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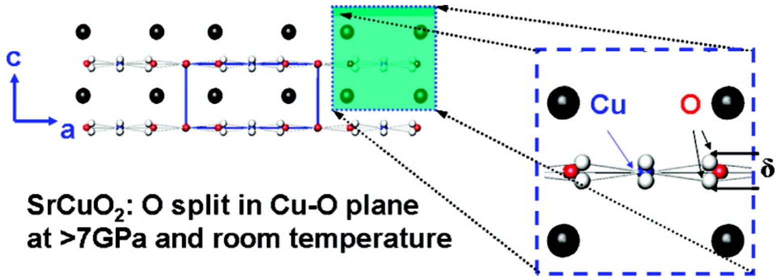

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# Pressure-Induced Splitting and Buckling of Cu−O Chains in the Low-Dimensional Structure of $SrCuO_2$

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***Abstract:*** A pressure-induced splitting of the Cu−O chains was found in $SrCuO_2$ at pressures >7 GPa and room temperature. The high-pressure phase is a superstructure of the infinite-layered tetragonal superconducting phase of $SrCuO_2$ and is not stable under ambient conditions. The Cu−O chains buckle with further increasing pressure, and a new high-density polymorph of $SrCuO_2$ is formed at 34.2 GPa.

## Introduction

Strontium copper oxides have been the subject of intensive investigation during recent years[1−6] because of their unique low-dimensional structural character. The orthorhombic $SrCuO_2$ (*Cmcm*),[7] which is the stable phase at normal pressure, contains a pair of corner-sharing Cu−O chains parallel to the *c*-axis, stacked along the *b*-direction (lattice parameters: $a = 3.5766$ Å, $b = 16.3354$ Å, $c = 3.9143$ Å, $Z = 4$). The electrons in the compound are likely to move along the Cu−O chains, and the coupling between neighboring chains is weak. At elevated pressure of 6 GPa and a temperature of 1000 °C, a metastable tetragonal polymorph of $SrCuO_2$ (*P4/mmm*) has been fabricated from the orthorhombic phase.[3] The tetragonal phase is a parent structure for superconductor and consists of two-dimensional $CuO_2$ sheets separated by layers of Sr atoms. Orthorhombic $SrCuO_2$ is one of these ideal one-dimensional (1-D) materials, which allows one to investigate fundamental physical phenomena in one dimension using both theoretical and experimental approaches, such as 1-D Mott insulators, and spin-charge separation.[2,8−12]

At ambient conditions, the tetragonal parent structure of superconductor was only obtained in a narrow compositional range, such as $Ca_{0.86}Sr_{0.14}CuO_2$,[13] and it is, in fact, an insulator. Small amount of Nd-doped $SrCuO_2$ is a superconductor with transition temperature $T_c = 40$ K.[14] Various doping in the tetragonal structure was realized at high pressures,[15−17] and the superconductivities with $T_c$ from 42−44 K in La-doped[16] $Sr_{1-x}La_xCuO_2$ to ∼110 K in Ca-doped[17] $(Sr,Ca)_{1-x}CuO_2$ were reported before. The orthorhombic to tetragonal phase transition in undoped $SrCuO_2$ can only be realized by high pressure and high-temperature treatment.[3] However, the mechanism of this phase transition is not well understood, and no pressure dependence of the structure of $SrCuO_2$ at room temperature has been determined until this study. The understanding of pressure-induced phase transitions at the atomic scale is always a challenge. In this paper, we show that the orthorhombic $SrCuO_2$ transforms to a superlattice (hp-I) of the infinite-layer tetragonal phase of $SrCuO_2$ at 7 GPa at room temperature. The formation of the superlattice is due to the splitting of one O site in the unit cell along the *c*-axis. The superstructure of the tetragonal phase is stable up to 34.2 GPa, but a new denser structure (hp-II) forms at higher pressures. The high-pressure phase-II is orthorhombic, and there is an 18% decrease in unit cell volume when it is transformed from the tetragonal phase. Both of the two pressure-induced phase transitions in $SrCuO_2$ are reversible.

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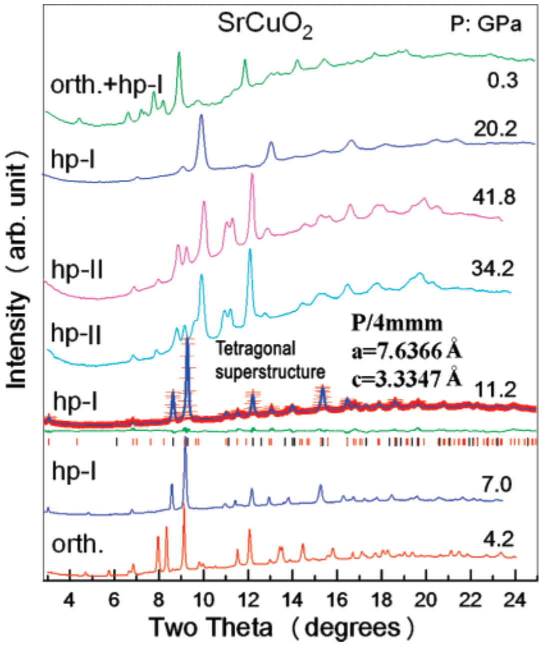

***Figure 1.*** The XRD patterns of $SrCuO_2$ at high pressures. Two phase transitions are clearly observed at pressures of ~7 and ~34.2 GPa, respectively. The XRD pattern at 11.2 GPa is refined using the Rietveld method in a superlattice ($2a \times 2b \times c$) of the superconducting tetragonal unit cell. The long vertical bars indicate the positions of Bragg diffractions from the basic tetragonal superconducting phase and the short ones indicate the diffraction peaks caused only by the superlattice. The green line above the bars represents the residual from the fit. The XRD patterns at 20.2 and 0.3 GPa are taken during release of pressure.

## Experimental Section

The powder sample of $SrCuO_2$ was synthesized by traditional solid-state reaction method at 900 °C for several days with intermediate grinding.[18] The synthesized sample is confirmed to be the pure orthorhombic phase by a lab XRD facility. High-pressure experiments were performed using a diamond anvil cell (DAC) with methanol/ethanol (4:1) liquid as pressure medium. The in situ XRD measurements were performed using a synchrotron radiation X-ray source (0.4066 Å) at the X17C station of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The Debye rings were recorded with image plate techniques and the XRD patterns were integrated from the images using the FIT2d software.[19] The pressure in all of the experiments was measured by the ruby fluorescence method.[20] A direct method was used to solve the crystal structure of the high-pressure phases with software EXPO.[21] The XRD patterns of the low-pressure orthorhombic phase and the tetragonal phase were refined with Rietveld method.[22] The energy calculations were carried out with CRYSTAL03 package.[23] B3LYP hybrid density functional was used for exchange and correlation. All-electron basis sets for Cu and O ions were of the form of 86-411(41d)G and 8-411G, respectively. A small-core Hay−Wadt pseudopotential basis set was used for Sr ion of the form of 31(3d)G.

## Results and Discussion

The XRD patterns of SrCuO2 at high pressures are shown in Figure 1. A phase transition is clearly observed at 7 GPa, and the strong peaks in the XRD pattern of the high-pressure phase are similar to those calculated from the tetragonal structural model reported previously.[4,13] However, several new peaks cannot be reconciled, such as the first diffraction maximum at a $2\theta$ of ~3°. Indexing using all the observed peaks resulted in a $2a \times 2b \times c$ superstructure, where $a$, $b$, and $c$ are the lattice constants of the tetragonal $SrCuO_2$. The phase transition at 7 GPa occurs over a very narrow pressure range (<0.5 GPa), and we never observed the coexistence of the tetragonal phase with the initial orthorhombic phase during several repeated experiments.

***Table 1.*** Atomic Coordinate of the Tetragonal Phase at 11.2 GPa Refined for Space Group *P4*/*mmm* and Lattice Parameters: $a = b = 7.6366(6)$ Å, $c = 3.3347(3)$ Å

| atom | Wyckoff | *x*/*a* | *y*/*b* | *z*/*c* | occupancy |
|---|---|---|---|---|---|
| Sr | 4k | 0.2196(4) | 0.2196(4) | 0.5 | 1 |
| Cu1 | 2f | 0.5 | 0 | 0 | 1 |
| Cu2 | 1c | 0.5 | 0.5 | 0 | 1 |
| Cu3 | 1a | 0 | 0 | 0 | 1 |
| O1 | 4l | 0.249(9) | 0 | 0 | 1 |
| O2 | 8t | 0.260(8) | 0.5 | 0.91(1) | 0.5 |

We solved the high-pressure structure directly from the XRD pattern taken at 11.2 GPa. The direct method generates six atomic positions in the space group *P4*/*mmm*. Assuming that the four sites with high electron densities are due to one Sr and 3 Cu atoms and the two sites with low electron densities are due to O atoms, a reasonable structure model can be proposed. The model structure is very close to that of the infinite-layer tetragonal phase. The structure was refined by the Rietveld method, and the refined atomic coordinates are listed in Table 1. The calculated XRD pattern fits the observed one quite well (Figure 1). The O2 atom occupies the 8*t* site, and the closest distance between sites that are occupied by O2 atoms is 0.6 Å at 11.2 GPa. The two closest O2 sites, in fact, are one single site split along the *c*-axis, and the occupancy is thus reduced by half. There are three Cu sites in the unit cell, which have different bonding environments with the O atoms. Cu3 atoms are surrounded by four O1, which have a typical bond length ($d = 1.902$ Å). Cu1 atoms bond with two O1 and two O2 atoms with bond lengths of 1.917 Å and 2.008 Å, respectively. Cu2 atoms reside in the center of the unit cell and bond with four O2 atoms and the bond length of Cu3−O2 is the shortest (1.857 Å). A schematic diagram of the superlattice is depicted in Figure 2b. Apparently, pressure-induced splitting of the O2 site along the *c*-axis is the reason of the formation of the superlattice. There is a 6% volume decrease with the transition from the orthorhombic phase to the tetragonal superlattice at 7 GPa. The pressure-induced tetragonal phase of $SrCuO_2$ cannot be quenched at room conditions; however, the simple tetragonal phase, which is fabricated from the orthorhombic phase by high-pressure and high-temperature treatment, can exist at room conditions as a metastable phase.

To compare the structural stability of the different tetragonal phases, we calculated the energy difference between the tetragonal phases without and with O-site splitting at 7 GPa using the density functional method as implemented by the program package *Crystal03*. In these calculations, O2 is placed on one of the two positions with full occupancy. We found that the superstructure has higher energy (0.13 eV per structural unit). To further understand the energetics of O2 site splitting of the

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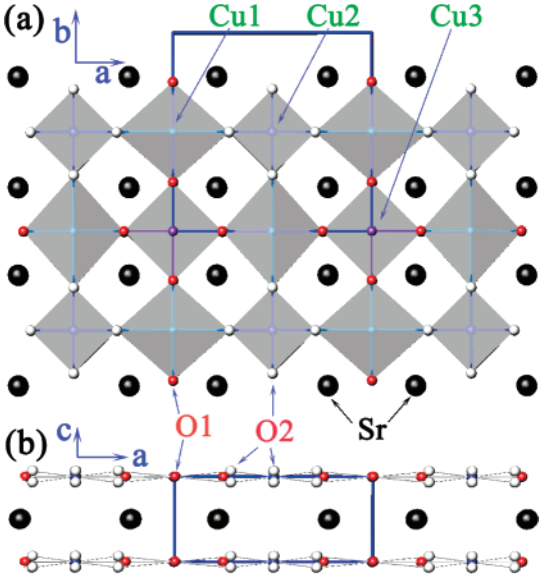

***Figure 2.*** Schematic crystal structure of the tetragonal superlattice at high pressures project along (a) (001) and (b) (010) directions, respectively. One of the O-sites (O2) is split along the *c*-axis in the unit cell.

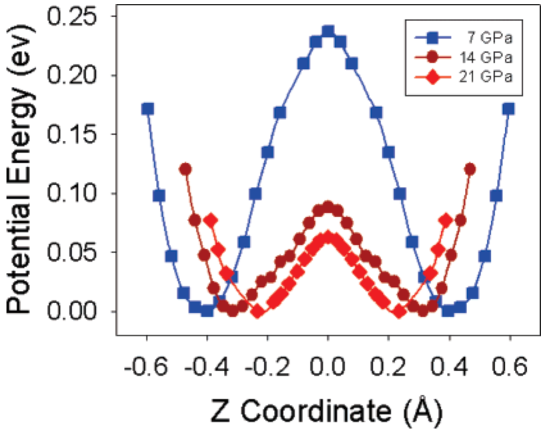

***Figure 3.*** The calculated lattice energy of the tetragonal $SrCuO_2$ phase and its dependence on the splitting of O2 atoms along the *c*-direction.

tetragonal phase under pressure, we have estimated the energy barrier by moving the O2 atom along the *c* direction and optimizing the coordinates of the rest atoms while keeping the experimental unit cell parameters constant. Figure 3 shows that the barrier at 7 GPa is about 0.24 eV, thus, about ten times higher than $k_BT$ at room temperature. Although the tetragonal phase with a simple structure seems to be more stable than that with a superstructure at 7 GPa, the energy barrier for the superstructure is high enough to prevent it from transforming to the basic tetragonal form at room temperature. High-temperature treatment or structural defects induced by chemical doping may provide the energy required to overcome the energetic barrier for the transformation.

With increasing pressure, the intensities of the diffraction peaks due to the superlattice structure are reduced gradually, which means a simple tetragonal structure may be formed at high enough pressure at room temperature. This is in agreement with our theoretical calculation results in Figure 3. The energy barrier and splitting distance of O2 atoms are reduced with increasing pressure, and the structure tends toward a simple tetragonal structure. However, the simple tetragonal structure is not formed by only increasing the pressure at room temperature because another phase transition occurs at 34.2 GPa (Figure 1). The XRD pattern at pressure above 34.2 GPa is completely different from that of the tetragonal superlattice structure. The transition from the tetragonal superlattice to the high-pressure phase-II has a large pressure range of ∼5 GPa, and the wide pressure range may be due to the non-hydrostatic conditions at higher pressures. Fortunately, most of the diffraction peaks from the high-pressure phase-II do not overlap, and they can be easily indexed in an orthorhombic unit cell. The indexing of the diffraction peaks at 41.8 GPa results in a unit cell with lattice constants of $a = 3.8441$Å, $b = 7.1256$ Å, and $c = 5.2665$ Å. The reflection restrictions ($k = 2n$ for $0kl$, $l = 2n$ for $h0l$, $k = 2n$ for $0k0$, and $l = 2n$ for $00l$) suggest a space group of $Pbc2_1$ (29) or *Pbcm* (57) for the high-pressure phase-II. High-pressure phases are usually denser than the normal phase, and the indexed results suggest that there are four formula units of $SrCuO_2$ in the unit cell of the high-pressure orthorhombic phase.

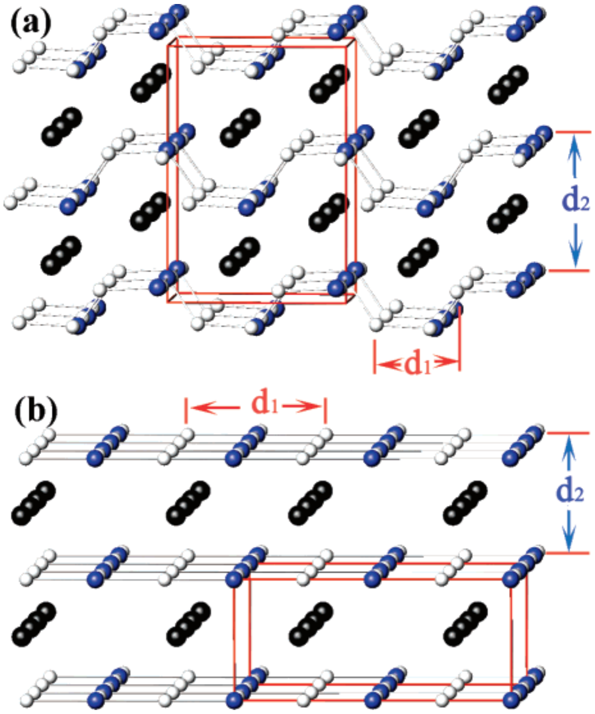

***Figure 4.*** (a) Schematic crystal structure of the high-pressure phase II and (b) the structure of the tetragonal phase. The big black balls represent Sr, small light balls and middle-sized blue balls are O and Cu atoms, respectively. The Cu−O chains are buckled in the high-pressure phase II, which is formed by compressing the tetragonal unit cell along the *b*-direction.

We tried to solve the structure from the XRD pattern taken at 41.8 GPa. The direct method generates six possible positions in the lower symmetry space group of $Pbc2_1$. All six positions are on the 4*a* site because only the general position (4*a*) is allowed in this space group. The two high electron density positions are assigned as Sr and Cu, respectively, and the remaining four sites with low electron densities are attributed to oxygen. However, two of the four oxygen positions have unreasonably short bond distances to the heavy atoms. After selecting the remaining two positions as the O sites, a reasonable structural model can be proposed (Figure 4a) for the high-pressure phase-II. The bonding environment of Cu maintains a

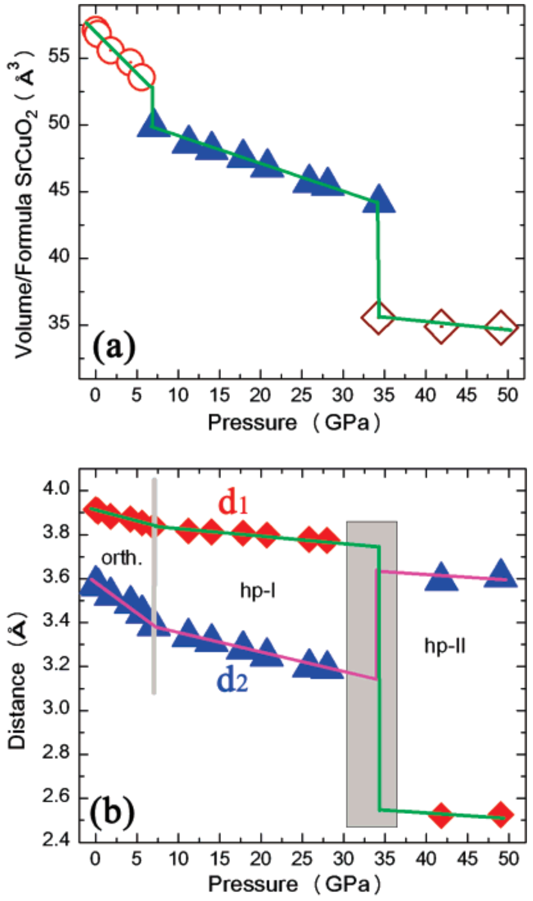

***Figure 5.*** (a) Pressure dependence of the unit cell volume (per $SrCuO_2$). (b) Pressure dependence of the distances between Cu−O chains or layers ($d_2$-triangles) and along the chains ($d_1$-diamonds). Definition of $d_1$ and $d_2$ is shown in Figure 4. During the phase transition from the orthorhombic to the tetragonal superlattice, compression between Cu−O2 sheets (or Cu−O layers) is dominant while the compression along Cu−O chains became dominant for the second phase transition.

similar topology as in the tetragonal phase (Figure 4b), but the Cu−O chains are buckled along the *c*-direction. In fact, a pressure-induced buckling of the $Cu_2O_3$ layers has been observed in a related compound $SrCu_2O_3$ at 3 GPa and at room temperature before,[24] and the high-pressure phase of $SrCu_2O_3$ is isostructural with the normal phase of $CaCu_2O_3$. The high-pressure phase II of $SrCuO_2$, however, is a new structure, and we cannot find a similar structure in any polymorphs of the alkaline copper oxides.

The pressure dependence of the unit cell volume of the different phases is plotted in Figure 5a. The volume decreases by ∼6% and ∼18% as one goes from the initial orthorhombic $SrCuO_2$ to the tetragonal superlattice structure and finally, to the high-pressure orthorhombic phase-II. The volume decrease from the tetragonal superlattice structure to the high-pressure phase II is very high and the ⟨Sr−O⟩ bond distances shorten to 0.21 nm at 41.8 GPa. The above structure model for high-pressure phase-II cannot be well refined using the Rietveld method because the relative intensities of the calculated diffraction peaks are somewhat different from the observed patterns. This may be due to the uncertainty of the O atom positions in the above structure model. The starting orthorhombic phase and the high-pressure phases have different compressibility. Fitting with Birch−Murnaghan equation of state, the bulk moduli for the orthorhombic and the tetragonal superlattice are 81(6) GPa and 158(4) GPa, respectively, if their derivatives at zero pressure are fixed at $B_o' = 4$. We cannot get a reliable bulk modulus for the second high-pressure phase from the three experimental data points only. The bonding distances between the Cu−O2 sheets and along the Cu−O chains in different phases are illustrated in Figure 5b. The compression between Cu−O layers is dominant in the starting orthorhombic phase and the tetragonal superlattice (hp-I). When the interplanar distance reaches a limit (e.g., ∼3.2 Å) in the tetragonal superlattice, further compression will buckle the Cu−O chains, and the compression along one direction of the Cu−O chains becomes dominant during the second phase transition. After the Cu−O chains are buckled, the distance between the layers in high-pressure phase-II is even a little larger than those in the orthorhombic and tetragonal phases.

## Conclusions

In summary, two new phases are discovered in $SrCuO_2$ at high pressures. The superstructure of the infinite-layer tetragonal structure of $SrCuO_2$ at pressures above 7 GPa is caused by the splitting of one of the O sites in the CuO2 sheets. Our results suggest that pressure alone can induce the structural transformation from the orthorhombic to the tetragonal phase, but the combination of high-temperature (more than 1000 °C) and high pressure can stabilize the O2 atoms into one nonsplit position, and thus stabilize the infinite-layer structure under ambient conditions. The second phase transition at 34.2 GPa is caused by the buckling of the Cu−O chains.

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