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Structure analysis of mutually incommensurate composite crystal $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$

Y. Gotoh [a,*], I. Yamaguchi [b], S. Takeya [a], H. Fujihisa [a], K. Honda [a], T. Ito [c], K. Oka [d], H. Yamaguchi [d]

[a] *Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan*

[b] *Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan*

[c] *Correlated Electron Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan*

[d] *Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan*

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Abstract

Single-crystal X-ray structure analysis of mutually incommensurate $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" has been performed by the composite approach which leads to average substructures and their relative arrangement. The composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ has the CuO_2 substructure and the $Ca_{0.5}Y_{0.5}$ substructure. The CuO_2 substructure with $a_1 = 10.598(2)$ Å, $b = 6.189(2)$ Å, $c_1 = 2.825(2)$ Å, $\beta_1 = 90.19(4)^\circ$, $V_1 = 185.4(1)$ Å^3, $Z = 4$ and space group $F2/m$ has the plane of edge-shared one-dimensional CuO_2 chains along the c-axis. The $Ca_{0.5}Y_{0.5}$ substructure with $a_2 = 10.629(2)$ Å, $b = 6.189(2)$ Å, $c_2 = 3.517(1)$ Å, $\beta_2 = 94.36(3)^\circ$, $V_2 = 230.7(1)$ Å^3, $Z = 4$ and space group $F2/m$ forms the sheet of (Ca, Y) atoms in the ac-plane. By considering (3 + 1)-dimensional superspace group symmetry, it is concluded that the incommensurate composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ should be described by the combination of $F2/m$ for the CuO_2 substructure and $F2/c$ for the $Ca_{0.5}Y_{0.5}$ substructure. The composite approach has made clear that the plane of CuO_2 chains and the sheet of (Ca, Y) atoms stack alternately to form a mutually incommensurate composite crystal with layered substructures.

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1. Introduction

Recently, many cuprates with quasi-one-dimensional CuO_2 chain have attracted much attention because low-dimensional Heisenberg antiferromagnets with the $S = 1/2$ spins enhance quantum fluctuations in the spin liquid state [1–4]. This phenomenon seems to be related to the occurrence of superconductivity in low-dimensional electron systems. It is known that some compounds of them form composite crystals with mutually incommensurate substructures. In the $(Sr_{2-x}(Ca, La, Y)_xCu_2O_3)_{0.7+\delta}CuO_2$, "$Sr_{14-x}(Ca, La, Y)_xCu_{24}O_{41}$" series, the CuO_2 chain in the CuO_2 substructure shows unique structural modulations and acts as hole reservoir of the two-legged Cu_2O_3 ladder in the $Sr_{2-x}(Ca, La, Y)_xCu_2O_3$ substructure [5]. By the use of polycrystalline sample [6], on the other hand, it has been preliminarily revealed that so-called $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ series [7]

* Corresponding author. Tel.: +81 29 861 4555; fax: +81 298 61 4555.
E-mail address: y-gotoh@aist.go.jp (Y. Gotoh).

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also form composite crystal structures with the CuO_2 substructure and the $Ca_{0.5+x}Y_{0.5-x}$ one and that it is expressed as $(Ca_{0.5+x}Y_{0.5-x})_{0.8+\delta}CuO_2$.

In many compounds containing CuO_2 chains, $(Sr_{2-x}(Ca, La, Y)_xCu_2O_3)_{0.7+\delta}CuO_2$ and $(Ca_{0.5+x}Y_{0.5-x})_{0.8+\delta}CuO_2$ are especially interesting because the amount of holes in the CuO_2 chain can be easily controlled by doping the trivalent atoms. According to the amount of holes in the CuO_2 chain, they show a variety of magnetic features with very complicated spin arrangements. To understand their magnetic properties, it is profitable to clarify the mutually incommensurate composite structure by using single-crystalline sample.

In the present study, single-crystal X-ray structure analysis of mutually incommensurate $(Ca_{0.5}Y_{0.5})_{0.8+\delta}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" has been performed by the composite approach which leads to average substructures and their relative arrangement [8].

2. Experimental

Single composite crystals of $(Ca_{0.5}Y_{0.5})_{0.8+\delta}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" were grown by the traveling solvent floating zone (TSFZ) method [9,10]. A single composite crystal of $(Ca_{0.5}Y_{0.5})_{0.8+\delta}CuO_2$ with dimensions about 0.2 mm × 0.2 mm × 0.05 mm was used for the structure analysis. The composite diffraction patterns of $(Ca_{0.5}Y_{0.5})_{0.8+\delta}CuO_2$ were identified by X-ray precession method with Mo Kα radiation (λ = 0.71073 Å). In the procedure of the camera technique, imaging plate (BAS UR 5 in. × 5 in. type, Fuji Photo Film Co. Ltd.) was used to detect the weak satellite reflections of composite structure of $(Ca_{0.5}Y_{0.5})_{0.8+\delta}CuO_2$. We have taken the c-axis as the mutually incommensurate direction in accord with the structure determination of $(Sr_2Cu_2O_3)_{0.70}CuO_2$, "$Sr_{14}Cu_{24}O_{41}$" in the $(Sr_{2-x}Ca_xCu_2O_3)_{0.7+\delta}CuO_2$ series [5]. The X-ray diffraction data of both substructures were collected together with common reflections at room temperature using Rigaku AFC5 diffractometer (Mo Kα radiation). The lattice parameters and data collection process are summarized in Table 1. The δ in the formula of $(Ca_{0.5}Y_{0.5})_{0.8+\delta}CuO_2$ was calculated as $(c_1/c_2) - 0.8 = 0.003$. All the calculations for the structure refinement of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ were carried out using the FMLSM system [11]. The mutually incommensurate composite structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ was drawn by the use of PRJMS in the REMOS system [12].

3. Results and discussion

By means of X-ray diffraction method, we have observed the composite diffraction pattern of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" with the first CuO_2 substructure and the second $Ca_{0.5}Y_{0.5}$ substructure (Fig. 1). In the present study, it was proved that a minimal reciprocal set (a^*, b^*, c_1^*, c_2^*) forms the monoclinic quasi-lattice of the composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ and $c_2{}^* = (a^*, b^*, c_1^*)\sigma(\alpha\,0\,\gamma)^{\mathrm{T}}$. This shows that the mutually incommensurate composite structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ obeys the symmetry of (3 + 1)-dimensional superspace group [11,12]. As illustrated in Fig. 2, the composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ is commensurate along the direction normal to the c-axis because the orthogonal projections a_1' of a_1 and a_2' of a_2 are equivalent together. The mutual incommensurability between the average substructures are expressed as $\sigma(\alpha\,0\,\gamma)$,

Table 1
Experimental summary for $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$"

Substructure	CuO_2	$Ca_{0.5}Y_{0.5}$
Crystal system	Monoclinic	Monoclinic
a (Å)	10.598(2)	10.629(2)
b (Å)	6.189(2)	6.189(2)
c (Å)	2.825(2)	3.517(1)
β (°)	90.19(4)	94.36(3)
Z	4	4
Diffractometer	Rigaku AFC-5	
Radiation (Å)	Mo Kα 0.71073	
θ range: min, max (°)	1.5, 45.0	
Scan mode	$2\theta-\omega$	
Data set	h: 0–21	h: 0–21
	k: 0–12	k: 0–12
	l: −6–6	l: −7–7
Unique reflections	414	512

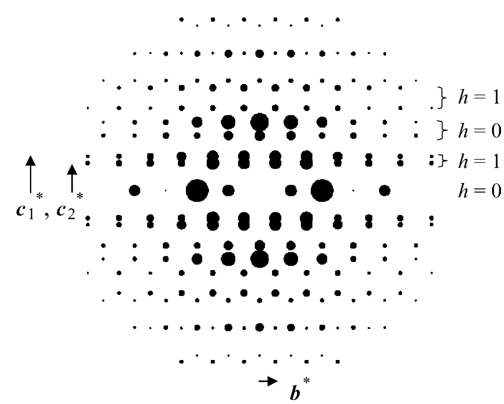

Fig. 1. The schematic drawing of the composite diffraction pattern of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" with $0\,k\,l\,m$ and $1\,k\,l\,m$-type X-ray reflections.

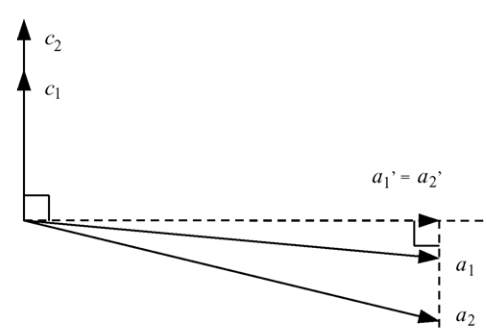

Fig. 2. The mutually incommensurate in-plane relation between the CuO_2 substructure and the $Ca_{0.5}Y_{0.5}$ substructure in $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$.

where $\alpha = [\sin(\beta_2 - 90) - \sin(\beta_1 - 90)](a_2/c_2) = 0.219$ and $\gamma = c_1/c_2 = 0.803$.

The average substructure of the CuO_2, defined by the monoclinic space group $F2/m$, has been determined with the edge-shared one-dimensional CuO_2 chains running along the c-axis. Because the reflections with $l = 0$ are common to both substructures, we have excluded these reflections to refine each substructure. The final refinement converged with R-value of 0.057 and R_w-value of 0.067 using 361 reflections excluding $h\,k\,0$ type. The CuO_2 substructure is essentially isostructural with that of $Ca_{0.83}CuO_2$, which was preliminarily investigated using the polycrystalline sample [13,14].

The average substructure of the $Ca_{0.5}Y_{0.5}$, defined by the monoclinic space group $F2/m$, has been determined with the sheet of (Ca, Y) atoms in the ac-plane. Because no superstructure reflections that suggest the ordering of Ca or Y atoms have been observed, we have employed the structure model with Ca and Y statistically distributed in the sheet of (Ca, Y) atoms. The final refinement converged with R-value of 0.113 and R_w-value of 0.152 using 450 reflections excluding $h\,k\,0$ type. The rather high values of R and R_w suggest that Ca and Y atoms form the positionally modulated structure that will be discussed in our future studies. All of the atomic parameters of each substructure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ are listed in Table 2.

The common $h\,k\,0$ reflections are essential to show clearly that $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" is a composite crystal with the CuO_2 substructure and the $Ca_{0.5}Y_{0.5}$ substructure. By considering (3 + 1)-dimensional superspace group symmetry, the reflection condition for $h\,0\,l$ of the $Ca_{0.5}Y_{0.5}$ substructure as $l = 2n$ indicates that the origin of the $Ca_{0.5}Y_{0.5}$ should be shifted by (1/4 1/4 0). This means that the space group of the $Ca_{0.5}Y_{0.5}$ should be converted into $F2/c$. The refinement of the commensurate section smoothly converged to an R-value of 0.082 and an R_w-value of 0.092 with 47 common reflections. The corresponding atomic parameters are listed in Table 3. By the composite approach in the present study, we have successfully demonstrated that $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" forms a composite crystal with two interpenetrating substructures. The mutually incommensurate composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ is drawn in Fig. 3.

Table 2
Atomic parameters and equivalent temperature factors (Å^2) of the CuO_2 substructure and the $Ca_{0.5}Y_{0.5}$ substructure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$"

	Occupancy	x	y	z	$B_{eq.}$
Cu	1.0	0.0	0.0	0.0	0.68(2)
O	1.0	0.6242(5)	0.0	0.001(2)	4.9(3)
Ca	0.48(2)	0.0	0.0	0.0	0.78(2)
Y	0.52	0.0	0.0	0.0	1.0(1)

The estimated standard deviations are given in parentheses. In each substructure analysis, all of the atomic parameters are refined by monoclinic $F2/m$ symmetry.

Table 3
Atomic parameters and isotropic temperature factors (Å^2) of the composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" projected along the mutually incommensurate c_1- and c_2-axes

	Occupancy	x	y	z	$B_{iso.}$
Cu	1.0	0.0	0.0	–	0.35(9)
O	1.0	0.626(4)	0.0	–	4.5(11)
Ca	0.52(3)	0.25	0.25	–	0.6(9)
Y	0.48	0.25	0.25	–	0.3(4)

The estimated standard deviations are given in parentheses. The occupancy of Y atom, Occ.(Y), is constrained as Occ.(Y) = 1 − Occ.(Ca).

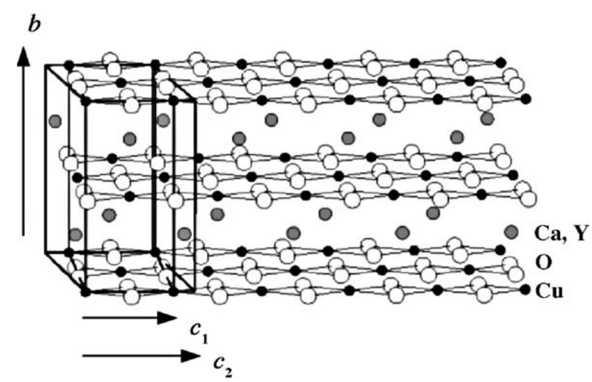

Fig. 3. The perspective view of the mutually incommensurate composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$.

In the present structure analysis, it is confirmed that the amount of doped Y atom is equivalent to that of Ca atom in our sample. From the chemical composition of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, therefore, it is expected that the average valence of Cu atom is +2.0 in the CuO_2 chain. With the results in Table 2, in fact, the calculated Cu–O distances and bond–valence sum [15] of Cu atom in the CuO_2 chain are 1.931(5) Å and 2.02, respectively. The agreement between the formal valence and the bond–valence sum indicates that Y-doping certainly control the valence of Cu atom in the $(Ca_{0.5+x}Y_{0.5-x})_{0.8+\delta}CuO_2$, "$Ca_{2+x}Y_{2-x}Cu_5O_{10}$" series. Since holes are not doped in the average substructure of the CuO_2 chain in $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, accordingly, magnetic interaction between nearest-neighbor Cu^{2+} ions are possible in the CuO_2 chain. Mizuno et al. theoretically predicted that the exchange interaction between the nearest-neighbor Cu^{2+} ions in the edge-shared CuO_2 chain turns out to be ferromagnetic if Cu–O–Cu angle is below 95° [16]. In the average CuO_2 chain in $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, the Cu–O–Cu angle is 94.1(2)°. Evidently, our results obtained by the composite approach well explain the ferromagnetic feature in the CuO_2 chain in $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" [7].

4. Conclusions

In the present study, single-crystal X-ray structure analysis of mutually incommensurate $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$,

"$Ca_2Y_2Cu_5O_{10}$" has been performed by the composite approach which leads to average substructures and their relative arrangement. The average substructures of the CuO_2 and the $Ca_{0.5}Y_{0.5}$ have been determined with the plane of edge-shared one-dimensional CuO_2 chains running along the *c*-axis and the sheet of (Ca, Y) atoms in the *ac*-plane, respectively. By considering (3 + 1)-dimensional superspace group symmetry, it is concluded that the mutually incommensurate composite crystal structure of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ should be described by the combination of monoclinic $F2/m$ for the CuO_2 substructure and monoclinic $F2/c$ for the $Ca_{0.5}Y_{0.5}$ substructure. The composite approach has made clear that the plane of CuO_2 chains and the sheet of (Ca, Y) atoms stack alternately to form a mutually incommensurate composite crystal. According to the results on the chemical composition of $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$ and the bond–valence sum calculation of Cu atom in the CuO_2 chain, it is confirmed that Y-doping certainly control the valence of Cu atom in the $(Ca_{0.5+x}Y_{0.5-x})_{0.8+\delta}CuO_2$,"$Ca_{2+x}Y_{2-x}Cu_5O_{10}$" series. The ferromagnetic feature in the CuO_2 chain in $(Ca_{0.5}Y_{0.5})_{0.80}CuO_2$, "$Ca_2Y_2Cu_5O_{10}$" has been well explained by considering the Cu–O–Cu angle in the average CuO_2 chain.

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