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BRIEF COMMUNICATION

$Nd_4Cu_2O_7$: A Copper(I) Oxide with a Novel Cooperatively Distorted T′ Type Structure

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The crystal structure of $Nd_4Cu_2O_7$ (monoclinic, space group $A2/m$, $a = 8.4493(2)$ Å, $b = 3.7591(1)$ Å, $c = 12.6006(5)$ Å, $\beta = 109.576(4)^\circ$, $Z = 2$), prepared by topotactic reduction of the high-T_c superconductor parent phase Nd_2CuO_4, has been determined by Rietveld fitting of time-of-flight neutron powder diffraction data ($R_{wp} = 1.90\%$). A novel oxygen-vacancy-ordered arrangement of cooperatively distorted Cu_2O_3 planes containing 2- and 4-coordinate Cu^+ sites is found. © 1998 Academic Press

Ln_2CuO_4 compounds (Ln = lanthanide) adopt two different structure types: the K_2NiF_4 (T) structure containing octahedrally coordinated Cu^{2+}, as found for La_2CuO_4, and the Nd_2CuO_4 (T′) structure containing Cu^{2+} in a square-planar site. Hole-doped superconductivity can be induced by oxidizing La_2CuO_4 through divalent cation substitution to yield the solid solution phases $La_{2-x}M_xCuO_4$ (M = Ca, Sr, Ba) or by insertion of excess oxygen to give $La_2CuO_{4+\delta}$ (1–3). By contrast, Nd_2CuO_4 can be reduced through Ce^{4+} substitution to yield the electron-doped superconductor $Nd_{2-x}Ce_xCuO_4$ (4, 5); however, attempts to prepare partially reduced $Nd_2CuO_{4-\delta}$ phases have resulted in the formation of an apparent Cu^+ oxide, $Nd_2CuO_{3.5}$ (6), for which a disordered Sr_2CuO_3 type structure (a vacancy-ordered T type structure) was determined using integrated powder X-ray intensities (7). We have optimized the synthesis of large (4*g*), phase-pure, polycrystalline samples of $Nd_2CuO_{3.5}$ by low-temperature hydrogen reduction, giving sufficient material for structure determination from time-of-flight neutron powder diffraction. This shows the product to be a stoichiometric phase $Nd_4Cu_2O_7$ with a novel oxygen-defect-ordered T′ structure containing cooperatively distorted $Cu^I_2O_3$ layers.

Polycrystalline Nd_2CuO_4 was prepared by solid-state reaction of Nd_2O_3 and CuO at 1025°C. Four grams of this powder was spread evenly in an alumina boat and heated at 335°C for 11 h in a tube furnace under a flowing 0.05 : 0.95 H_2–N_2 mixture to give the reduced phase $Nd_4Cu_2O_7$, which was identified by powder X-ray diffraction (7). Longer reaction times or higher temperatures resulted in decomposition to Nd_2O_3 and Cu, whereas shorter times or lower temperatures gave a mixture of Nd_2CuO_4 and $Nd_4Cu_2O_7$, and no intermediate Nd_2CuO_{4-x} phases were observed. The oxygen content of $Nd_4Cu_2O_7$ was confirmed by thermogravimetric analyses. Heating under 0.05 : 0.95 H_2–N_2 gave the products Nd_2O_3 and Cu, and the mass loss of 1.9(1)% corresponds to the composition $Nd_2CuO_{3.47(2)}$. Heating $Nd_4Cu_2O_7$ in O_2 re-formed the parent compound Nd_2CuO_4, and the mass increase of 2.0(1)% gives the formula $Nd_2CuO_{3.49(2)}$, assuming the product to be oxygen stoichiometric. Time-of-flight neutron powder diffraction data were collected at 4 K on the POLARIS instrument at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, U.K. Rietveld refinement (8) of the structure was performed using the GSAS package (9).

The powder X-ray diffraction pattern of $Nd_4Cu_2O_7$ was indexed on a body-centered orthorhombic cell with parameters $a_0 = 4.2427(2)$ Å, $b_0 = 3.7725(2)$ Å, and $c_0 = 11.9262(6)$ Å, similar to that of Sr_2CuO_3, and three additional weak reflections could be indexed on the $2a_0 \times b_0 \times 2c_0$ supercell observed previously by selected-area electron diffraction (10). Many intense superstructure peaks in the neutron diffraction pattern could also be indexed using this supercell (Fig. 1). The previously reported Sr_2CuO_3 type model (7) yielded poor Rietveld fits to the neutron data and so a series of models based on the T′ structure with oxygen defects in the CuO_2 planes and oxygen occupancy of possible sites in the Nd layers were tested. The only one to give a good fit to the neutron data is that shown in Fig. 1 and Table 1 and no significant occupancy of any other oxygen site was found. The structure has an A-centered monoclinic cell (space group $A2/m$) with lattice

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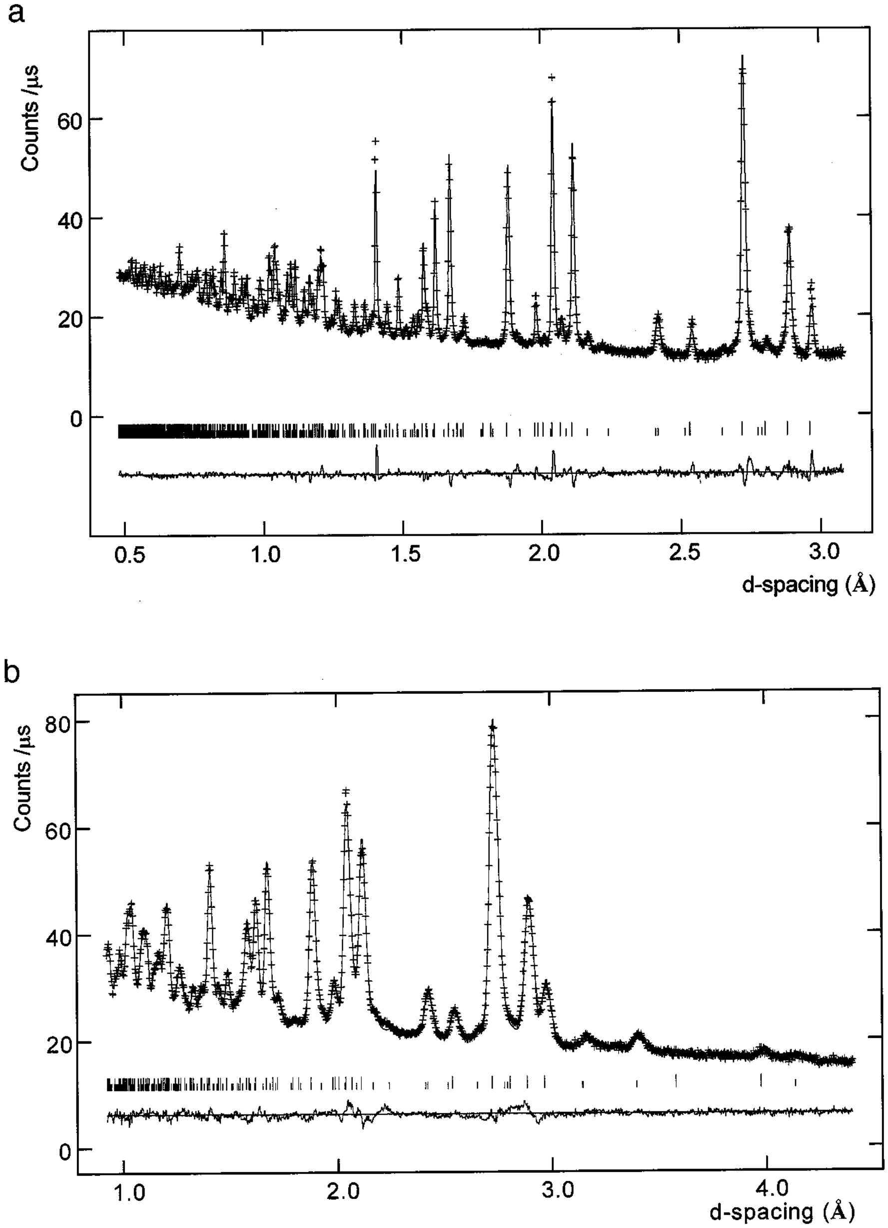

FIG. 1. Observed, calculated, and difference time-of-flight neutron powder diffraction profiles for $Nd_4Cu_2O_7$ based on data collected on (a) the backscattering and (b) the low-angle detectors of POLARIS. Long and short markers indicate Bragg reflections for an orthorhombic Sr_2CuO_3 type cell and the additional supercell reflections, respectively.

vectors $\mathbf{a} = 2\mathbf{a}_0$, $\mathbf{b} = \mathbf{b}_0$, and $\mathbf{c} = \mathbf{c}_0 - \mathbf{a}_0$. This model was refined simultaneously using data from both the low-angle ($2\theta = 35°$) and backscattering ($2\theta = 145°$) POLARIS detectors covering *d*-space ranges of 0.9–4.4 and 0.5–3.1 Å, respectively (Fig. 1).

The structure of $Nd_4Cu_2O_7$ is derived from that of Nd_2CuO_4 by ordered removal of one-quarter of the oxygens in the CuO_2 layers, as shown in Fig. 2. This gives rise to seven-coordinate Nd sites and alternating four- and two-coordinate Cu sites along the *a* axis. The Cu(1) coordination is a very distorted square plane with distances of 2×1.88 Å to O(1) and 2×2.40 Å to O(2), in contrast to the regular coordination (4×1.97 Å) of Cu^{2+} in the parent compound Nd_2CuO_4 (11). Cu(2) has a linear twofold coordination with Cu(2)–O(2) bond distances of 1.831(1) Å. Hence, the Cu_2O_3 planes are cooperatively distorted to give each Cu site a linear coordination geometry with two short Cu–O bonds characteristic of Cu^{+}. This distortion results in a puckering of the planes, giving a Cu(1)–O(2)–Cu(2) bond angle of 173°. Bond valence calculations (Table 1) using the method of

TABLE 1
Refinement Results[a] for $Nd_4Cu_2O_7$ in Space Group *A*2/*m* at 4 K and Calculated Bond Distances with Esd's in Parentheses

Profile data

$2\theta = 145°$	No. of reflections = 2203	No. of points = 3715	$R_{wp} = 1.82\%$	$R_p = 2.21\%$	$R_F = 1.40\%$
$2\theta = 35°$	No. of reflections = 404	No. of points = 3116	$R_{wp} = 2.22\%$	$R_p = 1.82\%$	$R_F = 1.60\%$
Total	No. of parameters = 52	$\chi^2 = 1.90$	$R_{wp} = 1.90\%$	$R_p = 2.06\%$	$R_F = 1.60\%$

Cell parameters

$a = 8.4493(2)$ Å $b = 3.7591(1)$ Å $c = 12.6006(5)$ Å $\beta = 109.576(4)°$

Atomic parameters[b]

Atom	Symmetry position	*x*	*y*	*z*	BVS[c]
Nd(1)	4*i*	0.1668(2)	0	0.3586(1)	2.92
Nd(2)	4*i*	0.3180(2)	0.5	0.1589(1)	2.82
Cu(1)	2*a*	0	0	0	1.02
Cu(2)	2*d*	0.5	0	0	0.94
O(1)	2*b*	0	0.5	0	1.66
O(2)	4*i*	0.2887(2)	0	0.0098(2)	1.57
O(3)	4*i*	0.1214(4)	0	0.7492(1)	2.31
O(4)	4*i*	0.3845(4)	0	0.2755(1)	2.01

Interatomic distances (Å)

Nd(1)–O(1) × 1	2.616(2)	Nd(2)–O(1) × 1	2.761(1)
Nd(1)–O(2) × 2	2.629(2)	Nd(2)–O(2) × 2	2.610(2)
Nd(1)–O(3) × 1	2.357(3)	Nd(2)–O(3) × 1	2.307(4)
Nd(1)–O(3′) × 2	2.286(1)	Nd(2)–O(4) × 2	2.336(1)
Nd(1)–O(4) × 1	2.402(3)	Nd(2)–O(4′) × 1	2.368(3)
Cu(1)–O(1) × 2	1.8796(1)	Cu(2)–O(2) × 2	1.831(1)
Cu(1)–O(2) × 2	2.400(1)		

[a] Further details are available from the authors.

[b] Constrained isotropic thermal *U* factors were 0.0004(1) Å^2 for the metal atoms and 0.0026(2) Å^2 for the oxygen atoms.

[c] Bond valence sums were calculated using the method and parameters in ref 12.

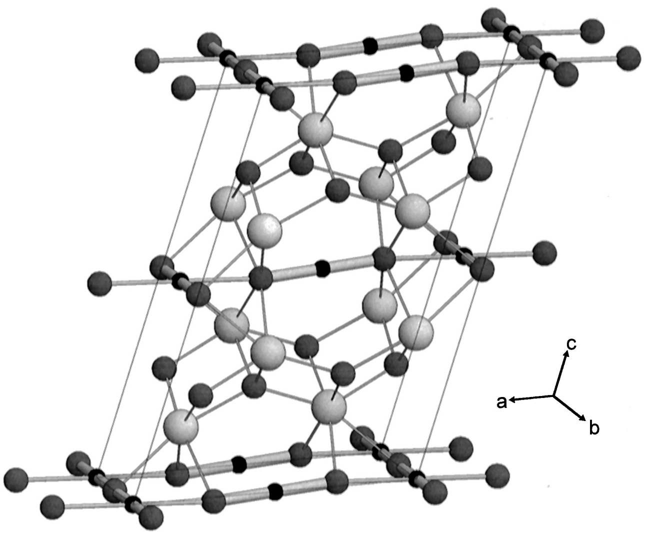

FIG. 2. Crystal structure of $Nd_4Cu_2O_7$, in which black, dark gray, and light gray spheres represent Cu, O, and Nd atoms, respectively, and the two short Cu–O bonds around each Cu^+ are emphasized.

Brown and Altermatt (12) confirm the presence of Cu^+ and Nd^{3+}. It is notable that bond valence sums for the O(1) and O(2) sites within the Cu_2O_3 planes are significantly less than the expected value of 2. Such deviations reflect internal stresses in the coordination polyhedron of an atom due to geometric constraints imposed by the rest of the structure (13) and evidence a stress within the Cu_2O_3 planes. By contrast, the O(3) and O(4) sites in the fluorite type Nd_2O_2 layers appear to be unstressed with mean Nd–O–Nd bond angles of 109.5° and 109.1°, respectively, very close to the ideal tetrahedral value.

Previous high-temperature studies of the Nd_2O_3–Cu_2O system have found only the Delafossite type phase $NdCuO_2$ (14), whereas $Nd_4Cu_2O_7$ is formed by the topotactic reduction of Nd_2CuO_4 at low temperatures and decomposes to $NdCuO_2$ and Nd_2O_3 above 650°C. $Nd_4Cu_2O_7$ is the only reported example of a Cu(I) oxide obtained by topotactic reduction of a high-T_c superconductor type structure. This unique reaction results from the expansive stress within the CuO_2 planes in Nd_2CuO_4, which also makes it the only simple copper oxide structure that can be electron-doped by Ce^{4+} substitution to give a superconducting phase.

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