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# A Structural Study of the Solid Solution Phase $Sr_{1+x}Cu_2O_3$ by HREM

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A Sr–Cu–O material with nominal composition of $Sr_4Cu_7O_{11}$ has been prepared and its structure investigated by high resolution electron microscopy in conjunction with image simulation studies. The basic unit cell has been determined to be orthorhombic with $a = 11.47$, $b = 13.40$, and $c = 3.95$ Å. Cu cations are square coordinated by four oxygen anions, existing in edge sharing double $CuO_4$ chains, sandwiched by Sr cation layers. A commensurate 1 × 1 × 9 superlattice has been observed. It is proposed that additional Sr cations can insert in the Sr layers to form the superlattice and a solid solution exists, $Sr_{1+x}Cu_2O_3$, $0 < x < 0.167$.

## Introduction

Superconductivity at 30 K in the La–Ba–Cu–O system was discovered by Bednorz and Muller (*1*), and, subsequently, other workers reported that the corresponding Sr system became superconducting at about 40 K (*2*). In contrast, it is now believed that the substitution of Sr for Ba in the superconductor $YBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0$) results in a large decrease in $T_c$ (*3*). Such remarkable differences in electronic properties arising out of substitutional effects have led us to undertake a study of the Y–(Ba, Sr)–Cu–O phase diagrams by a variety of structural and spectroscopic techniques (*4*). In the present work, we concentrate on the structure of the new binary phase "$Sr_4Cu_7O_{11}$."

Several compounds in the binary oxide system SrO–CuO have previously been reported (*5*). $Sr_2CuO_3$ has a body-centered orthorhombic symmetry, space group *Immm*, with unit cell parameters of $a = 12.68$, $b = 3.91$, and $c = 3.48$ Å. Cu cations are in square coordination by oxygen and these $CuO_4$ units share corners to form a chain sandwiched by (double) Sr cation layers (Fig. 1a). $SrCuO_2$ is also orthorhombic, space group *Cmcm*, with $a = 3.56$, $b = 16.32$, and $c = 3.92$ Å. This structure includes a $Cu_2O_3$ sheet sandwiched by (double) Sr cation layers (Fig. 1b). The structure of $SrCu_2O_3$ was first studied in 1970 (*5c*) and determined to be body-centered tetragonal with $a = 5.48$ and $c = 9.82$ Å. All Sr cations are octahedrally coordinated by oxygen and Cu cations occupy the interstices of the $SrO_6$ network, as shown in Fig. 1c. According to recent reports, there is no pure $SrCu_2O_3$ compound found, but a new phase "$Sr_{14}Cu_{24}O_{41}$" has been reported (*6*). Using X-ray single-crystal diffraction techniques, McCarron *et al.* determined the structure of $Sr_{14}Cu_{24}O_{41}$ as two interpenetrating structures: one with Sr–($Cu_2O_3$ sheets)–Sr layers in an orthorhombic cell with dimensions of $a = 11.459$, $b = 13.368$, and $c = 3.931$ Å and a second structure with layers of $CuO_2$ chains, in a cell having identical *a* and *b* values but with $c = 2.749$

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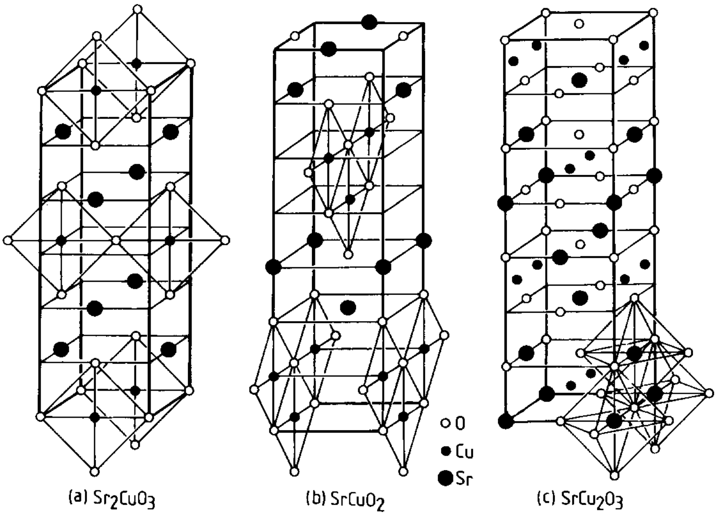


FIG. 1. Previously determined structural models of (a) $Sr_2CuO_3$, (b) $SrCuO_2$, (c) $SrCu_2O_3$.

Å. The interpretation of these two sublattices results a large superlattice with $a$ = 11.459, $b$ = 13.368 Å, and $c$ parameter being approximately 27.52 Å, which is 7 times of $c$ sheets or 10 times of $c$ chains. When Roth *et al.* (*7*) re-investigated this material, they found that the ratio of Sr : Cu was likely to close 4 : 7 rather than 14 : 24 and the compound should be considered to be a nonstoichiometric phase $Sr_{1+x}Cu_{2-x}O_3$ ($x$ = 0.1).

The structure determination of very large superlattices, and solid–solutions, gives rise to many difficulties in X-ray and neutron diffraction studies. In contrast, the technique of high resolution electron microscopy (HREM) is a powerful technique in this field. Many very complicated superstructures of solid–solution materials in the $Bi_2O_3$–$M_2O_5$ ($M$ = Nb, Ta, V) systems have been successfully determined by HREM in these laboratories (*8*).

In the present work, a compound with the nominal starting composition of 4SrO–7CuO has been prepared and investigated by HREM. The ratio of Sr : Cu determined experimentally is slightly smaller than both 14 : 24 and 4 : 7. Although the basic unit cell of this new phase is orthorhombic with $a$ = 11.47, $b$ = 13.40, and $c$ = 3.95 Å, which is similar to the previous result for $Sr_{14}Cu_{24}O_{41}$ from X-ray single-crystal diffraction studies, HREM studies indicate that the structure includes Sr–($Cu_2O_3$ sheets)–Sr layers without $CuO_2$ chain components. There also exists a 1 × 1 × 9 superlattice derived from this sublattice, indicated by selected area electron diffraction (SAED) patterns. Thus we report a study of the new phase $Sr_{1+x}Cu_2O_3$ by HREM and energy dispersive X-ray spectrometry in combination with computer simulations of HREM images and SAED patterns.

## Experimental

The Sr,Cu binary oxide with the starting composition of 4SrO–7CuO has been prepared by solid–solid reaction of raw materials $SrCO_3$ and CuO (BDH or Aldrich) at 1000°C for 72 hr, followed by cooling down to room temperature in furnace.

Initial characterization of the specimen was by X-ray powder diffractometry and neutron diffractometry. Most of the intense lines in both of the diffraction spectra could be indexed onto a *Fmmm* orthorhombic unit cell with $a$ = 11.47, $b$ = 13.40, and $c$ = 3.95 Å, in good agreement with the previously reported subunit cell for $Sr_{14}Cu_{24}O_{41}$ (*6*). There were also many extra lines observed, indicating superlattice formation. However, these diffraction lines were difficult to index onto a 7× superlattice, as proposed by McCarron *et al.* (*6*).

The composition of the sample was determined by energy dispersive X-ray spectrometry (EDS), using a Link 860 EDS facility within a Jeol JEM-200CX electron microscope operating at 200 kV. Twenty particles were randomly chosen for examination and the average intensity ratio of the Sr*Kα*/Cu*Kα* emission lines from all particles is 0.34 (*2*). This value corresponds to an atomic ratio Sr/Cu of 0.53, using freshly prepared $Sr_2CuO_3$ as a reference. Selected area electron diffraction patterns were recorded at a ±45° double tilt specimen stage in the same electron microscope. HREM images were recorded at a magnification of 500,000× over a range of objective lens focal increments on another Jeol JEM-200CX electron microscope, where a developed side-entry specimen stage ($C_s$ = 0.52 mm, $C_c$ = 1.05 mm, with absolute information limit ca. 1.8 Å) (*9*) was used. Computer-simulated model images were calculated according to the multislice method (*10, 11*) using programs especially developed for use with very large unit cells (*12*).

## Results and Discussion

Several sets of selected area electron diffraction patterns have been recorded from single microcrystals through tilting the specimen grid. One set of such SAED patterns, rotated around the $a$ axis, is shown in Fig. 2. All of the strong diffraction spots can be indexed onto the face-centered orthorhombic basic lattice with $a$ = 11.47, $b$ = 13.40, and $c$ = 3.95 Å, which is in agreement with the X-ray diffraction results. However, no incommensurate satellite spots fitting a 1 × 1 × 7 superlattice nor any evidence of $CuO_2$ chain sublattice reported by McCarron *et al.* (*6*) were observed. All satellite diffraction spots that appeared on these SAED patterns can be indexed onto a commensurate 1 × 1 × 9 superlattice with $a$ = 11.47, $b$ = 13.40, and $c$ = 35.55 Å.

Details of this new structure were studied by the simulation of HREM images. Two principal images are shown in Fig. 3, viewed down the [010] and [01$\bar{1}$] directions of the subunit cell, respectively. It is very clear that the basic structure is layered in an *A–B–B–A–B–B* arrangement along the $a$ axis. Considering the composition, a likely arrangement of cations in the sublattice is Sr–Cu–Cu–Sr–Cu–Cu along this direction. We propose the final model for the following reasons:

First, the structure must not be the same as that of $SrCu_2O_3$ determined by Teske and Muller-Buschbaum (5; Fig. 1c), because the unit cells are quite different and, using this structural model, it is impossible to derive the observed HREM images shown in Fig. 3.

Second, in $SrCuO_2$, $Sr_2CuO_3$, and the new phase, there is a common unit cell parameter, about 3.9 Å. Along this particular axis, Cu cations are square coordinated by four oxygen anions and these square $CuO_4$ units link each other by sharing corners to form a single chain in the case of $Sr_2CuO_3$ (Fig. 1a). Two such single chains share $CuO_4$ edges to form double chains in the case of $SrCuO_2$ (Fig. 1b). In the new phase, double $CuO_4$ chains are therefore possible. Interestingly, these double $CuO_4$ chains have also been reported in $YBa_2Cu_4O_8$ (*13*). Unlike $SrCuO_2$ and $Sr_2CuO_3$, the double $CuO_4$ chains link together on the $a$ direction, but leave enough room for Sr in these middle planes. The three-layer structure,

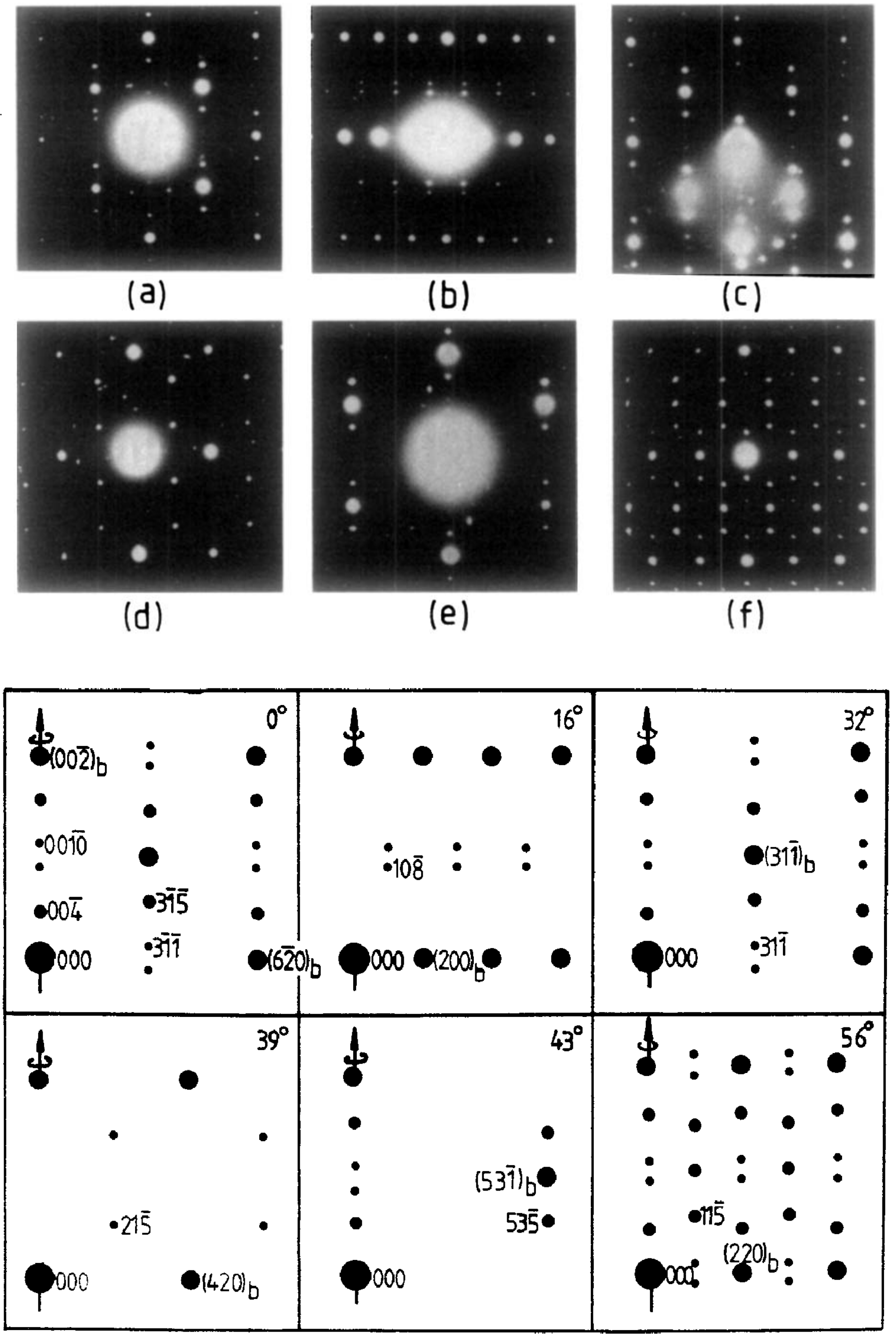
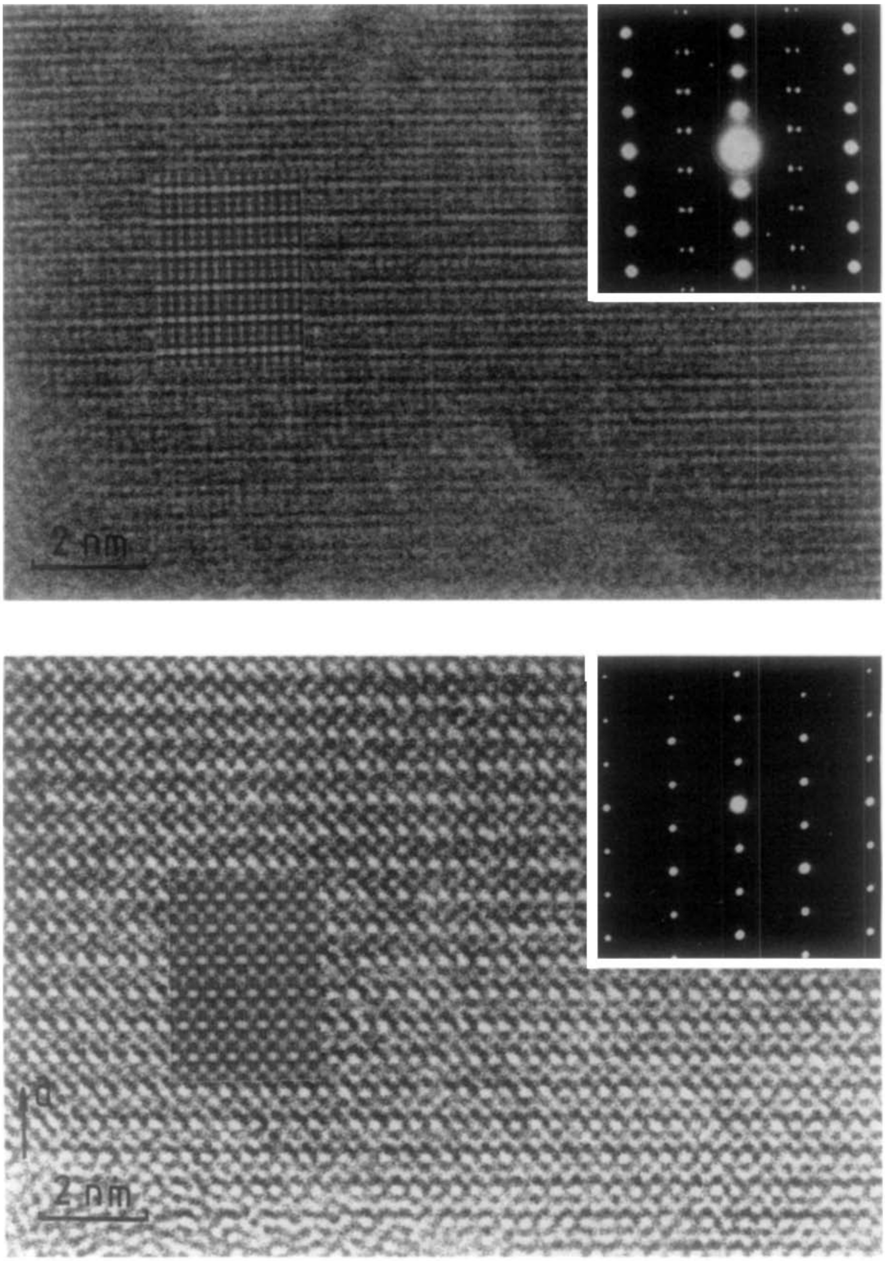


FIG. 2. SAED patterns taken from same microcrystal of $Sr_{1+x}Cu_2O_3$, through tilting the specimen grid around $c$ axis, indexed onto the subunit cell with $a = 11.47$, $b = 13.40$, and $c = 3.95$ Å by $(hkl)_b$ and onto a 1 × 1 × 9 commensurate superlattice by $(hkl)$. The angles tilted from the pattern (a) on one direction are shown at the top right corners.



(b)

FIG. 3. HREM images of $Sr_{1+x}Cu_2O_3$, viewed down the projections on (a) [010] and (b) $[01\bar{1}]$ directions of the basic unit cell. The insets show the computer-simulated images using the basic model of Fig. 4, with conditions of (a) 60 Å specimen thickness, 800 Å lens defocus, and (b) 80 Å thickness, 1200 Å defocus.

Sr–($Cu_2O_3$ sheets)–Sr, is therefore proposed.

Third, since there are no zigzag fringes on the image (Fig. 3a) when viewed down the [010] direction, the displacement of $CuO_4$ chains along the *c* direction is possible. Such a displacement is reasonable since all Cu cations will then have five, instead of four, coordinated oxygen ions. This will have the effect of decreasing the number of Cu–Cu bonding interactions and stabilizing the structure, also because the basic structure is face centered. The final basic structure is then shown in Fig. 4. Note that the shift of some $Cu_2O_3$ sheets leave two different kinds of positions for Sr cations. As shown in Fig. 5a, half of the Sr cations are in the centers of the square oxygen flats and half in the centers of diamond oxygen flats.

Finally, two different types of Sr coordination by oxygen might give a possible explanation for the superlattice formation and compositional variation observed in these materials. Square coordinated Sr cations are relatively stable. However, those in the centers of the diamond $O_4$ flats need less energy to move to the center of triangle $O_3$. Therefore we propose that additional Sr cations might be inserted into the structure and Fig. 5b shows a possible arrangement on one Sr–O plane with extra Sr cations to form a 1 × 9 superlattice. In the second Sr–O plane, all the atomic positions are shifted by $\frac{5}{9}$ of a unit cell on the *c* direction. The composition of this model is therefore $Sr_{19}Cu_{36}O_{54}$, which is close to the experimentally determined composition of the sample. Perhaps even more Sr cations may be inserted in the Sr–O planes. For example, if another two Sr cations are introduced into each Sr–O plane, this will result in a composition $Sr_{20}Cu_{36}O_{54}$; introducing a further two Sr cations will lead to a composition $Sr_{21}Cu_{36}O_{54}$ or $Sr_{14}Cu_{24}O_{36}$. This is the limiting stoichiometry and it has the same cation ratio as $Sr_{14}Cu_{24}O_{41}$ as reported previously. The probable arrangement of Sr cations in the Sr–O plane for a material with the cation ratio Sr : Cu of 14 : 24 is shown in Fig. 5c. In terms of structural chemistry, therefore, the phase is probably a solid solution,

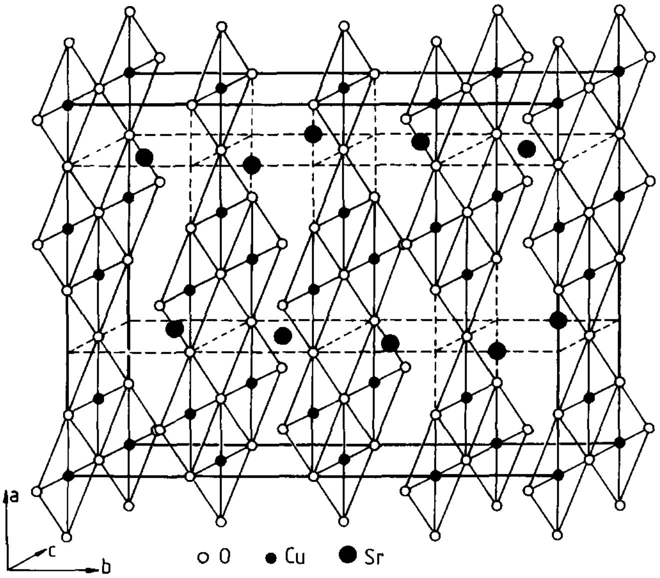


FIG. 4. The model of the basic structure with the ideal composition of $SrCu_2O_3$.

$Sr_{1+x}Cu_2O_3$, $0 \le x \ge 0.1667$, covering the compositional range from $SrCu_2O_3$ to $Sr_{14}Cu_{24}O_{36}$.

Using the model shown in Fig. 5b, we have found that HREM image simulations can match the experimental ones in both the [010] and [$01\bar{1}$] directions of the basic unit cell (see the insets of Fig. 3). Consequently, the basic structure shown in Fig. 4 seems acceptable. The superlattice gives no significant image contrast even on the *c* direction. However, model simulation of selected area electron diffraction patterns is more sensitive to the superstructure. Figure 6a shows one such computer simulation of SAED pattern in the [010] direction. The pairs of satellite diffraction spots clearly appeared. On the other hand, using the recently proposed model of McCarron *et al.* when viewed down the same direction, the SAED simulation shows a significantly different pattern (Fig. 6b).

## Conclusion

The structure of a solid-solution material $Sr_{1+x}Cu_2O_3$ has been investigated by HREM. The details of the basic structure has been determined by both HREM image and SAED pattern simulations to be Sr–

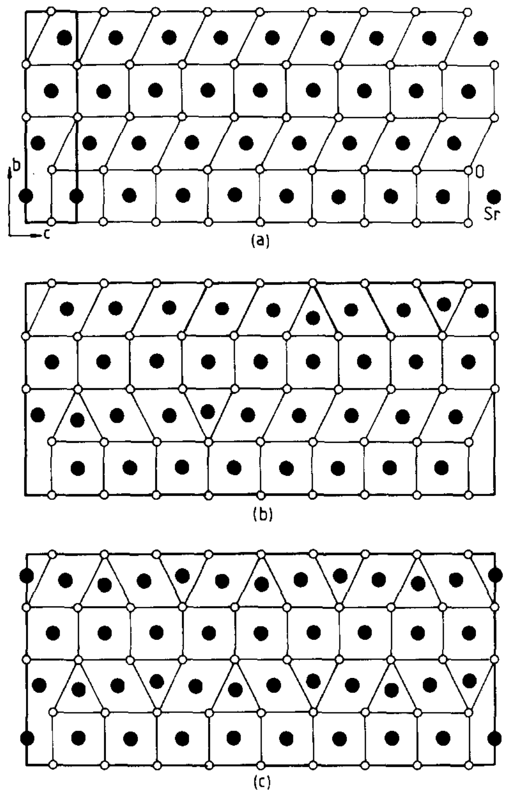


FIG. 5. (a) Atomic arrangement on the Sr–O planes in the model shown in Fig. 4. (b) Possible atomic arrangement of the Sr–O planes when additional Sr cations insert, forming the 1 × 9 superlattice. (c) A superlattice formed by inserting more additional Sr cations with the limiting composition $Sr_{14}Cu_{24}O_{36}$.

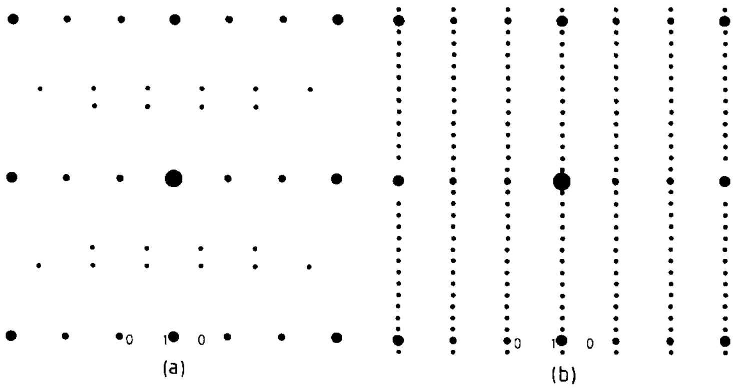


FIG. 6. Computer simulations of SAED patterns, viewed down the [010] direction using (a) the structural model shown in Fig. 5b and (b) the model of $Sr_{14}Cu_{24}O_{41}$ given by McCarron *et al.* (6).

($Cu_2O_3$ sheet)–Sr layered arrangement in a face-centered orthorhombic unit cell. Sr cations exist in two kinds of coordinations in the Sr–O planes. A 1 × 1 × 9 commensurate superlattice derived from this substructure was observed and it is proposed that this superlattice results from extra Sr cations inserting in the Sr–O layers. No previously determined $SrCu_2O_3$ phase nor $Sr_{14}Cu_{24}O_{41}$ phase was observed. Further refinement of the superstructure by computer simulation of SAED patterns is necessary. Analysis of oxygen content and measurements of physicochemical properties are also currently under investigation.

## References

1. G. Bednorz and K. A. Muller, *Z. Phys. B* **64,** 188 (1986).
2. J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, *Phys. Rev. Lett.* **61,** 1127 (1988).
3. A. Ono, T. Tanaka, H. Nozaki and Y. Ishizawa, *Japan J. Appl. Phys., Part 2* **26**(10), L1687 (1987).
4. R. Jones, W. Zhou, D. A. Jefferson, and P. P. Edwards, in preparation.
5. C. L. Teske and H. Muller-Buschbaum, (a) *Z. Anorg. Allg. Chem.* **371,** 325 (1969); (b) *Z. Anorg. Allg. Chem.* **379,** 234 (1970); (c) *Z. Anorg. Allg. Chem.* **379,** 113 (1970).
6. E. M. McCarron, M. A. Subramanian, J. C. Calabress, and R. L. Harlow, *Mater. Res. Bull.* **23,** 1355–1365 (1988).
7. R. S. Roth, C. L. Rawn, J. D. Whitler, C. K. Chiang, and W. K. Wong-Ng, *J. Amer. Ceram. Soc.* **72**(3), 395 (1989).
8. (a) W. Zhou, D. A. Jefferson, and J. M. Thomas, *Proc. R. Soc. London Ser. A* **406,** 173 (1986); (b) W. Zhou, D. A. Jefferson, and J. M. Thomas, *J. Solid State Chem.* **70,** 129 (1987); (c) W. Zhou, *J. Solid State Chem.* **76,** 290 (1988); (d) W. Zhou, D. A. Jefferson, and J. M. Thomas, *in "Geophys. Monograph"* (A. Navrotsky and P. J. Weidner, Eds.), Vol. 45, p. 113 (1989).
9. D. A. Jefferson, J. M. Thomas, G. R. Millward, K. Tsuno, A. Harriman, and R. D. Brydson, *Nature (London)* **323,** 428 (1986).
10. J. M. Cowley and A. F. Moodie, *Acta Crystallogr.* **16,** 609 (1957).
11. P. Goodman and A. F. Moodie, *Acta Crystallogr. Sect. A* **30,** 280 (1974).
12. D. A. Jefferson, G. R. Millward, and J. M. Thomas, *Acta Crystallogr. Sect. A* **32,** 823 (1976).
13. P. Marsh, R. M. Fleming, M. L. Mandich, A. M. DeSantolo, J. Kwo, M. Hong, and L. J. Martinez-Miranda, *Nature (London)* **334,** 141 (1988).