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Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71571 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1067]

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Structure of CePdAl

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Abstract

The cerium palladium aluminide, CePdAl, was found to crystallize with a hexagonal ZrNiAl-type structure, which is an ordered Fe_2P-type derivative.

Comment

The structure determination of CePdAl was carried out as part of an investigation of Ln*TX* compounds (Ln = rare-earth element, *T* = transition-metal element, *X* = B-group element). The structure of CePdAl was found to crystallize in the ZrNiAl-type structure found, for example, in CeNiAl and HoNiAl (Dwight, Mueller, Conner, Downey & Knott, 1968), CeNiGa (Yarmolyuk, Gryn & Gladyshevskii, 1979), and ScRuSi and Sc*T*Ge (*T* = Ru, Rh, Pd or Os) (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982).

The sample was synthesized by arc melting the constituent elements under purified Ar in a water-cooled copper hearth. Traces of a second phase were detectable on the Guinier powder photograph taken with Cu $K\alpha_1$ radiation. All crystals found in the crushed ingot were intergrown or twinned. The best crystal, which showed only slight twinning, was used for the data collection.

The structure consists of strongly distorted hexagonal close packing (*ABAB*) of Ce and Al atoms with all the Ce atoms in the *A* layers, all the Al atoms in the *B* layers, and with one third of the Pd atoms inserted in the *A* layers and two thirds [Pd in 2(*d*)] inserted in the *B* layers. Thus, each Pd atom in a 1(*a*) site is located at the centre of a trigonal prism of Al atoms [at a distance of 2.685 (6) Å] and has three Ce neighbours in the equatorial plane at 3.038 (2) Å. Pd in 2(*d*), on the other hand, is at the centre of a similar polyhedron formed by six Ce atoms at 3.025 (1) Å and three Al atoms at 2.859 (6) Å. The nonequivalence of the 1(*a*) and 2(*d*) sites was discussed by Rundqvist & Jellinek (1959), who predicted that ternary phases would exist with an ordered Fe_2P-type structure (their unit cell is shifted by $z = \frac{1}{2}$). The Al atom is surrounded by a tetragonal pyramid of five Pd atoms, while the Ce atom is surrounded by a tetrahedron of four Pd atoms. The structure of CePdAl is a further example which obeys the rule, demonstrated by Hovestreydt *et al.* (1982) in the

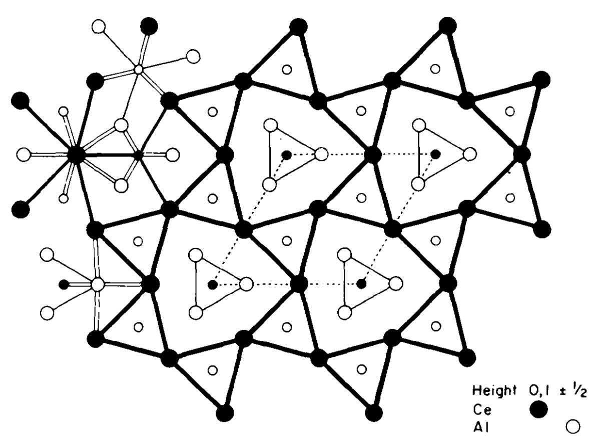

Fig. 1. The ZrNiAl-type structure of CePdAl projected onto the basal plane; the hexagonal unit cell is indicated by dashed lines, the trigonal prisms around the Pd atoms are shown in the main part and on the left-hand side the bonds are indicated for each kind of atom.

cases of HoNiAl, CeNiAl, CeNiGa and ZrRuSi, NbCrSi, *etc.* and ScRuGe, that the smallest element is always found on the prismatic site.

The observed bond lengths and angles are comparable with those of CeNiAl (Dwight *et al.*, 1968), but slightly larger since Pd is larger than Ni. Similar Al—Ce, Al—Al, Ce—Ce, Ce—Pd and Pd—Pd distances are also found in related compounds such as Ce_3Al (Havinga, 1975) and $CePd_3$ (Rossi, Ferro & Marazza, 1975).

A comparison of the d_n/d_{min} histogram for each point set was made with that given by Daams, Villars & van Vucht (1991) for the Fe_2P type. A similar *n versus* d_n/d_{min} relationship was found between Pd(*a*) and P1(*b*), Pd(*d*) and P2(*c*), Ce(*f*) and Fe2(*g*), whereas the coordination of Al(*g*) differs markedly from that of Fe3(*f*) (in the original setting).

Experimental

Crystal data

CePdAl
$M_r = 273.52$
Hexagonal
$P\bar{6}2m$
$a = 7.2198$ (7) Å
$c = 4.2329$ (7) Å
$V = 191.08$ (5) $Å^3$
$Z = 3$
$D_x = 7.130$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 3.26$-$35.03°$
$\mu = 24.63$ mm^{-1}
$T = 295$ K
Lath shaped (slight twinning)
0.10 × 0.05 × 0.02 mm
Silvery
Crystal source: arc melting

Data collection

Siemens *P*3/*PC* diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian by integration from crystal shape (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.255$, $T_{max} = 0.551$
3402 measured reflections
3351 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0993$
$\theta_{max} = 35.07°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -6 \rightarrow 6$
2 standard reflections monitored every 48 reflections, intensity variation: 1.2%

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.113$
$S = 1.857$
348 unique reflections
18 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 6.40P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 1.127$
$\Delta\rho_{max} = 5.28$ e $Å^{-3}$
$\Delta\rho_{min} = -5.12$ e $Å^{-3}$
Extinction correction: *SHELXL*92 (Sheldrick, 1992)
Extinction coefficient: 0.000 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8, 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	U_{eq}
Al	3(*g*)	0.2288 (12)	0	1/2	0.0084 (12)
Ce	3(*f*)	0.5792 (2)	0	0	0.0069 (3)
Pd	2(*d*)	1/3	2/3	1/2	0.0097 (4)
Pd	1(*a*)	0	0	0	0.0079 (5)

Table 2. *Selected geometric parameters* (Å)

Ce(*f*)—4 Pd(*d*)	3.025 (1)	Al(*g*)—2 Pd(*a*)	2.685 (6)
1 Pd(*a*)	3.038 (2)	2 Pd(*d*)	2.859 (6)
2 Al(*g*)	3.298 (7)	2 Al(*g*)	2.861 (11)
4 Al(*g*)	3.379 (2)	2 Ce(*f*)	3.298 (7)
4 Ce(*f*)	3.743 (2)	4 Ce(*f*)	3.379 (2)
Pd(*d*)—3 Al(*g*)	2.859 (6)	Pd(*a*)—6 Al(*g*)	2.685 (6)
6 Ce(*f*)	3.025 (1)	3 Ce(*f*)	3.038 (2)

The structure refinement was carried out with *SHELXL*92 (Sheldrick, 1992), leading to the structure data listed in the tables. Parallel refinement with *SHELX*76 (Sheldrick, 1976) yielded similar positional parameters but better *R* values: $R = 0.0416$ and $wR = 0.0367$ (atomic scattering factors were taken from Cromer & Mann, 1968). Instead of the usual refinement against *F*, *SHELXL*92 refines against F^2 and therefore yields larger *R* values. Both refinements were carried out by full-matrix least-squares methods. Data collection: *P*3/*PC Diffractometer Program* (Siemens, 1989). Cell refinement: *P*3/*PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991).

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(Fe,Ni)$Zn_{6.5}$, a Superstructure of γ-Brass

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Abstract

The structure of (Fe,Ni)$Zn_{6.5}$ (Pearson symbol *cF*412) is closely related to that of $Fe_{22}Zn_{78}$ [*cF*408; Koster & Schoone (1981). *Acta Cryst.* **B37**, 1905–1907]. Both structures may be considered as superstructures of γ-brass, but in the title structure the occupation of two fourfold positions that are vacant in $Fe_{22}Zn_{78}$ leads to further distortions away from the parent structure.

Comment

The binary systems Fe–Zn and Ni–Zn contain a plethora of complex phases, several being structurally related to γ-brass. To date, few of the compounds reported from these systems have been structurally characterized (Bastin, van Loo & Rieck, 1974).

In an attempt to grow crystals of suitable quality and size for an X-ray crystallographic study of the Zn-rich phases in the Fe–Zn system, Zn, in large excess, and Fe were mixed with equal portions (by volume) of ZnO to provide a porous matrix for the easier extraction of single crystals. The mixture was placed in stainless steel ampoules and sealed under Ar, heated to 1300 K in 2 h and cooled to room temperature at a rate of 30 K h^{-1}. The reaction product contained thin hexagonal plates, stacked together like a deck of playing cards. Single crystals were separated by cutting the 'deck' with a scalpel. The crystals were subjected to primary X-ray analysis (symmetry, crystal quality) using photographic methods. Microprobe analysis gave an approximate composition of $FeNiZn_{18}$, showing that the Zn had attacked the ampoule material.

The reciprocal lattice was examined meticulously for signs of further superstructure. A doubling of the unit cell along the $\langle 111 \rangle$ direction would yield a hexagonal unit cell, about 60 × 12.5 × 12.5 Å; this is a possible candidate for the structure of the phase '$FeZn_{10}$' (Bastin, van Loo & Rieck, 1974). No signs of superstructure reflections were detected, however, either by X-ray or electron diffraction.

The crystal structure of (Fe,Ni)$Zn_{6.5}$ is closely related to that of $Fe_{22}Zn_{78}$ (Koster & Schoone, 1981) and both may be considered as superstructures of γ-brass. One salient feature that all three structures have in common is a cluster built up from four slightly distorted icosahedra meeting around an empty central tetrahedron (Westman, 1972). In Fig. 1(*a*) the structure of γ-brass is shown as two identical interpenetrating f.c.c. (diamond) nets (grey–green and marine–light blue) of such clusters. Between the two nets a separating surface may be inserted. This is the infinite periodic minimal surface *D*, first described by Schwarz (1890). If one of the cluster nets that make up γ-brass is exchanged for a net consisting of truncated tetrahedra (light blue) and icosahedra (dark blue) meeting four-by-four around an octahedron, the structure of $Fe_{22}Zn_{78}$ is achieved (Fig. 1*b*). The dark blue icosahedra form pieces of the pyrochlore structure. The truncated tetrahedra (light blue) are empty and hence constitute a 16-atom f.c.c. block. In the structure of (Fe,Ni)$Zn_{6.5}$, two of the fourfold positions in the spacegroup $F\bar{4}3m$ (No. 216) are occupied. The position at the origin, which is the centre of the empty tetrahedron in one of the remaining γ-brass clusters (there are two symmetrically inequivalent γ-brass clusters in $Fe_{22}Zn_{78}$), is partially occupied (about $\frac{2}{3}$) and this leads to a split position and two different configurations around this site (*cf.* Table 1). If the origin is unoccupied, a classical γ-brass cluster results and the position of the Fe,Ni3 atom is that of Fe,Ni32. Where the origin is occupied, the cluster of icosahedra distorts to a cluster of four rhombic dodecahedra (grey, Fig. 1*c*), each missing one vertex (Fig. 2). The rhombic faces are slightly bent as can be seen in Fig. 2. This cluster constitutes a substantial b.c.c. block.

Further, in the title compound the position $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ is fully occupied and the positions at the faces of the truncated tetrahedron are forced outwards, generating a Frihauf polyhedron. This change is clearly seen in Figs. 1(*b*) and 1(*c*). The faces of the truncated tetrahedron (light blue) are planar in Fig. 1(*b*), while the corresponding faces of the Frihauf polyhedron in Fig. 1(*c*) are convex, showing only the outer positions. This Frihauf polyhedron is unusual in the sense that the vertices and the centre are occupied by

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