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Structural Order/Disorder in the $AlSr_2YCu_2O_7$ Compound

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From X-ray diffraction (XRD) data, $AlSr_2YCu_2O_7$ phase shows a tetragonal unit cell and space group *P4/mmm*, with lattice parameters $a = b = 3.862(5)$ Å and $c = 11.095(5)$ Å. From selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) studies, a superstructure with related parameters $a_s = 2a_t$, $b_s = 4a_t$, and $c_s = 2c_t$ was found, which is considered to be due to the existence of two types of symmetry-related zigzag AlO_4 chains along the *a*-direction. Simultaneously, some interlayer disordering occurs, which can be due to the disordered arrangement of these two AlO_4 chains along the *c*-axis. © 1997 Academic Press

INTRODUCTION

It was found recently that several elements, such as B (1, 2), S (3), C (4–7), Ga (8–11), and Al (12–14), can replace some of Cu sites of the so-called M-12$(n-1)n$ high T_c superconductors. The structures of these new structural types have been investigated succesfully by selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM), and some new superstructures have been reported.

For instance, a new homologous series of high-pressure superconductors, with general formula $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$ (8–11), was reported to show intralayer ordering between two different types of [GaO_4] chains (L and R), leading to a doubled periodicity along the *b*-direction normal to the chains. Also, interlayer disordering can occur simultaneously between both L- and R-[GaO_4] chains, along the *c*-axis, i.e., deviations from the regular alternations of L- and R-[GaO_4] chains (10, 11).

Isobe *et al.* (12), on the other hand, reported the high-pressure synthesis of Al-based superconductors, with the general formula $AlSr_2(Y_{1-x}Ca_x)Cu_2O_7$ ($0 \le x \le 0.8$), using the phase $AlSr_2YCu_2O_7$ as a precursor. From X-ray diffraction (XRD) data, all samples showed a tetragonal unit cell, although small changes with increasing x were obtained. SAED and HRTEM studies confirmed that these samples contained intergrowths, due to the Al-1234 phase, that cannot be detected in the XRD patterns. In any case, it was concluded that the unit cell of this Ca-containing material is tetragonal.

In this paper, we examined the $AlSr_2YCu_2O_7$ phase by means of SAED and HRTEM, and an ordered/disordred structure was found. A structural model is proposed.

EXPERIMENTAL

The $AlSr_2YCu_2O_7$ sample was prepared by the conventional solid state reaction from mixtures of Al_2O_3, Sr_2O_2, Y_2O_3 and CuO. Sr_2O_2 was prepared by adding NH_4OH to an aqueous solution of $SrCl_2$ and H_2O_2, which was then dried at 150°C (12).

The X-ray diffraction (XRD) study was performed on a diffractometer (Philips-PW 1800) using Cu$K\alpha$ radiation. Reticular parameters were calculated using the least squares method, with Si as an internal standard.

SAED and HRTEM observations were carried out on a Hitachi H-1500 electron microscope operated at 800 kV. The sample was ultrasonically dispersed in CCl_4 and transferred to carbon-coated copper grids.

RESULTS AND DISCUSSION

The sample showed semiconductor behavior, according to the dc electrical resistivity measurements performed by a standard four-probe method. Also, magnetic data did not show any diamagnetic signal. From these data, we concluded that the sample is not superconducting (12).

According to the crystal data for $AlSr_2YCu_2O_7$ phase, previously reported by Isobe *et al.* (12), all XRD maxima could be indexed as the 1212 structure with a tetragonal unit cell, space group *P*4/*mmm*, and lattice parameters $a_t = b_t = 3.862(5)$ Å and $c_t = 11.095(5)$ Å (where t denotes the basic tetragonal unit cell). However, SAED and HRTEM studies revealed a more complex structural situation.

Figure 1 shows the SAED pattern along $[001]_s$ (the s subindex refers to the new superstructure unit cell) of the

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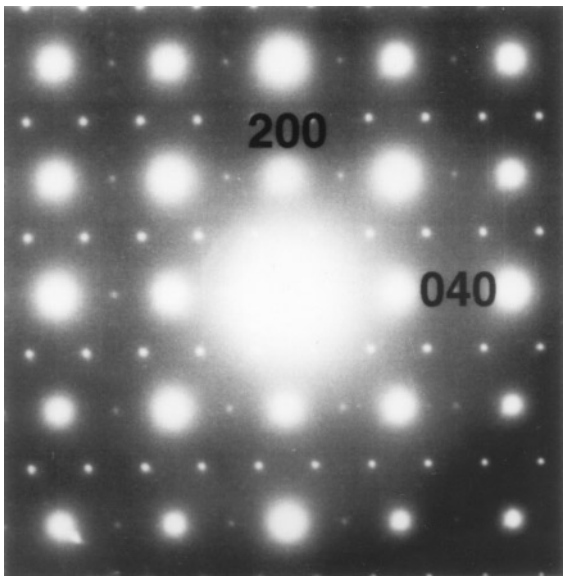

FIG. 1. SAED pattern along the $[001]_s$ direction of the $AlSr_2YCu_2O_7$ phase.

$AlSr_2YCu_2O_7$ phase. The main spots can be indexed on the basis of the above mentioned tetragonal subcell. However, it can be clearly observed that some extra weak spots exist along both a^*- and b^*-axes (note that indices are given on the basis of the new superlattice superlattice). These extra spots indicate the superlattice structure for $AlSr_2YCu_2O_7$.

Figure 2a shows the SAED pattern along $[010]_s$, confirming that $(101)_s$ and equivalent spots are absent. Figure 3b shows the corresponding HRTEM image along $[010]_s$ zone axis. A different contrast in the Al- and Cu-planes can be clearly distinguished, as a result of the ordering between both cations, separated by the Sr- or Ca-planes, respectivelly. It can be observed that the d spacing along the c-axis is 11.1 Å. However, the periodicity along a-axis seems to be 3.86 Å in this image.

In the SAED pattern along $[100]_s$ (Fig. 3a), however, it can be observed that a diffraction maximum appears at $(021)_s$ and equivalent reflexions. From these data, we can conclude that this phase shows an orthorhombic supercell with related parameters $a_s = 2a_t$, $b_s = 4a_t$, and $c_s = 2c_t$. Figure 3b shows the HRTEM images obtained for the $AlSr_2YCu_2O_7$ phase along the $[100]_s$. It can be observed that a different constrast exists in the Al layers along the b-direction, as a consequence of the existence of order between two types of symmetry zigzag AlO_4 chains. Note that some irregularity in the fringe spacing can be observed in the image as a result of the formation of some intergrowth defects. In this sense, it is important to note that a similar situation was previously observed in the Ga-based system (8, 10, 11).

From these SAED data, we can propose a base-centered orthorhombic space group, such as *Bmmm*.

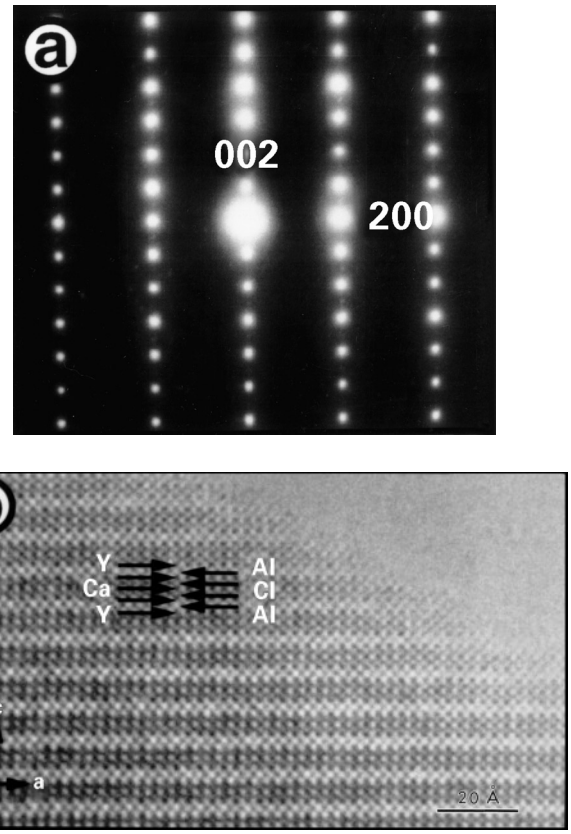

FIG. 2. (a) SAED pattern along the $[010]_s$ direction and (b) corresponding HRTEM image.

For comparison, Isobe *et al.* (13) reported the high-pressure synthesis, structural study, and physical properties on a new series of high T_c superconductors $AlSr_2Ca_{n-1}Cu_nO_{2n+3}$ ($n = 4$ and 5). From XRD and HRTEM data, it was also concluded that these phases have tetragonal cells and that they are essentially isomorphous with the Tl (or Hg)-based superconductors.

On the basis of these results, we can conclude definitely that the compound, $AlSr_2YCu_2O_7$, has essentially the 1212-type structure, except for the extra periodicity along both the a- and the b-axis. In a first approximation, we also considered that this superstructure was due to the ordering of Y atoms. If this superstructure is due to the order/disorder of Y atoms, then the superstructure should appear more easily in Ca/Y mixed compounds; however, these samples showed a tetragonal unit cell. These results suggest that only superstructures seem to exist in this Al-based system when Ca is fully replaced by Y.

Moreover, we also observed, in some crystals, the SAED pattern depicted in Fig. 4a. The almost continuous streaking along alternate rows of extra spots parallel to the c^*-direction can be observed in SAED pattern along $[110]_s$, suggesting that structural disorder occurs along the

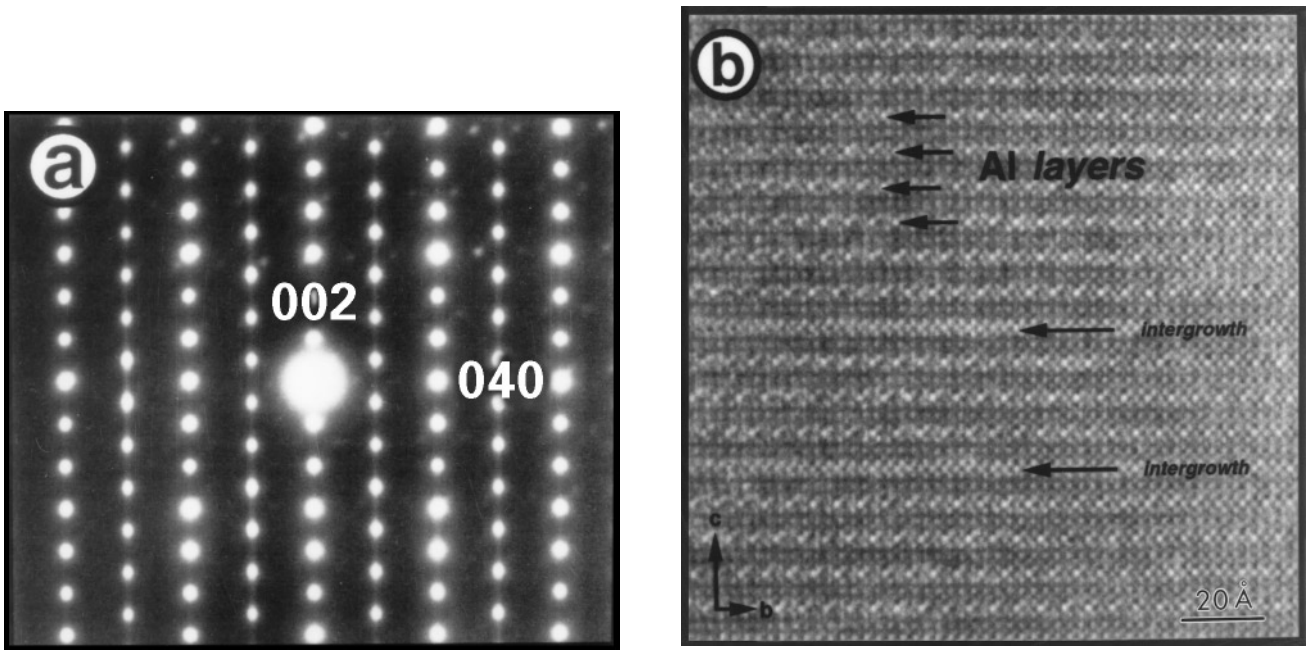

FIG. 3. (a) SAED pattern along the $[100]_s$ direction and (b) corresponding HRTEM image.

c-direction. In the HRTEM image along the $[110]_s$-direction (Fig. 4b), the existence of an interlayer disorder in the Al positions can be observed.

In some crystals, however, we observed the SAED pattern along the same direction $[110]_s$ depicted in Fig. 5, which shows a weaker streaking, i.e., the streaked lines are more spotty, indicating that in some crystals a more ordered structure exists. Moreover, it can be also observed that the weak extra spots appear between the main spots, suggesting a different arrangement in the AlO_4 tetrahedra.

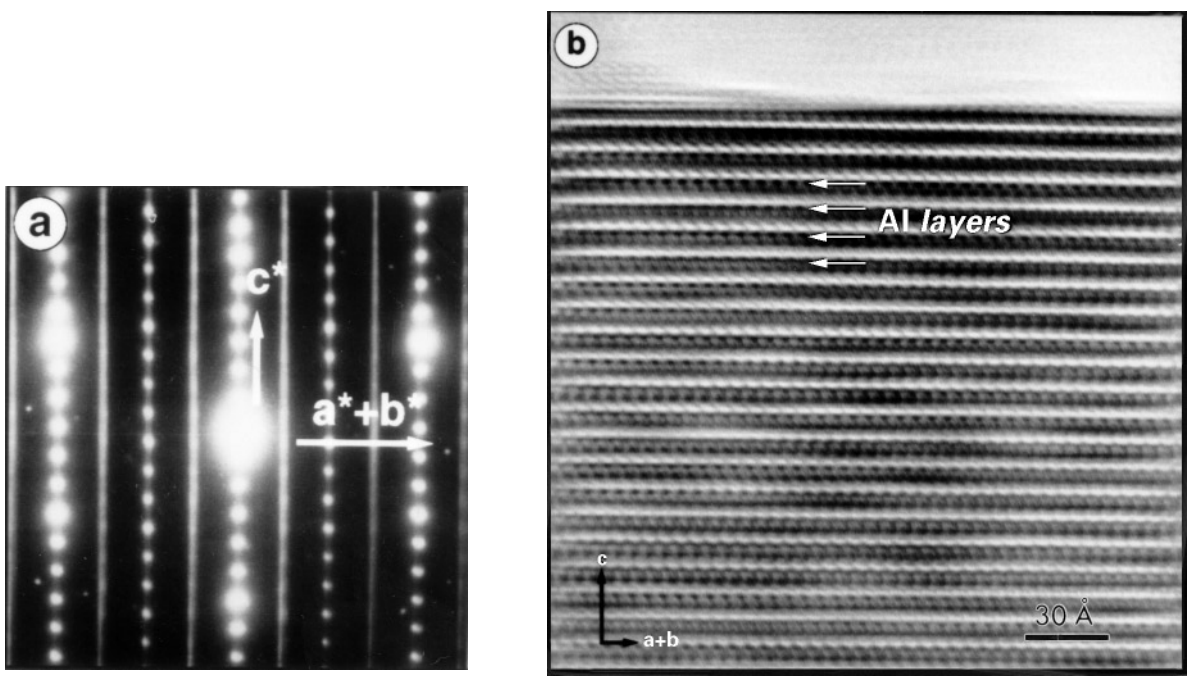

FIG. 4. (a) SAED pattern along the $[110]_s$ direction and (b) corresponding HRTEM image.

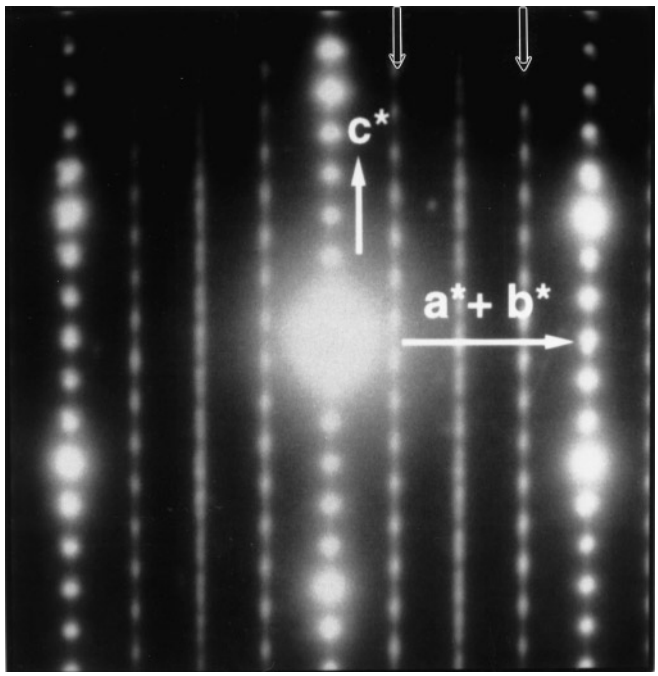

FIG. 5. SAED pattern along the $[110]_s$ direction, which shows a different symmetry in the weak extra spots.

Milat *et al.* (15) reported similar results in the $(Y_{0.75}Ce_{0.25})_2(Sr_{0.85}Y_{0.15})_2AlCu_2O_{9+x}$ compound. Considering that Al has a strong tendency to be tetrahedrally coordinated by oxygen, it is expected that the structure of this compound should be related to that induced by other ions *M* substituted for Cu in the CuO chain layer such a Co and Ga (16), which similarly have a strong tendency to form MO_4 tetrahedra. In the GaO layers the superstructure was a consequence of the ocurrence of different senses of rotation in successive parallel chains. However, the absence of coupled rotations in the AlO case eliminates the possibility for similar longer period structures. Thus, in the Al-2212 compound, a similar tendency is not expected. Neutron diffraction experiments showed that the title Al-2212 has an average body-centered tetragonal structure, with a double fluorite lamella. However, from a very detailed structural study from SAED and HRTEM data (15), it was reported that a superstructure by either meandering chains or square loops of corner-sharing AlO_4 tetrahedra are formed in the Al-2212 specimen. Moreover, a modulation was also observed, which is due to chemical ordering of Y and Sr and/or to deformation of the (Y, Sr)O framework.

When these structural considerations are taken into account, we can propose a related structural model for the Al-1212 phase. The AlO layer is the layer which most prominently exhibits the superstructure (15). We assume that Al atoms are bonded to four oxygens, attaining a tetrahedral AlO_4 configuration, with the tetrahedra oriented along the *c*-axis. One possible explanation of this structure is to consider that, in the *a–b* plane, the corner-sharing tetrahedra lead to the formation of two different chains running along the b_0 direction, in a similiar way as in the Ga-based superconducting system; however, it is important to note that in this case, GaO_4 chains are running along the $[110]_0$ direction (8, 10, 11). Figure 6a shows the tetrahedra

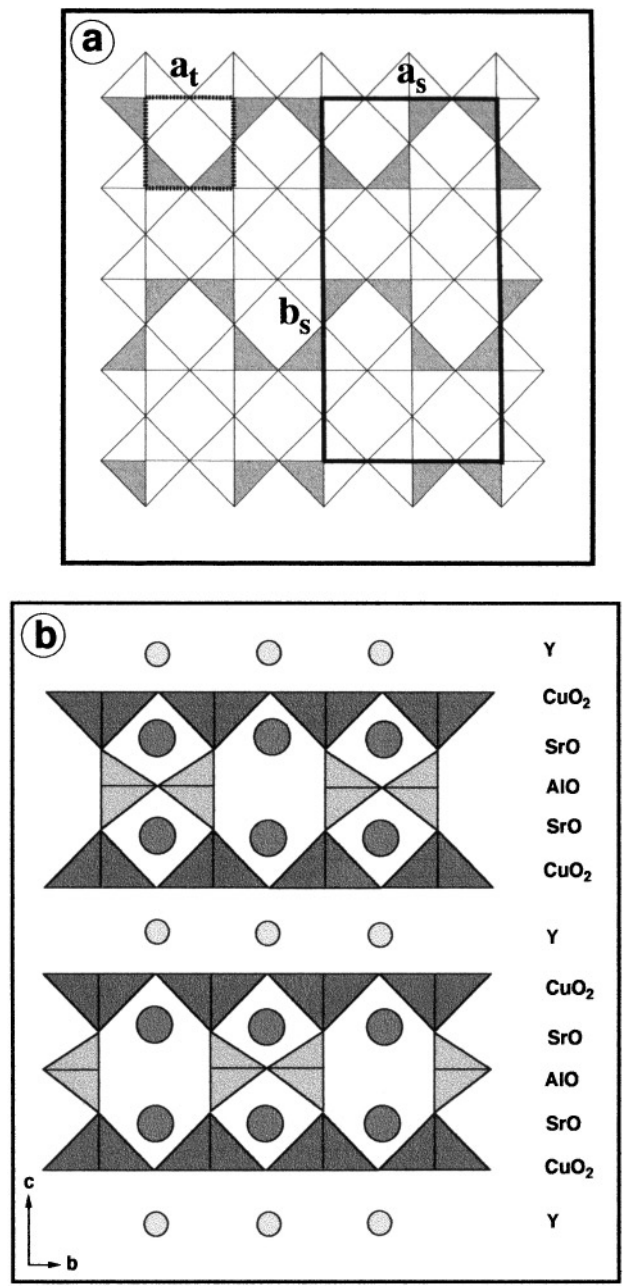

FIG. 6. (a) Schematic representation of the arrangement of AlO_4 tetrahedra chains running along the [010]-direction, leading to a periodicity of $a_s = 2a_t$, $b_s = 4b_t$, and $c_s = c_t$, and (b) tentative structural model of the $AlSr_2YCu_2O_7$ phase.

arrangement leading to the formation of a new superstructure whose unit cell parameters are related to that of the orthorhombic subcell (a_t, b_t, and c_t) by means of the expressions $a_s = 2a_t$, $b_s = 4b_t$, and $c_s = 2c_t$. In other words, our data are consistent with the removal of two oxygen atoms in the [AlO_6] octahedra planes, present in the basic tetragonal structure, to form locally ordered [AlO_4] tetrahedral chains in the ordered superstructure.

Figure 6b shows the full structural model proposed for the Al-1212 phase. The structure can be described as an ordered intergrowth of the CuO_5 pyramids and the AlO_4 tetrahedra layers, alternating along the *c*-axis between the SrO layers, with a resulting stacking sequence

$$\ldots\text{–AlO–SrO–}CuO_2\text{–Y–}CuO_2\text{–SrO–AlO–}\ldots$$

However, structural disorder was also observed, which is considered to be due to the existence of crystallographic shifting of the AlO_4 chains, introduced along $[010]_o$ by a_o. Taking this information into account, we can propose the tentative structural model of the $AlSr_2YCu_2O_7$ phase shown in Fig. 6.

In conclusion, by HRTEM study we have found a new superstructure in the $AlSr_2YCu_2O_7$ phase, which seems to be due to the intralayer ordering between two diferent AlO_4 chains along the *b*-direction. However, at the present stage, we could not conclude definitely which is the real reason for such superstructure. More structural studies are necessary for a more conclusive determination. On the other hand, some interlayer disordering occurs simultaneously along the *c**-axis. This disorder can be due to the existence of crystallographic shifting of the AlO_4 chains, which gives rise to the streaking observed in the SAED pattern showed in Fig. 4b.

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