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Influence of the Substitution of Y by In on the Structure and Magnetic Property of $Y_2Cu_2O_5$

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In_2CuO_5 is isostructural to $Y_2Cu_2O_5$ both in its crystal and magnetic structure. In and Y can be substituted by each other in any ratio to make new compounds $Y_{2-x}In_xCu_2O_5$ (x = 0–2) which were identified by XRD and IR spectrum. The structural change in $Y_{2-x}In_xCu_2O_5$ influences its magnetic property. The magnetism of $Y_{2-x}In_xCu_2O_5$ was studied between 77 K and room temperature. © 1994 Academic Press, Inc.

INTRODUCTION

The discovery of the high-T_c superconductors has intensified the interest in related oxide compounds, which, although not superconductors, are close to them in chemical composition and crystal structure.

So far, three groups of rare-earth copper oxides have been synthesized: R_2CuO_4 (R = La, Pr–Gd), $R_2Cu_2O_5$ (R = Tb–La, In, Sc), and $RCuO_3$ (R = La, Y) (1, 2). In the first group, La_2CuO_4 is a semiconductor and becomes a superconductor when part of La^{3+} is substituted by Sr^{2+} or Ba^{2+}. Many efforts have concentrated on the study of its magnetism. $RCuO_3$ can be synthesized only under high pressure and at high temperature (2).

$R_2Cu_2O_5$ are semiconductors with high electrical resistivity (1). $Y_2Cu_2O_5$ is one of the contaminants in the 123-type high-T_c superconductors (3, 4). For this reason, it is necessary to understand especially the magnetic properties of this compound in order to evaluate the magnetic interactions in the related 90 K superconductors.

$Y_2Cu_2O_5$ is special both in its magnetism and in its structure. It is orthorombic and isostructural to $Ho_2Cu_2O_5$ (5, 6). Cu^{2+} atoms in $Y_2Cu_2O_5$ have coordination 4 + 1. Four oxygen atoms located at distances 1.9–2.1 Å from Cu^{2+} form a diagonal-broken CuO_4 "square." The fifth Cu–O distance is significantly larger (2.7–2.9 Å). Two Cu^{2+} are joined together by two Cu–O–Cu bridges whose bond angles are close to 90°, forming Cu_2O_8–dimeric units. Apparently, the electronic configuration of Cu^{2+} ($3d^9$) is $(t_{2g})^6(3d_{z^2}^2, 3d_{x^2-y^2}^1)$. In the magnetic structure of $Y_2Cu_2O_5$, both ferromagnetic and antiferromagnetic interactions exist (5–7). It is proposed that the magnetic moments are aligned along the Cu_2O_8–dimer chain. This chain is ferromagnetic. These ferromagnetic chains order antiferromagnetically at low temperature. The exact magnetic structure of $Y_2Cu_2O_5$ has been identified by neutron diffraction (6).

$In_2Cu_2O_5$ has not been studied as much comparatively (2, 5, 6), but according to the fact that it is isostructural to $Y_2Cu_2O_5$ (8), it is reasonable to propose that its magnetism is similar to that of $Y_2Cu_2O_5$. Since the ionic radius of In^{3+} is similar to that of Y^{3+} (γ_{In}^{3+} = 0.92 Å, γ_Y^{3+} = 0.95 Å), it will be easy for these two ions to be substituted by each other, and the crystal structure and the magnetism will change systematically. This will be useful for better understanding the influence of the structure on the magnetism of $R_2Cu_2O_5$ compounds. This is the purpose of this work.

The structure of $Y_2Cu_2O_5$ is shown in Fig. 1. Different authors (1, 5–7) have different opinions about the selection of crystallographic axes and cell volume, but these do not affect the overall structure.

EXPERIMENTAL

Compounds $Y_{2-x}In_xCu_2O_5$ were prepared by a solid-state reaction method. The mixture of Y_2O_3 (99.99%), In_2O_3 (99.9%), and CuO (99.5%) in a proper ratio was fired at 1000°C for 10 days with five intermittent grindings and annealed at 550°C for 12 hr, and then removed from the furnace.

XRD experiments were finished on a Model-2028 (Rigaku) X-ray diffractometer with copper target ($K_{\alpha 1}$ = 1.5405 Å). A MB-2 magnetic balance (Naruse-Kagakukikai Co., Ltd.) was used for the determination of magnetic susceptibility. The IR measurement was carried out on a JASCO model IR-810 spectrometer using solid KBr as the solvent.

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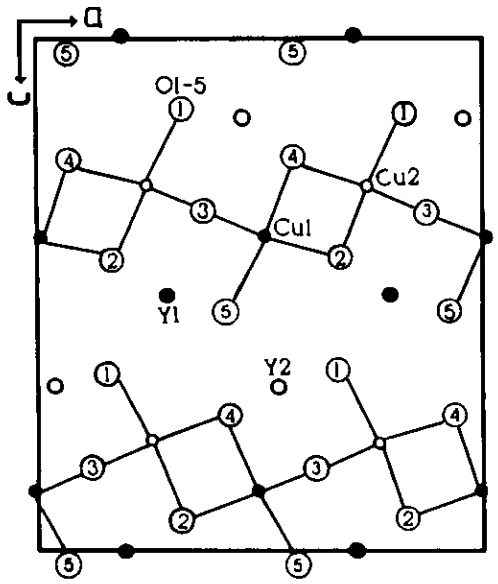

FIG. 1. Crystal structure of $Y_2Cu_2O_5$ (*ac* projection).

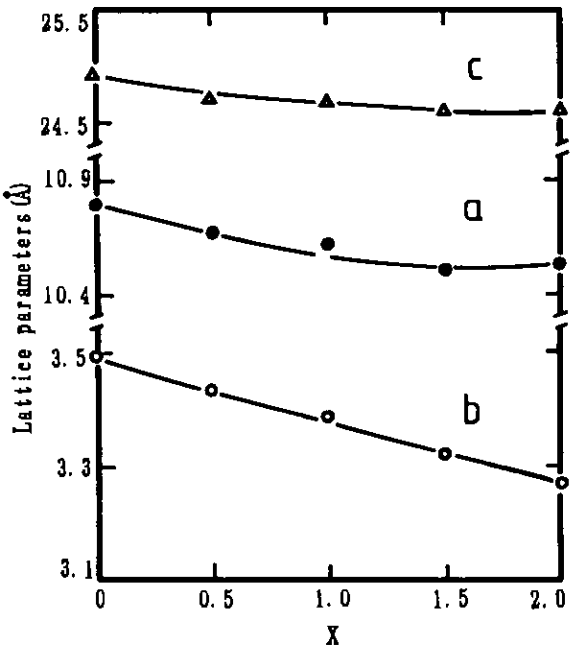

FIG. 3. Variation of lattice parameters with x for $Y_{2-x}In_xCu_2O_5$.

RESULTS AND DISCUSSION

Figure 2 shows the XRD (X-ray diffraction) patterns of $Y_{2-x}In_xCu_2O_5$ (x = 0, 0.5, 1, 1.5, 2). The XRD patterns of $Y_2Cu_2O_5$ and $In_2Cu_2O_5$ are the same as those of JCPDS. It is obvious that no impurities appear in $Y_{2-x}In_xCu_2O_5$. $Y_{2-x}In_xCu_2O_5$ is not just a mixture of $Y_2Cu_2O_5$ and $In_2Cu_2O_5$.

By the method of computer analysis of XRD patterns, it is found that $Y_{2-x}In_xCu_2O_5$ keeps the orthorhombic structure but the space group has been changed. The lattice-parameter changes of $Y_{2-x}In_xCu_2O_5$ are shown in Fig. 3 and Table 1. The lattice parameters do not change linearly with the change of the In^{3+} concentration, so Vegard's law is not obeyed (9). The lattice parameter *b* decreases more than *a*, and *a* decreases more than *c* comparatively.

The IR spectra of $Y_{2-x}In_xCu_2O_5$ are shown in Fig. 4, together with the spectra of the starting materials CuO, In_2O_3, and Y_2O_3 for comparison. The wave numbers of

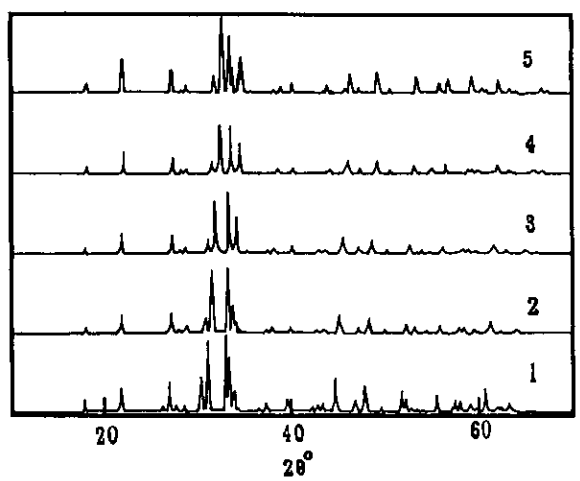

FIG. 2. XRD patterns of $Y_{2-x}In_xCu_2O_5$. (1) $Y_2Cu_2O_5$, (2) $Y_{1.5}In_{0.5}Cu_2O_5$, (3) $YInCu_2O_5$, (4) $Y_{0.5}In_{1.5}Cu_2O_5$ and (5) $In_2Cu_2O_5$.

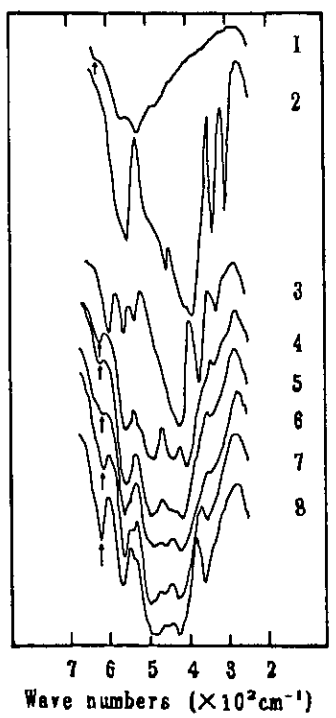

FIG. 4. IR absorption spectra of (1) CuO, (2) Y_2O_3, (3) In_2O_3, (4) $Y_2Cu_2O_5$, (5) $Y_{1.5}In_{0.5}Cu_2O_5$, (6) $YInCu_2O_5$, (7) $Y_{0.5}In_{1.5}Cu_2O_5$, and (8) $In_2Cu_2O_5$.

TABLE 1
Some Structural and Magnetical Parameters of $Y_{2-x}In_xCu_2O_5$

	a(Å)	b(Å)	c(Å)	c/a	$\mu_{eff}(\mu_B)$	θ(k)	T_{AF}(K)
$Y_2Cu_2O_5$	10.8010	3.4950	12.4600	1.154	2.070	45	180
$Y_{1.5}In_{0.5}Cu_2O_5$	10.6649	3.4320	12.3656	1.160	1.984	42	160
$YInCu_2O_5$	10.6349	3.3880	12.3576	1.162	1.906	40	160
$Y_{0.5}In_{1.5}Cu_2O_5$	10.5200	3.3244	12.2590	1.166	1.905	38	160
$In_2Cu_2O_5$	10.5270	3.2700	12.2640	1.165	1.926	38	160

the peaks in the spectra are listed in Table 2. It is not easy to identify all these peaks. It can be found that all these peaks (in the range 200–600 cm^{-1}) change systematically, their wave numbers becoming higher when Y^{3+} is substituted by In^{3+}. The radius of In^{3+} is smaller than that of Y^{3+}, and the atomic weight of In^{3+} is greater than that of Y^{3+}. The vibrational frequences of In–O bonds should be higher than those of Y–O bonds. However, one peak (marked with arrows, wave numbers about 620 cm^{-1}) changes very little, becoming a little stronger. This peak does not appear in the spectra of the starting materials Y_2O_3 and In_2O_5. The IR spectra of R_2CuO_4 (R = La, Pr, Nd, Sm) (10) are very different from those of $Y_{2-x}In_xCu_2O_5$. In compounds with square-planar coordination of Cu^{2+} such as Pr_2CuO_4, Nd_2CuO_4, and Sm_2CuO_4, the Cu–O asymmetric stretching vibration band appears as a single band near 500–550 cm^{-1}, but it is split into a doublet (about 620 and 520 cm^{-1}) in La_2CuO_4 (suggesting D_{4h} symmetry of the isolated octahedron). Cu^{2+} atoms in $Y_{2-x}In_xCu_2O_5$ have coordination 4 + 1, where four oxygen atoms around Cu^{2+} form a diagonal-broken CuO_4 "square" and the fifth Cu–O distance is significantly larger. Their IR spectra are more complicated, suggesting a low symmetry of the CuO_4 square.

The IR spectra of $Y_{2-x}In_xCu_2O_5$ demonstrate that the crystal structure or the coordination condition of Y^{3+}, In^{3+}, and Cu^{2+} is unchanged when Y^{3+} is substituted by In^{3+}. It is reasonable to propose that the Cu_2O_8–dimer chain in $Y_2Cu_2O_5$ or $In_2Cu_2O_5$ is kept when Y^{3+} and In^{3+} are substituted by each other.

The magnetic behavior of $Y_{2-x}In_xCu_2O_5$ has been determined on powder samples between 77 and 300 K. The results are given in Fig. 5 as $\chi_M^{-1} = f(T)$. As shown in these figures, the magnetic susceptibilities for various concentrations of $Y_{2-x}In_xCu_2O_5$ are similar. They obey Curie–Weiss' law above 160 and 180 K, with θ (Weiss constant) ranging between 38–45 K. The deviation of the $\chi_M^{-1} = f(T)$ curve from Curie–Weiss behavior at low temperature may be caused by the antiferromagnetic interactions (6, 7) (here T_{AF} represents the temperature at which the antiferromagnetic interaction begins to be apparent). The θ, T_{AF} values for $Y_{2-x}In_xCu_2O_5$ are listed in Table I.

The effective magnetic moments (μ_{eff}) decrease with the increase of the concentration of In^{3+} in $Y_{2-x}In_xCu_2O_5$ (Fig. 6, Table I), but deviate from a linear change. The magnetic susceptibility change does not obey Wiedemann's additive law (11). This deviation implies that the magnetism of $Y_{2-x}In_xCu_2O_5$ is not just a mixture of $Y_2Cu_2O_5$ and $In_2Cu_2O_5$.

At room temperature, the values of μ_{eff} of Cu^{2+} in $Y_{2-x}In_xCu_2O_5$ are 2.07 (x = 0), 1.984 (x = 0.5), 1.906 (x = 1), 1.905 (x = 1.5), and 1.926 (x = 2) μ_B. All these values are higher than the theoretical value 1.7–1.8 μ_B for free cupric ions assuming g = 2.1 and $S = \frac{1}{2}$. The high μ_{eff} values and positive θ values indicate the presence of ferromagnetic interactions. The results of Figs. 5 and 6 indi-

TABLE 2
IR Spectrum Wave Numbers for $Y_{2-x}In_xCu_2O_5$ and Starting Materials

CuO	640w	573w	530m	482w	440w	400w	310w		
In_2O_3		593m	557m	530m	420vs	366s	326m	302w	
Y_2O_3		580m	556vs	490w	458w	412m	390vs	338vs	306vs
$Y_2Cu_2O_5$	620w	560m	490m	435m	405m	330m			
$Y_{1.8}In_{0.2}Cu_2O_5$	620w	560m	485m	440m	410m	335m			
$Y_{1.5}In_{0.5}Cu_2O_5$	625w	560m	490w	460w	420w	340w			
$YInCu_2O_5$	620w	560m	490w	460w	425w	340m			
$Y_{0.5}In_{1.5}Cu_2O_5$	620w	560m	490w	465m	430m	360m			
$In_2Cu_2O_5$	625m	570s	505w	475w	430w	360s			

Note. s, strong; vs, very strong; m, middle; w, weak.

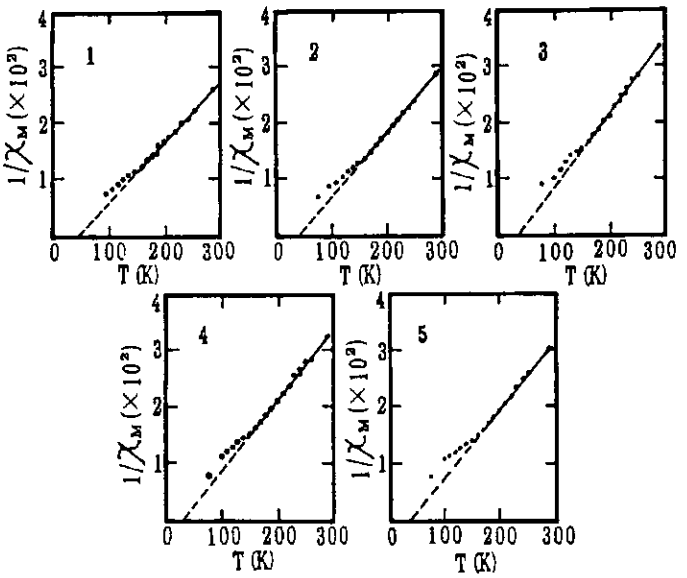

FIG. 5. Plot of $1/\chi_M$ vs temperature of $Y_{2-x}In_xCu_2O_5$. (1) $Y_2Cu_2O_5$, (2) $Y_{1.5}In_{0.5}Cu_2O_5$, (3) $YInCu_2O_5$, (4) $Y_{0.5}In_{1.5}Cu_2O_5$, and (5) $In_2Cu_2O_5$.

cate that both ferromagnetic and antiferromagnetic interactions also exist in the magnetic structure of $Y_{2-x}In_xCu_2O_5$, as in that of $Y_2Cu_2O_5$. Ferromagnetic interactions are prevalent at high temperatures and antiferromagnetic interactions are prevalent at lower temperatures. In (6), it is proved by the neutron diffraction experiment that the ferromagnetic interaction exists in the Cu_2O_8–dimer chain through two Cu_1–O_3–Cu_2 and two Cu_1–$O_{2,4}$–Cu_2 bonds along the *a*-axis and between dimer chains along the *b*-axis through two $Cu_{1,2}$–O_5–$Cu_{1,2}$ bonds. The antiferromagnetic interaction exists between the Cu_2O_8–dimer chains along the *c*-axis through two two-oxygen pathways Cu_2–O_1–O_2–Cu_2 and Cu_1–O_4–O_5–Cu_1.

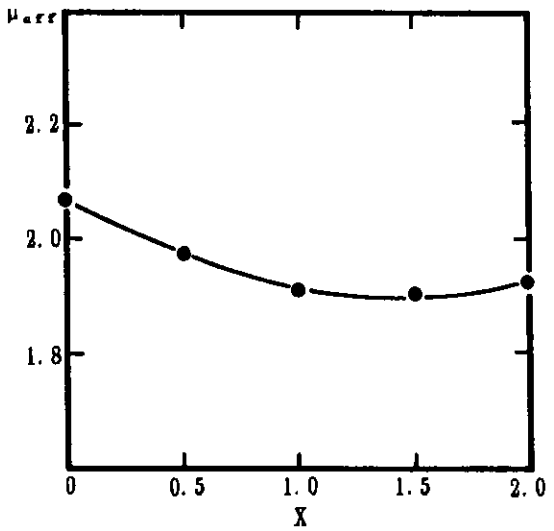

FIG. 6. Effective Bohr magnetons (μ_{eff}) of $Y_{2-x}In_xCu_2O_5$.

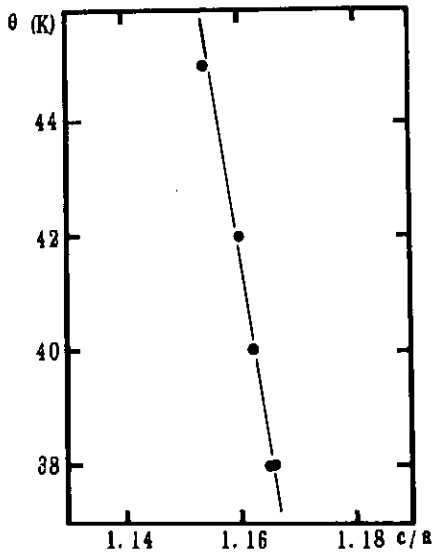

FIG. 7. Plot of θ (Weiss constant) vs c/a (ratio of lattice parameters).

(This seems to be impossible because (i) the distance between O_1 and O_2 or O_4 and O_5 is at least 3.2 Å, the two oxygen atoms cannot contact each other; (ii) O_1 and O_2 or O_4 and O_5 are interrupted by Y^{3+} or In^{3+} atoms. The superexchange pathway Cu_2–O_1–R–O_2–Cu_2 or Cu_1–O_4–R–O_5–Cu_1 is more possible than the direct oxygen–oxygen pathway although Y^{3+} and In^{3+} are diamagnetic. In (12, 13) examples have been given of a diamagnetic ion Zn^{2+}, Be^{2+}, or Bi^{3+} as the antiferromagnetic superexchange pathway.)

When Y^{3+} is substituted by In^{3+}, the distance between two Cu_2O_8–dimer chains becomes shorter (Fig. 3, parameter c) and the antiferromagnetic interaction will be stronger; at the same time, the substitution of Y^{3+} by In^{3+} makes the Cu–O distance in the dimer chain along the *a*-axis and between dimer chains along the *b*-axis become shorter (Fig. 3, parameters a and b), and the ferromagnetic interaction will also be stronger. These two opposite effects together make the effective magnetic moments of $Y_{2-x}In_xCu_2O_5$ deviate from a linear change (Fig. 6). The lattice parameter *c* (and *b*) of $In_2Cu_2O_5$ is even larger (and smaller) than that of $Y_{0.5}In_{1.5}Cu_2O_5$. So, the μ_{eff} value of $In_2Cu_2O_5$ is even higher than that of $Y_{0.5}In_{1.5}Cu_2O_5$.

The θ values of $Y_{2-x}In_xCu_2O_5$ decrease with the increase of In^{3+} concentration (Table 1). Figure 7 gives the variation of θ values with the c/a ratio of lattice parameters, showing a good linear relationship between θ and c/a. The increase of c/a makes the antiferromagnetic interaction between two layers of Cu_2O_8–dimer chains become stronger.

In summary, we have studied the influence of the substitution of Y^{3+} by In^{3+} on the structure and magnetic properties of $Y_{2-x}In_xCu_2O_5$. The substitution of Y^{3+} by In^{3+}

makes the lattice parameters decrease nonlinearily and also makes the μ_{eff} value decrease nonlinearily. This substitution effect further proves the proposal about the magnetic structure of $Y_2Cu_2O_5$ suggested by various authors (6, 7, 14).

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