

## Pressure Effect on the Crystal Structure and Electrical Conductivity of $\text{LiCuO}_2$

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Pressure dependence of the unit-cell parameters in  $\text{LiCuO}_2$ , composed of a bundle of infinite one-dimensional Cu-O chains, has been investigated under hydrostatic conditions up to 6.3 GPa. The axes perpendicular to the chains show a considerable decrease with an increase in pressure, whereas the axis parallel to the chains show low contraction with compression. These behaviors are directly related to the chain structure of  $\text{LiCuO}_2$ : the compressibility along the edge-shared  $\text{CuO}_2$  chains is very low and vice versa. The electrical resistivities up to 8 GPa show a semiconductive behavior between room temperature and 77 K with slight pressure dependence. © 1993 Academic Press, Inc.

### Introduction

Oxocuprate compounds containing formally trivalent copper ions have been investigated because these ions often play an essential role in inducing high- $T_c$  superconductivity. The compounds  $\text{ACuO}_2$ , with  $A$  = alkali ions, are typical of the most simple oxocuprates(III) and are expected to have a potentiality for elucidating the physical and chemical properties of Cu(III) in oxides (1-3). These compounds have related structures with infinite, one-dimensional Cu-O chains which are constructed of the edge-sharing  $\text{CuO}_4$  square planar units.

Quite recently, stoichiometric  $\text{LiCuO}_2$  has been first prepared in our group by Li-extraction of  $\text{Li}_2\text{CuO}_2$  with  $\text{I}_2$  and was determined by X-ray analyses to be orthorhombic with the space group of  $Cmmm$  (4). The crystal structure analysed by Riedvelt method (4) is, as illustrated in Fig. 1, essentially made of a bundle of infinite Cu-O

chains and lines of Li ions are located at the interspace of the chains. The other  $\text{ACuO}_2$  compounds with  $A$  = K through Cs have a related structure to  $\text{LiCuO}_2$  with the orthorhombic space group  $Cmcm$  (5, 6), where the coordination around  $A$  ions is slightly different and the mutual distance of Cu-O chains is much larger.  $\text{NaCuO}_2$  is nearly isostructural with  $\text{LiCuO}_2$  but is distorted monoclinically with a space group of  $C2/m$  (7, 8).

Crystals composed of such a bundle of one-dimensional, infinite chains commonly show anisotropic behavior between parallel and perpendicular to the chain-axis because of the significant difference in interactions of intra- and interchains. The interchain interactions should be changed by changing the mutual distance of chains, whereas those for the intrachains are expected to be not so significant.

The present paper describes a pressure-induced change in the lattice parameters of  $\text{LiCuO}_2$  which is thought to be a typical orthogonally  $\text{ACuO}_2$  compound having such a

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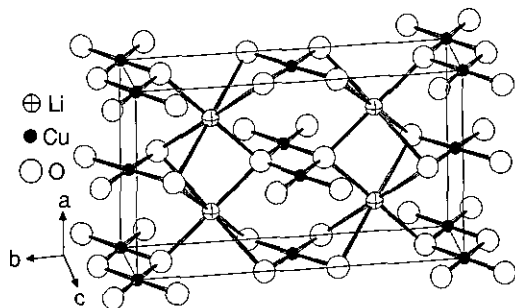


FIG. 1. Crystal structure of  $\text{LiCuO}_2$  (4).

$\text{Cu(III)-O}$  chain. A significant anisotropy in compressibility was observed between perpendicular and parallel to the  $\text{Cu-O}$  chain axis.

### Experimental

Powders of  $\text{LiCuO}_2$  were synthesized by a chemical treatment of Li-ion extraction (delithiation) from a raw material  $\text{Li}_2\text{CuO}_2$  which was prepared using a standard solid state reaction technique. The delithiation progressed in an  $\text{I}_2$ -acetonitrile solution following the reaction formula:



Details of the synthesis as well as the results of structure analysis have already been reported elsewhere (4). The obtained powders were checked to be a single phase of  $\text{LiCuO}_2$  with X-ray powder diffraction and with ordinary chemical analysis. The orthorhombic lattice constants were  $a_0 = 5.708(6) \text{ \AA}$ ,  $b_0 = 9.639(2) \text{ \AA}$  and  $c_0 = 2.7172(3) \text{ \AA}$ , and the ratio  $\text{Li/Cu}$  was between 0.98 and 1.09. Impurity phase of less than 1 wt%  $\text{I}_2$ , which was included on the delithiation process (1), was detected.

*In-situ* X-ray powder diffraction study under high pressure was conducted up to 6.3 GPa at room temperature with a cubic anvil type apparatus named "MAX90," which was installed at the Photon Factory in the National Institute for High Energy Physics (KEK), Tsukuba, Japan, and was combined with a synchrotron radiation beam (9, 10).

Figure 2 shows a cell assembly of the present experiment. Powdered sample was stuffed in a Teflon capsule with a mixed fluid of methanol and ethanol (4 : 1) which has a high freezing pressure up to 10 GPa at room temperature. Thus, the sample is compressed hydrostatically. A high intensity beam of white X-ray collimated to  $0.1 \times 0.3 \text{ mm}^2$  from a vertical Wiggler was introduced to the compressed sample through the shallow gap between the anvils, and the diffracted beam was detected at the opposite side of the incident beam with a fixed glancing angle  $2\theta = 6^\circ$  using an energy dispersive type solid state detector in the energy range from 20 to 80 keV. The pressure values were calibrated by measuring the lattice constant of Au placed at the bottom of the Teflon capsule.

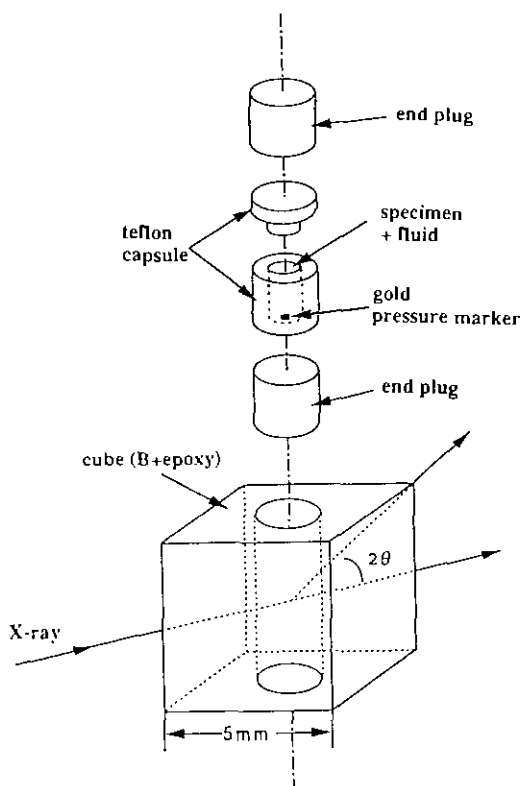


FIG. 2. A schematic drawing of X-ray powder diffraction experiment under high pressure using the cubic anvil type apparatus "MAX90."

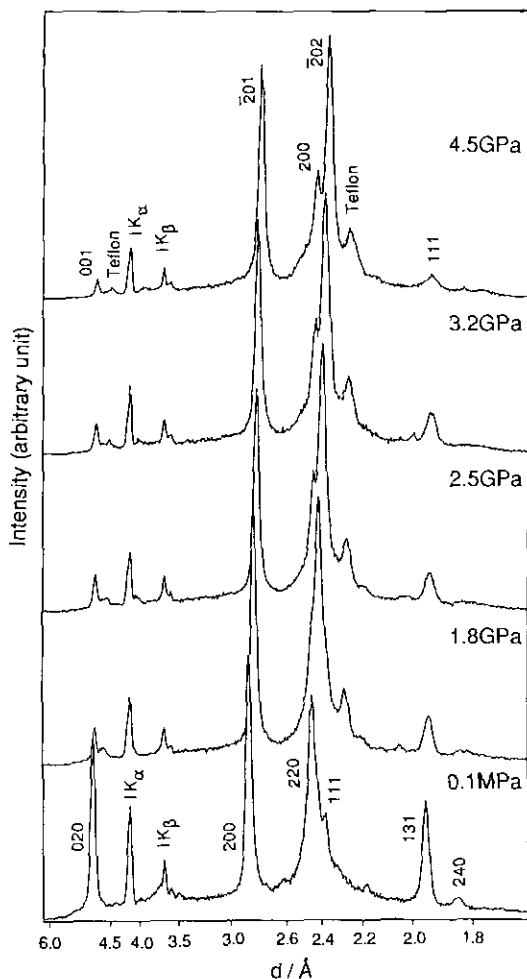


FIG. 3. X-ray powder diffraction patterns of  $\text{LiCuO}_2$  under various pressure conditions at room temperature. An energy dispersive type pure Ge detector was used.

Four-point electrical resistance of powder samples at high pressure was measured under uniaxial compression up to 8 GPa using a high pressure apparatus with a cubic-type anvil between room temperature and 77 K. The electrodes were Au strips and the powder sample was sandwiched between Teflon sheets. The current in the specimen was fixed at  $10 \mu\text{A}$ .

### Results and Discussion

Figure 3 represents typical X-ray diffraction patterns of  $\text{LiCuO}_2$  before and under

compression in the high pressure apparatus at room temperature. The apparent peaks at normal state correspond to those of  $\text{LiCuO}_2$  and are easily indexed by the data already reported (4), as shown at the lowest part of Fig. 3. The additional two peaks observed between 3.5 and 4.5 Å belong to fluorescences of included solid  $\text{I}_2$ . With increasing pressure, all the diffraction peaks shifted slightly but apparently toward the right-hand side. This corresponds to becoming smaller in  $d$  values. It should be noted that the  $2\ 2\ 0$  peak at atmospheric pressure separated into two peaks with compression, suggesting a structural transformation to the high pressure phase in this pressure range. The changes were completely reversible in both the peak positions and profiles on release of pressure.

To obtain accurate  $d$  values, a curve fitting technique was applied to the diffraction peaks, and the lattice constants were calculated from these values where those of  $\text{I}_2$  and of crystallized Teflon originated by compression were excluded. It became clear that the observed peaks at high pressures were successfully indexed by a monoclinic  $\text{NaCuO}_2$ -like structure, as also shown in the upper part of Fig. 3. The lattice parameters at 4.9 GPa were determined to be:  $a_{\text{hp}} = 5.53(2) \text{ \AA}$ ,  $b_{\text{hp}} = 2.674(8) \text{ \AA}$ ,  $c_{\text{hp}} = 5.42(3) \text{ \AA}$ ,  $\beta_{\text{hp}} = 118.9(3)^\circ$  and  $V_{\text{hp}} = 70.2(5) \text{ \AA}^3$ , respectively, where the subscript  $hp$  means high pressure state. Figure 3 also indicates that the monoclinic distortion by compression started in the low pressure range below 1.8 GPa.

Figure 4a is an ORTEP drawing of  $\text{LiCuO}_2$  projected on the  $a, b$  plane along the chain axis (4), representing the packing of Li, Cu, and O atoms, and Fig. 4b is a similar projection of  $\text{NaCuO}_2$  on the  $a, c$  plane. It is easy to recognize from two figures that the packing features are very close to each other, although the  $\text{NaCuO}_2$  crystal is monoclinically distorted from the orthogonal  $\text{LiCuO}_2$  structure. Thus, the change in compression from the normal to high pressure phase can readily be understood by only a slight distor-

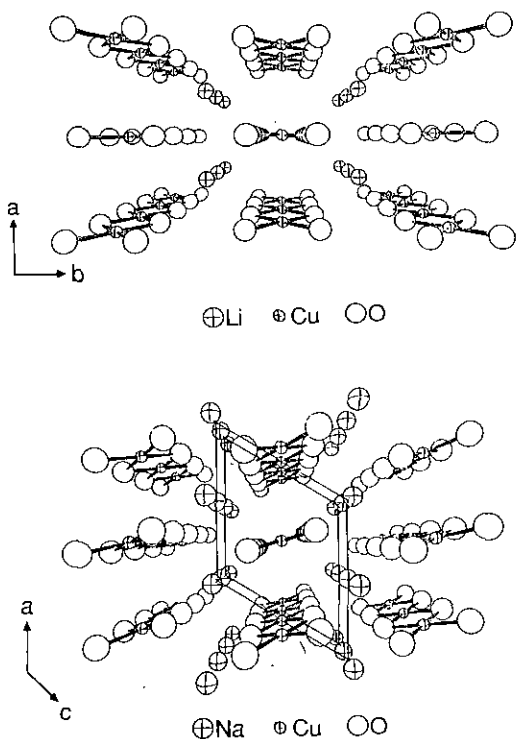


FIG. 4. The ORTEP projections of the orthorhombic  $\text{LiCuO}_2$  (upper) and monoclinic  $\text{NaCuO}_2$  (lower). The chain axis in  $\text{LiCuO}_2$  is along the  $c$  axis, whereas that in  $\text{NaCuO}_2$  is along the  $b$  axis.

tion with following relations:  $a_0/a_{\text{hp}}$ ,  $(110)_0/c_{\text{hp}}$  and  $c_0/b_{\text{hp}}$ , where the subscript 0 stands for normal state. This means that the Cu-O chain axis at compressed states is parallel to  $b_{\text{hp}}$ . In order to avoid confusion induced by the exchange in the nomenclature of the unit cell parameters, the tentative monoclinic symmetry is used hereafter for indexing the normal pressure phase with the subscript hp,0.

Pressure dependence of the lattice spacings is listed in Table I. Using these data, changes in the unit cell volume ( $V_{\text{hp}}/V_{\text{hp},0}$ ), lengths ( $a_{\text{hp}}/a_{\text{hp},0}$ ), ( $b_{\text{hp}}/b_{\text{hp},0}$ ) and ( $c_{\text{hp}}/c_{\text{hp},0}$ ), and angle  $\beta_{\text{hp}}$  were calculated as a function of pressure. As shown in Fig. 5, the unit cell parameters monotonically decreased with increasing pressure. Although data for unit cell calculation contain some ambiguities because of unfortunate overlappings of the neighboring peaks, the tendency was quite reproducible in several compression-decompression experiments.

The  $b_{\text{hp}}$  axis is most incompressible with the value ( $\Delta b_{\text{hp}}/b_{\text{hp},0}$ ) of about 0.01 at 3 GPa, which is one third of ( $\Delta c_{\text{hp}}/c_{\text{hp},0}$ ). The origin of the low compressibility along the  $b_{\text{hp}}$  axis is explained by considering the crystal struc-

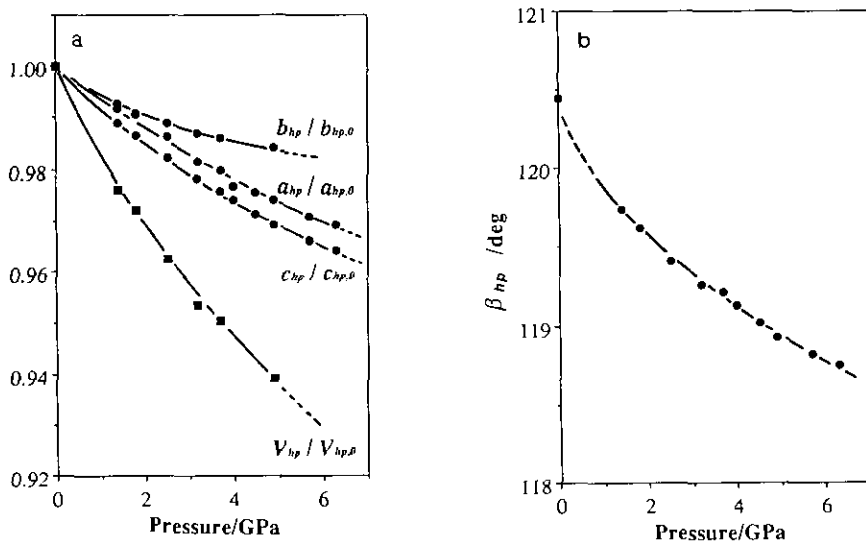


FIG. 5. (a), Changes in the monoclinic unit cell lengths and volumes of  $\text{LiCuO}_2$  with pressure. The data are expressed in ratios of the cell parameters in compressed state to those in normal state. (b), Change in the unit cell angle  $\beta_{\text{hp}}$  with compression.

TABLE I  
CHANGES IN THE LATTICE SPACING OF  $\text{LiCuO}_2$  WITH PRESSURE

Pressure (GPa)	Lattice spacings $hkl$ in Å						Ref.
	020	200	220	111	131 <sup>a</sup>		
0.0	4.820	2.854	2.456	2.378	1.950		(4)
0.0	4.826	2.854	2.452	2.372	1.950		
	001	-201	200	-202	110	111 <sup>b</sup>	
1.4	4.792	2.822	2.451	2.413	2.363	1.943	
1.8	4.787	2.814	2.448	2.408	2.361	1.941	
2.5	4.772	2.801	2.443	2.395		1.937	
3.2	4.760	2.790	2.436	2.382		1.933	
3.7	4.751	2.783	2.432	2.377		1.932	
4.0	4.746	2.779	2.429	2.370			
4.5	4.737	2.769	2.425	2.364			
4.9	4.731	2.762	2.422	2.359		1.928	
5.7	4.718	2.753	2.417	2.350			
6.3	4.711	2.747	2.414	2.345			

<sup>a</sup> Indexed as an orthorhombic structure.

<sup>b</sup> Indexed as a monoclinic structure.

ture of  $\text{LiCuO}_2$ , as shown in Figs. 1 and 4, where the straight chains are made by two-dimensional edge-sharing of the square planar  $\text{CuO}_4$  units extended toward the  $b_{\text{hp}}$  axis.

On the other hand, the  $a_{\text{hp}}$  and  $c_{\text{hp}}$  axes are expected to be more compressible because the packing feature of  $\text{LiCuO}_2$  except for the chain axis is apparently loose, as shown in Fig. 1, where the structure is constructed by a stacking of the Cu-O chains with loose linkages of octahedrally coordinated Li ions.

Resistance measurements under uniaxial compression up to 8 GPa showed that compressed  $\text{LiCuO}_2$  powders always behaved semiconductive between room temperature and 77 K, and the data displayed very slight pressure dependence, as shown in Fig. 6, where a very slight decrease was observed between the data of 4 and 8 GPa. The resistances at room temperature and at 77 K were about  $10^3$  and  $10^6 \Omega$ , respectively, with activation energies in the range of 0.1–0.2 eV. Wizansky *et al.* (11) reported the resistivity of  $\text{Li}_{2-x}\text{CuO}_2$  with  $x \approx 0.5$  to be  $71 \Omega \text{ cm}$  at room temperature, but found no superconductivity down to 4 K. The weak pressure dependence in the present specimen may partly support the foregoing suggestion that the large contraction perpendicular to the chain axis is effective only for decreasing

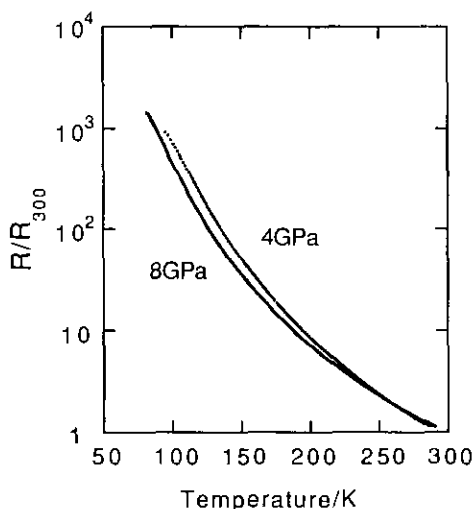


FIG. 6. Temperature dependence in the resistance ratio  $R/R_{300}$  of  $\text{LiCuO}_2$  powder between room temperature and 77 K at pressures of 4 and 8 GPa, showing a semiconductive behavior.  $R_{300}$  means the resistance at 300 K of approximately  $10^3 \Omega$ .

the Li-O distances but not for increasing an interaction of intra- or interchains which would have a considerable effect for changing such physical properties.

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