

Pressure-Induced Buckling of Spin Ladder in SrCu₂O₃Masaki Azuma,^{*,†,‡} Hirofumi Yoshida,[†] Takashi Saito,[†] Takahiro Yamada,[§] and Mikio Takano[†]

Contribution from the Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan; PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan; and Japan Synchrotron Radiation Research Institute, Kouto Mikazuki-cho Sayo-gun, Hyogo 679-5198, Japan

Received February 13, 2004; E-mail: masaki@scl.kyoto-u.ac.jp

Abstract: Pressure-induced structural phase transition of spin ladder compound SrCu₂O₃ was investigated by synchrotron X-ray powder diffraction with a diamond anvil cell (DAC). The change was characterized by a buckling of the Cu₂O₃ plane in the rung direction of the ladder. The structure of the high-pressure phase was found to be essentially the same as that of CaCu₂O₃. Application of an external pressure of 3.4 GPa therefore affected the structure in the same manner that the chemical (internal) pressure does.

1. Introduction

High-pressure (HP) synthesis is a powerful technique in searching for new functional materials. To obtain a compound with a designed structure, it is necessary to understand how pressure affects a crystal structure. For example, SrCuO₂ changes from a one-dimensional zigzag chain structure to a so-called infinite layer after treatment at 3 GPa and 700 °C.¹ The infinite layer phase can only be obtained in the vicinity of Sr_{0.84}Ca_{0.16}CuO₂ at ambient pressure (AP). Therefore, the heat treatment at a high pressure of 3 GPa stabilizes the structure obtained by substituting the smaller Ca ions for Sr ions. Such ionic radius control is called application of chemical (internal) pressure.

In the case of SrCuO₂, the HP phase can be quenched to ambient conditions as a metastable phase, so the investigation of the obtained product is rather easy. On the other hand, when the structure is stable only at a high pressure, observation of the pressure-induced structural transition and the structure determination of the HP phase are quite difficult. The combination of synchrotron radiation X-ray, an imaging plate, and a diamond anvil cell is a powerful tool to study crystal structures at high pressures. The effect of pressure was extensively studied for the inorganic spin-Peierls compound CuGeO₃ in the past decade. Since the lattice dimerization is the origin of the singlet ground state of this compound, it is expected that the pressure affects both the transition temperature (T_{SP}) and the magnitude of spin gap. Several HP polymorphs were found during the investigation of the pressure effects, and the crystal structures of some of them were determined by means of single-crystal X-ray diffraction (XRD) studies.^{2,3} SrCu₂O₃⁴ is another class

of spin gap compound. This compound, prepared at 4 GPa, comprises $S = 1/2$ quantum spin ladders.⁵ It has a large spin gap of 420 K without any structural distortion. In the course of powder XRD study at high pressure and temperature, to determine the single-crystal growth condition,^{6–8} we found an unexpected pressure-induced structural transition at room temperature. The result of the structure determination of the HP phase is reported here. It is shown that the application of pressure affected the crystal structure of this complex oxide in the same way that the chemical pressure does.

2. Experimental Section

The sample was prepared by treating a mixture of SrCuO₂ and CuO at 4 GPa and 1050 °C for 30 min. in a cubic anvil type HP apparatus.⁴ The structural parameters at room temperature and at ambient pressure were refined by Rietveld analysis of the powder XRD data (Cu K α radiation) with Rietan 2000⁹ and are summarized in Table 1. Sr–O and Cu–O bond lengths are also given in Table 2. The obtained SrCu₂O₃ was then carefully crushed into fine powders and put in a screw type DAC with a methanol/ethanol 4:1 pressure medium. The pressure was determined using the ruby fluorescence method. The powder diffraction data obtained by monochromated X-ray ($\lambda = 0.327$ Å) were recorded on a flat imaging plate at the BL04B2 beam line of SPring-8 with a sample-to-detector length of 227 mm.

3. Results and Discussion

The powder XRD patterns taken at various pressures and at room temperature are shown in Figure 1. The data at 0.65 to

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[†] Institute for Chemical Research, Kyoto University.

[‡] PRESTO, Japan Science and Technology Agency (JST).

[§] Japan Synchrotron Radiation Research Institute. Present address: National Institute of Advanced Industrial Science and Technology, (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

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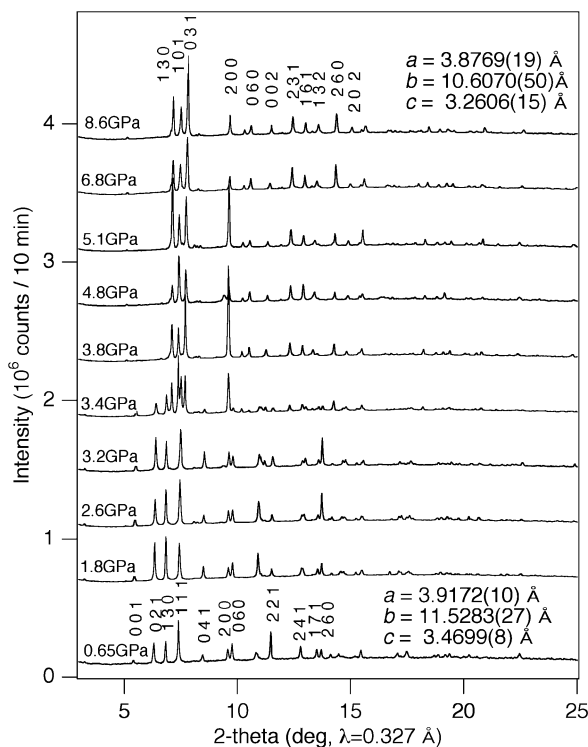
Table 1. Refined Crystal Parameters for SrCu₂O₃ at 0.1 MPa and 6.7 GPa^a

	atom	site	x	y	z	B (Å ²)
0.1 MPa Cmmm (65)	Sr	2d	0	0	0.5	0.6
	Cu	4i	0	0.3342(1)	0.0	0.8
	O1	2b	0.5	0.0	0.0	1.0
	O2	4i	0.0	0.1699(5)	0.0	1.0
6.8 GPa Pmmn (59)	Sr	2a	0.25	0.25	0.7530(51)	0.6
	Cu	4f	0.75	0.0711(3)	0.2456(38)	0.8
	O1	4f	0.25	0.0698(14)	0.2405(183)	1.0
	O2	2b	0.75	0.25	0.5095(87)	1.0

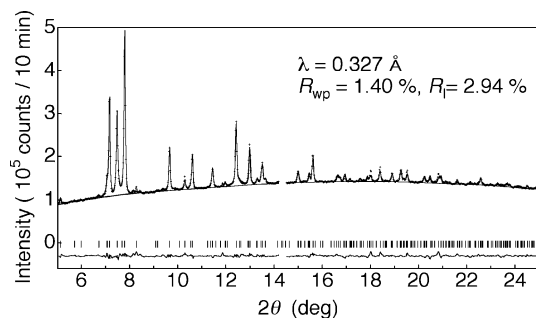
^a $R_{wp} = 2.78\%$ and $R_1 = 2.50\%$ for 0.1 MPa data. $R_{wp} = 1.40\%$ and $R_1 = 2.94\%$ for 6.8 GPa data. $Z = 2$ for both compounds. Isotropic atomic displacement parameters (B) were fixed in the refinements.

Table 2. Selected Bond Lengths for SrCu₂O₃ at 0.1 MPa and at 6.8 GPa

	bond	length
0.1 MPa	Cu–O1	1.917(1)
	Cu–O2	1.900(6)
	Cu–O2 × 2	1.966(0)
	Sr–O1 × 4	2.628(4)
	Sr–O2 × 4	2.629(0)
6.8 GPa	Cu–O1 × 2 (in-plane)	1.942(1)
	Cu–O2 (in-plane)	2.088(14)
	Cu–O1 (in-plane)	2.187(46)
	Cu–O1 (apical)	2.254(47)
	Cu–O2 (apical)	3.072(26)
	Sr–O2 × 2	2.100(14)
	Sr–O1 × 2	2.493(46)
	Sr–O1 × 2	2.547(48)
	Sr–O2 × 2	3.150(30)

**Figure 1.** Powder XRD patterns of SrCu₂O₃ collected at 0.65 to 8.6 GPa at room temperature.

3.2 GPa were consistent with the spin ladder phase of SrCu₂O₃. The variety of the intensity ratios among the data collected at different pressures occurred because of the inhomogeneity of the Debye rings resulting from the inclusion of relatively large

**Figure 2.** Observed (+), calculated (solid line) and the difference of the powder XRD pattern of SrCu₂O₃ at 6.8 GPa. The ticks show the peak positions. The data between 14.2° and 14.5° corresponding to the 2 6 0 peak were excluded from the fitting.

particles. The pattern changed significantly above 3.8 GPa indicating that a structural transition took place. All the peaks of the HP phase could be indexed assuming an orthorhombic cell of $\sim 3.9 \times 10.6 \times 3.3 \text{ \AA}^3$. The data collected at 6.8 GPa was chosen for the structure determination because the influence of the large particles was the smallest in these data. In other words, the Debye rings were the most homogeneous, and thus the intensity ratio was the most reliable.

Since the unit cell was close to that of CaCu₂O₃¹⁰ and the reflection condition ($h + k = 2n$ for $hk0$, $h = 2n$ for $h00$, and $k = 2n$ for $0k0$) satisfied the space group $Pmmn$, the CaCu₂O₃ crystal structure was chosen as the initial model. It should be noted that the ab initio determination using EXPO software¹¹ gave the same structure. The refinement of the structural parameters was performed by means of the Rietveld method. Only the 2 6 0 peak was excluded from the fitting because of the inhomogeneous Debye-ring for this reflection.

The observed, calculated, and difference of the XRD pattern taken at 6.8 GPa were shown in Figure 2. The refined atomic positions and Sr–O and Cu–O bond lengths are listed in Tables 1 and 2, respectively. Thus, the determined structure of the HP phase of SrCu₂O₃ is shown in Figure 3 with those of the AP phase and CaCu₂O₃ for comparison. At ambient pressure, SrCu₂O₃ consists of Sr layers and Cu₂O₃ ladder layers that alternate along the c -axis. In the Cu₂O₃ plane, 2 –O–Cu–O–Cu–O– chains are connected with each other through linear Cu–O–Cu bonds to form a ladder. The ladders are assembled to make a sheet. The most significant difference of the structure at 6.8 GPa was the buckling of the Cu₂O₃ plane in the rung direction of the ladder. Consequently Sr ions were shifted upward or downward. Because of the buckling, oxygen atoms in the adjacent Cu₂O₃ planes go to the apical positions of a Cu ion. However, a Cu ion was not at the center of an octahedron, so the coordination was rather pyramidal. As a result, the coordination number of Cu increased from 4 to 5, while that of Sr was the same, 8, for both the ladder and the HP phases. The lattice parameters, as well as the unit cell volume, are plotted as functions of pressure in Figure 4. Two sets of markers were plotted for 3.4 GPa data because the AP and the HP phases coexisted at this pressure. The change was anisotropic. The c -axis contracted drastically at the transition pressure, while the a -axis changed little, and even expanded. It reflects the stiff

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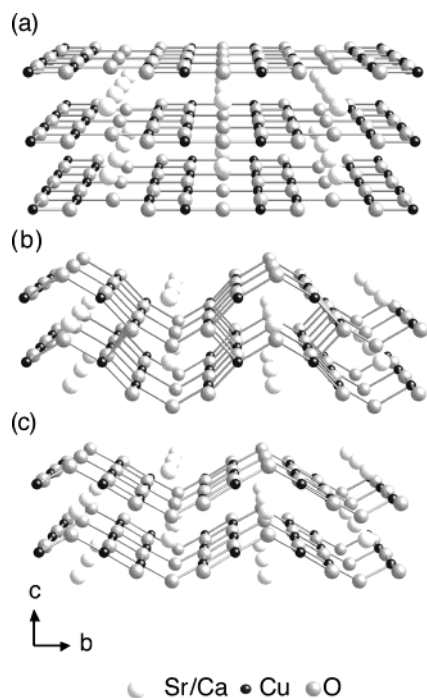


Figure 3. Crystal structures of SrCu_2O_3 at (a) 0.1 MPa and (b) 6.8 GPa and that of (c) CaCu_2O_3 at 0.1 MPa.

covalent nature of the Cu–O bonds. The b -axis contracted by 6.6% due to the buckling of the Cu_2O_3 plane in this direction. The sharp drop in the volume and the coexistence of the two phases observed in the pattern collected at 3.4 GPa indicated that the transition was of first-order. The transition was quite sharp; however, no hysteresis was observed in the experimental resolution. The pressure was applied and released twice in the order indicated in Figure 4. Each time the pressure was released, the ladder phase was recovered.

From the magnetic point of view, this finding is not an encouraging one to promote further measurements at high pressures. The singlet ground state of this novel spin ladder compound should be switched to an antiferromagnetic long-range order as observed in CaCu_2O_3 .¹² However, from a crystallographic point of view, the present result is quite interesting. SrCu_2O_3 transformed from the ladder phase to the CaCu_2O_3 structure at 3.4 GPa. This shows that the application of the external, and the chemical pressures drive the system to undergo the same structural change. It might be interesting to estimate the critical ionic size of alkaline earth (the Sr/Ca ratio) at ambient pressure. The compressibility of the SrCu_2O_3 spin ladder phase was 1.1%/GPa in volume. On the other hand, 10% substitution of Ca for Sr compressed SrCu_2O_3 by 0.87%.¹³

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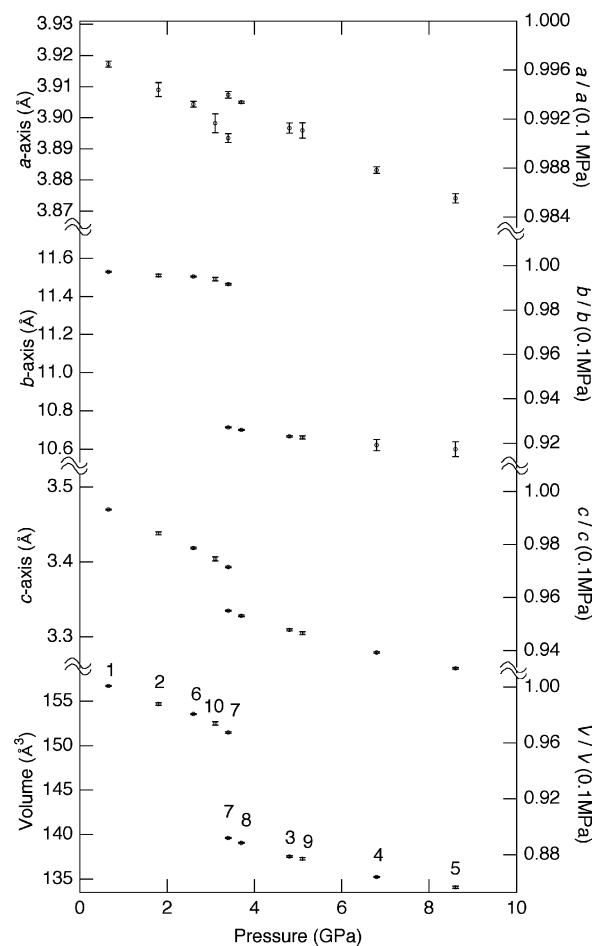


Figure 4. Lattice parameters and volume of SrCu_2O_3 as functions of pressure. The numbers in the figure correspond to the order of the experiment. The values relative to those at 0.1 MPa are shown on the left axis.

Application of 3.4 GPa thus corresponds to a 43% substitution of Ca for Sr. Unfortunately this cannot be experimentally confirmed because of the low solubility limit (15%) of Ca for Sr in $\text{Sr}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_3$.¹³

In conclusion, we have found a pressure-induced structural phase transition in spin ladder compound SrCu_2O_3 at 3.4 GPa and at room temperature. The HP phase had essentially the same structure as CaCu_2O_3 . The same structures were obtained by applications of external and chemical pressures on this complex oxide.

Acknowledgment. The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute. The authors express their thanks to the Ministry of Education, Culture, Sports, Science and Technology, Japan, for Grants-in-Aid No. 12CE2005, for COE Research on Elements Science, and No. 13440111.

JA049212C