ACTA CHEMICA SCANDINAVICA 24 (1970) 3471–3479

Determination of the Structure of Cubic Gamma-Pt,Zn; a Phase of Gamma Brass Type with an 18 Å Superstructure

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The gamma brass like phase with the approximate composition Pt_3Zn_{10} is face centered cubic, with a lattice parameter of ~18.11 Å. The space group is $F\bar{4}3m$. The structure may be described in terms of four different types of "cluster"; each cluster consisting of an inner tetrahedral, an outer tetrahedral, an octahedral, and a cubo-octahedral position. The octahedral position in one cluster is unoccupied. In another cluster either the inner *or* the outer tetrahedral position is unoccupied; the two versions of this cluster are statistically distributed over the structure in equal numbers. The outer tetrahedral positions in all clusters are filled with Pt and some excess Pt together with Zn distributed over the octahedral positions in the three clusters where that position is occupied.

The γ phase in the system Pt–Zn was first discovered by Ekman [1] in 1931. He published powder diffraction data from an alloy with 81.1 atomic % Zn. The structure was found to be face centered cubic with a lattice parameter of 18.116 Å. (This value is recalculated from kX units.)

No determination of an atomic ordering scheme for this phase or even of the number of atoms in the unit cell has been reported in the literature. The present investigation of γ-Pt,Zn is part of a program aimed at establishing the crystal structures of different types of gamma brass like phases.

EXPERIMENTAL

Weighed amounts of platinum (dust, Johnson & Mathews, spectroscopically pure) and zinc (granular, Mallinkrodt Analytical Reagent) were melted together in sealed evacuated silica capsules at 1000°C for one day. After the heat treatment the capsules were quenched in water, and then reheated at 700°C (*i.e.* somewhat below the peritectic decomposition temperature of the prepared phase) for three days. At the end of that period they were again quenched in water.

Density measurements were performed by weighing of alloy specimens in air and in CCl_4.

Guinier photographs were taken with $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å) and with KCl ($a = 6.2919$ Å) as an internal standard.

Photographic single crystal X-ray data were obtained from two crystals picked out from the same preparation. For some reason one of these, with a lattice parameter $a \approx 9$ Å, had apparently not reached the same degree of ordering as the other in which a superstructure with $a \approx 18$ Å was quite prominent. The data were collected with a Weissenberg camera (Cu$K\alpha$ radiation) using multiple film technique. The intensities were estimated visually by comparison with an intensity scale obtained from a similar alloy crystal (Γ-Ni,Zn). From the first crystal ~200, and from the other ~800 intensities were collected. After scaling by intercomparison of equivalent reflexions from several layer lines, 54 and 168 independent structure factors, respectively, were finally obtained from the two crystals. No absorption corrections were attempted since both crystals were quite irregular fragments with maximum diameters of ~0.04 mm. (This corresponds to a minimum transmission factor of 0.7.)

Single crystal X-ray diffractometer data were also collected with an SAED (Siemens Automatisches Einkristall-Diffraktometer) instrument from a third crystal picked out from a later preparation which yielded a sharper X-ray powder photograph. This was a quite irregular fragment, measuring approximately $0.05 \times 0.05 \times 0.06$ mm^3. 218 independent intensities ($\neq 0$) were obtained and absorption correction was carried out ($\mu = 82.36$ cm^{-1}) together with the calculation of Lp-factors.

Atomic scattering factors were taken from Cromer and Waber [2] and corrected for dispersion according to Cromer.[3] Least-squares structure refinements were carried out with the program LALS (World list [4] No. 384) on the IBM 360/75 computer at Stockholms datacentral. In the final stages, Cruickshank's weighting scheme with $w = (1500 + |F_o|)$ was employed.

RESULTS

The powder diffraction record from the investigated sample could be indexed on the basis of a face centered cubic lattice with $a = 18.1128 \pm 6$ Å. The Weissenberg diffraction data were collected from the two single crystals (with $a \approx 9$ and with $a \approx 18$ Å, respectively) picked out from that preparation.

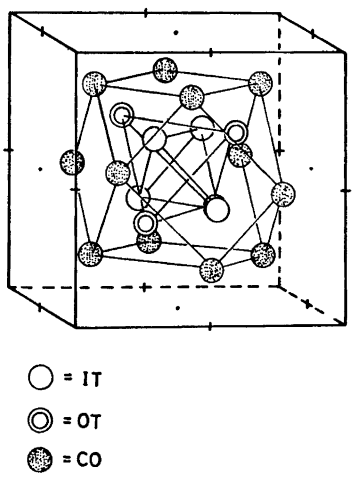

Fig. 1. Atomic sites in cluster A centered around 000. IT=inner tetrahedral(Zn), OT=outer tetrahedral(Pt), and CO=cubo-octahedral(Zn) position. The octahedral position is totally unoccupied.

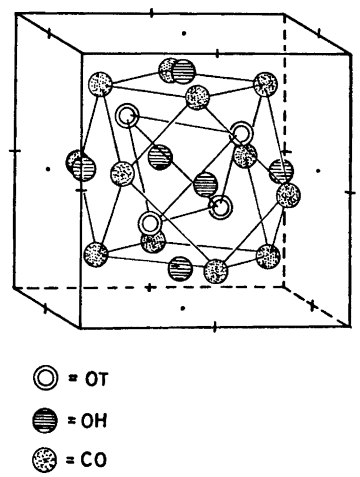

Fig. 2. Atomic sites in cluster B, centered around $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. In this figure the inner tetrahedral position is unoccupied. OT=outer tetrahedral(Pt,Zn), OH=octahedral(Pt, Zn), and CO=cubo-octahedral(Zn) position.

The first crystal yielded a rather diffuse diffraction pattern which, otherwise, appeared quite normal for a body centered cubic gamma brass type phase with $a = 9$ Å. From the second crystal, however, we obtained a sharper pattern, with superstructure reflections present. On rotation photographs of the two patterns, the positions of the substructure reflections matched one another exactly. We therefore assumed the first crystal to have the same composition as the second, but a less wellordered structure.

We started to analyze the structure with the assumption that, like other gamma brass type phases, it could be described as being built up of atomic clusters,[5] such as shown in Fig. 4.

Commencing with an attempt to construct a substructure, we first investigated a body-centered cubic model with a unit cell edge of ~9 Å (containing two clusters – one centered on 000, the other on $\frac{1}{2}\frac{1}{2}\frac{1}{2}$), and with all atoms identical (Zn). Refinements were carried out with the complete set of Weissenberg data from the 9 Å crystal, and with a set consisting of the diffractometer reflections with $h+k+l=4n$, collected from the third crystal mentioned above, with $a \approx 18$ Å.

Both refinements yielded fairly normal atomic position parameters and thermal parameters which were negative for the OT and OH positions. From this result, it could be inferred that the substructure ought to be approximately of the Pd_6Zn_{20} type,[6] with Pt and Zn distributed over the OT and OH sites. In the best substructure model obtained, the OT position was filled with Pt, and 1/3 Pt + 2/3 Zn distributed over the OH site. The composition of this model does not match exactly the weighed-in formula, ~Pt_4Zn_{22}, but is still

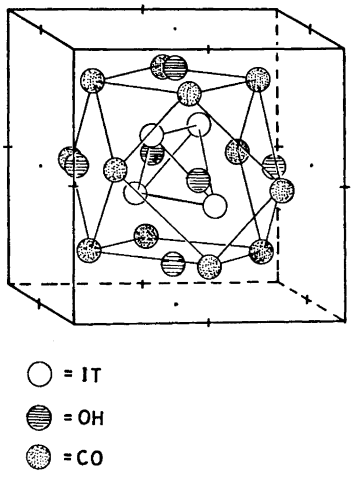

Fig. 3. Atomic sites in cluster B centered around $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. In this figure the outer tetrahedral position is unoccupied. IT = inner tetrahedral(Zn(Pt)), OH = octahedral(Pt, Zn) and CO = cubo-octahedral(Zn) position.

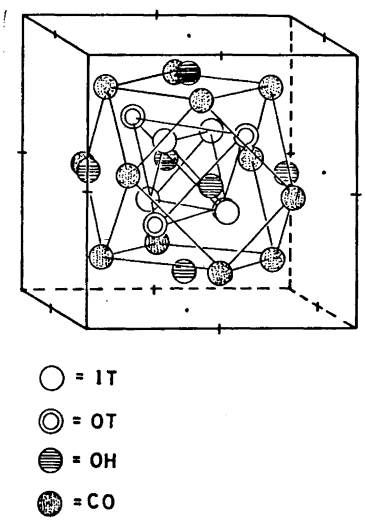

Fig. 4. Atomic sites in cluster C centered around $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, or in cluster D centered around $\frac{3}{4}\frac{3}{4}\frac{3}{4}$. IT = inner tetrahedral(Zn), OT = outer tetrahedral(Pt), OH = octahedral(in C Pt, Zn and in D Zn(Pt)), and CO = cubo-octahedral(Zn) position.

within the homogeneity range of the phase (as indicated by other alloy specimens prepared for the present investigation). At this stage, the unweighted R-value was 10 % and all temperature factors positive, although B_{IT} was still somewhat high (~3 Å^2). The 18 Å structure, then, could be assumed to be a more or less ordered version of the atomic distribution thus arrived at.

A model for the complete structure should consist of four different clusters centered around: A, 000; B, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; C, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; and D, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$; plus equivalent face centered cubic positions. If one assumes all symmetry elements (except body centering) of the 9 Å structure (space group $I\bar{4}3m$) to be retained in the complete model, it ought to have the symmetry described by space group $F\bar{4}3m$ (No. 216), with the following positions utilized:

			A	B	C	D
IT	16	(e) $x\,x\,x$	$x=$ 0.05	$x=0.55$	$x=0.30$	$x=0.80$
OT	16	(e) $x\,x\,x$	$x=-0.09$	$x=0.41$	$x=0.16$	$x=0.66$
OH	24	(f) $x\,0\,0$ (or $x\,\frac{1}{2}\,\frac{1}{2}$)	$x=$ 0.18	$x=0.68$		
	24	(g) $x\,\frac{1}{4}\,\frac{1}{4}$ (or $x\,\frac{3}{4}\,\frac{3}{4}$)			$x=0.43$	$x=0.93$
CO	48	(h) $x\,y\,y$	$x=$ 0.03	$x=0.53$	$x=0.28$	$x=0.78$
			$y=$ 0.15	$y=0.65$	$y=0.40$	$y=0.90$

(The tentative parameters in the table above are borrowed from earlier investigations [5] of gamma brass like phases. The numerical values are, of course, halved, in order to match the doubled unit cell edge.)

The distribution of atoms can be expected to be different in the four clusters. For a start, it was assumed that all OT sites contained Pt and that the OH position (which, in the substructure model was occupied by $\frac{1}{3}$ Pt + $\frac{2}{3}$ Zn) contained only Zn in cluster A, and $\frac{1}{3}$ Pt + $\frac{2}{3}$ Zn in the other clusters. That model, with the composition $Pt_{11}Zn_{41}$, has a calculated density of 11.0 g cm^{-3} compared with the measured value 10.1 ± 1 g cm^{-3}. Refinement of the model led to the following result:

The temperature factor of OH(A) increased rapidly, indicating that this position might be unoccupied. Also, the position parameter, x, of $Zn_{OH(A)}$ was shifted so that impossibly short interatomic distances were created in the model.

Next, models with the OH(A) position completely empty were refined. All these refinements yielded extremely short interatomic distances, 2.1 Å, between the IT(B) and OT(B) atoms. Furthermore, in all these attempts, either of the two thermal parameters $B_{IT(B)}$ and $B_{OT(B)}$, became too high to be acceptable. This situation could eventually be remedied by assignment of two Zn atoms to position IT(B) and two Pt atoms to OT(B). The calculated interatomic IT(B) – OT(B) distance remained very short, however. If this structural feature, *viz.* the apparent coexistence of two half-filled, mutually crowding tetrahedra in the same cluster, is interpreted in terms of a statistical distribution of equal numbers of completely filled Zn(IT) and Pt(OT) tetrahedra in different clusters, the short distances disappear from the model.

The calculated density for this model ($Pt_{10}Zn_{37}$) is 9.8 g cm^{-3}, which is lower than the measured density (10.1 ± 1 g cm^{-3}). Apparently, the structure may contain more Pt which, judging from the thermal parameters obtained

Table 1. Atomic distributions, positional and thermal parameters of the refined structure.

		$a \pm \sigma$ Å	18.1128±6 Å		
		Cluster A	Cluster B	Cluster C	Cluster D
IT	Atom	Zn	$\frac{1}{12}\frac{1}{2}$Zn+$\frac{1}{12}\frac{1}{2}$Pt [a,b]	Zn	Zn
	$x \pm \sigma$	0.0577±11	0.5506±18	0.3024±10	0.8251±17
	$B \pm \sigma$ Å²	0.2±5	0.2±9	0.5±5	3.1±9
OT	Atom	Pt	$\frac{1}{2}$Zn+$\frac{1}{2}$Pt [a,b]	Pt	Pt
	$x \pm \sigma$	−0.0896±4	0.4350±11	0.1611±4	0.6655±5
	$B \pm \sigma$ Å²	1.2±2	1.1±6	1.6±3	1.0±2
OH	Atom	vacant	$\frac{1}{3}$Zn+$\frac{2}{3}$Pt [b]	$\frac{1}{3}$Zn+$\frac{2}{3}$Pt [b]	$\frac{1}{12}\frac{1}{2}$Zn+$\frac{1}{12}$Pt [b]
	$x \pm \sigma$		0.6806±5	0.4296±6	0.9263±12
	$B \pm \sigma$ Å²		0.01±20	0.3±3	0.2±4
CO	Atom	Zn	Zn	Zn	Zn
	$x \pm \sigma$	0.0216±10	0.5204±20	0.2701±13	0.7591±10
	$y \pm \sigma$	0.1550±6	0.6499±14	0.4065±8	0.9112±6
	$B \pm \sigma$ Å²	0.5±3	0.8±6	1.8±5	−0.4±2

[a] *Either* IT(B) *or* OT(B) is occupied by the atomic distribution indicated.
[b] Note that the occupancy parameter is not exactly determined.

Table 2. X-Ray structure factors from the final model of γ-Pt,Zn. R=9.3 %.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	2	413	678	5	7	9	558	591	4	10	12	319	321	4	12	14	499	345	2	14	16	458	522
2	2	2	387	520	7	7	9	483	439	6	10	12	329	392	8	12	14	370	271	4	14	16	176	357
1	1	3	537	349	1	9	9	425	331	8	10	12	257	287	0	14	14	401	272	1	1	17	956	942
1	3	3	649	881	3	9	9	894	954	10	10	12	854	805	4	14	14	1712	1518	1	3	17	199	253
3	3	3	1823	1654	5	9	9	303	420	0	12	12	3771	3750	8	14	14	2658	2823	3	5	17	283	287
0	0	4	950	605	7	9	9	835	980	2	12	12	425	513	1	1	15	512	612	5	5	17	1165	1144
2	2	4	1765	1722	9	9	9	797	791	4	12	12	705	735	1	3	15	335	429	1	7	17	314	284
0	4	4	788	737	0	2	10	187	134	6	12	12	264	317	3	3	15	642	693	5	7	17	843	831
4	4	4	554	482	2	4	10	301	385	8	12	12	320	359	1	5	15	618	625	7	7	17	543	461
1	1	5	1450	1359	0	6	10	479	442	12	12	12	2378	2325	3	5	15	427	439	3	9	17	152	134
1	3	5	482	278	4	6	10	1085	1180	1	1	13	685	677	5	5	15	1038	1005	5	9	17	355	305
3	3	5	217	350	2	8	10	725	843	1	3	13	236	275	1	7	15	439	544	7	9	17	463	396
5	5	5	2538	2395	0	10	10	2733	2753	3	3	13	1706	1586	1	9	15	372	434	9	9	17	320	115
0	2	6	428	444	2	10	10	358	367	3	5	13	566	498	3	9	15	622	664	1	11	17	538	904
2	2	6	144	399	4	10	10	970	818	5	5	13	454	454	9	9	15	591	659	1	13	17	543	504
4	4	6	369	390	6	10	10	249	260	3	7	13	671	661	1	11	15	731	590	3	13	17	501	388
0	6	6	7887	8391	8	10	10	778	704	5	7	13	193	330	3	11	15	213	181	0	2	18	451	310
4	6	6	1017	973	1	1	11	188	194	7	7	13	1083	1094	5	11	15	508	520	2	4	18	209	333
6	6	6	149	318	1	3	11	158	180	1	9	13	780	599	7	11	15	471	465	0	6	18	2550	2475
1	1	7	441	315	1	5	11	1575	1539	3	9	13	1014	994	9	11	15	344	269	2	6	18	142	522
1	3	7	434	352	3	5	11	162	112	7	9	13	338	105	11	11	15	837	709	2	8	18	1044	1220
3	3	7	1772	1686	1	7	11	633	775	9	9	13	806	747	3	13	15	443	406	4	8	18	481	325
1	5	7	210	246	3	7	11	377	465	3	11	13	338	321	5	13	15	348	440	8	8	18	510	441
3	5	7	354	329	7	7	11	275	244	5	11	13	531	506	7	13	15	398	444	6	10	18	154	132
5	5	7	764	717	1	9	11	639	656	7	11	13	418	359	1	15	15	376	60	1	3	19	533	536
1	7	7	637	434	5	9	11	649	581	1	13	13	665	718	3	15	15	571	636	3	3	19	1132	1044
3	7	7	385	405	9	9	11	255	160	3	13	13	640	614	0	0	16	455	432	1	5	19	437	483
5	7	7	333	490	3	11	11	400	378	7	13	13	386	679	2	2	16	397	348	3	5	19	313	376
7	7	7	556	393	5	11	11	1705	1674	9	13	13	617	589	0	4	16	1910	1715	5	5	19	336	357
2	2	8	4262	4209	7	11	11	972	832	2	2	14	393	378	2	4	16	371	358	1	7	19	719	825
2	4	8	173	364	0	0	12	5524	5429	2	4	14	2514	2451	4	4	16	848	777	3	7	19	493	412
4	4	8	1865	1856	2	2	12	811	810	4	4	14	397	366	2	6	16	555	604	1	9	19	297	92
0	6	8	402	416	0	4	12	409	229	0	6	14	464	531	4	6	16	346	305	3	9	19	907	824
0	8	8	488	516	2	4	12	257	402	2	6	14	352	346	6	6	16	455	433	0	0	20	1186	1337
4	8	8	2635	2519	4	4	12	273	92	4	6	14	328	384	8	8	16	155	357	2	2	20	1960	1881
6	8	8	319	273	0	6	12	340	260	6	6	14	465	412	2	10	16	373	359	2	4	20	290	214
8	8	8	4552	4450	2	6	12	618	649	2	8	14	3052	2992	4	10	16	366	451	4	4	20	1408	1410
1	1	9	373	348	4	6	12	316	537	6	8	14	612	546	6	10	16	2010	2144	0	6	20	317	382
1	3	9	802	972	6	6	12	4370	4442	0	10	14	298	21	8	10	16	386	418	4	6	20	324	313
3	3	9	1211	1122	0	8	12	575	396	2	10	14	281	323	10	10	16	890	764	0	8	20	493	442
1	5	9	196	525	2	8	12	363	453	4	10	14	1005	1016	4	12	16	908	886	1	1	21	724	658
3	5	9	466	402	4	8	12	342	287	8	10	14	1243	1205	8	12	16	216	273	3	3	21	506	451
5	5	9	637	451	8	8	12	1062	1109	2	12	14	396	451	0	14	16	336	289	1	5	21	776	797
3	7	9	922	894	2	10	12	524	456															

in the refinement, should preferably be introduced into the OH(B) position which had a markedly negative B value.

Several attempts to determine the exact distribution of Pt and Zn over the OH positions of the B, C, and D clusters yielded inconclusive results. One of the best refined models, selected because it had the lowest R value, is described by the atomic distributions, position and thermal parameters given in Table 1. Observed and calculated structure factors for this model are listed in Table 2. The model contains 23 atomic % $Pt = Pt_3Zn_{10}$ (weighed-in composition 19.2 % Pt; preferential loss of Zn through evaporation may have occurred) and has a calculated density of 10.1 g cm^{-3} (*cf.* $d_{obs} = 10.1 \pm 1$ g cm^{-3}). $R = 9.3$ % is based on 205 out of the 218 non-zero reflections. Excluded are only 13 very weak reflections with $|F_o|/|F_c| > 2$ or $< 1/2$.

The thermal parameter $B_{IT(B)}$ tended to become negative in the refinements. An attempt to equalize the distribution of Pt and Zn over the IT(B) and OT(B) positions resulted in a somewhat lower R value ($R = 9.0$ %). However, $B_{IT(B)}$ became too high, $\sim$(5 Å^2), which seems to indicate that Zn and Pt occur preferentially as IT and OT, respectively, even though the ordering may not be complete. The final model described in Table 1 contains $\sim$10 % Pt and 90 % Zn the IT(B) position.

It should be emphasized that, although the refinement process described has produced certain final values for the occupancy of various positions, different criteria for the selection of a "best model" would yield different occupancy parameters (see, *e.g.*, Ref. 6). Thus, the results of the present investigation should be considered to be:

(a) a reasonably well established set of atomic position parameters,
(b) an idealized ordering scheme for the Zn and Pt atoms on the positions found, and
(c) an indication of where in the idealized structure Pt may to some extent substitute for Zn.

DISCUSSION

The best description of the final model derived for this Pt-Zn alloy phase may be based on the γ-Pd,Zn type structure,[6] containing ordered defects. A γ-Pd,Zn cluster consists of an OT position completely occupied by transition metal atoms, an OH position containing a disordered distribution of zinc and transition metal and, finally, IT and CO positions completely occupied by zinc.

This description accurately fits also the 18 Å Pt–Zn structure, with the additional requirement that the OH(A) position be completely unoccupied and that cluster B contain either Zn in the IT or Pt in the OT position, with the other position empty.

The ordering of "vacancies" naturally causes some displacement of the atoms from the positions they might be expected to occupy in a structure without these defects. The most remarkable displacements are observed for the Pt atoms of the OT(B) position which has shrunk to little more than IT size, and for the Zn atoms of IT(D), which has expanded so that it almost forms a regular cube together with the OT(D) position.

Table 3. Coordination, number and type of contacts, interatomic distances (Å) with standard deviations. Pt,Zn or Zn(Pt) means the distribution given in Table 1.

3	IT(A)—IT(A)	Zn—Zn 2.958±44
3	—OT(A)	—Pt 2.792±14
3	—CO(A)	—Zn 2.576±27
(1	—OT(C)	—Pt 3.242±37)
3	OT(A)—IT(A)	Pt—Zn 2.792±14
3	—CO(A)	—Zn 2.619±17
1	—IT(D)	—Zn 2.675±42
3	—CO(D)	—Zn 2.740±19
1	CO(A)—IT(A)	Zn—Zn 2.576±27
1	—OT(A)	—Pt 2.619±17
1	—OT(C)	—Pt 2.532±20
1	—OH(C)	—(Pt,Zn) 2.590±16
2	—CO(C)	—Zn 2.699±21
1	—OH(D)	—Zn(Pt) 2.983±21
2	—CO(D)	—Zn 2.803±16
3	IT(B)—IT(B)	Zn(Pt)—Zn(Pt) 2.592±92
3	—OH(B)	—(Pt,Zn) 2.688±37
3	—CO(B)	—Zn 2.601±58
(3	OT(B)—OT(B)	(Pt,Zn)—(Pt,Zn) 3.331±42)
3	—OH(B)	—(Pt,Zn) 2.675±26
3	—CO(B)	—Zn 2.668±45
3	—CO(C)	—Zn 3.074±32
2	OH(B)—IT(B)	(Pt,Zn)—Zn(Pt) 2.688±37
2	—OT(B)	—(Pt,Zn) 2.675±26
4	—CO(B)	—Zn 2.795±20
2	—CO(C)	—Zn 2.557±23
2	—CO(D)	—Zn 2.683±16
1	CO(B)—IT(B)	Zn—Zn(Pt) 2.601±58
1	—OT(B)	—(Pt,Zn) 2.668±45
2	—OH(B)	—(Pt,Zn) 2.795±20
1	—OH(C)	—(Pt,Zn) 3.047±37
2	—CO(C)	—Zn 2.720±32
1	—OT(D)	—Pt 2.659±38
1	—OH(D)	—Zn(Pt) 2.741±37
2	—CO(D)	—Zn 2.583±24
3	IT(C)—IT(C)	Zn—Zn 2.683±42
3	—OT(C)	—Pt 2.725±14
3	—OH(C)	—(Pt,Zn) 2.666±10
3	—CO(C)	—Zn 2.730±32
(1	OT(C)—IT(A)	Pt—Zn 3.242±37)
3	—CO(A)	—Zn 2.532±20
3	—IT(C)	—Zn 2.725±14
3	—OH(C)	—(Pt,Zn) 2.808±8
3	—CO(C)	—Zn 2.626±23
2	OH(C)—CO(A)	(Pt,Zn)—Zn 2.590±16
2	—CO(B)	—Zn 3.042±37
2	—IT(C)	—Zn 2.666±10
2	—OT(C)	—Pt 2.808±8
4	—CO(C)	—Zn 2.888±14
1	—OH(D)	—Zn(Pt) 2.610±25
2	CO(C)—CO(A)	Zn—Zn 2.699±21
1	—OT(B)	—(Pt,Zn) 3.074±34
1	—OH(B)	—(Pt,Zn) 2.557±23
2	—CO(B)	—Zn 2.720±32

Table 3. Continued.

1	—IT(C)	—Zn	2	OH(D)—CO(A)	Zn(Pt)—Zn
		2.730±32			2.983±21
1	—OT(C)	—Pt	2	—CO(B)	—Zn
		2.626±23			2.741±37
2	—OH(C)	—(Pt,Zn)	1	—OH(C)	—(Pt,Zn)
		2.888±14			2.610±25
(2	—CO(D)	—Zn	2	—IT(D)	—Zn
		3.346±19)			2.657±42
			2	—OT(D)	—Pt
1	IT(D)—OT(A)	Zn—Pt			2.730±14
		2.675±42	4	—CO(D)	—Zn
3	—OT(D)	—Pt			2.937±9
		2.900±31			
3	—OH(D)	—Zn(Pt)	1	CO(D)—OT(A)	Zn—Pt
		2.657±42			2.740±19
3	—CO(D)	—Zn	2	—CO(A)	—Zn
		2.508±45			2.803±16
			1	—OH(B)	—(Pt,Zn)
3	OT(D)—CO(B)	Pt—Zn			2.683±16
		2.659±38	2	—CO(B)	—Zn
3	—IT(D)	—Zn			2.583±24
		2.900±31	(2	—CO(C)	—Zn
3	—OH(D)	—Zn(Pt)			3.346±19)
		2.730±14	1	—IT(D)	—Zn
3	—CO(D)	—Zn			2.508±45
		2.595±16	1	—OT(D)	—Pt
					2.595±16
			2	—OH(D)	—Zn(Pt)
					2.937±9

It might be natural to expect this shrinkage of the outer tetrahedron of cluster B, when there is no inner tetrahedron to support it. One ought to observe, however, that the effect is not present in the gamma Ni,Cd structure [7] which also contains a cluster with the IT position unoccupied.

The expansion of the Zn tetrahedron in cluster D is more difficult to explain. In fact, as may be seen from Table 3 where interatomic distances and coordination numbers are listed, the $Zn_{IT(D)}$ atoms establish rather short contacts, 2.51±24 Å, with their $Zn_{CO(D)}$ neighbors—in fact the shortest interatomic distances in the whole structure.

This is all the more remarkable, considering the fact that $Zn_{CO(D)}$ is 10-coordinated, whereas neither the 9-coordinated $Zn_{CO(C)}$ nor the, also 9-coordinated, $Zn_{CO(A)}$ atoms form any such short contacts. The expansion does, however, establish one Zn—Pt contact (2.68 Å), between IT(D) and OT(A), which makes IT(D) 10-coordinated.

All refinements of structural models with $Zn_{IT(D)}$ displaced so as to form more normal contacts have, however, converged to the model already described.

Acknowledgements. This investigation has been carried out within a research program sponsered by the *Swedish Natural Science Research Council.*

We wish to express our sincere gratitude to Professor Arne Magnéli, for providing us with research facilities, for his continued interest in this work and for critical reading of the manuscript.

We also wish to acknowledge the technical assistance of Mrs. Gunvor Winlöf, who took the Guinier photographs.

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Received April 21, 1970.