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STRUCTURAL STUDY OF CuO AT LOW TEMPERATURES

H. Yamada[1], Y. Soejima[2], X. G. Zheng[3] and M. Kawaminami[4]

[1]VBL, KYUSHU UNIVERSITY, FUKUOKA 812-8581, JAPAN

Fax: 81-092-642-2553, e-mail: hiro6scp@mbox.nc.kyushu-u.ac.jp

[2]DEPARTMENT OF PHYSICS, KYUSHU UNIVERSITY, FUKUOKA 812-8581, JAPAN

Fax: 81-092-642-2553, e-mail: oko6scp@mbox.nc.kyushu-u.ac.jp

[3]DEPARTMENT OF PHYSICS, SAGA UNIVERSITY, SAGA 840-8502, JAPAN

Fax: 81-0952-28-6547, e-mail: zheng@cc.saga-u.ac.jp

[4]DEPARTMENT OF PHYSICS, KAGOSHIMA UNIVERSITY, KAGOSHIMA , JAPAN

Fax: 81-099-285-8975, e-mail: kawamina@sci.kagoshima-u.ac.jp

Cupric oxide (CuO) shows unusual magnetic and dielectric properties. In order to study the origin of these properties, the structure determination of CuO at low temperatures has been made by means of the single crystal four-circle X-ray diffractometry. No drastic change in the crystal structure is observed, however, it is found that the lattice constant β indicates the novel temperature dependence. The behaviour is induced by the change in the bond length and bonding angle of the Cu-O chain running along the $[1\,0\,\bar{1}]$ direction, and thus the results suggest that the magnetic interaction between Cu^{2+} ions is anisotropic.

Key words: crystal structure, X-ray diffraction, Cu-O bond length

1. Introduction

The two dimensional CuO_2 plane in the superconducting copper oxide plays an important role for the superconductivity. Since the cupric oxide (CuO) contains the CuO_2 planes like as that of the superconductors and consists of the simple constituents in comparison with high-T_C superconductor $La_{2-x}Sr_xCuO_4$ and $YBa_2C0_3O_{7-\delta}$ etc., the various experimental and theoretical studies on CuO has been done in terms of the electric-magnetic properties of the CuO_2 planes.[1,2] Recently, X. G. Zheng et. al. have found a novel ferroelectricity that coexists with the antiferromagnetic behavior below 230 K[3]: at 212 K, the antiferromaganetic phase transition to commensurate state from incommensurate one. For understanding the correlation between the antiferromagnetism and the ferroelectricity, the information of the crystal structure at low temperatures is required to discuss that the origin of the property in connection with the structural modulation.

In spite of well knowledge of the structure at room temperature,[4] that at low temperatures is still ambiguous. In this report, we investigate the structural modulation at low temperature using X-ray structure determination on single crystal.

2. Experiments

Recently X. G. Zheng et. al. succeeded to make high quality single crystal by the method of vapor phase growth[5]. In order to compensate for oxygen, single crystal obtained by the method is annealed with flowing oxygen gas at 673 K for 24 h. The crystal is shiny black appearance and plate-shaped: the dimensions of the specimen chosen for the measurements were $0.14 \times 0.14 \times 0.04 \quad mm^3$.

Two kinds of the measurement have been made; one is the data collection for the determination of the crystal structure, and another is for refinement of the lattice constants. The measurements are made by CAD4 (Enraf Nonius Co.) diffractometer with Mo Kα radiation monochromatized by Ge (111) diffraction. The specimen temperature was controlled with the low temperature controller FR558-S (Enraf Nonius Co.) installed in the N_2 flow cryostat system. The stability of the temperature was within 0.5 K during the measurements: the data collection at 96, 148, 199, 220, 293 K have been carried in addition of the refinements of the lattice constants at 169, 190, 211, 230, 250, 269 K.

Table I The result of the refinements for the crystal structure analysis.

	96 K	148 K	199 K	220 K	293 K
a(Å)	4.6809(9)	4.6844(11)	4.682(1)	4.683(1)	4.6894(7)
b(Å)	3.4176(7)	3.4192(9)	3.4199(6)	3.4203(6)	3.4222(7)
c(Å)	5.122(1)	5.1231(13)	5.1252(9)	5.1245(9)	5.1299(8)
β	99.744(19)	99.76(2)	99.73(1)	99.707(16)	99.591(14)
Refl.	216	211	205	205	188
R	0.098	0.094	0.087	0.092	0.091
R_w	0.114	0.111	0.104	0.105	0.104
y	0.417(4)	0.417(4)	0.416(4)	0.417(4)	0.417(4)

Lorentz, polarization and absorption correction are taken into the observed intensities and the structure determination is performed with the program MolEN (Enraf Nonius Co.). Some results of the refinement were listed in Table I .

3. Results and Discussion

By taking the rotation photograph, it is confirmed that neither appearance nor disappearance of diffraction spots due to a change in the space group is observed at any temperatures. The space group is determined C2/c(No.15). In the symmetry, four chemical units of CuO are in the unit cell (i.e. Z=4), and the Cu ions occupy symmetry site 4(c), $(x,y,z)=(\frac{1}{4},\frac{1}{4},0)$, and the oxygen ions are at the symmetry site 4(e), $(x,y,z)=(0,y,\frac{1}{4})$. The coordinate y for the oxygen position is variable, however, that is almost constant at any temperature. The results guarantees that the structure and symmetry is kept in the temperature range of the present measurements, even below the antiferromagnetic phase transition at 230 and 212 K.

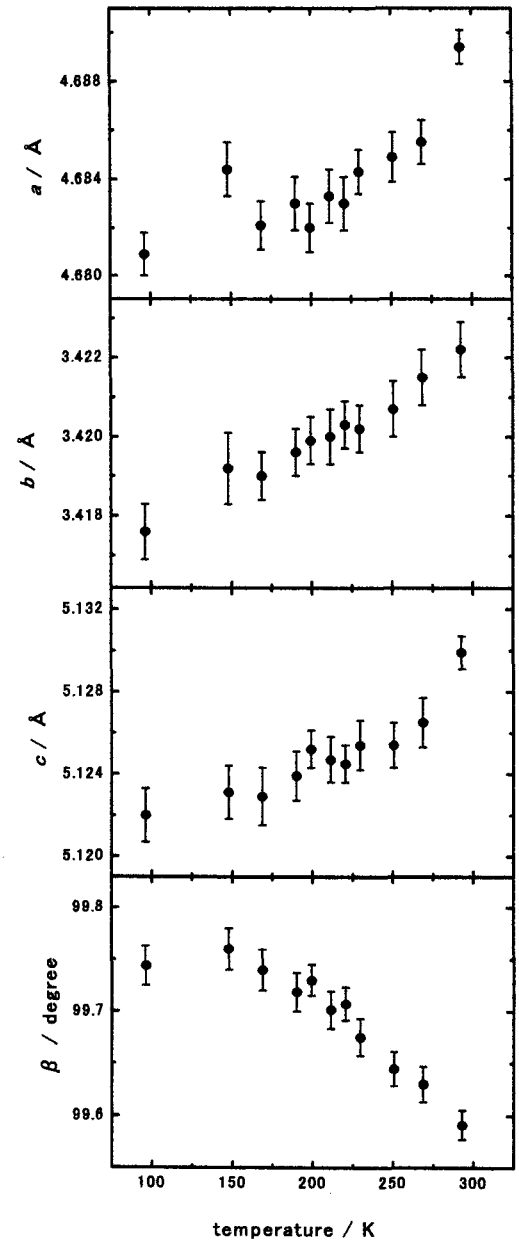

Fig. 1 The temperature dependence of the lattice constants *a*, *b*, *c* and β.

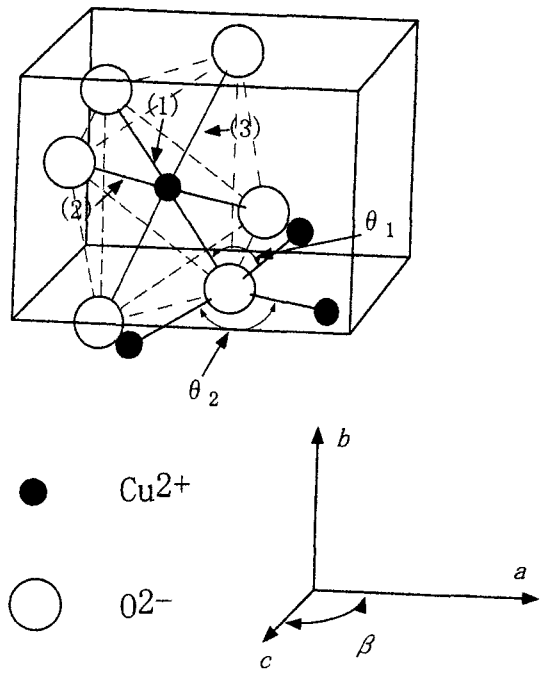

Fig. 2 The distorted octahedral CuO_6 and the unit cell of CuO. The label (1), (2), (3) and θ_1, θ_2 in the figure indicate the bond lengths and the bond angles between the nearest neighboring atoms, respectively.

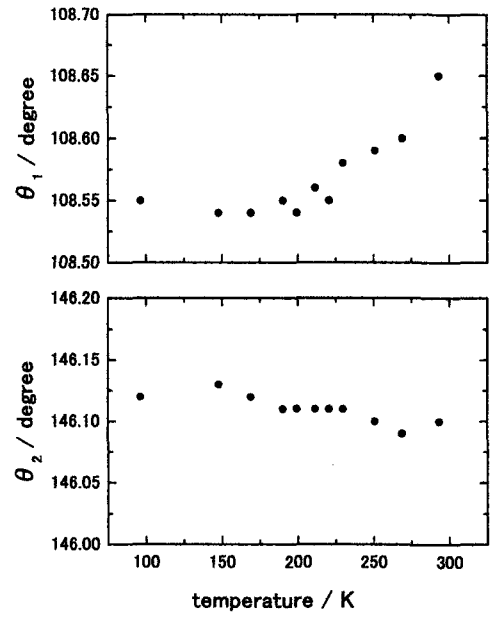

Fig. 4 The temperature dependence of the bond angles θ_1 and θ_2. The angles are defined in Fig.2.

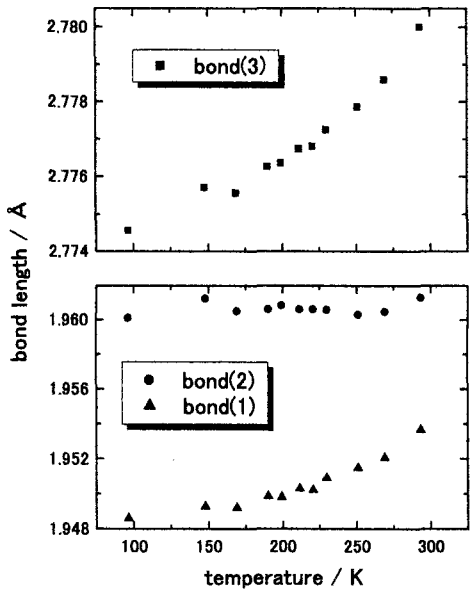

Fig. 3 The temperature dependence of the bond lengths in the CuO_6 octahedra. The labels (1), (2) and (3) are shown in Fig. 2.

In contrast, the remarkable feature is found in the temperature dependence of the lattice constants: the temperature dependence of the lattice constants *a*, *b*, *c* and β are shown in Fig. 1. The parameter β increases with decreasing temperature, while *a*, *b* and *c* decrease in normal manner. It is noted that β below 150 K is nearly constant. In order to discuss the bond length and the bonding angle of Cu-O, the temperature dependence of the lengths (1), (2), (3) and the angle θ_1, θ_2, defined in Figure 2, are determined from the result of the crystal structure analysis assuming the oxygen position $y = 0.4174$: the results are shown in Fig.s 3 and 4.

As shown in Fig. 2, the Cu-O bonds consist of two different types: diagonal and axial bond in CuO_6 octahedron. According to this, the length (1) and (2) are almost identical, and (3) is long due to the Jahn-Teller effect of Cu^{2+}. In fact, the bond length (3) shows large

temperature sensitivity in comparison with (1) and (2). The Cu-O bonds are composed of Cu-O zigzag chains running along the $[1\,0\,1]$ and $[1\,0\,\bar{1}]$ directions. As shown in Figure 4, the angles θ_1 and θ_2 shows different temperature sensitivity and this indicates that the structure of CuO is anisotropic in $[1\,0\,1]$ and $[1\,0\,\bar{1}]$ directions. According to the anisotropy, we conclude that the two Cu-O chains behaves differently and they are independent likely as one-dimensional, at low temperature. This idea will be identified by the study of the crystal structure at high temperature.

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