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The crystal structure of $CeCu_2$.*

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As part of a program of structural studies of intermetallic compounds of Ce and of Pu the crystal structure of $CeCu_2$ has been determined. The structure of $CeCu_6$ has recently been reported by Cromer, Larson & Roof (1960).

A Ce–Cu alloy containing 66 at.% Cu was melted in vacuum at 1080 °C. in a MgO crucible and slowly cooled. The density of the ingot was found to be 7·51 g.cm.$^{-3}$. The ingot was crushed and single crystals were fairly common among the smaller fragments. This alloy oxidized rather quickly in air to give a black powder, probably CeO. The powder was likely to be pyrophoric when disturbed. Crystals were sealed in thin Pyrex tubes and examined with a precession camera. The crystals were found to be orthorhombic, space group *Imma* (if centric), with

$$a = 4{\cdot}43 \pm 0{\cdot}01,\ b = 7{\cdot}05 \pm 0{\cdot}02,\ c = 7{\cdot}45 \pm 0{\cdot}02\ \text{Å}$$
$$(\lambda = 0{\cdot}7107\ \text{Å})\ .$$

The calculated density with four $CeCu_2$ per unit cell is 7·62 g.cm.$^{-3}$. A satisfactory structure was found in space group *Imma* so that the non-centric space group *Im*2*a* was not considered.

The short *a* axis with a mirror perpendicular to it requires that all atoms lie on this mirror and a trial structure was derived from spatial considerations alone. This structure had the Ce atoms in 4*e* with $z \approx 0{\cdot}55$ and the Cu atoms in 8*h* with $y \approx 0{\cdot}05$ and $z \approx 0{\cdot}16$. A crystal was mounted on the *b* axis and a series of timed exposures was taken on a precession camera with Mo $K\alpha$ radiation for the 0*kl* and 1*kl* reciprocal lattice levels. The intensities were estimated visually and *Lp* corrections (Waser, 1951) were computed on an IBM 704 and applied to give relative values of F^2. Near the edge of the film and also near the center, particularly on upper levels, computed *Lp* corrections are much superior to graphical corrections because of the very steep slope of the correction curve.

An 0*kl* Patterson projection was computed and the trial structure was quickly confirmed. The trial structure was refined by the least-squares method, the results of which are given in Table 1. Data from the two reciprocal lattice levels were given separate scale factors. The full matrix was used to determine shifts and the matrix was inverted for standard deviation calculations. The form factors were used in exponential form with the coefficients given by Forsyth & Wells (1959). Anomalous dispersion corrections of $-1{\cdot}3$ and $+0{\cdot}4$ electrons were applied to the Ce and Cu form factors, respectively. The final observed and calculated structure factors, for which $R = 10{\cdot}8\%$, are listed in Table 2.

Table 1. *Final parameters in* $CeCu_2$ *from the least-squares refinement*

Atom	Position	*x*	*y*	*z*	*B* (Å^2)
Ce	4*e*	0	$\frac{1}{4}$	0·5377 ± 0·0006	0·82 ± 0·12
Cu	8*h*	0	0·0510 ± 0·0011	0·1648 ± 0·0010	1·13 ± 0·18

Table 2. *Observed and calculated structure factors for* $CeCu_2$

If $F_o = 0$ the reflection occurred at too small an angle to be observed satisfactorily. If F_o is negative the reflection was too weak to be observed and the minus sign should be interpreted as 'less than'

H	K	L	F_o	F_c	H	K	L	F_o	F_c
0	0	2	49	40	1	0	1	0	-45
0	0	4	12	3	1	0	3	126	-146
0	0	6	78	62	1	0	5	14	3
0	0	8	37	-30	1	0	7	36	29
0	0	10	44	-40	1	0	9	19	-10
0	1	1	0	-5	1	1	2	63	-67
0	1	3	62	55	1	1	4	41	-39
0	1	5	94	78	1	1	6	61	-54
0	1	7	46	39	1	1	8	56	-51
0	1	9	32	32	1	1	10	22	-17
0	2	0	17	-18	1	2	1	131	124
0	2	2	106	-114	1	2	3	-10	-3
0	2	4	78	-71	1	2	5	43	43
0	2	6	38	32	1	2	7	19	14
0	2	8	-15	2	1	2	9	44	-43
0	2	10	13	12	1	3	2	25	-19
0	3	1	69	-80	1	3	4	92	92
0	3	3	50	-49	1	3	6	47	53
0	3	5	16	-15	1	3	8	19	14
0	3	7	68	-73	1	3	10	41	36
0	3	9	30	-33	1	4	1	68	-58
0	4	0	89	94	1	4	3	71	-64
0	4	2	53	52	1	4	5	16	-14
0	4	4	27	26	1	4	7	18	9
0	4	6	17	19	1	4	9	-19	11
0	4	8	15	-16	1	5	2	79	-74
0	5	1	30	-36	1	5	4	-16	-4
0	5	3	33	35	1	5	6	39	-40
0	5	5	80	83	1	5	8	54	-58
0	5	7	-14	13	1	5	10	-18	-3
0	5	9	19	24	1	6	1	48	43
0	6	0	71	-72	1	6	3	53	52
0	6	2	36	-39	1	6	5	-17	11
0	6	4	24	-20	1	6	7	-19	-9
0	6	6	17	-17	1	6	9	-19	-8
0	6	8	14	14	1	7	2	-17	-5
0	7	1	32	-39	1	7	4	51	55
0	7	3	30	-30	1	7	6	30	36
0	7	5	14	-14	1	7	8	-19	12
0	7	7	43	-48	1	8	1	55	-53
0	8	0	15	13	1	8	3	-19	-4
0	8	2	46	49	1	8	5	24	-22
0	8	4	32	35	1	8	7	-19	-7
0	8	6	11	-15	1	8	9	21	25
0	9	1	-12	2	1	9	2	22	-21
0	9	3	21	22	1	9	4	22	-20
					1	9	6	-18	-26
					1	9	8	22	-25

Table 3. *Interatomic distances in* $CeCu_2$

The standard deviation of Ce–Ce distances is about 0·01 Å and of the other distances about 0·02 Å

Ce–2 Ce	3·568 Å	Cu–2 Ce	3·023 Å
–2 Ce	3·859	–1 Ce	3·067
–4 Cu	3·023	–1 Ce	3·111
–2 Cu	3·067	–2 Ce	3·209
–2 Cu	3·111	–2 Cu	2·552
–4 Cu	3·209	–1 Cu	2·557
		–1 Cu	2·805

The interatomic distances are given in Table 3. This structure, although formally a distortion of the AlB_2 structure (C32 structure type) can be considered as a new type because the coordination numbers of the two structure types are different. Consider a hypothetical $CeCu_2$

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compound having the hexagonal C32 structure. The Ce atoms are in layers normal to the *c* axis. In one layer, those Ce atoms in alternate rows parallel to *b* are moved slightly in the $+a^*$ direction. In the other rows the Ce atoms are moved in the $-a^*$ direction. In the next layer above, these movements are reversed. The Cu atoms are then moved in the *c* direction to relieve the strain produced by the Ce atom movement. These small movements change the symmetry to *Imma* and the two cells are related by the transformation

$$\begin{aligned}\mathbf{A}&=\mathbf{a}\\ \mathbf{B}&=2\mathbf{c}\\ \mathbf{C}&=\mathbf{a}-2\mathbf{b}\end{aligned}$$

where **A**, **B** and **C** refer to the orthorhombic cell and **a**, **b** and **c** to the hexagonal C32 cell.

Each Ce atom has four Ce neighbors in a distorted tetrahedron and twelve Cu neighbors in two distorted hexagons, one hexagon on each side of the Ce atom. Two Ce atoms are pushed in between these hexagons of Cu atoms so that the hexagons are separated from each other more on one side than the other.

Each Cu atom has six Ce neighbors and four Cu neighbors. The Ce atoms are arranged in a trigonal prism but the atoms at one end of the prism are spread apart somewhat. There are three Cu neighbors co-planar with the central Cu atom and the fourth Cu neighbor is displaced outward from the center of the larger end of the trigonal prism of Ce neighbors.

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The β-$\mathrm{Ag_3In}$ phase.

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It is well-known that a body-centred cubic 3:2 electron compound, usually called the β-phase, occurs in binary alloys of copper with aluminium, indium, gallium, and tin, and of silver with aluminium and indium. The factors affecting their formation have been fully discussed by Hume-Rothery *et al.* (1940*a*). The structures are stable only at high temperature and decompose in a complex way on quenching. The lattice parameters of these phases are all known except for β-$\mathrm{Ag_3In}$, where the only high-temperature X-ray investigations (Hume-Rothery *et al.*, 1940*b*) appear to have been confined to the $(\alpha+\beta)$ region.

In connection with recent work on silver-based Heusler alloys (Morris *et al.*, 1959), we have had occasion to examine the β-$\mathrm{Ag_3In}$ phase. According to the phase diagram published in *Structure Reports*, **11**, 1947–8, the β-phase extends over a narrow range of composition around 25 at.% In and between temperature limits 660 to 693 °C. The alloy investigated was made from spectroscopically standardized silver and indium to the exact composition $\mathrm{Ag_3In}$, the weight loss on melting the elements in an evacuated silica tube being negligible. High-temperature X-ray photographs confirmed that the β-phase structure was body-centred cubic, and the absence of extra reflections showed that the alloy was single-phase at 684 °C., with $a=3{\cdot}3682$ Å. Wavelengths were taken from Lonsdale (1950). The lattice parameters of all the β-phases of the copper and silver alloys are set out below (Pearson, 1958). The factor ($\times 1{\cdot}00202$) was used to convert kX. units to Å.

β-$\mathrm{Ag_3Al}$ 3·302 Å at 700 °C.
β-$\mathrm{Ag_3In}$ 3·3682 Å at 684 °C.
β-$\mathrm{Cu_3Al}$ 2·9564 Å at 672 °C. at $\alpha/(\alpha+\beta)$ boundary
β-$\mathrm{Cu_4In}$ 3·0461 Å at 672 °C. at $\alpha/(\alpha+\beta)$ boundary
β-$\mathrm{Cu_3Ga}$ 2·9671 Å at 672 °C. at $\alpha/(\alpha+\beta)$ boundary
β-$\mathrm{Cu_5Sn}$ 3·0200 Å at 672 °C. at $\alpha/(\alpha+\beta)$ boundary

Addition of manganese to the β-phases of the copper alloys permits the high-temperature structures to be retained by quenching, and also leads to the development of order, until ultimately at compositions $\mathrm{Cu_2Mn}X$ the alloys have the Heusler structure and are ferromagnetic. It has been shown however (Morris *et al.*, 1959) that no Heusler structure exists at either $\mathrm{Ag_2MnAl}$ or $\mathrm{Ag_2MnIn}$, and Hall (1959) has established that the β-$\mathrm{Ag_3Al}$ phase is not stabilized by addition of manganese and that the high-temperature β-phase does not extend to the composition $\mathrm{Ag_2MAl}$. In both Ag–Mn–Al and Ag–Mn–In the extension of the β-phase into the ternary system is thus considerably less than in the corresponding copper series. Since the magnetic properties of the Heusler alloys suggest that the manganese atoms are univalent, this difference in behaviour may be attributed to size-factor effects, substitution of copper by manganese in the β-phases being favoured by their similar atomic diameters, but not substitution of silver by manganese.

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