical anion position. In this work we have demonstrated that these two latter possibilities are inconsistent with the neutron-powder-diffraction measurements. We conclude that Na substitution is likely to be the dominant doping mechanism. However, neither starting composition (as used by Hiroi, Kobayashi, and Takano or neutron diffraction (as reported here) can give an accurate measure of the Na content. Bond valence sums calculated from the refined bond lengths indicate that the effective charge of the Cu atom varies from 2.23 in nonsuperconducting $Ca_2CuO_2Cl_2$ to 2.28 in superconducting $(Ca,Na)_2CuO_2Cl_2$. The latter value is in good agreement with the effective Cu valence determined for $Sr_2CuO_2F_{2+\delta}$ (Ref. 1) but lower than that in $La_{1.85}Sr_{0.15}CuO_4$, which has a value of 2.44. The small difference in effective charge of the Cu atom as estimate from bond valence sums between the nonsuperconducting and superconducting samples may well indicate that this material is not optimally doped. In part this would offer an explanation for the lower T_c observed for this material as opposed to other materials which belong to the same structural family.

IV. CONCLUSION

Neutron-powder-diffraction measurements of $Ca_2CuO_2Cl_2$ and $(Ca,Na)_2CuO_2Cl_2$ demonstrated that for both compounds the apical anion position is fully occupied by Cl. For the superconductor $(Ca,Na)_2CuO_2Cl_2$ we do not measure significant occupancy at the interstitial anion position, nor do we see any static displacements in the structure that would suggest additional defects. Doping is evidenced by a decrease of the Cu-O bond and an increase of the Cu-Cl bond. Bond valence sums indicate that valence of the Cu atom increases. Although our direct sensitivity to Na substitution on the Ca site is limited, we conclude that such a substitution is likely to be the doping mechanism.

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[1] M. Al-Mamouri, P. P. Edwards, C. Greaves, and M. Slaski, Nature (London) **369**, 382 (1994).

[2] Z. Hiroi, N. Kobayashi, and M. Takano, Nature (London) **371**, 139 (1994).

[3] N. Kobayashi, Z. Hiroi, and M. Takano (unpublished).

[4] J. D. Jorgensen, J. J. Faber, 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).

[5] A. C. Larson and R. B. von Dreele, Los Alamos National Laboratory Report No. LAUR 86-78, 1990 (unpublished).

[6] R. B. von Dreele, J. D. Jorgensen, and C. G. Windsor, J. Appl. Crystallogr. **15**, 581 (1982).

[7] W. A. Dollase, J. Appl. Crystallogr. **19**, 267 (1986).

[8] A. March, Z. Kristallogr. **81**, 285 (1932).

[9] P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, B. A. Hunter, J. L. Wagner, F. C. Chou, and D. C. Johnston, Phys. Rev. B **48**, 499 (1993).

[10] P. Lightfoot, S. Pei, J. D. Jorgensen, X. X. Tang, A. Manthiram, and J. B. Goodenough, Physica C **169**, 15 (1990).

[11] J. B. Goodenough and A. Manthiram, J. Solid State Chem. **88**, 115 (1990).