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The Structures of the γ-Phases in the Pd–Cd and Pt–Cd Systems

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Abstract

The primitive cubic γ-Pd_8Cd_{43} and γ-Pt_8Cd_{40} phases have structures similar to that of γ-brass-like Ni_8Cd_{40}, in that they have vacancies in the inner-tetrahedral positions. In Pt_8Cd_{40}, all Pt atoms have entered the outer-tetrahedral positions. Alloys of the approximate composition T_8Cd_{41} in both systems have body-centered cubic superstructures with lattice parameters of ~20 Å. The superstructure of Pt_8Cd_{41} can be described in terms of three different 'clusters', all similar to γ-brass clusters, although two of them have lower symmetry. Atoms are totally absent from the inner-tetrahedral position of one type of cluster, while Cd atoms occupy that position in the others. The outer-tetrahedral positions of all clusters are occupied by Pt.

In the Pd–Cd and Pt–Cd systems there exist cubic phases with ~83 at.% Cd; in both systems they are designated γ. Novotny, Stempfl & Bittner (1951) (Pd–Cd) and Novotny, Bauer, Stempfl & Bittner (1952) (Pt–Cd) have suggested that the phases have γ-brass-like structures although the composition T_5Cd_{21}, which could be expected from the Hume-Rothery rule, is outside the homogeneity range of both phases; these ranges are 80·7–83·3 at.% Cd for Pd–Cd, and 82·5–85·5 at.% Cd for Pt–Cd. The authors have reported cubic lattice parameters, a = 9·960 and a = 9·897 Å for the 82·5% Cd–Pd and 83·9% Cd–Pt alloys, respectively. In the Ni–Cd system there is a γ-brass-like phase in the same composition range. The structure of this phase, Ni_8Cd_{40}, has been determined by Ljung & Westman (1970). The cubic unit cell, a = 9·7878 Å, is primitive and contains 48 atoms, leaving the inner-tetrahedral position of one cluster vacant. The present investigation was undertaken in order to establish relationships between the γ-phases of Cd and Ni, Pd and Pt.

Experimental

The starting materials, cadmium (very pure sticks, the British Drug Houses, 99·9% Cd), palladium (wire, Koch–Light, 99·99% Pd) and platinum (dust, Johnson & Mathews, spectroscopically pure), were weighed out to match several different compositions around 83 at.% Cd. The Pd–Cd mixtures were heated together at 973 K and the Pt–Cd mixtures at 1013 K in evacuated silica capsules for 2 d. The alloys were then quenched in water, weighed and crushed. The alloys were reheated in the same manner: Pd–Cd at 733 K for 12 weeks, Pt–Cd at 933 K for 6 weeks, and then quenched in water. Subsequent weighing showed that the Pt–Cd alloys had suffered some weight loss (~0·5%) presumably due to evaporation of Cd, which has the higher vapor pressure. The observation that the metallic deposits found in the top of the capsules were soft and not brittle like the rest of the preparations supported the assumption that they consisted of only Cd. The final compositions were calculated from the weighed-in amounts of the reactants, corrected for the loss of cadmium. No chemical analyses were performed, since it has been observed in other γ-brasses, synthesized as above, that the mole fractions calculated from the weighed-in amounts differ from those derived from chemical analysis only by a few units in the third decimal place (Westman, 1972). Density measurements were performed by weighing the alloys in air and in $CHCl_3$.

Single crystals were picked from three of the samples. Subsequent comparisons between the diffraction patterns of the bulk powder materials and those of the corresponding single crystals showed that the compositions were the same. Crystal data are given in Table 1. The lattice parameters were calculated from Guinier photographs. Rotation and zero-level Weissenberg photographs were obtained from all three single crystals. Single-crystal X-ray data for $Pd_{0\cdot156}Cd_{0\cdot844}$ were collected on a Siemens automatic single-crystal diffractometer (SAED) with Mo $K\alpha$ radiation. 699 intensities were recorded in the range 5° ≤ θ ≤ 40° with the θ–2θ scan technique, and were reduced to 343 independent structure factors. 213 of these, with $\sigma(I)/I$ < 0·4, were used in the initial refinements.

The X-ray data from the single crystal of $Pt_{0\cdot168}Cd_{0\cdot832}$ were collected with Mo $K\alpha$ radiation on a Pailred linear single-crystal diffractometer controlled by an IBM 1800 computer. Intensities from 568 reflections with 5° ≤ θ ≤ 30·3° were evaluated from

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Table 1. *Crystal data*

Compound	Pd_8Cd_{43}	Pt_8Cd_{40}	Pt_8Cd_{41}
Composition	$Pd_{0\cdot156}Cd_{0\cdot844} = Pd_8Cd_{43\cdot2}$	$Pt_{0\cdot168}Cd_{0\cdot832} = Pt_8Cd_{39\cdot6}$	$Pt_{0\cdot164}Cd_{0\cdot836} = Pt_8Cd_{40\cdot8}$
Lattice parameter a (Å)	9·9415 ± 5	9·9200 ± 3	19·8042 ± 9
Measured density (Mg m^{-3})	9·62 ± 4	10·38 ± 4	10·51 ± 7
Calculated density (Mg m^{-3})	9·64	10·30	10·51
Z	1	1	8
Space group	$P\bar{4}3m$	$P\bar{4}3m$	$I\bar{4}3m$
Crystal size (μm)	50 × 50 × 30	70 × 30 × 20	100 × 20 × 20
Linear absorption coefficient μ(mm^{-1})	26·2	50·6	232·7

the Gaussian profile analysis described by Norrestam (1972). These intensities were then reduced to 149 independent structure factors.

For the compound $Pt_{0\cdot164}Cd_{0\cdot836}$, single-crystal film data were collected with an integrating Weissenberg camera using Cu $K\alpha$ radiation, and evaluated by means of an automatic SAAB film scanner–IBM 1800 computer system. A description of the program system has been published by Werner (1969). 1207 intensities were recorded and reduced to 333 independent structure factors.

A satisfactory absorption correction could only be applied on the Pd–Cd alloy data. Attempts to correct the Pt–Cd intensities for absorption did not decrease the differences between equivalent reflections.

In the structure determination the programs *MULTAN* (Germain, Main & Woolfson, 1971), *CRYM* (Duchamp, 1964) and *UPALS* were used for phase determination, Fourier calculations and least-squares calculations, respectively. Scattering factors were taken from Cromer & Mann (1968) and dispersion corrections from Cromer & Liberman (1970). The calculations were carried out on an IBM 370/165 computer.

The γ-Pd–Cd structure

Two of the Pd–Cd preparations were single phase. The alloy with the composition $Pd_{0\cdot156}Cd_{0\cdot844}$ showed a primitive cubic Guinier pattern with a lattice parameter a = 9·9415 ± 5 Å. At a somewhat lower Cd concentration, $Pd_{0\cdot167}Cd_{0\cdot833}$, the lattice parameter was a = 9·9417 ± 6 Å. This powder pattern also showed a few very weak lines which could be indexed as superstructure reflections of a body-centered cubic cell with a doubled lattice parameter: a = 19·8834 ± 8 Å. A single crystal was picked of $Pd_{0\cdot156}Cd_{0\cdot844}$ only, since the additional reflections from the other sample were too weak to be measured with the accuracy needed to solve the superstructure. The rotation and Weissenberg photographs showed no superstructure reflections, and they indicated the Laue symmetry $m3m$.

In order to obtain an independent starting model for the structure refinement, the data set was phased by direct methods in space group $P\bar{4}3m$. Only the strongest reflections, with $h + k + l = 2n$, could be phased accurately; consequently the structure model arrived at was body-centered. This model was indeed a normal γ-brass-like structure, but contained a split octahedral position: $z_{\rm OH}$ = 0·36 and 0·33. The starting model for refinement of the primitive cell was one with two identical γ-brass-like clusters, except that cluster A, centered on 0,0,0, had the smaller octahedron [$z_{{\rm OH}(A)}$ = 0·33] and cluster B, around $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, had the larger one [$z_{{\rm OH}(B)} = \frac{1}{2}$ + 0·36]. Both clusters contained Cd at all sites. A refinement of this model converged to an R value of 10·8%. The value of the temperature factor $B_{{\rm IT}(B)}$ was somewhat higher than the others: 2·7 $Å^2$ compared to 0·2–1·5 $Å^2$.

Since the composition and density indicate the presence of one Cd vacancy per unit cell, the next model chosen for refinement was one with only three of the four IT(B) sites occupied. This refinement converged to R = 10·4%. $B_{{\rm IT}(B)}$ decreased to 1·1 $Å^2$ while the rest of the parameters remained generally unaffected. In a recent investigation by Arnberg, Hovmöller & Westman (1979), it was recommended that the weak reflections should also be included in the final refinement of a structure from which data have been collected in a constant-time diffractometer experiment. In the next refinement the 130 weakest reflections with $\sigma(I)/(I) \geq 0\cdot4$ were therefore included. The R value increased to 14·4%, the standard deviations of the positional parameters decreased, albeit very slightly, and some of the atoms shifted by more than one standard deviation. $B_{{\rm IT}(A)}$ increased to 2·9 $Å^2$ while $B_{{\rm IT}(B)}$ decreased to 0·3 $Å^2$. The result clearly indicated that the structure model obtained from the strong reflections was wrong and that the vacancy should occur in cluster A instead of B. This is, moreover, a more reasonable model, since there is less space in cluster A due to the smaller octahedron. A refinement from all reflections, with the vacancy in cluster A, converged to R = 13·2%. The temperature factors of IT(A) and IT(B) were now 1·6 and 1·3 $Å^2$, respectively and the standard deviations of the positional coordinates were about 60% of those from the refinement with only the strong reflections.

Attempts were also made to refine structure models with either IT(A) or IT(B) completely empty by analogy with the Ni_8Cd_{40} structure. These refinements gave R values around 20%, and the B_{OH} of the cluster without IT atoms became very high (~ 15 Å^2). The data quality did not permit determination of the Pd sites, *i.e.* no attempts to substitute Cd for Pd at any of the sites improved the refinement results significantly. This is not surprising, considering the small difference in scattering power between Pd and Cd. A neutron diffraction experiment would certainly establish the Pd sites, but this requires more material than was available.

Table 2. *Refined structural parameters of* Pd_8Cd_{43}

Estimated standard deviations are given in parentheses in units of the last digit. Thermal parameters are in Å^2.

		Cluster A	Cluster B
		$\frac{3}{4}$ Cd	Cd
IT 4(e) xxx	x	0·1048 (9)	0·6073 (6)
Inner tetrahedron	B	1·6 (2)	1·3 (1)
		Pd	Pd
OT 4(e) xxx	x	−0·1734 (6)	0·3292 (5)
Outer tetrahedron	B	0·8 (1)	0·4 (1)
		Cd	Cd
OH 6(g) 00z	z	0·3493 (9)	
6(f) $\frac{1}{2}\frac{1}{2}z$	z		0·8556 (7)
Octahedron	B	1·5 (1)	0·7 (1)
		Cd	Cd
CO 12(i) xxz	x	0·3038 (4)	0·8076 (4)
Cubo-octahedron	z	0·0474 (6)	0·5448 (5)
	B	1·1 (1)	1·0 (1)

Table 3. *Coordination numbers of* Pd_8Cd_{43}, Pt_8Cd_{40} *and* Pt_8Cd_{41}

Cd—Cd distances <3·5 Å and Cd—Pd, Pt distances <3·1 Å have been counted. γ-Brass and Ni_8Cd_{40} are included for comparison.

	Pd_8Cd_{43}*		Pt_8Cd_{40}		Pt_8Cd_{41}*			γ-Brass	Ni_8Cd_{40}	
	A	B	A	B	A	C	B		A	B
IT1	12	12		12	12		12	12		12
IT2							12			
OT1	12	12	9	12	12	9	12	12	9	12
OT2							12			
OH1	13	13	11	13	12	8	13	13	12	13
OH2			8			10	11			
CO1	11	11	12	10	11	12	10	11	12	10
CO2						11	11			
CO3							11			

* Coordination numbers have been calculated as though all positions were completely occupied. For Pd_8Cd_{43} and Pt_8Cd_{41}, with partially vacant IT(A) sites, some of the actual CN values are slightly lower.

The positional parameters given in Table 2* and the coordination numbers in Table 3 originate from the 51 atom/cell model described above.

A calculation of the mean distance from each atom to its nearest neighbors gives the three smallest values of 2·894, 2·901 and 2·908 Å for the IT(A), OT(A) and OT(B) atoms, respectively. It is reasonable to assume that the eight smaller Pd atoms enter two of these three sites. Westman (1972) pointed out that there is a tendency in γ-brasses for the transition-metal atoms to concentrate at the OT sites. This is also the case for γ-Pt–Cd; the small difference in atomic radius between Pd and Pt, $r_{Pd} = 1 \cdot 37$ Å and $r_{Pt} = 1 \cdot 39$ Å, implies that the distribution of the transition-metal atoms is similar. The assumption that the Pd atoms occupy the OT sites leaves some rather short Cd—Cd distances in the structure. The shortest, three IT(A)—OH(A) and three IT(A)—CO(A) are 2·842 and 2·856 Å, respectively. These six short contacts occur, as could be expected, around IT(A) which is only partially occupied. There is another short contact, OH(B)—OH(B) (2·871 Å), which also occurs in the Ni_8Cd_{40} structure. This is, however, a single contact in a coordination polyhedron where the mean distance from OH(B) to the 13 neighbors is 3·059 Å.

The γ-Pt–Cd structure

The Guinier powder diffraction patterns from the Pt–Cd alloys were very similar to those from the Pd–Cd system. In the Pt–Cd system the two alloys were also single phase. One of them, with the composition $Pt_{0 \cdot 168}Cd_{0 \cdot 832}$, had a primitive cubic lattice with $a = 9 \cdot 9200 \pm 3$ Å; and the other, with the composition $Pt_{0 \cdot 164}Cd_{0 \cdot 836}$, had a body-centered cubic superstructure with $a = 19 \cdot 8042 \pm 9$ Å. The superstructure reflections were, however, stronger than those from the corresponding Pd–Cd alloy, and hence single crystals were picked for both Pt–Cd alloys. Weissenberg photographs of $Pt_{0 \cdot 164}Cd_{0 \cdot 836}$ showed observable superstructure reflections, while $Pt_{0 \cdot 168}Cd_{0 \cdot 832}$ films did not.

The structure determination of $Pt_{0 \cdot 168}Cd_{0 \cdot 832}$ followed the procedure of the γ-Pd–Cd determination. The body-centered structure model obtained by direct methods was γ-brass-like, with a high OT peak indicating Pt at this site, and two peaks at OH: one at $z = 0 \cdot 35$ and the other at $z = 0 \cdot 26$.

The starting model for refinement of the primitive cell had one γ-brass cluster, A, around 0,0,0, with the smaller octahedron [$z_{OH(A)} = 0 \cdot 26$] and an empty inner

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* Lists of structure factors for the three structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34935 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tetrahedron as in Ni_8Cd_{40}, and another cluster, *B*, around $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, containing the larger octahedron [$z_{OH(B)} =$ 0·35] and an inner tetrahedron occupied by Cd. The positional parameters of the OT and CO sites were identical in *A* and *B*, and the OT sites of both clusters were occupied by Pt.

The vacancy concentration, ~4 Cd atoms absent/cell, was calculated from the composition and the density. A refinement of the starting model converged to R = 14·4%. The thermal parameter of OH(*A*) was large (4·5 Å^2) compared to those of the other atoms, which ranged from –0·2 to 1·8 Å^2, indicating either too high an assumed occupancy or disorder at this site. A difference Fourier map revealed two peaks at the OH(*A*) site, one of them at z = 0·35 and the other at z = 0·25. This indication of disorder at the OH(*A*) site led to a model in which the OH(*A*) atoms are situated either at $z_{OH1(A)}$ = 0·25 or $z_{OH2(A)}$ = 0·35. A model with one half of the OH(*A*) atoms at OH1(*A*) and the remainder at OH2(*A*) converged to an *R* value of 12·0%. After removal of the three strongest reflections, which were found to suffer from extinction, the occupancy parameters of OH1(*A*) and OH2(*A*) were refined. This resulted in an occupancy of 3·6 ± 0·8 atoms at OH1(*A*) and 2·4 ± 0·6 atoms at OH2(*A*). The temperature factors were now not unduly scattered (0·4–2·7), and the *R* value was 10·7%. All attempts to refine structure models with atoms at the IT(*A*) site or at the origin resulted in temperature factors in the region of 10 Å^2 for these atoms. The positional parameters of the disordered structure model with the composition Pt_8Cd_{40} are given in Table 4* and the corresponding coordination numbers in Table 3.

Table 4. *Refined structural parameters of* Pt_8Cd_{40}

Estimated standard deviations are given in parentheses in units of the last digit. Thermal parameters are in Å^2.

		Cluster *A*	Cluster *B*
		Vacant	Cd
IT 4(*e*) *xxx*	*x*		0·610 (2)
Inner tetrahedron	*B*		2·7 (6)
		Pt	Pt
OT 4(*e*) *xxx*	*x*	–0·1832 (8)	0·3312 (9)
Outer tetrahedron	*B*	1·3 (3)	0·4 (2)
		0·6 Cd	Cd
OH1 6(*g*) 00*z*	*z*	0·337 (6)	
6(*f*) $\frac{1}{2}\frac{1}{2}z$	*z*		0·856 (2)
Octahedron	*B*	1·6 (8)	1·0 (3)
		0·4 Cd	
OH2 6(*g*) 00*z*	*z*	0·260 (4)	
Octahedron	*B*	2·3 (7)	
		Cd	Cd
CO 12(*i*) *xxz*	*x*	0·296 (1)	0·818 (1)
Cubo-octahedron	*z*	0·051 (1)	0·536 (2)
	B	1·0 (2)	2·3 (4)

The starting model for refinement of the $Pt_{0.164}Cd_{0.836}$ superstructure in space group $I\bar{4}3m$ was derived from the Pt_8Cd_{40} structure as follows: the cell contains sixteen clusters of which two identical ones, *A*, are centered on 0,0,0 *etc.*; six other identical clusters, *C*, are grouped around 0,$\frac{1}{2}$,$\frac{1}{2}$ *etc.*, and eight identical clusters, *B*, are centered on $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ *etc.* The *B* and *C* clusters will, of course, have lower symmetry than the ordinary γ-brass-like cluster. Clusters *A* and *C* of the superstructure will then correspond to cluster *A* of the primitive subcell, and cluster *B* of the superstructure to cluster *B* of the subcell. The model was based on the assumption that clusters *A* and *C* differ with respect to their octahedra, as was indicated by the disorder of the subcell. It was further assumed that the larger subcell octahedron, with the lowest occupancy factor, should occur in cluster *A*.

Table 5 shows the relationship between the starting structure model of $Pt_{0.164}Cd_{0.836}$ and the structure of Pt_8Cd_{40}. A refinement of this model converged to R = 17·6%. A difference Fourier map at this stage showed a peak at x,x,x, ≃ 0·05, indicating that the IT(*A*) site

Table 5. *Relationships between positional parameters in the superstructure of* γ-Pt–Cd *and the structure of* Pt_8Cd_{40}

	Site in the superstructure	
Cluster *A* centered on 2(*a*) at 0,0,0	OT 8(*c*) *x,x,x*	$x = \frac{1}{2}x_{OT(A)}$*
	OH 12(*d*) 0,0,*z*	$z = \frac{1}{2}x_{OH2(A)}$
	CO 24(*g*) *x,x,z*	$x = \frac{1}{2}x_{CO(A)}$
		$z = \frac{1}{2}z_{CO(A)}$
Cluster *C* centered on 6(*b*) at at 0,$\frac{1}{2}$,$\frac{1}{2}$	OT 24(*g*) *x,x,z*	$x = \frac{1}{2}x_{OT(A)}$
		$z = \frac{1}{2}[1 - x_{OT(A)}]$
	OH1 12(*d*) 0,0,*z*	$z = \frac{1}{2}[1 + x_{OH1(A)}]$
	OH2 24(*f*) *x*,0,$\frac{1}{2}$	$x = \frac{1}{2}x_{OH1(A)}$
	CO1 24(*g*) *x,x,z*	$x = \frac{1}{2}x_{CO(A)}$
		$z = \frac{1}{2}[1 + z_{CO(A)}]$
	CO2 48(*h*) *x,y,z*	$x = \frac{1}{2}x_{CO(A)}$
		$y = \frac{1}{2}z_{CO(A)}$
		$z = \frac{1}{2}[1 + x_{CO(A)}]$
Cluster *B* centered on 8(*c*) at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$	IT1 8(*c*) *x,x,x*	$x = \frac{1}{4} + \frac{1}{2}x_{IT(B)}$
	IT2 24(*g*) *x,x,z*	$x = \frac{1}{4} - \frac{1}{2}x_{IT(B)}$
		$z = \frac{1}{4} + \frac{1}{2}x_{IT(B)}$
	OT1 8(*c*) *x,x,x*	$x = \frac{1}{4} + \frac{1}{2}x_{OT(B)}$
	OT2 24(*g*) *x,x,z*	$x = \frac{1}{4} - \frac{1}{2}x_{OT(B)}$
		$z = \frac{1}{4} + \frac{1}{2}x_{OT(B)}$
	OH1 24(*g*) *x,x,z*	$x = \frac{1}{4}$
		$z = \frac{1}{4} + \frac{1}{2}x_{OH(B)}$
	OH2 24(*g*) *x,x,z*	$x = \frac{1}{4}$
		$z = \frac{1}{4} - \frac{1}{2}x_{OH(B)}$
	CO1 24(*g*) *x,x,z*	$x = \frac{1}{4} + \frac{1}{2}x_{CO(B)}$
		$z = \frac{1}{4} + \frac{1}{2}z_{CO(B)}$
	CO2 24(*g*) *x,x,z*	$x = \frac{1}{4} - \frac{1}{2}x_{CO(B)}$
		$z = \frac{1}{4} + \frac{1}{2}z_{CO(B)}$
	CO3 48(*h*) *x,y,z*	$x = \frac{1}{4} - \frac{1}{2}z_{CO(B)}$
		$y = \frac{1}{4} - \frac{1}{2}x_{CO(B)}$
		$z = \frac{1}{4} + \frac{1}{2}x_{CO(B)}$

* These parameters relate to the Pt_8Cd_{40} structure.

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* See deposition footnote.

Table 6. *Refined structural parameters of* Pt_8Cd_{41}

Estimated standard deviations are given in parentheses in units of the last digit. Thermal parameters are in Å^2.

Cluster *A*

IT	8(*c*)	*xxx*	0·8 Cd		
				x	0·043 (5)
				B	4 (3)
OT	8(*c*)	*xxx*	Pt		
				x	−0·0840 (5)
				B	−3·2 (2)
OH	12(*d*)	00*z*	Cd		
				z	0·178 (2)
				B	−1·0 (6)
CO	24(*g*)	*xxz*	Cd		
				x	0·151 (1)
				z	0·023 (1)
				B	−1·8 (3)

Cluster *C*

OT	24(*g*)	*xxz*	Pt		
				x	−0·0985 (6)
				z	0·4112 (8)
				B	−1·2 (3)
OH1	12(*d*)	00*z*	Cd		
				z	0·627 (2)
				B	−0·2 (7)
OH2	24(*f*)	*x*0½	Cd		
				x	0·158 (3)
				B	2·0 (7)
CO1	24(*g*)	*xxz*	Cd		
				x	0·149 (1)
				z	0·521 (1)
				B	−2·0 (3)
CO2	48(*h*)	*xyz*	Cd		
				x	0·140 (1)
				y	0·032 (1)
				z	0·642 (1)
				B	−0·4 (4)

Cluster *B*

IT1	8(*c*)	*xxx*	Cd		
				x	0·299 (1)
				B	−2·3 (6)
IT2	24(*g*)	*xxz*	Cd		
				x	0·194 (1)
				z	0·314 (2)
				B	−1·0 (5)
OT1	8(*c*)	*xxx*	Pt		
				x	0·1699 (9)
				B	−1·2 (5)
OT2	24(*g*)	*xxz*	Pt		
				x	0·3343 (7)
				z	0·164 (1)
				B	−1·6 (2)
OH1	24(*g*)	*xxz*	Cd		
				x	0·247 (1)
				z	0·428 (2)
				B	−2·2 (3)
OH2	24(*g*)	*xxz*	Cd		
				x	0·255 (1)
				z	0·069 (3)
				B	0·4 (6)
CO1	24(*g*)	*xxz*	Cd		
				x	0·411 (1)
				z	0·266 (1)
				B	−1·6 (5)
CO2	24(*g*)	*xxz*	Cd		
				x	0·096 (1)
				z	0·270 (2)
				B	−0·2 (6)
CO3	48(*h*)	*xyz*	Cd		
				x	0·229 (2)
				y	0·097 (1)
				z	0·414 (1)
				B	−0·5 (4)

should be occupied. Since the observed composition and density required a somewhat higher cell content of cadmium, the next model to be refined had the IT(*A*) site occupied by Cd. A few of the other atoms in the model were given slight initial displacements according to the difference Fourier map, and before the refinement the three strongest reflections were deleted since they were appreciably affected by extinction.

The model refined to an *R* value of 14·6%. The temperature factor of IT(*A*) was large (5·6 Å^2) compared to the others which ranged from −3·3 to 1·3 Å^2. The occupancy factor of IT(*A*) was therefore refined; it converged to 2·9 ± 0·8 atoms/IT(*A*) site. The value of $B_{\mathrm{IT}(A)}$ decreased to 4·3 Å^2 and the *R* value to 14·3%. Several attempts were made to refine models with atoms differently distributed around the origin, at the origin and at the IT(*C*) site, but they yielded temperature factors of 10 Å^2 or more for the corresponding atoms. The model with the partially occupied IT(*A*) site was thus considered to be the best one, although the large temperature factor of IT(*A*), the corresponding positional parameter of which gives Cd—Cd distances of 2·4 Å, and the large standard deviation of $x_{\mathrm{IT}(A)}$ clearly indicate disorder around the origin.

The positional parameters are given in Table 6* and the coordination numbers in Table 3. There are some rather short Cd—Cd distances in the structure, namely OH(*A*)—CO1(*B*) and IT2(*B*)—OH1(*B*) of 2·72 and 2·69 Å, respectively. These are, however, single bonds in coordination polyhedra with considerably longer mean Cd—Cd distances. The shortest Pt—Cd distances are between OT(*B*) and CO3(*B*) (2·58 Å), and OT(*B*) and CO1(*C*) (2·59 Å).

As can be seen from Table 3, the temperature factors are rather scattered [even disregarding $B_{\mathrm{IT}(A)}$] and many of them have negative values. This is probably a consequence of the lack of absorption correction. A better determination of the structure could certainly be obtained from a single crystal prepared according to the procedure described by Arnberg & Westman (1978).

Discussion of the structures

There are several similarities between the structures of γ-Ni–Cd, γ-Pd–Cd and γ-Pt–Cd, although the transition-metal distribution is not the same in γ-Ni–Cd as in γ-Pd–Cd and γ-Pt–Cd. One common feature is the presence of vacancies in the inner tetrahedron of one of the clusters. The number of atoms at this site seems to vary from zero to at least three.

The distortion of the structures in certain vacancy-concentration ranges causes cubic superstructures with doubled cell parameters. This feature has also been observed in the Ni–Cd system by Lihl & Buhl (1955), who found a γ-brass-like alloy with a = 19·545 Å at 18·5 at.% Ni. The superstructure model suggested for γ-Pt–Cd permits ideally ordered structures at the compositions T_8Cd_{41} [with IT(*A*) occupied and IT(*C*) vacant] and T_8Cd_{43} [IT(*A*) vacant and IT(*B*) occupied]. It is possible that Pd_8Cd_{43} represents the latter structure type, although the superstructure reflections were too weak to be observed.

As can be seen from Table 3, the structure most similar to γ-brass is Pd_8Cd_{43}. This is quite natural, since the number of vacancies is low (one per unit cell).

The structures of Pt_8Cd_{40} and Ni_8Cd_{40} differ with respect to the OH(*A*) atom. Four OH(*A*)—OH(*A*) contacts occur in Ni_8Cd_{40}. These are mainly Ni—Ni distances of 3·471 Å. In Pt_8Cd_{40} OH(*A*) is occupied by Cd, and the corresponding distance [OH2(*A*)—OH2(*A*)] is consequently longer (3·653 Å).

The *A* cluster of the Pt_8Cd_{41} structure can be regarded as a normal γ-brass cluster without the OH(*A*)—OH(*A*)′ contact. This distance [here OH(*A*)—OH1(*C*)] is 3·831 Å. The *C* cluster of this structure is very similar to the corresponding cluster of the subcell (Pt_8Cd_{40} cluster *A*). OH2(*C*) has, however, two contacts to CO2(*B*) which do not occur for the

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* See deposition footnote.

OH2(*A*) atom of Pt_8Cd_{40}. The *B* clusters of the two Pt–Cd structures are also very similar. The two OH(*B*)–CO(*B*) contacts are lost for one of the atoms [OH2(*B*)], reducing the CN for this atom from 13 to 11. Two of the CO(*B*) atoms in Pt_8Cd_{41} have CO(*B*)–OH(*B*) contacts which are longer (2·739 Å) in the Pt_8Cd_{40} structure.

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Structure Reinvestigation of the High-Temperature Form of K_2SO_4

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Abstract

The crystal structure of the high-temperature form of K_2SO_4 was redetermined from three-dimensional X-ray diffractometer data at 1073 K and refined to an *R* value of 0·086 for 66 observed reflexions. The structure belongs to the hexagonal space group $P6_3/mmc$, with $a = 5{\cdot}947$ (2), $c = 8{\cdot}375$ (3) Å, $Z = 2$, and $D_x = 2{\cdot}26$ Mg m^{-3}. The SO_4^{2-} tetrahedron has two orientations with one of the apices of the SO_4^{2-} tetrahedron pointing statistically in opposite directions along the *c* axis. The net entropy change, $\Delta S = 5{\cdot}02$ J mol^{-1} K^{-1} at the phase-transition point (860 K), was explained successfully by the configurational change of the SO_4^{2-} tetrahedron in the low- and high-temperature forms. The SO_4^{2-} tetrahedron is approximately undistorted with a corrected mean S–O distance of 1·43 Å. Two crystallographically independent K atoms are coordinated by 9 and 13 O atoms with mean K–O distances of 3·20 and 3·37 Å, respectively.

Introduction

Two modifications of potassium sulphate, K_2SO_4, were reported by Bredig (1942), Bernard & Hocart (1961) and Fischmeister (1962). The first-order phase transition between them occurs at 860 K. The space group and structure of the low-temperature form are well established (Robinson, 1958; McGinnety, 1972).

The space groups reported for the high-temperature form of K_2SO_4 were inconsistent. Bredig (1942) and Eysel & Hahn (1970) proposed the space groups $P\bar{3}m1$ and $P6_3mc$, respectively, from powder X-ray diffraction analyses. Iwai, Sakai & Watanabè (1973) carried out a structure analysis using a high-temperature Weissenberg technique. They concluded that the space group is $P6_3mc$, but ambiguity in the structure remains unexplored. The ferroelastic study of Shiozaki, Sawada, Ishibashi & Takagi (1977) suggests that the space group is $P6_3/mmc$.

Recently, van den Berg & Tuinstra (1978) refined the

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