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Neutron Powder Diffraction Study of the Crystal Structure of $YSr_2AlCu_2O_7$

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The structure of $YSr_2AlCu_2O_7$ has been analyzed by neutron powder diffraction techniques. This compound crystallizes with space group $P4/mmm$ symmetry and with lattice parameters $a = 3.8646(1)$, $c = 11.1139(3)$Å. The general structural features of $YSr_2AlCu_2O_7$ are similar to those found for the 123 superconductor $YBa_2Cu_3O_{6+x}$, and in particular the sequence of layers is the same in the two materials, with SrO substituting for BaO. The Al ions substitute for the copper ions of the chain sites of the 123 parent structure and have tetrahedral coordination. The tetrahedra form chains propagating along the a and b axes on the basal plane of the unit cell. Thus the structure is made of short-range domains within which the local symmetry is orthorhombic. All the oxygen atoms in this compound have a disordered configuration around the specialized positions of the 123 structure. This arrangement results in tilting of the CuO_5 pyramids and in significant distortions of the coordination polyhedra of the other cations.

Introduction

In order to establish the structural conditions that favor or inhibit the occurrence of superconductivity in materials with the structure of $YBa_2Cu_3O_{7-x}$, it is important to analyze the changes that take place when the copper ions are totally or partially replaced by metal ions with different coordinations, and to correlate such changes with the electrical properties of the resulting materials. Thus, it is not surprising that compounds of the general formula $LnSr_2MCu_2O_7$ (Ln = Er, . . . , La, Y; M = Ga, Co, Al, Pb, Fe) have recently received considerable attention because of their chemical and structural relationship to the 123 superconductor (*1–3*). The compounds $YSr_2GaCu_2O_7$ and $NdSr_2GaCu_2O_7$ (*2*), as well as $YSr_2CoCu_2O_7$ (*3*), have been characterized by X-ray and/or neutron diffraction methods and in all cases they have been found to be orthorhombic and to have striking similarities with the structure of the 123 superconductor. In particular, the atomic arrangement in the blocks of layers $(SrO)(CuO_2)(Ln)(CuO_2)(SrO)$ and $(BaO)(CuO_2)(Y)(CuO_2)(BaO)$ is quite similar in the two structural types, showing identical double layers of CuO_2 separated by a layer of the trivalent rare-earth ion. Layers of SrO replace BaO and, as a result, the copper ions have fivefold pyramidal coordination in both cases. The significant differences between the two structures result from the fact that the copper ions of the square-planar chains

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are replaced by Ga or Co ions having tetrahedral coordination, with the GaO_4 or CoO_4 tetrahedra arranged in chains running along the diagonal of the basal plane of the 123 unit cell. Although the atomic configuration of the GaO and CoO layers and that of the CuO_x layers are different, the transformation from one to the other can be accomplished by means of simple shifts of the oxygen atoms (*3*). It would be of interest to inquire if the same relationship holds in systems in which metal ions other than Ga and Co replace the chain copper of $YBa_2Cu_3O_{7-x}$.

The compound $YSr_2AlCu_2O_7$ has been prepared in single phase form and has been found to have an apparent tetragonal symmetry (*1*, *2*). Attempts to refine the structure from X-ray powder diffraction data showed, however, a pronounced disorder in the basal plane, involving both the cation and the oxygen sites (*2*). In fact, the disordering of the atoms proved to be so complex that it was not even possible to establish the type of Al coordination from the available data. Our neutron powder diffraction study of $YSr_2AlCu_2O_7$ was therefore initiated to clarify the nature of this disorder, and to relate the structure of the compound to those of $YSr_2GaCu_2O_7$ and $YSr_2CoCu_2O_7$. The results of our structural analysis are reported in the present paper.

Experimental

Ceramic samples were prepared by standard ceramic techniques using $Sr(NO_3)_2$, CuO, Y_2O_3, and $Al(NO_3)_3 \cdot 9H_2O$. Typical sample preparation involved slow heating of the starting materials in an alumina crucible to 900°C and cooling. The resulting powder was well ground and subjected to several cycles of grinding and firing at 950–1050°C with a final anneal at 500°C in flowing O_2. Neutron powder diffraction measurements were made at room temperature with the high-resolution five-counter diffractometer at the Reactor of the National Institute of Standards and Technology, using the experimental conditions given in Table I. All refinements were made with the Rietveld method (*4*), adapted to the multicounter diffractometer and modified to include background parameters (*5*). In all cases, the peak shapes were described by means of Pearson functions.

The first refinements were made assuming a model based on the symmetry of space group *Pmmm*, with the structure of the 123 superconductor in which Al replaces the chain copper Cu(1) and Sr replaces Ba. The results of these calculations were not quite satisfactory, but they showed a great degree of disorder in the structure, reflected in the high values of the thermal factors of almost all the atoms. It was therefore natural to generalize this initial model by splitting the positions occupied by the oxygen atoms in ways that would improve the agreement between observed and calculated intensities and result in acceptable values of the atomic thermal parameters. The cases analyzed and the *R* factors obtained for each configuration of the oxygen atoms are shown in Table II in the order in which they were considered. Clearly, the best agreement was achieved for the tetragonal structure V in which all the oxygen atoms are disordered around their idealized positions. This last model was then refined with anisotropic thermal parameters for the metal atoms. The B_{ii} values obtained for the Al atom were $B_{11} = B_{22} = 4.7(4)$, $B_{33} = -0.2(3)$ Å. Since this anomalous result may be due to static disorder, a further refinement was carried out with the Al sites split over the positions $x, y, 0$ of space group *P4/mmm*. During the refinement the high correlation (over 95%) between the coordinates x and y made it necessary to constrain these two parameters to be equal. In addition, the Al isotropic thermal parameter was kept fixed at a reasonable value ($B = 0.4$ Å^2), again because its high correlation with the displacement x (over 75%) makes it dif-

TABLE I

COLLECTION OF INTENSITY DATA

Monochromatic beam:	220 reflection of a Cu monochromator
Wavelength:	1.545(1) Å
Horizontal divergences:	10′, 20′, 10′ of arc for the in-pile, monochromatic-beam, and diffracted-beam collimators, respectively
Sample container:	Vanadium can of about 10 mm diameter
2θ angular range:	5°–120°; steps, 0.05°
Scattering amplitudes ($\times 10^{-12}$):	b(Y) = 0.775, b(Sr) = 0.702, b(Al) = 0.345, b(Cu) = 0.772, b(O) = 0.581
Peak shape:	Pearson VII

ficult to vary these two parameters together. The final results of these calculations are given in Table III. Selected bond distances are reported in Table IV and Fig. 1 shows the agreement between observed and calculated intensities for the five counters of the diffractometer.

Discussion of the Structure

The unit cell of $YSr_2AlCu_2O_7$ is schematically represented in Fig. 2. A comparison of this structure with those of $YSr_2GaCu_2O_7$ (*2*) and $YSr_2CoCu_2O_7$ (*3*) shows similarities as well as differences in the atomic configurations. The block of layers $(SrO)(CuO_2)(Y)(CuO_2)(SrO)$ is common to the three structures and, therefore, the coordination and the bond distances of the yttrium and copper cations are basically similar to the three materials. However, the distribution of the oxygen atoms O(1) located on the basal plane of the M ions (M = Ga, Co, Al) varies from compound to compound. The possible oxygen sites on the MO layers (Fig. 3) are closely related to those on the CuO_y basal plane of the parent structure of the superconductor $YBa_2Cu_3O_{6+y}$. The shifts from the idealized positions $\frac{1}{2}, 0, 0$ and $0, \frac{1}{2}, 0$ are undoubtedly caused by the coordination

TABLE II

SHIFTS OF THE OXYGEN ATOMS IN $YSr_2AlCu_2O_7$ AT ROOM TEMPERATURE[a]

	I	II	III	IV	V
O(11)	$0, \frac{1}{2}, 0$	$x, \frac{1}{2}, 0$	$x, \frac{1}{2}, 0$	$x, \frac{1}{2}, 0$	$x, \frac{1}{2}, 0$
O(12)			$\frac{1}{2}, y, 0$	$\frac{1}{2}, y, 0$	
O(2)	$\frac{1}{2}, 0, z$	$\frac{1}{2}, 0, z$	$\frac{1}{2}, 0, z$	$\frac{1}{2}, 0, z$	$\frac{1}{2}, 0, z$
O(3)	$0, \frac{1}{2}, z$	$0, \frac{1}{2}, z$	$0, \frac{1}{2}, z$	$0, \frac{1}{2}, z$	$\frac{1}{2}, 0, z$
O(4)	$0, 0, z$	$x, 0, z$	$x, 0, z$	x, x, z	x, x, z
R_N	12.56	9.35	8.26	7.87	5.97
R_P	9.29	8.34	7.84	7.65	7.09
R_W	12.29	11.17	10.26	10.03	9.49
R_E	4.49	4.49	4.49	4.49	4.49
χ	2.74	2.49	2.29	2.23	2.11

[a] *Pmmm* symmetry is used in I, II, III, and IV with $a = b$, $x_{O(11)} = y_{O(12)}$, and $z_{O(2)} = z_{O(3)}$; *P4/mmm* symmetry is used in *V* with $z_{O(2)} \neq z_{O(3)}$; i.e., the position is split along the c axis. In all refinements the temperature factors of all atoms were varied isotropically.

TABLE III

REFINED STRUCTURAL PARAMETERS OF $YSr_2AlCu_2O_7$[a] AT ROOM TEMPERATURE

Atom	Position		x	y	z	B(Å^2)	Occupancy
Y	1*d*	4/*mmm*	½	½	½	0.90	1
Sr	2*h*	4*mm*	½	½	0.1933(2)	1.32	2
Al	4*j*	*m* . 2*m*	0.055(2)	0.055(2)	0	0.40	1
Cu	2*g*	4*mm*	0	0	0.3476(2)	0.51	2
O(1)	4*n*	*m*2*m* .	−0.077(2)	½	0	1.6(2)	1
O(2)	4*i*	2*mm* .	½	0	0.3488(4)	0.72(5)	2
O(3)	4*i*	2*mm* .	½	0	0.3766(4)	0.72(5)	2
O(4)	8*r*	. . *m*	0.0844(9)	0.0844(9)	0.1375(4)	2.0(2)	2

Anisotropic temperature factors of cations

	B(11)	B(22)	B(33)
Y	0.4(1)	0.4(1)	1.9(2)
Sr	1.5(1)	1.5(1)	0.9(1)
Cu	0.37(5)	0.37(5)	0.8(1)

Note. [a] Space group: *P*4/*mmm*, $n = 1$, $M_r = 530.21$, $\rho_c = 5.30$ g/cm^3.
$a = 3.8646(1)$, $c = 11.1139(3)$ Å, $V = 165.99(1)$ Å^3.
$R_N = 5.81$, $R_p = 6.87$, $R_W = 9.24$, $R_E = 4.49$, $\chi = 2.06$.

TABLE IV

BOND LENGTHS (Å) AND VALENCE CHARGES V_i FOR $YSr_2AlCu_2O_7$ AT ROOM TEMPERATURE, WHERE $V_i = \sum_j V_{ij} = \sum_j \exp[(R_{ij} - d_{ij})/b]$ (6)

Y	–O(2) × 4	2.369(3)
	–O(3) × 4	2.561(3)
	V	2.444
Sr	–O(1)	2.698(5)
	–O(1)	3.098(6)
	–O(2) × 2	2.593(4)
	–O(3) × 2	2.808(4)
	–O(4)	2.354(5)
	–O(4)	3.254(5)
	–O(4) × 2	2.840(1)
	V	2.002
Al	–O(1)	1.721(8)
	–O(1)	1.794(6)
	–O(4) × 2	1.708(7)
	V	3.221
Cu	–O(2) × 2	1.9591(8)
	–O(3) × 2	1.9324(1)
	–O(4)	2.3801(5)
	V	2.097

requirements of the cations Ga, Co, and Al. Basically only the O(1*a*) sites are occupied in the gallium compound, while in YSr_2Co-Cu_2O_7 the oxygen occupies the O(1*a*) and O(1*b*) sites in almost equal numbers. In the case of the aluminum compound, our present results show the O(1) atoms evenly distributed over all the sites *a*, *b*, *c*, and *d*. A consequence of this configuration is that the average symmetry of the structure is *P*4/*mmm*, instead of *Ima*2, and that the unit cell is smaller than those of the Ga and Co compounds (i.e., $c_{Al} \simeq \frac{1}{2} a_{Co}$; a_{Al}, $b_{Al} \simeq (b_{Co}, c_{Co})/\sqrt{2}$.

Since the oxygen atoms can be located in any of the sites shown in Fig. 3, several coordination polyhedra are possible for the aluminum ions; e.g., octahedra, pyramids, and tetrahedra. Of these only the last are possible, since the atomic configuration necessary to form octahedral and fivefold pyramidal coordination would result in at least

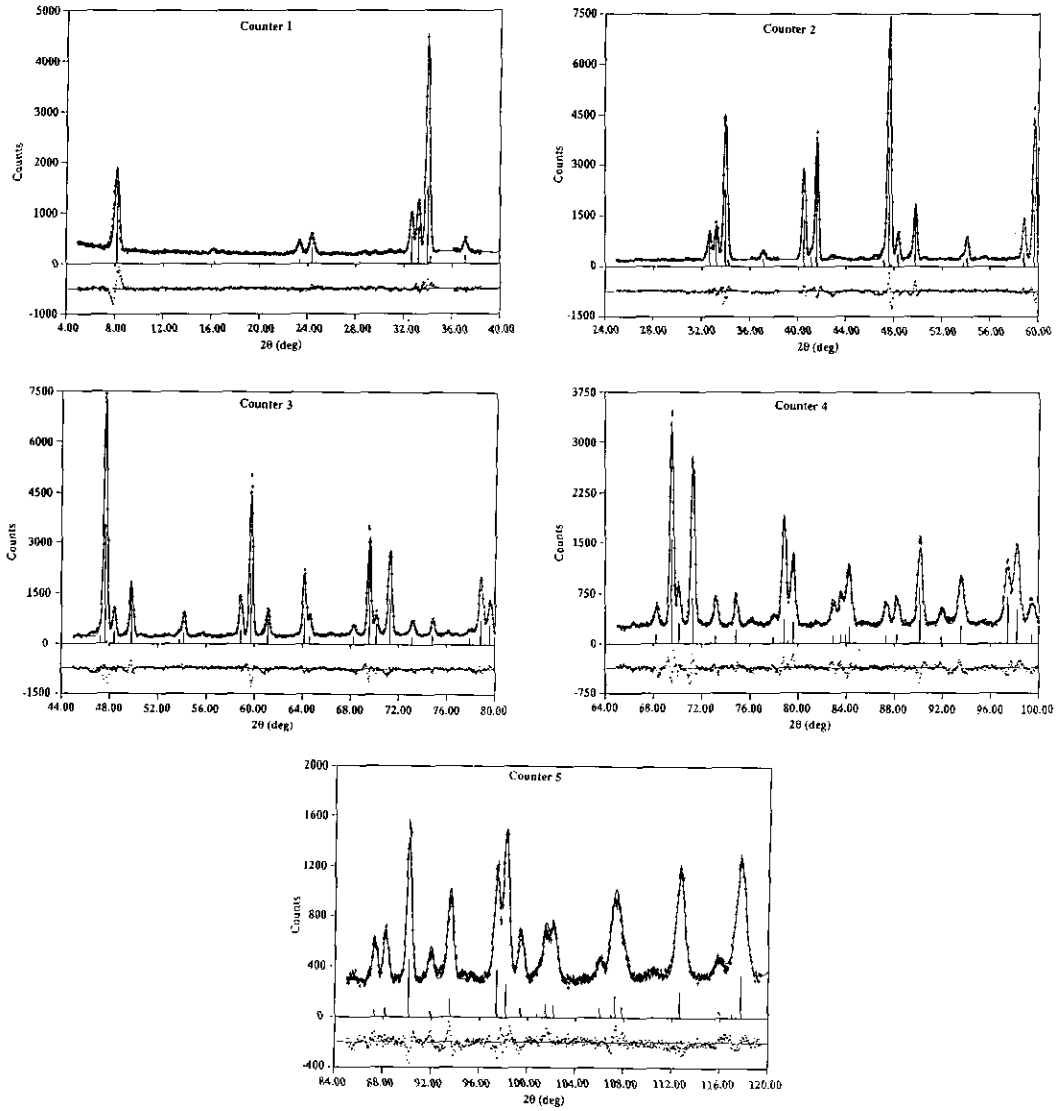

FIG. 1. Observed (small circles) and calculated (continuous line) intensities for the structure of $YSr_2Al-Cu_2O_7$. The differences I(cal.)-I(obs.) are shown at the bottom of each plot. The regions at $2\theta \sim 36°$ and $\sim 39°$ are excluded because they were affected by weak impurity peaks.

one O(1)–O(4) distance being unacceptably short, as shown by the oxygen–oxygen separations indicated on Fig. 3. As in the case of the gallium and cobalt compounds, the AlO_4 tetrahedra share corners and form chains. However, in order to explain the even distribution of the O(1) atoms over positions a, b, c, and d, we have to assume that in $YSr_2AlCu_2O_7$ these chains run in both the a and b directions on the basal plane. A possible model of the atomic configuration of the AlO_4 tetrahedra is represented in Fig.

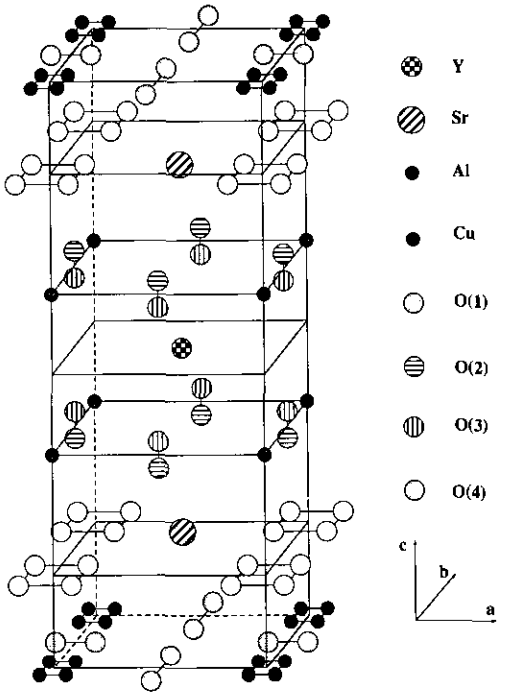

FIG. 2. Schematic representation of the structure of $YSr_2AlCu_2O_7$. Only one-fourth of the O(1) and O(4) sites and half of the O(2) and O(3) sites are occupied by oxygen atoms.

4. According to this scheme, the structure of the AlO layers is made up of domains in each of which the symmetry is orthorhombic, with chains propagating either along *a* or along *b*. The domains are related to one another by reflections across the (100) plane ((011), if referred to the large cell of the Ga and Co compounds), which may be considered a twin plane for all practical purposes. The tetragonal symmetry observed in our diffraction experiment results from the fact that the orthorhombic configuration of each domain is of short-range nature.

The disordering of the oxygen atoms O(4) around the ideal positions 0, 0, *z* on the SrO layers can be easily explained by the consideration that without such displacements the AlO_4 tetrahedra would be considerably distorted and, more important, the O(1)–O(4) and Al–O(4) distances would be unreasonably short. Another consequence of this disordering is that the apical O(4) ions are not located exactly above and below the copper ions, causing a tilting of the CuO_5 pyramids. The resulting tilt pattern is determined by the distribution of the AlO_4 tetrahedra on the AlO layer and it is much more complex than that found in the case of the gallium and cobalt compounds (*2*, *3*). One of its effects on the structure of $YSr_2AlCu_2O_7$ is to cause the splitting (into O(2) and O(3) in Fig. 2) of the oxygen atoms of the CuO_2 layers from the positions $\frac{1}{2}$, 0, *z* and 0, $\frac{1}{2}$, *z*. A model of the tilting of the CuO_5 pyramids, matching the configuration of Fig. 4, is schematically represented in Fig. 5.

The shift of the Al ions from the position at 0, 0, 0 is about 0.3 Å along the diagonal

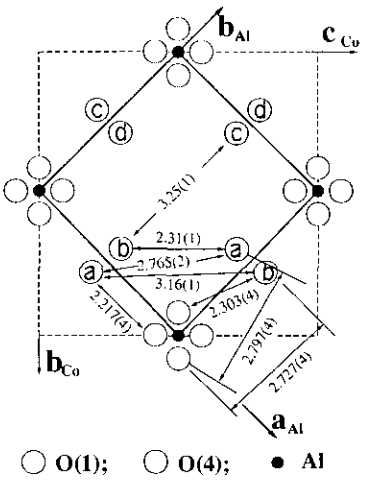

FIG. 3. Distribution of the oxygen sites on the layer AlO. The sites O(4) are located above and below the plane of the figure on the SrO layers. The unit cell of the aluminum compound is outlined by the heavy lines. The unit cell of the structures of $YSr_2GaCu_2O_7$ and $YSr_2CoCu_2O_7$, outlined by the broken lines, is shown for comparison purposes. The distances shown in the figure indicate what sites may or may not be occupied by oxygen atoms.

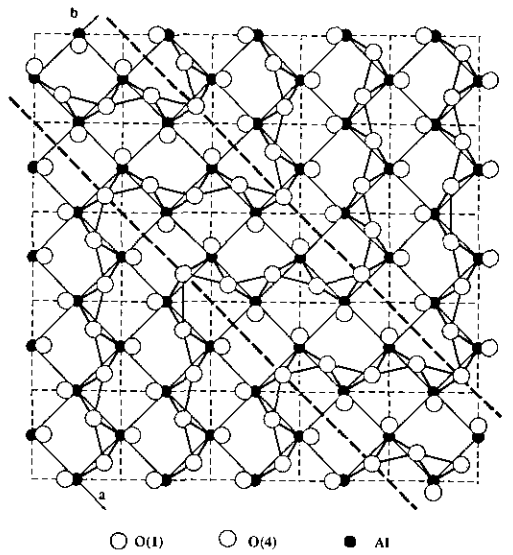

FIG. 4. A possible configuration of the oxygen atoms forming the AlO_4 tetrahedra. As in Fig. 3, the atoms O(4) are located above and below the plane of the figure. This model explains the even distribution of the oxygen atoms over the O(1) sites and the average tetragonal symmetry of the structure. The heavy broken lines running along the [100] directions separate domains within which the symmetry is (locally) orthorhombic.

of the AlO mesh toward the midpoint of the O(1)–O(1) bond. Thus, this displacement results in an AlO_4 tetrahedron significantly more regular than that corresponding to the 0, 0, 0 position.

As mentioned earlier, the coordination of Sr and Y is basically the same in the Ga, Co, and Al compounds. The disordering of the oxygen atoms of the CuO_2 layers in $YSr_2Al-Cu_2O_7$, however, causes a distortion of the eightfold prismatic polyhedron surrounding yttrium, while that of the O(4) atoms of the SrO layers may result in a slight shift of the Sr ions in the plane of the layers. The values of the anisotropic temperature factors of Y and Sr seem to be consistent with the above considerations and with the general configuration of the oxygen atoms in the structure.

The sum of the valences V of the metal atoms reported in Table IV is 13.86 v.u. (valence unit), a result close to the value one would expect from the stoichiometry of the title compound. However, the values of 2.44 and 3.22 v.u. obtained for Y and Al indicate that some of the contributions to the valences of these atoms are only approximately determined. This is understandable for a structure in which most of the atoms are disordered over sites whose location is known only with a significant degree of uncertainty. However, although the valences of Table IV are approximate, they are sufficiently close to the expected values to show that the model proposed to account for the observed disorder is plausible.

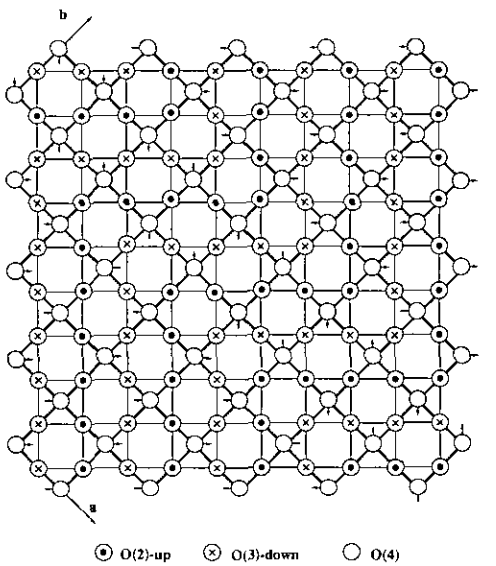

FIG. 5. Representation of the CuO_2 layer. The copper ions are located below (or above) O(4). The oxygen atoms occupying the O(4) sites are shifted from their positions as indicated by the arrows. The oxygen atoms occupy the O(2) and O(3) sites as indicated in the figure in order to avoid short O(4)–O(2) or O(4)–O(3) distances. The configuration causes a tilting of the CuO_5 pyramids. The model of this figure is consistent with that of Fig. 4.

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