We thank Professor J. D. H. Donnay for many helpful suggestions and our two anonymous referees for their constructive critique.

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The Crystal Structure of YCd_6*

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(*Received* 2 *November* 1970)

YCd_6 is cubic, $a=15{\cdot}482$ (3) Å with 24 formula units in space group $Im3$. The structure was solved by direct methods from counter data and is isomorphous with Ru_3Be_{17}, but with an additional Cd atom in a 24-fold $0yz$ position which is $\frac{1}{3}$ occupied. This fractional atom occupies the large void at the origin of the otherwise ordered structure. Least-squares refinement with anisotropic thermal parameters gave $R=3{\cdot}1$ and $R_w=2{\cdot}8\%$; with the fractional atom excluded, $R=6{\cdot}4$ and $R_w=5{\cdot}5\%$.

Introduction

A large number of MCd_6 compounds have been reported by Johnson, Schablaske, Tani & Anderson (1964) where M is yttrium or any of the rare earths except lanthanum and promethium. The compounds are cubic with a about 15·5 Å. This compound was accidentally prepared during an attempted preparation of $Y_2Cd_{\sim 9}$ (Cromer & Larson, 1970) and, because it was an unknown structure type, we decided to study it. Also, we hoped that this structure might help in solving the superstructure of $Y_2Cd_{\sim 9}$.

Experimental

Crystals of YCd_6 were formed by slowly cooling a melt of nominal composition $YCd_{4.5}$. A second phase, YCd_3 was presumably present although all single-crystal fragments examined were YCd_6. Crystals of $Y_2Cd_{\sim 9}$ are produced by rapidly cooling a melt of this composition. Preliminary precession photographs showed the crystals to be cubic, space group $Im3$, if centric.

Lattice constants and intensities were measured using graphite monochromated Mo $K\alpha$ radiation and a Picker four-circle goniometer interfaced with a PDP-8 computer. The orientation, least-squares, and data-collection programs were obtained from Busing, Ellison, Levy, King & Roseberry (1968). The lattice constant that was found, $a=15{\cdot}482$ (3) Å ($\lambda=0{\cdot}70926$ Å), is in good agreement with $a=15{\cdot}479$ (2) Å reported by Johnson *et al.* (1964). The θ–2θ scan mode was used for intensity measurements with steps of 0·05° 2θ over a scan range of 2° plus the α_1–α_2 dispersion. Two-second counts were taken at each step. The background was counted for 20 seconds at each extreme and assumed to vary linearly over the scan range. A total of 4462 reflections with $2\theta \leq 55°$ was measured in one

* Work performed under the auspices of the U.S. Atomic Energy Commission.

Table 1. *Least-squares parameters for* YCd_6

Position and thermal parameters are multiplied by 10^5.

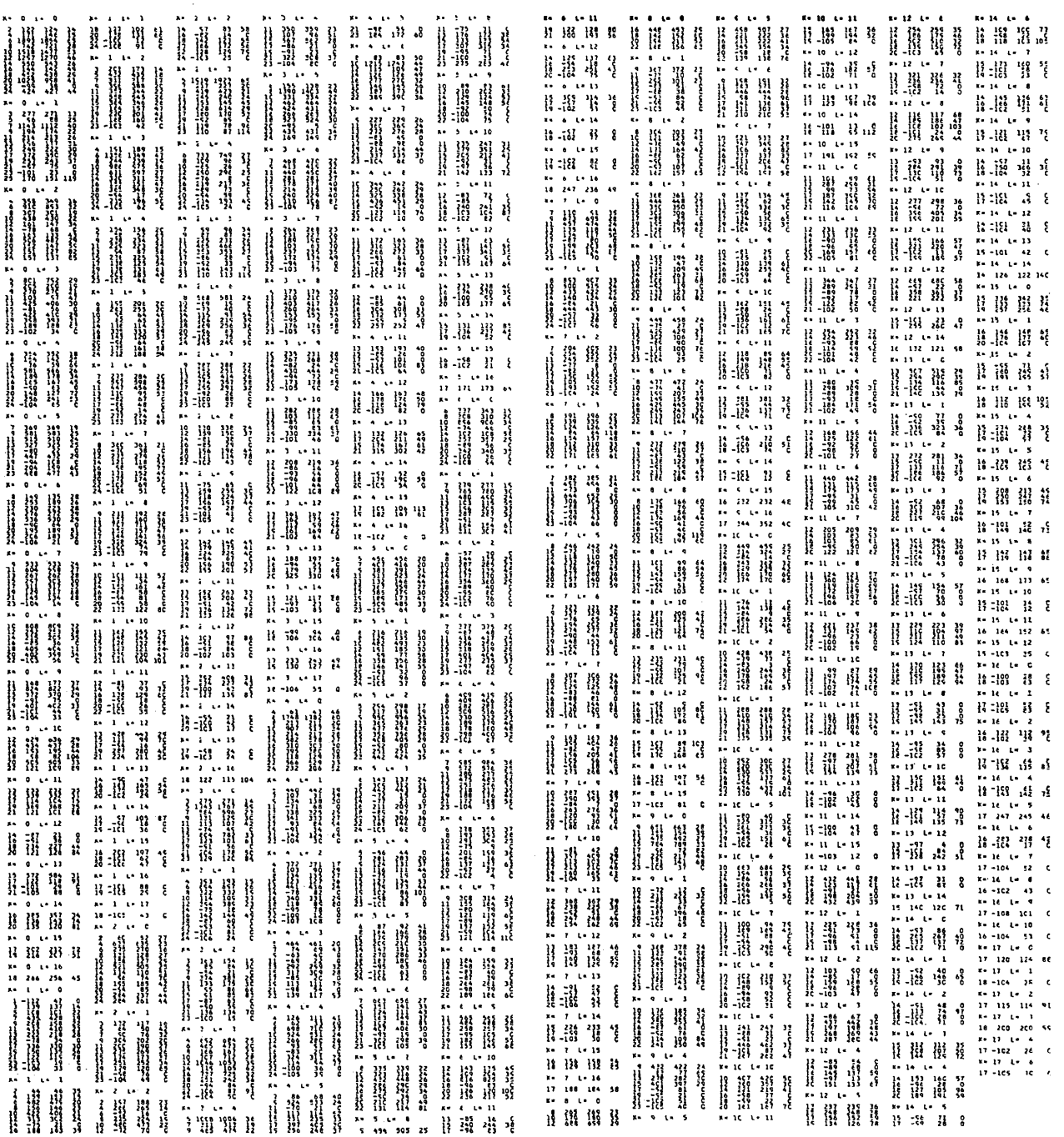
	Set	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Y	24(g)	0	29966 (7)	18985 (6)	75 (3)	102 (4)	100 (4)	0	0	18 (6)
Cd(1)	48(h)	11835 (4)	20031 (4)	34049 (4)	189 (2)	132 (2)	121 (2)	82 (4)	−51 (4)	−24 (4)
Cd(2)	24(g)	0	09227 (6)	24069 (8)	117 (3)	117 (3)	559 (6)	0	0	179 (8)
Cd(3)	24(g)	0	34603 (5)	40438 (5)	136 (3)	115 (3)	102 (3)	0	0	49 (5)
Cd(4)	16(f)	16081 (4)	—	—	191 (2)	β_{11}	β_{11}	179 (5)	β_{12}	β_{12}
Cd(5)	12(e)	0	19018 (7)	$\frac{1}{2}$	103 (4)	103 (4)	210 (5)	0	0	0
Cd(6)	12(d)	0	0	40551 (8)	140 (5)	473 (8)	124 (5)	0	0	0
Cd(7)	24(g)	0	0832 (3)	0741 (4)	1640 (45)	405 (25)	578 (30)	0	0	−667 (41)

Occupancy of Cd(7) = 0·331 (4).
$g=1{\cdot}78\ (10)\times 10^{-8}$.
The temperature factor is $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right]$.

quadrant of the cubic crystal. Thus, equivalent reflections, except for the class *hhh*, were measured in three different orientations. The crystal was fairly equant in shape, and absorption was approximated by a sphere with $\mu R = 1{\cdot}8$. Equivalent reflections were averaged to give the final unique data set. A disagreement index defined as $R_d = \sum_n \sum_i |\bar{F}_n - F_{i,n}| / \sum_i \bar{F}_n$ was 0·029, where $\bar{F}_n = \sum w_i F_i / \sum w_i$ and the summation is over each of the i measurements of the unique reflection F_n, provided F_i is observed greater than zero. A total of 1505 unique reflections was measured, of which 1000 were

Table 2. *Calculated and observed structure factors for* YCd_6.

Column headings are h, F_o/K, F_o^*/K and 10σ (F_{obs}/K). A minus sign preceding F_o/K means less than.



observed according to the criterion

$$(I-B) \geq 3\sigma(I) = 3\,[I+B+(kI)^2]^{\frac{1}{2}},$$

with $k=0{\cdot}0117$ as determined by the variation of a periodically measured standard reflection.

Solution and refinement of the structure

The structure was solved by the application of the symbolic addition method. The process went very smoothly and, after an origin choice was made, a unique solution with 497 signs was reached. An E map gave peaks corresponding to a formula Y_3Cd_{17}. At this point it was realized that the structure was the same as that of Ru_3Be_{17} (Sands, Johnson, Krikorian & Kromholtz, 1962). An interesting feature of this structure is the existence of a huge hole at the origin.

The Y_3Cd_{17} structure, determined from the E map, was refined by least-squares methods. The minimized function was $\sum w(F_o-F_c^*)^2$, where

$$F_c^* = KF_c / \left\{1+2g\ \mathrm{Lp}\ \left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right] F_c^2\right\}^{\frac{1}{4}}$$

in which K=scale factor, g=extinction parameter (Zachariasen, 1963, 1967; Larson, 1967, 1970), Lp=Lorentz and polarization factor, and F_c is the structure factor calculated in the usual way. Relativistic Hartree–Fock scattering factors were used for Y (Cromer & Waber, 1968) and Cd (Doyle & Turner, 1968). Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ were applied (Cromer & Liberman, 1970). The weights, w, were derived from $\sigma(I)$, [equation (1), Stout & Jensen, 1968]. The R indices quoted are $R=\sum |\Delta F| / \sum |F_o|$ and $R_w=(\sum w(\Delta F)^2 / \sum wF_o^2)^{1/2}$ (Hamilton, 1964), with unobserved reflections omitted. Refinement with anisotropic thermal parameters led to $R=0{\cdot}0643$ and $R_w=0{\cdot}0548$.

A difference Fourier map at this time showed a significant peak near the origin at a $0yz$ 24-fold position. However, an atom could not be in this position if the set were fully occupied, for the atom would be too close to its symmetry-related atoms. Therefore, a cadmium atom with an associated occupancy parameter was placed in this set and the least-squares refinement with anisotropic thermal parameters was continued. The fractional occupancy value became

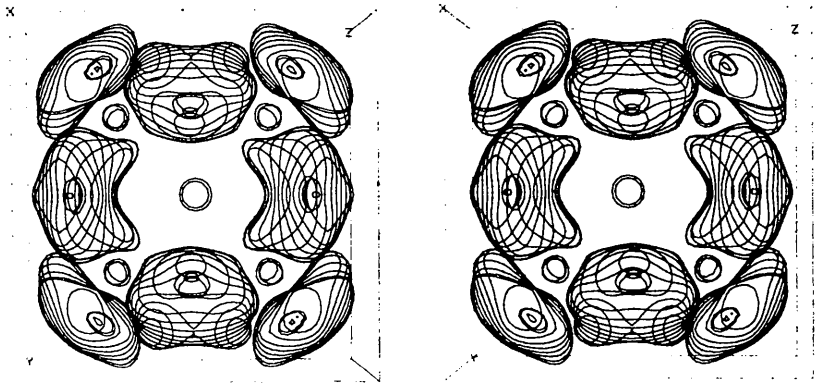


Fig. 1. Observed Fourier showing the region about the large hole at the origin. Contours are drawn for the 7 and 21 e.Å^{-3} levels

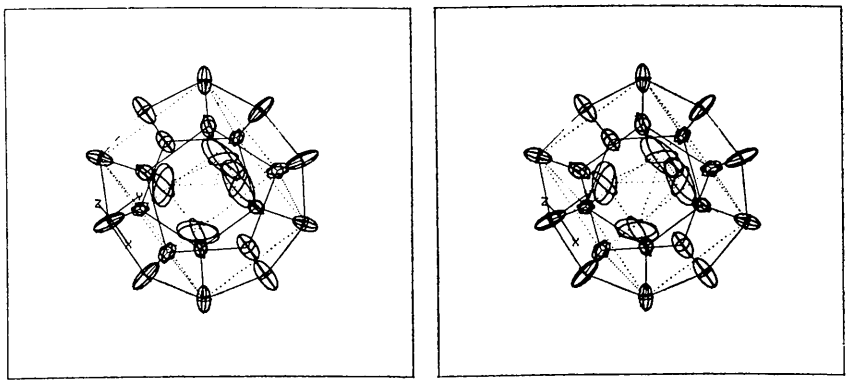


Fig. 2. Stereo drawing of the origin region. The Cd(7) atoms forming the tetrahedron about the origin are joined by dotted lines. The Cd(4) atoms which form a cube about the origin are also joined by dotted lines. The other atoms are Cd(2). In this and subsequent figures the symbols X, Y and Z are plotted at the positive ends of axial vectors to indicate the direction of view. The ellipsoids are scaled to five times the r.m.s. amplitude.

0·331 ± 0·004. With this 24-fold set $\frac{1}{3}$ occupied (within one standard deviation) the stoichiometry becomes exactly YCd_6. For this model $R=0·031$ and $R_w=0·028$. The final parameters are given in Table 1 and the observed and calculated structure factors are shown in Table 2. The calculated density is 8·196 g.cm^3.

Discussion

Graphic evidence for the fractional Cd(7) atom is shown in Fig. 1 which is a stereo observed Fourier map of the region around the origin. It is quite possible that a similar situation exists in Ru_3Be_{17} and that the compound is actually $RuBe_6$. However, it would be very difficult to detect a $\frac{1}{3}$ occupied Be set in the presence of the heavy atom Ru. A small peak at the origin can be seen in Fig. 1. Attempts to place a fractional atom at the origin were unsuccessful for the fraction went to zero and the thermal parameter became very large.

Fig. 2 is a stereo drawing showing the coordination about the origin. Eight Cd(4) and 12 Cd(2) atoms surround a tetrahedron of Cd(7) atoms. This tetrahedron is disposed in one of six possible orientations, this disorder leading to $\frac{1}{3}$ occupancy of the 24-fold Cd(7) site. Apparently, there is a rather short Cd(7)–Cd(7) distance of 2·295 Å within this tetrahedron. However, the very anisotropic thermal parameters (the three B_i's are 15·7, 1·4 and 8·0 Å^2) of this atom probably reflect a considerable positional disorder about the mean position and no two Cd atoms are actually at this short distance.

Interatomic distances are given in Table 3 and, except for the one mentioned above, are not unusual. The coordination polyhedra are as described by Sands *et al.* (1962) except that the atoms Cd(2), Cd(4) and Y have an additional Cd(7) neighbor. The polyhedra for these atoms are shown in Figs. 3 through 5.

Table 3. *Interatomic distances in* YCd(6)

Y–2Cd(1)	3·256 (1) Å	Cd(3)–Y	3·398 (1) Å
Y–2Cd(1)	3·341 (1)	Cd(3)–2Y	3·481 (1)
Y–2Cd(1)	3·353 (1)	Cd(3)–2Cd(1)	3·005 (1)
Y–Cd(2)	3·306 (1)	Cd(3)–2Cd(1)	3·070 (1)
Y–2Cd(2)	3·393 (1)	Cd(3)–Cd(3)	2·961 (2)
Y–Cd(3)	3·398 (1)	Cd(3)–Cd(5)	2·797 (1)
Y–2Cd(3)	3·481 (1)	Cd(3)–Cd(5)	2·831 (1)
Y–2Cd(4)	3·319 (1)	Cd(3)–2Cd(6)	3·165 (1)

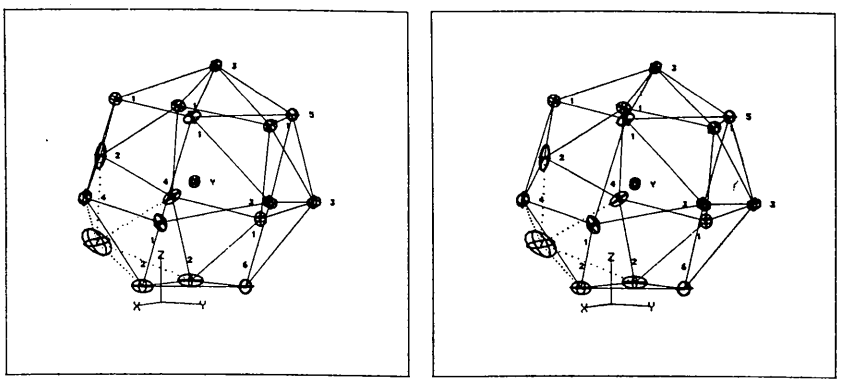


Fig. 3. Stereo drawing of the coordination about *Y*. Every crystallographic type of Cd is represented in the coordination polyhedron. The types of Cd are labeled 1–7.

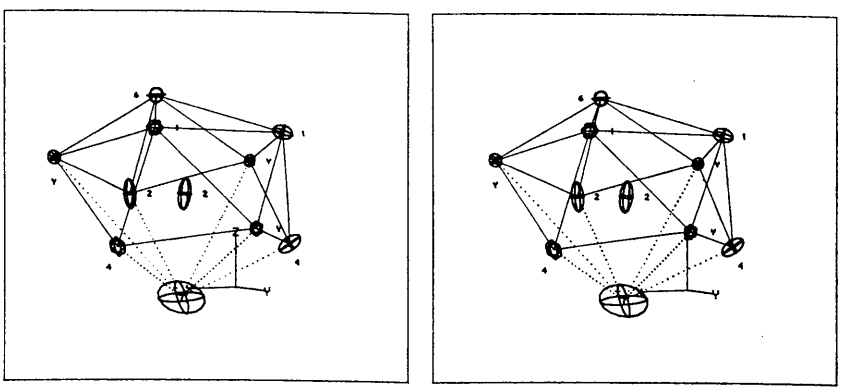


Fig. 4. Stereo drawing of the coordination about Cd(2). Details as in Figs. 2 and 3.

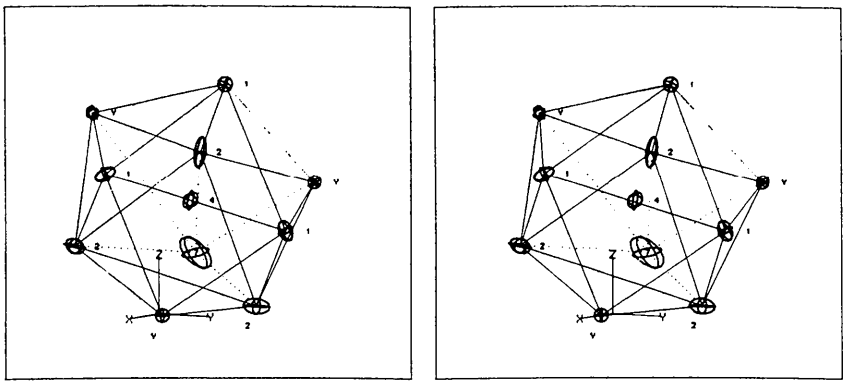


Fig. 5. Stereo drawing of the coordination about Cd(4). Details as in Figs. 2 and 3.

Table 3 (*cont.*)

Y–Cd(5)	3·614 (1)	Cd(4)–3Y	3·320 (7)
Y–Cd(6)	3·365 (1)	Cd(4)–3Cd(1)	2·922 (1)
Y–Cd(7)	3·801 (6)	Cd(4)–3Cd(2)	2·976 (1)
		Cd(4)–Cd(7)	3·074 (3)
Cd(1)–Y	3·256 (1)		
Cd(1)–Y	3·353 (1)	Cd(5)–4Cd(1)	3·079 (1)
Cd(1)–Y	3·341 (1)	Cd(5)–2Cd(3)	2·797 (1)
Cd(1)–2Cd(1)	2·948 (1)	Cd(5)–2Cd(3)	2·831 (1)
Cd(1)–Cd(2)	2·923 (1)	Cd(5)–2Cd(6)	3·288 (1)
Cd(1)–Cd(3)	3·005 (1)		
Cd(1)–Cd(3)	3·070 (1)	Cd(6)–2Y	3·365 (1)
Cd(1)–Cd(4)	2·922 (1)	Cd(6)–2Cd(2)	2·924 (2)
Cd(1)–Cd(5)	3·079 (1)	Cd(6)–4Cd(3)	3·165 (1)
		Cd(6)–2Cd(5)	3·288 (1)
Cd(2)–Y	3·306 (1)		
Cd(2)–2Y	3·393 (1)	Cd(7)–Cd(7)	2·296 (12)
Cd(2)–2Cd(1)	2·923 (1)	Cd(7)–Cd(7)	2·576 (10)
Cd(2)–Cd(2)	2·857 (2)	Cd(7)–2Cd(7)	2·985 (7)
Cd(2)–2Cd(4)	2·975 (1)		
Cd(2)–Cd(6)	2·924 (2)		
Cd(2)–Cd(7)	2·583 (6)		

We are indebted to V. O. Struebing for preparing the specimen.

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Refinement of the Crystal Structure of Tosyl-L-prolyl-L-hydroxyproline Monohydrate*

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The published X-ray diffraction data for tosyl-L-prolyl-L-hydroxyproline monohydrate have been refined by least-squares methods to an R index of 0·093. As a result, some structural parameters are markedly improved.

Introduction

This paper records briefly the refinement of the structure of tosyl-L-prolyl-L-hydroxyproline monohydrate (I) whose approximate structure was determined originally by Fridrichsons & Mathieson (1962). A straightforward refinement was thought desirable for two reasons: (*a*) interest in the accurate geometry and conformation of the proline ring, and (*b*) the nonplanarity of the peptide group in this structure. Fridrichsons & Mathieson stated that the peptide group is strictly

* Contribution No. 325 from the Centre of Advanced Study in Physics, University of Madras, Madras-25, India.