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Lanthanide-copper intermetallic compounds having the $CeCu_2$ and AlB_2 structures.

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Twelve rare-earth—copper intermetallic compounds (XCu_2, X = rare earth metal) have been prepared as part of a continuing study of the properties of rare earth alloys. From powder X-ray data only, it has been shown that all of these alloys, as well as YCu_2 are orthorhombic and isostructural with $CeCu_2$. The structure of $CeCu_2$ was recently reported by Larson and Cromer (1961).

The $CeCu_2$ structure belongs to space group $Imma\,(D_{2h}^{28})$ with Ce in positions $4e$: $(000;\ \frac{1}{2}\frac{1}{2}\frac{1}{2}) + 0,\ \frac{1}{4},\ z;\ 0,\ \frac{3}{4},\ \bar{z}$; and Cu in positions $8h$: $(000;\ \frac{1}{2}\frac{1}{2}\frac{1}{2}) + 0,\ y,\ z;\ 0,\ \bar{y},\ \bar{z};\ 0,\ \frac{1}{2}+y,\ \bar{z};\ 0,\ \frac{1}{2},\ z$. Larson and Cromer found the value of z for Ce to be $0{\cdot}5377 \pm 0{\cdot}0006$ while for Cu, $y = 0{\cdot}0510 \pm 0{\cdot}0011$ and $z = 0{\cdot}1648 \pm 0.0010$.

We have shown from powder X-ray data only that $LaCu_2$ has the hexagonal AlB_2 structure. The existence of a compound with this stoichiometry has been reported previously (Gschneider, 1961) but without crystal structure data. In this investigation it was found that 25-g ingots almost completely oxidize in air in a day and X-ray patterns must be taken soon after preparation. This relatively rapid oxidation could possibly account for the lack of structure data from previous investigators.

Table 1. *Crystallographic data for the* XCu_2 *compounds**

X	*a*	*b*	*c*	Density (comp.)
Y	4·305 Å	6·800 Å	7·315 Å	6·70 g.cm^{-3}
La†	4·346		3·807	7·07
Ce	4·425	7·057	7·475	7·61
Pr	4·400	7·024	7·435	7·75
Nd	4·387	7·059	7·420	7·92
Sm	4·360	6·925	7·375	8·27
Eu	4·45	7·25	7·54	7·62
Gd	4·320	6·858	7·330	8·69
Tb	4·310	6·825	7·320	8·83
Dy	4·300	6·792	7·300	9·02
Ho	4·280	6·759	7·290	9·20
Er	4·275	6·726	7·265	9·36
Tm	4·266	6·697	7·247	9·51
Yb	4·28	6·76	7·40	9·31
Lu	4·245	6·627	7·220	9·88

* All lattice constants are ± 0·005 Å except for Eu and Yb which are ± 0·01 Å.

† Hexagonal AlB_2 structure.

Powder diffraction data for YCu_2 had been reported by Domagala, Rausch & Levinson (1961) but no structure was given. As noted above, it was found that this compound also has the $CeCu_2$ structure. Crystallographic data for all of the XCu_2 compounds are shown in Table 1.

The compounds were prepared by melting stoichiometric amounts of the elements in quartz crucibles in an argon atmosphere by induction heating. The copper purity was 99·999% and the rare earths were 99 + % except Pr and Y which were 99.9 + %. Powder X-ray patterns were taken of all the compounds with Cr $K\alpha$ radiation using Straumanis type Norelco cameras of 114·6 mm diameter.

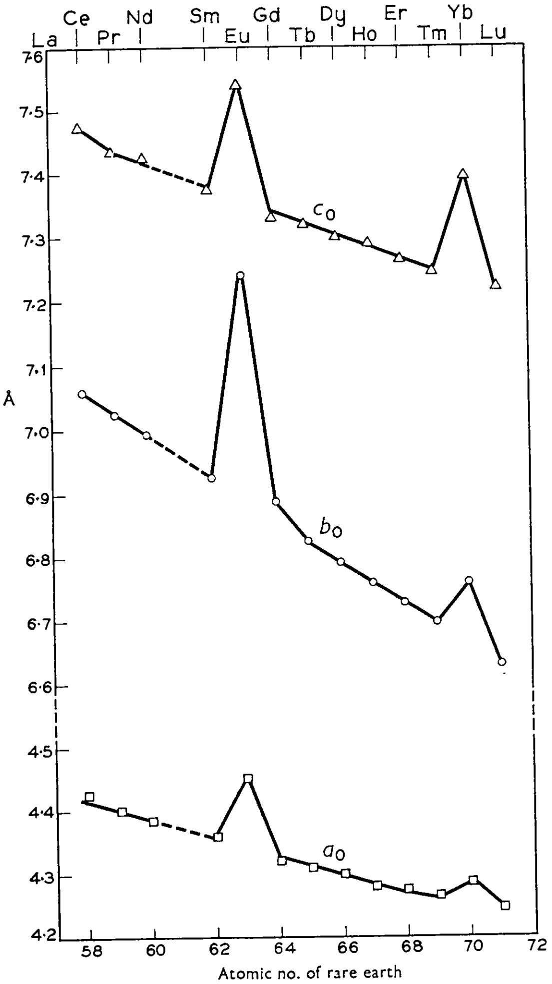

Fig. 1. The variation of the lattice parameters of the XCu_2 intermetallic compounds with atomic number of the lanthanide element.

Table 1 shows the crystallographic data for the XCu_2 compounds. Except for $EuCu_2$ and $YbCu_2$, a linear regression analysis program giving a least-squares fit to the lattice parameters was run and the results of this program were checked by using a d-spacing program. The calculated values of the interplanar spacings for high angles were all within 0·002 Å of the measured values and, in general, were within better than 0·001 Å. The variation of lattice constants with atomic number of the rare earth is shown in Fig. 1. The lanthanide contraction is apparent. Ce appears to be behaving trivalently, while Eu and Yb appear to be divalent.

As noted above, it has been determined from powder data only that $LaCu_2$ has the hexagonal AlB_2 structure and, therefore, belongs to the group $P_6mmm\,(D_{6h}^{1})$ with La in positions a: 000; and Cu in positions $2d$: $\pm\frac{1}{3},\ \frac{2}{3},\ \frac{1}{2})$. Computed and observed relative intensities and inter-

Table 2. *Observed and calculated interplanar spacings and intensities for* Cu_2La – Cr $K\alpha$ *radiation*

hk·l	d_o†	d_c	I_o*	I_c
00·1	n.o	3·807	—	0·5
10·0	3·742	3·764	vw	1·93
10·1	2·670	2·677	vs	30·73
11·0	2·169	2·173	s	15·15
00·2	1·905	1·904	w-m	3·28
11·1	n.o	1·887	—	0·75
20·0	n.o	1·882	—	0·20
10·2	n.o	1·699	—	0·29
20·1	1·6863	1·6871	m	7·06
11·2	1·4339	1·4319	S	10·72
21·0	n.o	1·4226	—	0·20
20·2	n.o	1·3384	—	0·20
00·3	n.o	1·2691	—	0·06
21·1	1·3326	1·3326	s	11·36
30·0	1·2546	1·2546	m	6·75
10·3‡	1·2044	1·2026	ms	8·99
30·1	n.o	1·1916	—	0·58

* s = strong m = medium w = weak v = very.

† n.o = not observed.

‡ *d* values for α_1 and α_2 averaged.

planar spacings are shown in Table 2. In the calculations of intensities, the Thomas and Umeda (1957) atomic scattering factors corrected for dispersion (Dauben & Templeton, 1955) were used. Corrections for absorption were not made. The good agrrement between observed and calculated interplanar spacings and intensities supports the correctness of the proposed structure.

Larson and Cromer have discussed the close relationship between the AlB_2 type and orthorhombic structure of $CeCu_2$. The fact that $LaCu_2$ has the AlB_2 structure corroborates this close relationship. Attempts were made to convert $LaCu_2$ to the orthorhombic form and convert YCu_2 to the hexagonal AlB_2 structure even though the available phase diagram information indicated no phase changes. $LaCu_2$ was quenched in ice water from 740 °C (melting point 834 °C) which YCu_2 was annealed at 400 °C for 70 hours. These compounds did not change structure after these treatments. However, we do not believe these experiments negate the possibility of the existence of phases with the AlB_2 structure type in the XCu_2 compounds.

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The water molecules in (+)-demethanolaconinone hydroiodide trihydrate.

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In the course of a survey of organic hydrate structures (Clark, 1963), the crystal structure for (+)-demethanolaconinone hydroiodide, $C_{19}H_{17}N.C_2H_5(OH)_4.O.(OCH_3)_3.HI.3H_2O$, described by Przybylska (1961), was examined with respect to the water molecules. The three water molecules (O9, O10 and O11) and the iodine atom (I″) form a sub-structure (Fig. 1) that is discussed briefly in the present note.

The sub-structure viewed along the *a* direction has a trapezoidal shape. Trapezoids related by the 2_1 axis parallel to *c* are linked to one another by a short hydrogen bond (2.50 Å) between two water molecules to form a zigzag chain along the *c* direction. The chain is held among neighboring alkaloid molecules by four hydrogen bonds, one involving hydroxyl (O8) to water (O9), and three involving hydroxyls to the iodine atom (Tables 1, 2).

Assignment of water-molecule protons among the hydrogen bonds is complicated by the close contacts (3.5 to 3.6 Å) to one iodine by five oxygen atoms, *i.e.* two water and three hydroxyl oxygens, all noted by Przybylska (1961). The following comment has been made by Przybylska (written communication, 1963) about the assignment of the hydroiodide proton: *Considering the very low ionic character of* HI *and the fact that the iodine atom is*

Table 1. *Hydrogen bond distances*

Atoms† *X*	*Y*	Location of *Y*	Distance‡ *X* – *Y*
O9	I″	1/2+*x*, 1/2−*y*, 1−*z*	3·58 Å
O10	I″	1/2+*x*, 1/2−*y*, 1−*z*	3·53
I	O5′	1/2−*x*, 1−*y*, *z*−1/2	3·52
I	O6′	1/2−*x*, 1−*y*, *z*−1/2	3·52
I	O7	1−*x*, *y*−1/2, 1/2−*z*	3·62
O9	O8′	3/2−*x*, 1−*y*, *z*+1/2	2·84
O10	O6	1−*x*, *y*−1/2, 1/2−*z*	2·83
O10	O11	*x*, *y*, *z*	2·81
O11	O9	*x*, *y*, *z*+1	2·81
O11	O9′	3/2−*x*, 1−*y*, *z*−1/2	2·50

† Atoms *X* are located at *x*, *y*, *z* (Table 1, Przybylska, 1961) except O9 which is at *x*, *y*, *z*+1. O5, O6, O7, O8 are hydroxyl oxygens; O9, O10, O11 are water molecules.

‡ All data taken from Przybylska (1961) for calculations of bond distances using SILLIAC program V-21 by Dr F. M. Lovell, University of Sydney. Errors estimated by present author: O–I ± 0·05 Å; O–O ± 0·10 Å. The crystals have space group $P2_12_12_1$, $a = 14·69 \pm 0·03$, $b = 22·08 \pm 0·03$, $c = 8·33 \pm 0·02$ Å.

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