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Structural Disorders in the Superconducting $GaSr_2Ca_3Cu_4O_y$

J. Ramírez-Castellanos,*,† Y. Matsui,*,[1] E. Takayama-Muromachi,* and M. Isobe*,‡

*National Institute for Research in Inorganic Materials (NIRIM), 1-1 Namiki, Tsukuba, Ibaraki 305, Japan; †Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan; and ‡Sony Corporation Research Center, 174 Fujitsuka-cho, Hodogaya-Ku, Yokohama 240, Japan

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Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) studies were performed on the new superconductor $GaSr_2Ca_3Cu_4O_y$ (Ga-1234), $n = 4$ member of the homologous series $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$ prepared under high pressure. Although it consists of rather irregular intergrowths of the blocks with $n = 3$, 4, and 5 [CuO_2] layers, the average number of [CuO_2] layers is close to 4. In addition, an intralayer ordering between two different types of [GaO_4] tetrahedral chains along the *b* axis, as well as an interlayer disordering of the chains along the *c* axis, are also observed. © 1996 Academic Press, Inc.

INTRODUCTION

Takayama-Muromachi *et al.* (1) have reported the high pressure synthesis of a homologous series of superconductors, with the general formula $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$ (Ga-12($n-1$)n, $n = 3$ and 4), and T_c ranging between 70 (for $n = 3$) and 107 K (for $n = 4$). It has been stated, from the X-ray diffraction (XRD) data, that the structures for these phases can be described by an orthorhombic lattice (*Ic*2*m*), with lattice parameters $a_0 \approx b_0 \approx \sqrt{2}a_p$ and $c_0 \approx (2n + 2)a_p$, where a_p is the lattice parameter for the basic cubic perovskite structure.

Several authors (2, 3) have already reported the structure of the $GaSr_2LnCu_2O_7$ (*Ln* = La, Y, Er, Yb, ...) (Ga-1212) from X-ray and neutron diffraction studies. The structure contains double layers of [CuO_5] pyramids separated by trivalent lanthanides, like $YBa_2Cu_3O_7$ (Cu-1212). [CuO_4] square planar chains of Cu-1212 are, however, replaced by [GaO_4] tetrahedral chains in Ga-1212. The chains run along the b_0 axis which corresponds to the diagonal of the basal plane of the Cu-1212 subcell. Recently, Roth *et al.* (4) reported the crystal structure of the semiconducting $GaSrLnCuO_5$ (*Ln* = La, Pr, Nd) (Ga-1201), which consists of almost planar nets of distorted corner-sharing [CuO_6] octahedra, connected along the longest axis, via [GaO_4] tetrahedral chains, with *Ln* and Sr ions filling the large voids between planes and chains.

SAED and HRTEM studies (5) on $CoSr_2YCu_2O_7$ (Co-1212) and $GaSr_2(Nd, Ce)_nCu_2O_{5+2n}$ (n = 1, 2, ...) (Ga-12n2), however, suggest the existence of more complicated superstructures, as a consequence of a regular alternation of two types of symmetry related [MO_4] tetrahedra chains (M = Ga, Co). This occurs because the [MO_4] tetrahedra can rotate in two different ways in the structure, giving two types of [MO_4] chains (L and R), and leading to double periodicity along the b_0 direction normal to the chains.

Recently, the present authors reported microstructural studies (6, 7) on both $GaSr_2CaCu_2O_{7+\delta}$ and $GaSr_2Ca_2Cu_3O_{9+\delta}$ phases ($n = 2$ and 3 members of the superconducting homologous series $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$) and observed the similar superstructures.

In this paper, we report the SAED and HRTEM data of the compound with nominal composition $GaSr_2Ca_3Cu_4O_y$, which is considered to be the $n = 4$ member of the superconducting homologous series $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$ (1), and we propose a tentative structural model based on these data.

EXPERIMENTAL

$GaSr_2Ca_3Cu_4O_y$ (y = 10.8, 10.9, 11.0, 11.1, and 11.5) samples were prepared at 1250°C for 1 h, under 6 GPa in a belt-type high-pressure apparatus, as previously reported.

Powder X-ray diffraction (XRD) patterns of samples were obtained using a diffractometer with Cu$K\alpha$ radiation. Lattice parameters were calculated by the least squares method from the X-ray data, using Si as an internal standard. All the XRD maxima corresponding to the Ga-1234 sample with $y = 10.8$ (except some peaks due to CuO and a secondary unknown impurity) can be indexed on the basis of an orthorhombic symmetry and space group *Ic*2*m*, with lattice parameters $a_0 = 5.417(4)$ Å, $b_0 = 5.462(4)$ Å, and $c_0 = 35.78(5)$ Å. However, broadness of some peaks, such as $11\underline{1}0$, strongly suggests the presence of intergrowths.

[1] To whom correspondence should be addressed.

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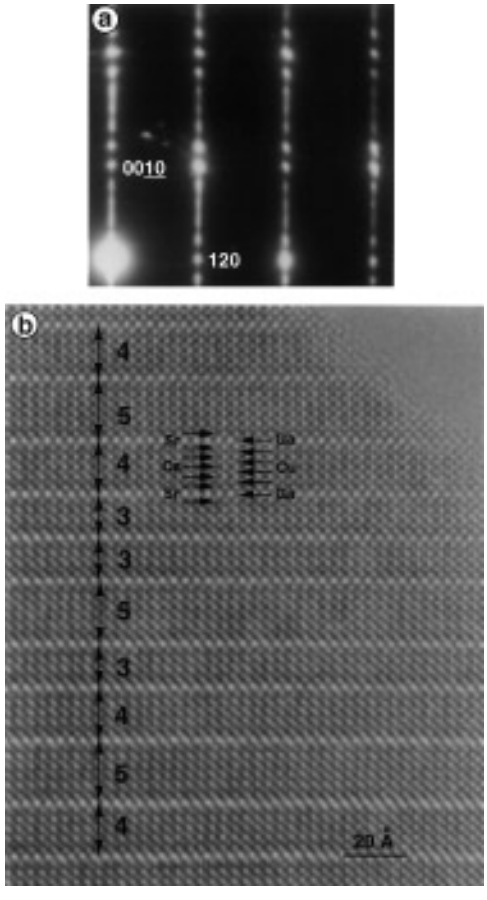

FIG. 1. (a) SAED pattern of $GaSr_2Ca_3Cu_4O_{10.8}$ taken with the electron beam along the $[210]_s$ direction and (b) the corresponding HRTEM micrograph.

The T_c of $GaSr_2Ca_3Cu_4O_y$ samples depends on the oxygen content, y. The sample with $y = 10.8$ showed almost single superconducting transition at 93 K, as observed from the dc electrical resistivity measurements, performed by a standard four-probe method for a sintered specimen, using colloidal silver as the electrode. Magnetic data for the Ga-1234 sample with $y = 10.8$ showed a diamagnetic transition temperature higher than 90 K, while other samples with higher oxygen content showed a second transition at lower temperatures.

For more details about sample preparation, X-ray diffraction, and physical properties, we refer to Ref. (1).

Selected area electron diffraction and high resolution transmission electron microscopic observation were carried out on a Hitachi H-1500 electron microscope, operated at 800 kV. The samples were ultrasonically dispersed in CCl_4 and transferred to carbon coated copper grids.

RESULTS AND DISCUSSION

Taking into account the quality of materials mentioned above, we focused the structural study on the $GaSr_2Ca_3Cu_4O_{10.8}$ sample. As we mention below, SAED patterns indicate that the b parameter should be doubled and, therefore, the new parameters $a_s = a_0$, $b_s = 2b_0$, and $c_s = c_0$ are used to index the diffraction patterns.

Basic Structure and Intergrowths

Figure 1a shows the SAED pattern taken along $[210]_s$ to confirm the basic layered structure. In the corresponding HRTEM image (Fig. 1b), the Ga and Cu planes separated by alkali-earth atomic planes, can be clearly observed. The streaking along the c^* axis observed in the diffraction pattern is reflected in the structural disorder in the micrograph. Irregular intergrowth of blocks with 3, 4, and 5 $[CuO_2]$ layers can be observed. But, the average number of $[CuO_2]$ layers is very close to 4.

Figure 2a shows the SAED pattern taken along the chain direction $[100]_s$, where the diffraction spot appears at $(021)_s$, since the chain position shifts by $b_s/4$ (or $b_0/2$) between the neighboring $[GaO_4]$ layers. Figure 2b shows the corresponding high resolution lattice image, where intergrowths of blocks are also observed. The periodical shift of chain positions are clearly observed. It is found again that the average number of $[CuO_2]$ layers is almost 4. In this way, we confirmed that the average chemical composi-

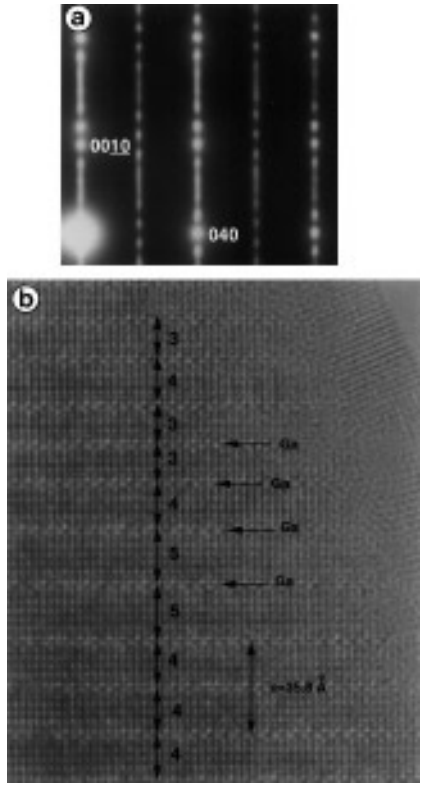

FIG. 2. (a) SAED pattern along the $[100]_s$ direction, and (b) the corresponding HRTEM micrograph.

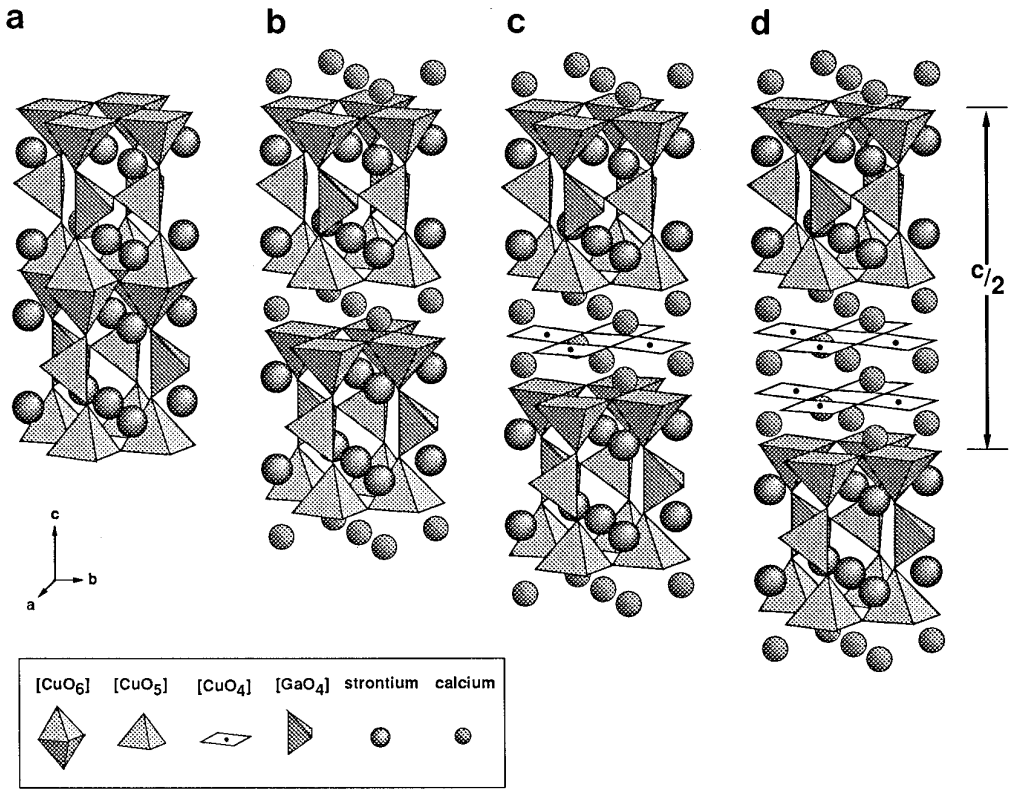

FIG. 3. Schematic representations of tentative structural models of $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$ (Ga-12(n − 1)n), for (a) n = 1 (Ga-1201 phase), (b) n = 2 (Ga-1212 phase), (c) n = 3 (Ga-1223 phase), and (d) n = 4 (Ga-1234 phase). [CuO_6] octahedra, [CuO_5] pyramids, and [GaO_4] tetrahedra are shaded. Cu atoms in planar square configuration are indicated by small black dots. Ca and Sr positions are represented as the shaded circles.

tion is close to that of Ga-1234, although it consists of rather irregular intergrowth of blocks with 3, 4, and 5 [CuO_2] layers.

Taking into account the above information, we propose a tentative model of the basic structure for this homologous series with the general formula $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$. They can be described as being formed by an alternation of n[CuO_2] layers with [GaO_4] tetrahedra layers, occurring between (n − 1) Ca and SrO layers, along the c axis, with a resulting stacking sequence

$$\ldots\text{–GaO–SrO–}CuO_2\text{–[Ca–}CuO_2]_{n-1}\text{–SrO–GaO–}\ldots$$

The c dimension increases linearly with n. The orthorhombic distortion, which is defined as the difference between the a_0 and b_0 dimensions, tends to decrease with n. The distortion is caused by the [GaO_4] tetrahedral planes. Their number per unit length along the c axis decreases linearly with increasing n. This seems to explain the systematic trend in the orthorhombicity (1).

Figure 3 shows the idealized structural model proposed for the n = 1, 2, 3, and 4 members. The structure of $GaSr_2CuO_5$ (n = 1 member) (Fig. 3a) can be described as an ordered intergrowth of the [CuO_6 octahedra and the [GaO_4] tetrahedra layers, alternating along the c axis between the SrO layers. The $GaSr_2Ca_1Cu_2O_7$ (n = 2 member) shown in Fig. 3b can be very easily described from the n = 1 member structure, just by the incorporation of one additional Ca layer between [CuO_5] pyramidal copper planes, which are linked by sharing corners. Note that Cu atoms are in fivefold coordination. However, for both n = 3 and 4 (Figs. 3c and 3d, respectively), there are two crystllographically different sites for Cu atoms: one with fivefold coordination in the [CuO_5] pyramids blocks, and one with square planar configuration in the additional (n − 1)[Ca–CuO_2] layers, between the pyramidal copper planes.

Ordering and Disordering of [GaO_4] *Chains*

The second feature of the structure of the Ga-1234 specimen is the intralayer ordering, as well as interlayer disordering of two different types of chains, L- and R-[GaO_4]. To distinguish these two types of chains, we must focus on some other diffraction patterns (5) as follows.

Figure 4a shows the SAED pattern taken along $[001]_s$, which contains weak extra spots along the b^* axis, indicat-

ing that the b^* reciprocal direction of the basic $Ic2m$ subcell is doubled (i.e., $b_s = 2b_0$). It has already been reported for other related compounds (5–7) that this double periodicity is a consequence of a regular alternation of two different types of symmetry (L and R) of the $[GaO_4]$ tetrahedra, along the b direction (intralayer ordering). Taking into account the information reported by Krekels *et al.* (5), $[GaO_4]$ tetrahedra are linked sharing corners to form chains. Tetrahedra can rotate in two different ways (left and right) along the c axis, giving rise to the formation of two types of zig-zag chains, an L chain and an R chain, respectively. This leads to a new superstructure whose unit cell parameters are related to that of the orthorhombic subcell (a_0, b_0, and c_0) by means of the expression $a_s = a_0$, $b_s = 2b_0$, and $c_s = c_0$.

On the basis of these results, we can conclude that such an ordering occurs as well in $GaSr_2Ca_3Cu_4O_y$.

On the other hand, Fig. 4b shows the SAED pattern along $[130]_s$. It can be clearly observed that $31l$ rows parallel to the c^* direction are continuously streaked. This can be attributed to structural disorder in the arrangement of paralle R- and L-$[GaO_4]$ chains along the c direction (interlayer disordering).

The intralayer ordering between both L- and R-$[GaO_4]$ chains leads to a doubled peridocity along the b direction normal to the chains (as shown in Fig. 5a) (5). However, some interlayer disordering occurs simultaneously between both L- and R-$[GaO_4]$ chains (Fig. 5b) along the c^* axis, i.e., deviations from the regular alternations of L- and R-$[GaO_4]$ chains. This disorder is due to a local change of the repeat periodicity between $c_s \approx 2c_p$ and $4c_p$, where c_p is the lattice parameter for the basic cubic perovskite structure. It gives rise to the streaking observed in the SAED pattern shown in Fig. 4b.

Detailed HRTEM study on such interlayer disorder of $[GaO_4]$ chains is in progress.

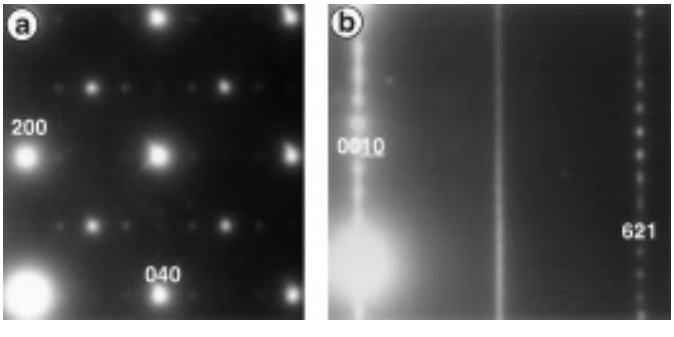

FIG. 4. SAED patterns of $Ga_1Sr_2Ca_3Cu_4O_{10.8}$ sample, along (a) the $[001]_s$ and (b) the $[130]_s$ zone axis. Existence of extra reflections in (a), as well as streaking along the c axis in (b), are apparent.

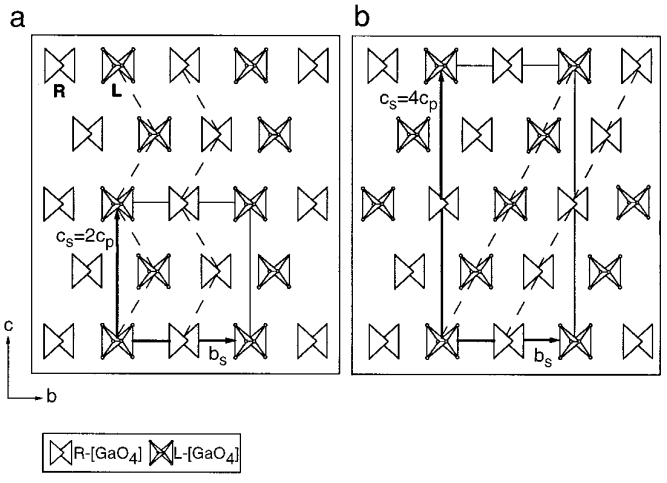

FIG. 5. Schematic representation of two different arrangement of L- and R-$[GaO_4]$ tetrahedra with a periodicity $c_s \approx 2c_p$ in (a) and $2c_s \approx 4c_p$ in (b), respectively (5).

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