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$Sr_6Nd_3Cu_6O_{17}$: An Intergrowth of the "123"-Phase and Rock Salt-Type Structure

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A new layered cuprate, $Sr_6Nd_3Cu_6O_{17}$, has been synthesized using an argon flow. The structure of this orthorhombic phase (a = 3.7547 Å, b = 11.4882 Å, c = 20.0976 Å) determined by neutron diffraction, is closely related to the "0212"-type and to the "123" structures. It can be described as an intergrowth of $YBa_2Cu_3O_7$-type layers with rock salt-type (RS) layers according to the formulation $[Sr_{7/6}Nd_{5/6}Cu_2O_{4.66}]^{\text{"123"}}[Sr_{5/6}Nd_{1/6}O]^{RS}$. The CuO_5 pyramids and especially the CuO_4 groups are strongly distorted. The distribution of the strontium and neodymium cations, which seems to be an important factor for the stabilization of this framework, is discussed.

The studies of the system "$Ln_2SrCu_2O_6$–$Sr_2LnCu_2O_{6-y}$" have shown the ability of the latter to form layered cuprates belonging to the family $[ACuO_{3-x}]_m[A'O]_n$ and characterized by an intergrowth of double oxygen deficient perovskite layers (m = 2) with single rock salt-type (RS) layers (n = 1). The oxides $Ln_{2-x}A_{1+x}Cu_2O_6$ (A = Ca, Sr) (*1, 2*) and $Sr_{2-x}Ln_{1+x}Cu_2O_{6-y}$ (*3–6*) indeed illustrate this point of view. However, the crystal chemistry of this system is very complex, owing to the issue of oxygen nonstoichiometry which may involve different possible distributions of the anionic vacancies in the perovskite layers. The lanthanide rich cuprates $Ln_{2-x}A_{1+x}Cu_2O_6$ (*1, 2*) indeed exhibit the classical intergrowth of double pyramidal copper layers $[Cu_2O_5]_\infty$ with single rock salt-type layers, whereas a tripling of one parameter (b = 3a) was observed for the strontium rich cuprates $Sr_{2-x}Ln_{1+x}Cu_2O_{6-y}$ (*3*). Recently, neutron diffraction studies of the oxides $Nd_{1.4}Sr_{1.6}Cu_2O_{5.79}$ (*4*) and $NdSr_2Cu_2O_{5.76}$ (*5*) allowed an ordered distribution of the oxygen vacancies in the structure, explaining for those phases the tripling of one of the cell parameters. The anionic distribution in these structures is fundamentally different from that observed for the lanthanide rich phases, since it shows the formation of groups of 2 × 2 corner-sharing CuO_5 pyramids whose basal plane is orthogonal to the layers. The analysis of the structure of $NdSr_2Cu_2O_{5.76}$ (*5*) led us to suggest that it was the result of the coexistence of two extreme structures with compositions $Sr_2NdCu_2O_6$ and $Sr_2NdCu_2O_{5.66}$, respectively. The very nice determination of the tunneled structure recently performed by Grasmeder and Weller (*4*) for $Nd_{1.4}Sr_{1.6}Cu_2O_{5.79}$ shows that it corresponds to the first composition. We report here on the synthesis and the structure determination by neutron diffraction of the oxide $Sr_6Nd_3Cu_6O_{17}$, which corresponds to the second composition.

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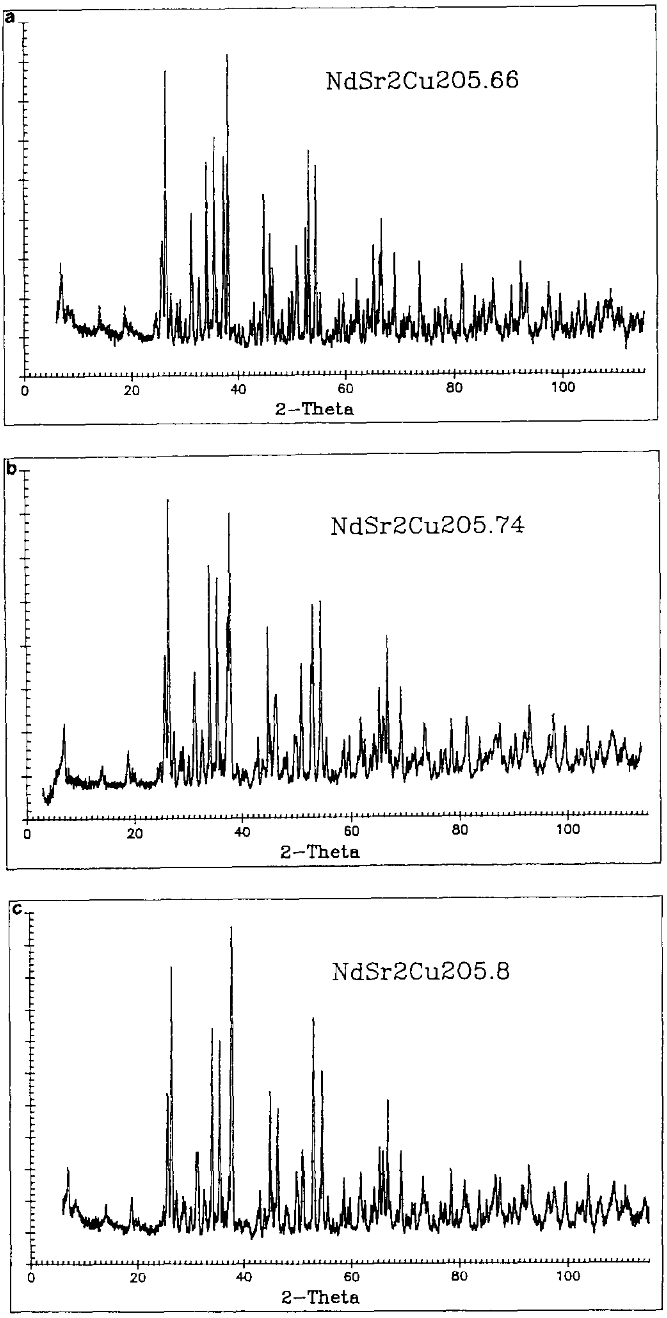

FIG. 1. Powder neutron diffraction patterns of the oxides $Sr_2NdCu_2O_y$ vs gas atmosphere: (a) argon, $Sr_6Nd_3Cu_6O_{17}$ (y = 5.66); (b) air, $Sr_2NdCu_2O_{5.76}$; (c) oxygen, $Sr_2NdCu_2O_{5.8}$; (d) results of refinements for $Sr_6Nd_3Cu_6O_{17}$: observed profile (dotted line), calculated profile and difference (solid lines).

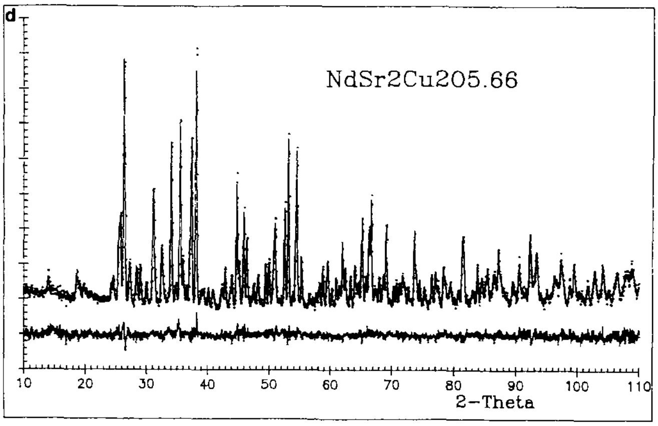

FIG. 1—*Continued*

Experimental

The oxide $Sr_2NdCu_2O_{5.76}$ (*5*) was synthetized by solid state reaction from neodymium and copper oxides and strontium carbonate. The mixture was intimately ground in an agate mortar and heated in air at 1100°C for 5 hr and then slowly cooled. The oxide "$Sr_2NdCu_2O_{5.66}$" was prepared by annealing $Sr_2NdCu_2O_{5.76}$ under flowing Ar gas at 600°C for 10 hr.

The purity of the sample was checked by X-ray diffraction using a Philips counter working with Cu$K\alpha$ radiation. The oxygen content was determined by chemical (redox titration) and thermogravimetric analyses (i.e., reduction under H_2/Ar).

The symmetry of the crystals was studied by electron diffraction using a JEOL 120CX electron microscope fitted with a side entry goniometer ($\pm 60°$).

The neutron diffraction pattern was registered using the multicounter 3t2, installed at the ORPHEE reactor of the Leon Brillouin laboratory, Saclay (*8*). A short neutron wavelength of 1.2269 Å was used to collect data by step scanning over an angular range of $6° < 2\theta < 115°$, in increment of 0.05 (2θ). The 4-cm^3 powder sample was introduced into a cylindrical vanadium can (ϕ = 6 mm) at room temperature. The analysis of the data was performed by the Rietveld profile method with the computer program DBW 3.2 (*9*). A gaussian peak shape was assumed for the 660 bragg peaks observed from 13° to 110°.

Results and Discussion

For the above experimental conditions, a pure phase was isolated whose oxygen content deduced from the chemical analysis led to the formula $Sr_6Nd_3Cu_6O_{17}$, i.e., $Sr_2NdCu_2O_{5.66}$ to be compared to the air-synthesized phase $Sr_2NdCu_2O_{5.76}$ (*5*).

The E.D. patterns of $Sr_6Nd_3Cu_6O_{17}$ are very similar to those observed for $Sr_2NdCu_2O_{5.76}$ (*5*). Both phases crystallize in an orthorhombic cell with $a \approx a_p$, $b \approx 3a_p$ and $c \approx 20$ Å, where a_p is the mean parameter of the ideal perovskite cell. The extra spots which imply a tripling of the b parameter ($b \approx 3a_p$) are generally very intense, leading to the reflection conditions hkl: $h + k + l = 2n$ characteristic of a I space group. The N.D. pattern of $Sr_6Nd_3Cu_6O_{17}$ (Fig. 1a) is also closely related to that of the air-synthesized phase $Sr_2NdCu_2O_{5.76}$ (Fig. 1b) and of the oxygen-synthesized oxide

TABLE I

CELL PARAMETERS OF THE OXIDES $Sr_2NdCu_2O_{6-x}$ OBTAINED FROM N.D. PATTERNS

	Gas flow	a (Å)	b (Å)	c (Å)	V (Å)
$Sr_2NdCu_2O_{5.80}$	O_2	3.7806 (1)	11.4054 (5)	20.1010 (8)	876.74
$Sr_2NdCu_2O_{5.76}$	Air	3.7701 (2)	11.4381 (5)	20.0938 (9)	866.50
$Sr_2NdCu_2O_{5.66}$ or $Sr_6Nd_3Cu_6O_{17}$	Argon	3.7547 (1)	11.4882 (4)	20.0976 (7)	866.90

$Sr_2NdCu_2O_{5.8}$ (Fig. 1c). However, the cell parameters of those three oxides (Table I) show a significant variation with the oxygen content. One indeed observes that *a* increases and *b* decreases as the oxygen content increases, whereas *c* remains approximately unchanged. This variation of the distortion is easily explained by an evolution of the oxygen distribution as the oxygen content changes. On the other extreme, the cell volume remains unchanged, owing to the small variation of the oxygen content (less than 2% per mole oxygen).

The neutron diffraction study was performed in the space group *Immm* using the structural parameters previously obtained for the air-synthesized oxide $Sr_2NdCu_2O_{5.76}$ as a starting model. Like for this latter oxide, the refinement of the cationic positions and oxygen positions, *B* factors, and occupancy factors successively showed that the metallic sites and the oxygen sites $O_{(1)}$, $O_{(2)}$, $O_{(5)}$, $O_{(6)}$, and $O_{(7)}$ are fully occupied. In the same way no oxygen was found in the $O_{(3)}$ positions, contrary to the $La_2SrCu_2O_6$-type oxides (*2*). But the important difference with respect to $Sr_2NdCu_2O_{5.76}$ deals with the $O_{(4)}$ sites, which are found to be absolutely empty for $Sr_6Nd_3Cu_6O_{17}$. The occupation of the split $O_{(8')}$ sites instead of $O_{(8)}$ is also confirmed. As deviations for ideal values were not observed, the oxygen occupation factors were all fixed in the final refinement. The final refinement of all atomic positions and of the thermal parameters led to the following reliability factors: $R_p = 4.84\%$, $R_{wp} = 6.25\%$, $R_I = 5.64\%$. (Reliability factors used here are described in (*9*)). The final atomic parameters are given in Table II. The final structural model corresponds to the formulation $Sr_6Nd_3Cu_6O_{17}$ and its oxygen content is in agreement with the TG analysis.

These results show definitely that a new layered structure, regular intergrowth of the $YBa_2Cu_3O_7$ [123]-type structure with the rock salt-type structure, can be synthesized in the form of a pure phase $Sr_6Ln_3Cu_6O_{17}$. The structure of this phase (Fig. 2) is indeed built up from "123"-type ribbons $[Sr_{7/6}Nd_{5/6}Cu_2O_{4.66}]_\infty$ running along **b**, and from $[Sr_{5/6}Nd_{1/6}O]_\infty$ rock salt-type layers parallel to (100). Thus, $Sr_6Nd_3Cu_6O_{17}$ can be considered as the second member ($m = 2$, $n = 1$) of a series of intergrowths of general formula $(ACuO_{2.33})_m^{\text{"123"}} \cdot (AO)_n^{\text{RS}}$, in which *A* will correspond to an adequate content of alkaline earth cations (Ca, Sr, Ba) and of lanthanides. The "123"-type ribbons, which are two CuO_5 or CuO_4 polyhedra wide along **c**, exhibit a significant difference with the classical $YBa_2Cu_3O_7$ structure (*10*). The Cu–O interatomic distances (Table III) show indeed that the CuO_4 groups as well as the CuO_5 pyramids are strongly distorted with Cu–O distances ranging from 1.85 to 2.22 Å. The apical Cu–O distance of the CuO_5 pyramid (2.22 Å) is shorter than that observed for $YBa_2Cu_3O_7$ (2.29 Å), whereas a large distortion is observed in the basal

TABLE II

$Sr_6Nd_3Cu_6O_{17}$: FINAL ATOMIC PARAMETERS

	x	y	z	B	SOF
$Nd_{(1)}$	0	0	0	0.20 (10)	1
$(Nd/Sr)_{(2)}$	0	0.2989 (4)	0	0.49 (12)	0.56/0.44 (16)
$(Nd/Sr)_{(3)}$	0	0	0.1962 (3)	0.42 (11)	0.44/0.56 (16)
$Sr_{(4)}$	0	0.3231 (4)	0.1772 (2)	0.71 (7)	1
$Cu_{(1)}$	0	0	0.5881 (3)	1.33 (9)	1
$Cu_{(2)}$	0	0.3521 (3)	0.6010 (2)	0.53 (5)	1
$O_{(1)}$	0	0.1610 (5)	0.4154 (2)	1.07 (8)	1
$O_{(2)}$	0	0.1352 (4)	0.0979 (3)	0.71 (6)	1
$O_{(3)}$	0	0	0.6849 (4)	1.40 (14)	1
$O_{(6)}$	0	0.3495 (5)	0.7013 (2)	0.97 (8)	1
$O_{(7)}$	0	0.3678 (5)	$\frac{1}{2}$	0.27 (11)	1
$O_{(8')}$	0.3077 (44)	0	$\frac{1}{2}$	2.81 (36)	0.5

Note. $R_p = 4.84\%$; $R_{wp} = 6.25\%$; $R_I = 5.64\%$.

plane (1.88 to 2.02 Å) compared to $YBa_2Cu_3O_7$ (1.93 to 1.96 Å). The CuO_4 groups are no more planar: two $O_{(1)}$ atoms and $O_{(5)}$ remain approximately in the same plane, whereas $O_{(8')}$, which ensures the junction between two CuO_4 groups, is significantly out of this plane, leading to a Cu–O–Cu angle of 147° instead of 180°. The configuration of copper is intermediate between square planar and flattened tetrahedron. Those features are easily understable if one considers the sequence of "123" ribbons

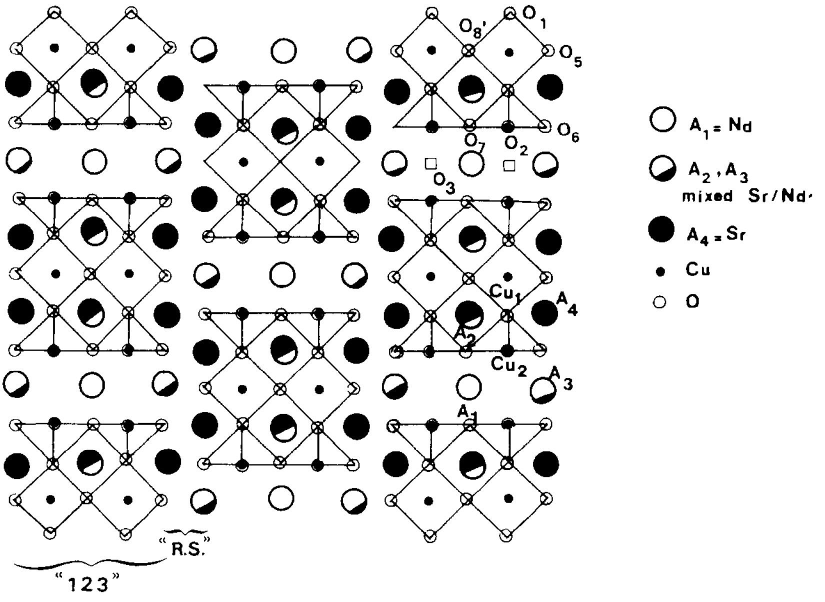

FIG. 2. $Sr_6Nd_3Cu_6O_{17}$ structure projected along [100]. The cations Sr and Nd are labeled A.

TABLE III

INTERATOMIC DISTANCES IN $Sr_6Nd_3Cu_6O_{17}$ CALCULATED STANDARD DEVIATIONS ARE IN PARENTHESES

$Nd_{(1)}–O_{(2)}$	2.507(6) Å ×4	$Cu_{(1)}–O_1$	1.851(6) Å ×2
$Nd_{(1)}–O_{(7)}$	2.415(4) Å ×4	$Cu_{(1)}–O_{8'}$	2.114(10) Å ×1
$(Nd/Sr)_{(2)}–O_{(1)}$	2.574(3) Å ×4	$Cu_{(1)}–O_5$	1.945(10) Å ×1
$(Nd/Sr)_{(2)}–O_{(2)}$	2.722(6) Å ×2	$Cu_{(2)}–O_1$	2.220(7) Å ×1
$(Nd/Sr)_{(2)}–O_{(7)}$	2.682(5) Å ×2	$Cu_{(2)}–O_2$	1.884(1) Å ×2
$(Nd/Sr)_{(2)}–O_{(8')}$	2.420(7) Å ×1	$Cu_{(2)}–O_6$	2.016(6) Å ×1
$(Nd/Sr)_{(3)}–O_{(2)}$	2.513(7) Å ×2	$Cu_{(2)}–O_7$	2.038(4) Å ×1
$(Nd/Sr)_{(3)}–O_{(5)}$	2.390(10) Å ×1		
$(Nd/Sr)_{(3)}–O_{(6)}$	2.555(4) Å ×4		
$Sr_{(4)}–O_{(1)}$	2.650(4) Å ×2		
$Sr_{(4)}–O_{(2)}$	2.683(7) Å ×1		
$Sr_{(4)}–O_{(5)}$	2.771(3) Å ×2		
$Sr_{(4)}–O_{(6)}$	2.772(6) Å ×2		
$Sr_{(4)}–O_{(6)}$	2.460(6) Å ×1		

along **c** (Fig. 2). Two successive ribbons are indeed shifted by about 3.8 Å along **b**, so that at a same level along this latter direction, a neodymium plane is replaced by a copper plane. Such an arrangement induces strains in the structure which can only be decreased by a distortion of the CuO_4 and CuO_5 polyhedra and by their tilting.

The distribution of the strontium and neodymium cations is remarkable and is certainly an important factor for the stabilization of such a structure. One indeed observes that in the middle of the "123"-type ribbons the smaller cations, neodymium, take the place of yttrium in eightfold coordination ($Nd_{(1)}$ sites), whereas in the rock salt-type layers, the sites which exhibit an eightfold coordination ($Sr_{(4)}$-sites) are only occupied by strontium. On the other extreme, the cationic sites which are located at the intersection of the rock salt layer and the basal planes of the CuO_5 pyramids ($(Nd/Sr)_{(3)}$ sites) are occupied half by strontium and half by neodymium. In the same sense it is worth pointing out that the barium sites, in the "123" ribbons, are occupied by much smaller cations, half neodymium and half strontium ($(Nd/Sr)_{(2)}$ sites). This latter occupancy may be at the origin of the distortion of the CuO_4 square groups and may allow an adjustment of the "123" and rock salt-type layers.

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