

## Crystal Structure of $RCu_4Ag$ and $RCu_4Al$ ( $R =$ Rare Earth) Intermetallic Compounds

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Crystallographic studies have been made on the ternary rare earth intermetallic compounds  $RCu_4Al$  and  $RCu_4Ag$ , where  $R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er,$  and  $Tm$ . All  $RCu_4Al$  compounds are found to crystallize in the hexagonal  $CaCu_5$  structure. However, in  $RCu_4Ag$  series, compounds with  $R = Nd$  to  $Tm$  form in the  $MgSnCu_4$ -type structure, while those with  $R = La, Ce,$  and  $Pr$  form only multiphase solids.

### Introduction

$RCu_5$  compounds are known to crystallize in the hexagonal  $CaCu_5$ -type structure and/or in the cubic  $AuBe_5$ -type structure depending on the rare earth elements involved and the heat treatments. The compounds with large-size rare earths ( $R = La-Sm$ ) crystallize only in the  $CaCu_5$ -type structure, while those with small-size rare earths ( $R = Ho-Tm$ ) occur only in the  $AuBe_5$ -type structure (1). In the medium-size rare earths ( $R = Gd, Tb$  and  $Dy$ ), both structures occur depending on the heat treatments;  $CaCu_5$ -type being stable at high temperatures (1). Rare earth intermetallic compounds,  $RCO_3$  and  $RNi_5$ , which have the hexagonal  $CaCu_5$ -type structure, have been extensively studied because of their important magnetic properties and hydrogen absorption capacity (2, 3). Little attention has been paid to  $RCu_5$  compounds since this system is not attractive in this respect, although some  $RCu_5$  compounds are reported to absorb hydrogen (4). It is known that the high coercivity of  $RCO_3$  compounds is due to their anisotropic (uniaxial) magnetization,

which arises from their unique crystal structure, i.e.,  $CaCu_5$  structure (2). Since  $RCu_5$  compounds can have two morphological modifications, it is thought that a study on the effects of the ternary substitution in this system will give some clue in understanding of their structural stabilities. The composition  $RCu_4X$  was chosen because this composition gives opportunities for possible interesting crystal structures, i.e., the ordered or disordered substitution in the  $CaCu_5$  and  $MgSnCu_4$  structures (5), the latter of which is derived from the cubic  $AuBe_5$  structure by ordered substitution. A study of the magnetic properties of some of the  $RCu_4Ag$  compounds has been reported elsewhere (6).

### Experimental

Alloys were prepared by induction melting of stoichiometric amounts of the constituent metals in a water-cooled copper boat under a continuous flow of purified argon gas. The purity of the starting materials was as follows: rare earth, 99.9%; Cu, Al, and Ag, 99.9999%. The alloy ingots were turned over and melted several times to ensure sample homogeneity. The weight loss during melting was negligible.

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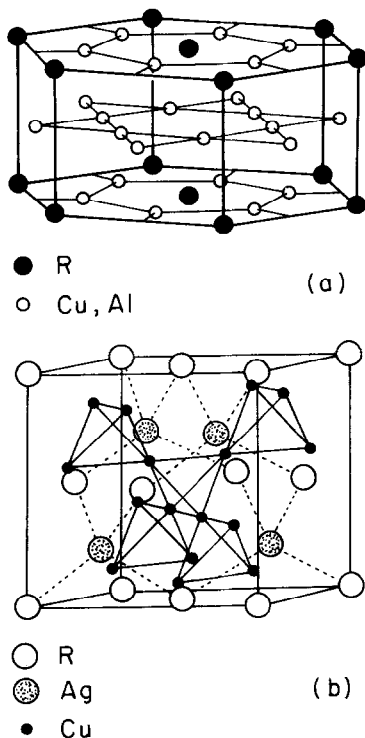


FIG. 1. (a) The unit cell of the hexagonal  $\text{CaCu}_5$ -type structure; (b) the unit cell of the cubic  $\text{MgSnCu}_4$ -type structure.

Powder X-ray diffraction patterns of as-cast samples were obtained on a Picker X-ray diffractometer using  $\text{CuK}\alpha$  radiation with a nickel filter. The lattice constants were obtained by using a least-squares-fit computer program.

TABLE I  
CRYSTALLOGRAPHIC DATA OF  $\text{RCu}_4\text{Al}$  COMPOUNDS

	$a$ (Å)	$c$ (Å)	$c/a$	$V$ (Å <sup>3</sup> )
$\text{LaCu}_4\text{Al}$	5.238	4.189	0.800	99.52
$\text{CeCu}_4\text{Al}$	5.195	4.188	0.806	97.90
$\text{PrCu}_4\text{Al}$	5.186	4.185	0.807	97.52
$\text{NdCu}_4\text{Al}$	5.150	4.181	0.812	96.03
$\text{SmCu}_4\text{Al}$	5.126	4.168	0.813	94.84
$\text{GdCu}_4\text{Al}$	5.096	4.152	0.815	93.35
$\text{TbCu}_4\text{Al}$	5.073	4.149	0.818	92.46
$\text{DyCu}_4\text{Al}$	5.064	4.152	0.820	92.16
$\text{HoCu}_4\text{Al}$	5.047	4.148	0.822	91.50
$\text{ErCu}_4\text{Al}$	5.039	4.139	0.821	91.00
$\text{TmCu}_4\text{Al}$	5.026	4.138	0.823	90.51

## Results and Discussion

All  $\text{RCu}_4\text{Al}$  compounds studied are found to crystallize in the hexagonal  $\text{CaCu}_5$ -type structure, which is shown in Fig. 1a. Their crystallographic data are given in Table I. Lattice parameters of  $\text{RCu}_4\text{Al}$  compounds together with those of hexagonal  $\text{RCu}_5$  compounds are plotted against the rare earth atomic numbers in Fig. 2. No anomaly in the lattice parameters of  $\text{CeCu}_4\text{Al}$  and  $\text{CeCu}_5$  is observed, from which it is inferred that cerium is trivalent in these compounds. It is noted that the aluminum substitution stabilizes the hexagonal  $\text{CaCu}_5$  structure for  $\text{RCu}_4\text{Al}$  compounds although  $\text{RCu}_5$  compounds with Ho, Er, and Tm occur only in the cubic  $\text{AuBe}_5$  structure (1). The unit cell of the  $\text{RCu}_4\text{Al}$  compounds has expanded with respect to that of the corresponding  $\text{RCu}_5$  compounds since the atomic radius of Al (1.432 Å) is larger than that of Cu (1.278 Å).<sup>1</sup> The expansion of the  $c$ -axis is larger than that of the  $a$ -axis, and this

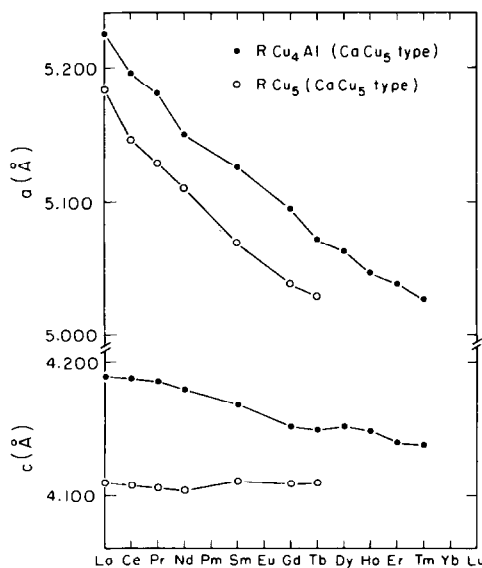


FIG. 2. The lattice constants of the hexagonal  $\text{RCu}_5$  and  $\text{RCu}_4\text{Al}$  vs the atomic number of rare earth elements.

<sup>1</sup> The radii of the elements of coordination number 12 are taken from the data in Ref. (7).

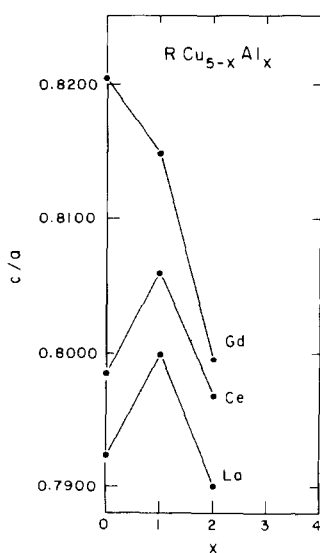


FIG. 3. The lattice constants ratio ( $c/a$ ) vs the aluminum contents ( $x$ ) for  $RCu_{5-x}Al_x$  ( $R = La, Ce,$  and  $Gd$ ).

trend is greater for compounds of larger-size rare earths. This indicates that the Al atom substitutes preferentially a Cu atom on the 3g site in larger-size rare earth compounds. X-ray diffraction intensity measurements also showed that in compounds of larger-size rare earths ( $R = La-Sm$ ), Al occupies preferentially the 3g site, but compounds of smaller rare earths ( $R = Gd-Tm$ ) are more consistent with the random substitution of Al for Cu. Attempts were made to prepare  $RCu_3Al_2$  and  $RCu_2Al_3$  compounds with  $R = La, Ce,$  and  $Gd$  and it was found that, for these rare earths,

TABLE II  
CRYSTALLOGRAPHIC DATA OF  $RCu_4Ag$  COMPOUNDS

	$a$ (Å)	$V$ (Å <sup>3</sup> )	$\frac{1}{4}V$ (Å <sup>3</sup> )
NdCu <sub>4</sub> Ag	7.234	378.56	94.64
SmCu <sub>4</sub> Ag	7.186	371.07	92.77
GdCu <sub>4</sub> Ag	7.163	367.52	91.88
TbCu <sub>4</sub> Ag	7.148	365.22	91.31
DyCu <sub>4</sub> Ag	7.112	359.73	89.93
HoCu <sub>4</sub> Ag	7.101	358.06	89.52
ErCu <sub>4</sub> Ag	7.097	357.46	89.37
TmCu <sub>4</sub> Ag	7.083	355.35	88.84

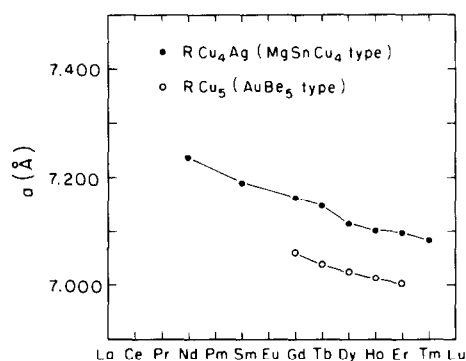


FIG. 4. The lattice constants of the cubic  $RCu_5$  and  $RCu_4Ag$  vs the atomic number of rare earth elements.

$RCu_3Al_2$  compounds crystallize in  $CaCu_5$  structure while  $RCu_2Al_3$  compounds are multiphase materials. In Fig. 3 the lattice parameter ratios,  $c/a$ , are plotted against the aluminum content in  $RCu_{5-x}Al_x$  ( $R = La, Ce,$  and  $Gd$ ) compounds. It is seen that this ratio has the maximum at  $x = 1$  for La and Ce but decreases continuously for Gd. This is also in agreement with the above conclusion, i.e., the preferential occupation of Al in the 3g site for larger rare earths (La-Sm) and the random substitution of Al in Cu sites for smaller rare earths (Gd-Tm).

In the ternary  $RCu_4Ag$  system, compounds of Nd to Tm are found to form single-phase solids, but those of La-Pr are found to be multiphase solids.  $RCu_4Ag$  compounds of  $R = Nd-Tm$  form the cubic  $MgSnCu_4$  structure, which is shown in Fig. 1b. This structure is derived from the cubic  $MgCu_2$  or  $AuBe_5$  structure by an ordered substitution of rare earth atom ( $MgCu_2$  type) or that of transition atom ( $AuBe_5$  type). Crystallographic information for the  $RCu_4Ag$  compounds is given in Table II. Lattice constants of these compounds together with those of cubic  $RCu_5$  compounds are plotted against atomic numbers of rare earths in Fig. 4. It is seen that the normal lanthanide contraction occurs in the  $RCu_4Ag$  series and, moreover, the lattice of  $RCu_4Ag$  compounds has expanded with respect to that of the parent  $RCu_5$  compounds.

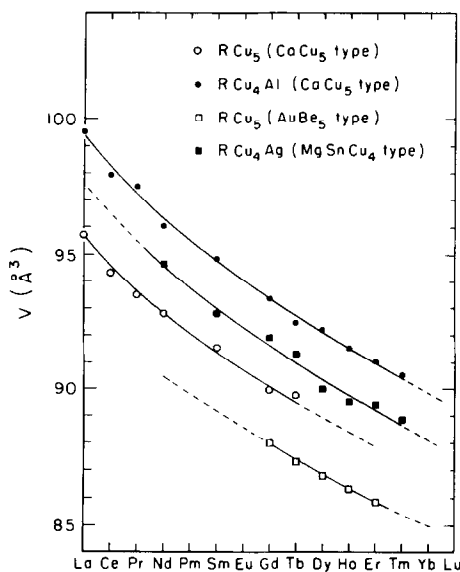


FIG. 5. The volume of one formula unit of  $RCu_5$ ,  $RCu_4Al$ , and  $RCu_4Ag$  vs the atomic number of rare earth elements.

This is due to the larger size of Ag (1.445 Å) than that of Cu (1.278 Å). It should be noted that the silver substitution has stabilized the cubic morphological structure. In fact, the compounds of Nd and Sm have the cubic  $MgSnCu_4$  structure although the corresponding  $RCu_5$  compounds exist only in the hexagonal  $CaCu_5$  structure. The unit cell of cubic  $RCu_5$  or  $RCu_4Ag$  contains four formula units and the hexagonal  $RCu_5$  or  $RCu_4Al$  has one formula unit in its unit cell. In Fig. 5, the volume per one formula unit for  $RCu_5$ ,  $RCu_4Al$ , and  $RCu_4Ag$  is plotted against the atomic number of rare earth elements. A comparison of these for the cubic  $RCu_5$  and the hexagonal  $RCu_5$  shows that the cubic morphological structure is more compact than the hexagonal one. A similar trend is seen for the cubic  $RCu_4Ag$  and the hexagonal  $RCu_4Al$  although the metallic radius of Ag (1.445 Å) is slightly larger than that of Al (1.432 Å).

It was reported that the cubic  $AuBe_5$  structure occurs in  $AB_5$  stoichiometry where the radius ratio of  $A$  and  $B$  elements is small, and the contrary is observed for the hexagonal  $CaCu_5$ -type structure (1, 8). The metallic

radius of Ag (1.445 Å) is larger than that of Cu (1.278 Å). The occurrence of the cubic structure in the silver ternary  $RCu_4Ag$  compounds ( $R = Nd$  to  $Tm$ ) is, therefore, in agreement with the statement of Dwight (8). Nonformation of the compounds  $LaCu_4Ag$ ,  $CeCu_4Ag$ , and  $PrCu_4Ag$  is also in accordance with this, since the size of the rare earths involved is large. The metallic radius of Al (1.432 Å) is slightly smaller than that of Ag (1.445 Å), but it is much larger than that of Cu (1.278 Å). It seems, therefore, that the  $RCu_4Al$  compounds are also expected to crystallize in the cubic structure according to Dwight. However, all  $RCu_4Al$  compounds studied ( $R = La$ – $Tm$ ) are found to crystallize in the hexagonal structure contrary to this expectation.

The electron concentration in the  $RCu_4Ag$  compounds is the same as that in the parent  $RCu_5$  compounds since one Cu atom or one Ag atom donates one electron to the conduction band giving an electron concentration of 1.33 per atom in these compounds. Therefore, the size of the element involved appears to be a major factor in the structural stabilization in the  $RCu_4Ag$  system. On the other hand, one Al atom gives three electrons to the conduction band. Consequently the electron concentration in the  $RCu_4Al$  compounds (1.67 per atom) is higher than that in the  $RCu_5$  compounds (1.33 per atom), which may overcome the size factor and stabilize the hexagonal structure in the  $RCu_4Al$  system, particularly for small-size rare earths (Ho, Er, and Tm). However, the electron concentration in the typical hexagonal compound  $CaCu_5$  is only 1.17 per atom and the simple electron concentration consideration alone does not appear to be enough for an understanding of the difference in the substitution effect of Ag and Al. As mentioned above, the unit cell volume of the hexagonal compound is larger than that of the corresponding cubic compound, and the volume expansion is smaller by Al than by Ag substitution. These observations indicate that the hexagonal  $CaCu_5$  structure is capable of

accommodating larger atoms in the Cu sites than was originally thought (8).

In this regard, the structural stability of the ternary systems studied is mainly due to the size of the substituting elements, and our results indicate that there is a critical radius of the substituting element for the occurrence of the cubic or the hexagonal structure in the ternaries studied.

In this study it has been shown that one Al atom substitution of a Cu atom in  $RCu_5$  stabilizes the hexagonal  $CaCu_5$  structure and the Al atom substitutes a Cu atom preferentially on the 3g site in larger-size rare earth compounds but enters randomly in smaller rare earth compounds. The one Ag atom substitution in  $RCu_5$  is shown to stabilize the cubic  $MgSnCu_4$  structure for medium to small rare earth (Nd–Tm) compounds, but larger rare earths (La–Pr) do not form single-phase compounds. Since the metallic radii of Al and Ag are 1.432 and 1.445 Å, respectively, the

effects of the ternary substitution of these metals are believed to be due to the size effect although some electronic effects must be involved. Similar studies are now in progress for  $RCO_4X$  and  $RNi_4X$  in our laboratory.

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