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Structure Refinement of the Composite Crystal $(Ca_{0.565}Y_{0.435})_{0.82}CuO_2$

Yuzuru Miyazaki[1,2] , Mitsuko Onoda[3], Akiji Yamamoto[3], Peter P. Edwards[2],
and Tsuyoshi Kajitani[1]

[1]*Department of Applied Physics, Graduate School of Engineering, Tohoku University,*
Aramaki Aoba, Aoba-ku, Sendai 980-8579, Japan
[2]*School of Chemistry, University of Birmingham, Edgbaston, Birmingham*
B15 2TT, United Kingdom
[3]*National Institute for Research in Inorganic Materials, 1-1 Namiki,*
Tsukuba, Ibaraki 305-0044, Japan

We have determined the crystal structure of the quasi one-dimensional compound $(Ca_{0.565}Y_{0.435})_{0.82}CuO_2$, known as $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ *etc.*, by a superspace group approach. Neutron diffraction experiment was carried out at 4 K using a TOF-type diffractometer, POLARIS, installed at the ISIS facility in Rutherford Appleton Laboratory. Structural parameters were refined with a superspace group of $F2/m(p0q)0s$ using a Rietveld refinement program, PREMOS. Remarkable displacive modulation is observed, even as low temperature as 4 K, for the O atoms, while such modulation is less significant for the Cu atoms. The [Ca,Y] atoms suitably sit in the center of the modulated oxygen octahedra, namely O_6.

KEYWORDS: composite crystal, superspace group, cuprate, Rietveld refinement

§1. Introduction

Recently, the quasi one-dimensional (1D) cuprate $(Ca_{1-x}Y_x)_{1-y}CuO_2$ ($y \sim 0.18$) has attracted much interest because it evolves different magnetic ordered states from a three-dimensional (3D) antiferromagnetic (AF) state to a 1D AF state, by controlling the formal Cu valence (Cu^{n+}) from +2.00 to +2.36 with the compositional parameter x.[1,2] The sample with $x = 0.435$ ($Cu^{n+}=2.00$) exhibits an AF transition at $T_N = 29$ K, while the sample with $x=0$ ($Cu^{n+}=2.36$) shows a broad maximum at 30 K in the magnetic susceptibility (χ) curve. With decreasing x (equivalent to increase copper valence), T_N decreases gradually and eventually disappears at around $x=0.20$ ($Cu^{n+}=2.20$), followed by emergence of the 1D state. Miyazaki *et al.*[3] have investigated the magnetic behavior of the solid solution in detail using the electron spin resonance (ESR) technique and found that the doped hole carriers appear to be localized and to dilute the long-range spin correlations along the CuO_2 chain. The $\chi(T)$ dependency can be well described in terms of a combination of the Curie-Weiss component and the alternating Heisenberg chain, the former is introduced by the doped holes. The crystal structure of the solid solution, on the other hand, has not yet been fully understood due to its incommensurate superstructure. [4,5] In fact, the solid solution belongs to a composite crystal, in which two incommensurate subsystems are interleaving each other parallel to the a-axis. Subsystem 1 consists of 1D $[CuO_2]$ chains with sharing opposite edges of CuO_4 squares, while subsystem 2 comprises a set of $[Ca_{1-x}Y_x]$ atoms locating in between the $[CuO_2]$ chains. Conventional structure refinement methods can not be applied to such a composite crystal for which a superspace group must be considered. In the present study, we employed a four-dimensional superspace group approach. Rietveld refinement of a time-of-flight (TOF) neutron diffraction (ND) data, has revealed a remarkable modulated arrangement of the "CuO_2-ribbons" along the a-axis.

§2. Experimental

Polycrystalline samples were prepared from high-purity $CaCO_3$ (99.9%), Y_2O_3 (99.99%) and CuO (99.99%) powders. These powders were intimately mixed in an agate mortar and pressed into pellets. The pellets were heated at 980 °C in oxygen-gas flow for 144 h with intermediate grindings. After the heating, the samples were furnace cooled to room temperature. Neutron powder diffraction data were collected at 4 K using a TOF diffractometer, POLARIS, installed at the ISIS facility, Rutherford Appleton Laboratory. The ND data were analyzed using a Rietveld refinement program, PREMOS.[6]

§3. Results and discussion

The structure model was constructed on the basis of our previous report.[5] Both the subsystems belong to monoclinic systems with common b-axis ($b \sim 6.21$ Å) and different a- and c- axes: $a_1 \sim 2.83$ Å for subsystem 1, and $a_2 \sim 3.45$ Å for subsystem 2. The relationship between the c-axis lengths of the both subsystems is $c_1 \sin\beta_1 = c_2 \sin\beta_2$. From the observe systematic extinction of Bragg reflections, we adopted suitable superspace group of $F2/m(p0q)0s$, which is equivalent to $B2/m(\alpha\beta 0)0s$ (No.12.2) in Table 9.8.3.5 in ref 7. Through the refinement, the fractional coordinates and isotropic thermal displacement parameters, B, of the atoms were fixed at the values shown in Table I.

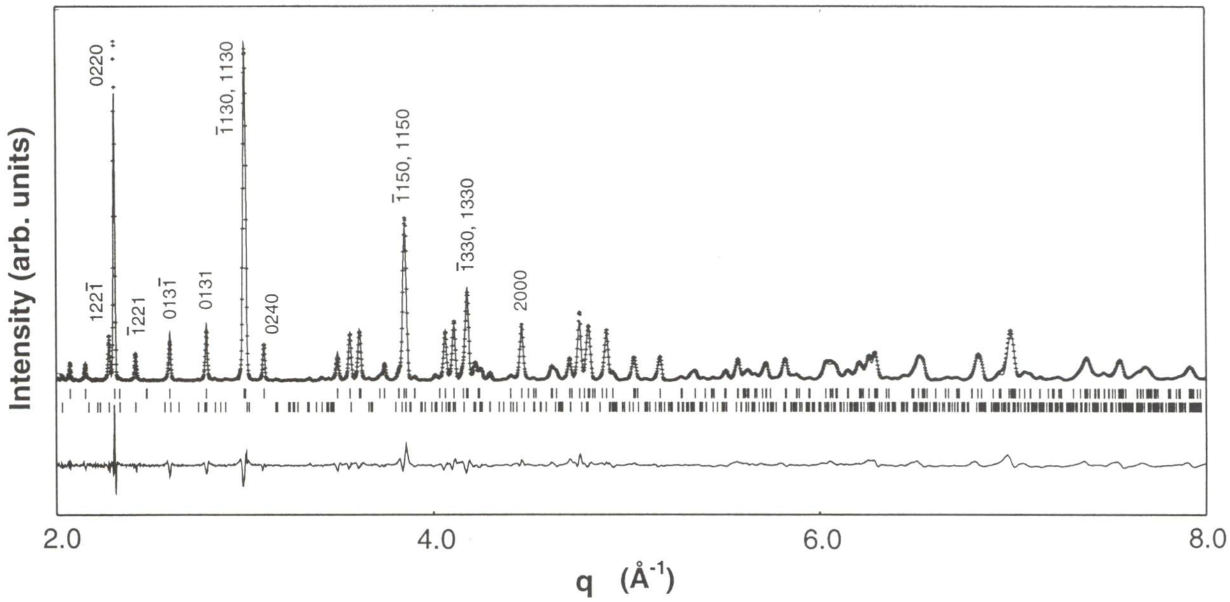

Fig. 1. Observed, calculated and difference time-of-flight neutron diffraction patterns for $(Ca_{0.565}Y_{0.435})_{0.82}CuO_2$ measured at 4 K. Short vertical lines below the pattern indicate the peak positions of main (upper) and satellite (lower) reflections for the two subsystems.

Table I. Initial fractional coordinates and isotropic atomic displacement parameters, B, for the fundamental structure of $(Ca_{0.565}Y_{0.435})_{0.82}CuO_2$.

Atom	Site	x	y	z	B (Å^2)
Subsystem 1: $[CuO_2]$					
Cu	$2a$	0.0	0.0	0.0	0.2
O	$4i$	0.002	0.0	0.380	0.2
Subsystem 2: $[Ca_{0.565}Y_{0.435}]$					
Ca/Y	$4e$	0.0	1/4	1/4	0.2

Then, the Fourier amplitudes of the modulation waves were refined, considering up to the second order of the Fourier terms of cosine and sine components, A_i (i=0, 1, 2) and B_i (i=1, 2), respectively. Table II summarizes refined Fourier amplitudes for the fractional coordinates and B factors. The refined modulation vector components along the a^*- and c^*- axes, p and q, are also shown in the table. Numbers in parentheses representestimated standard deviations of the last significant digits. Averaged structure can be obtained by adding A_0 terms to the corresponding parameters of the fundamental structure shown in Table I. Figure 1 shows observed, calculated and difference profiles for the TOF-ND data collected at 4 K. We observed very few and relatively small magnetic Bragg peaks in the measured q region and their contribution was thus ignored in the refinement. Four integers, $hklm$, are required to index both the main and satellite reflections. The peaks of $hkl0$ and $0klm$ are originated from subsystem 1 and subsystem 2, respectively. The final R_{WP} was 5.5% and the lattice parameters were refined to be a_1=2.8244(3) Å, b=6.1987(2) Å, c_1=10.5795(2) Å and β_1=90.23(1)° for subsystem 1 and a_2=3.4862(3) Å, c_2=10.6142(2) Å and β_2=94.64(1)° for subsystem 2. The resulting a_1/a_2 (=p) ratio of 0.8101(2) yields the stoichiometry of the sample, $(Ca_{0.565}Y_{0.435})_{0.8101}CuO_2$. In most papers, the chemical formulas of the solid solution are expressed like "$Ca_{2+x}Y_{2-x}Cu_5O_{10}$". However, the two subsystems connect incommensurately and the a_1/a_2 ratio varies with Ca/Y composition, approximately from 0.80 to 0.83, as we have already demonstrated.$^{5)}$ *Therefore, the formula should be expressed as* $(Ca,Y)_{a_1/a_2}CuO_2$.

In Figure 2, we show the refined crystal structure viewed from a-axis. One may clearly recognize ribbon-like modulation of the CuO_2 chains, where CuO_2 squares are buckled due to the interaction with [Ca,Y] subsystem. Such displacive modulation of the O atoms is much significant in b-direction, whereas the Cu atoms

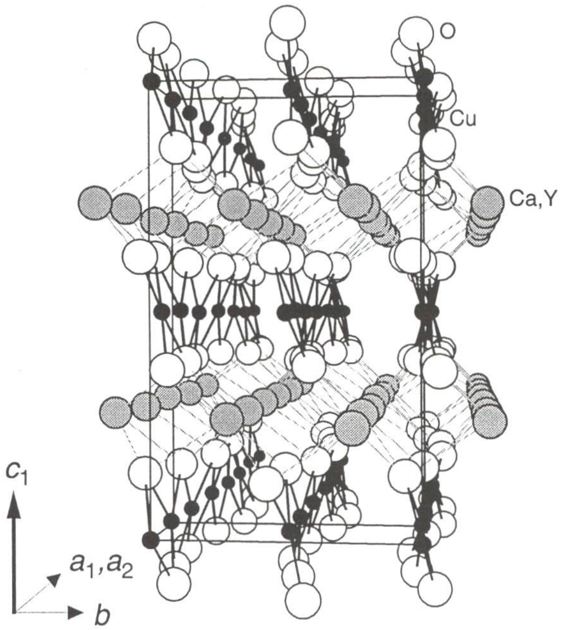

Fig. 2. The modulated crystal structure of $(Ca_{0.565}Y_{0.435})_{0.82}CuO_2$ at 4 K viewed perspectively from the a-axis.

Table II. Refined Fourier amplitudes and modulation vector components ($(p0q)$) of $(\mathrm{Ca}_{0.565}\mathrm{Y}_{0.435})_{0.82}\mathrm{CuO}_2$ measured at 4 K.

Atom		A_0	A_1	B_1	A_2	B_2
Subsystem 1: $[\mathrm{CuO}_2]$						
Cu	x	0	0	0	0	-0.013(4)
	y	0	0	-0.0117(7)	0	0
	z	0	0	0	0	-0.003(1)
	B	-0.22(6)	0	0	1.2(2)	0
O	x	-0.001(1)	0	0	0.003(4)	-0.017(3)
	y	0	-0.0700(8)	-0.013(1)	0	0
	z	-0.0013(2)	0	0	-0.0016(9)	-0.005(1)
	B	0.12(8)	0	0	0.3(2)	-0.3(2)
Subsystem 2: $[\mathrm{Ca}_{0.565}\mathrm{Y}_{0.435}]$						
Ca/Y	x	0	0	0	0	-0.034(5)
	y	0	0	-0.002(2)	0	0
	z	0	0	0	0	0.005(2)
	B	0.5(1)	0	0	0.5(4)	0
modulation vector components: p=0.8101(2), q=0.2372(2)						

small deviation show from the $2a$ site. The Cu-O bond lengths vary from 1.82 to 1.98 Å depending on the t parameter; the complementary coordinate in the 4D superspace. Similar displacive modulation of the CuO_2 chain has been reported in $(\mathrm{Ca,Sr})_{14}\mathrm{Cu}_{24+y}\mathrm{O}_{41+z}$.[8)] Interestingly, the O atoms appear to deviate so as to locate the [Ca,Y] atoms in the center of O_6 cages. The effective ionic radius of the $[\mathrm{Ca}^{2+}_{0.565}\mathrm{Y}^{3+}_{0.435}]$ averaged ion under such coodination is 0.957 Å,[9)] and corresponding bond distance to the surrounding six O atoms is estimated to be 2.357 Å, which is too long to be realized in the solid solution without modulation. Although diffraction data were collected at low temperatures, no remarkable structural change was observed between 4 K and 300 K. Larger Sr^{2+} ion is found to substitute the [Ca,Y] site up to 20 % under 1 atm of oxygen atmosphere. This substitution leads the stoichiometry towards cation-deficient one as $M_x\mathrm{CuO}_2$ ($x = a_1/a_2 \sim 0.75$). The resulting copper valence becomes as high as 2.5, where a half of the Cu ions are at the low spin state. We are currently determining detailed crystal and magnetic structures of the entire range of the solid solution including Sr-analogue.

§4. Summary

Modulated crystal structure of $(\mathrm{Ca}_{0.565}\mathrm{Y}_{0.435})_{0.82}\mathrm{CuO}_2$ is successfully determined from neutron powder diffraction data assuming the superspace group of $F2/m(p0q)0s$. The O atoms in the $[\mathrm{CuO}_2]$chain are found to be markedly displaced to accommodate the [Ca,Y] atoms in the O_6 cages, while the Cu sites deviate very little from the ideal squre-coordinated positions.

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