# Crystal Structures of the High Pressure Phases ZnAs and CdAs

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The structure of the high pressure compounds ZnAs and CdAs have been determined using Guinier film and counter methods. The compounds are orthorhombic, (space group Pbca; Z = 8), with a = 5.679(2) Å, b = 7.277(4) Å, c = 7.559(4) Å and a = 5.993(4) Å, b = 7.819(6) Å, c = 8.011(6) Å respectively.

ZnAs and CdAs are isostructural with the normal pressure phases ZnSb and CdSb, which are related to the high pressure phase Si III. Structural relationships are discussed including the Si III-diamond structure relationship.

#### Introduction

The previously unknown compounds ZnAs and CdAs could be prepared by high-pressure decomposition of ZnAs<sub>2</sub> and CdAs<sub>2</sub> or by high-pressure synthesis from Me<sub>3</sub>As<sub>2</sub>-As mixtures<sup>1</sup>. In the present paper we describe the crystal structures of the new high-pressure phases.

Besides the well-characterized compounds with 1:1 stoichiometry, pressure temperature treatment of ZnAs<sub>2</sub> and CdAs<sub>2</sub> yielded further quenchable phases whose stability and exact composition are not known<sup>1</sup>. The diffraction data obtained for these phases is presented as an appendix for comparison purposes. All efforts to index this data were without success.

#### Experimental

The experimental details concerning the synthesis of the high-pressure phases have been discussed<sup>1</sup>. ZnAs could be synthesized practically without impurities, while CdAs still had fair amounts of Cd<sub>3</sub>As<sub>2</sub> and As present. However, the diffraction lines due to the impurities were not as sharp, and thus were easy to recognize and remove. The

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Requests for reprints should be sent to Dr. J. B. CLARK, National Physical Research Laboratory, C.S.I.R., P.O. Box 395, *Pretoria 0001*, South Africa, or to Prof. Dr. KLAUS-JÜRGEN RANCE, Institut für Chemie der Universität Regensburg, *D-8400 Regensburg*, Universitätsstraße 31, FRG. retained phases were fine, well-compacted powders. All efforts to grow single crystals of ZnAs and CdAs under high pressure and temperature using fluxes of  $ZnI_2$  and As were without success.

The diffraction patterns were obtained using a Huber Guinier Camera (film and counter methods) and monochromatized  $\operatorname{CuK}_{a1}$  ( $\lambda = 1,5405$  Å) radiation. The intensity data are for the areas of the peaks (counter methods) and were measured using a planimeter.

### **Structure Determination**

The powder patterns obtained for ZnAs and CdAs are listed in Tables I and II respectively. In each case the observed peaks could be readily indexed using the method of DE WOLFF<sup>2</sup>, and yielded orthorhombic cells with a = 5.679(2) Å, b = 7.277(4) Å, c = 7.559(4) Å and a = 5.993(4) Å, b = 7.819(6) Å, c = 8.011(6) Å, respectively. Systematic absences in both cases indicated that the space group is  $D_{2h}^{15}$ Pbca. From the experimentally determined density for ZnAs of 5.9 g  $\cdot$  cm<sup>-3</sup>, the unit cell must contain 16 atoms. The experimentally determined density of CdAs was less accurate due to the presence of Cd<sub>3</sub>As<sub>2</sub> and As. However, the value also indicated that 16 atoms were required in the unit cell. This structural data suggested that the compounds CdAs and ZnAs are isostructural with CdSb and ZnSb<sup>3</sup>. Using the published data for CdSb as a starting model, the structural parameters could be calculated and refined (Table III). The Iobs and Icale values are listed in Tables I and II. R-values of 0.121 and 0.137  $(R = \Sigma |I_{obs} - I_{calc}| / \Sigma I_{obs})$  were obtained for ZnAs and CdAs respectively.

Table 1. Guinier powder data for ZnAs.

Table I cont.

dobs [Å]	d <sub>calc</sub> [Å]	hkl	Tobs	Icalc	dobs [Å]	dcale [Å]	hkl	I <sub>obs</sub>	Icalc
3.852	3.852	111	0.6	0.1	1.1241	1.1236	325)	20	90
3.781	3.779	002	1.0	1.1	1.1217	1.1216	414∫	0.0	0.0
3.638	3.638	020	23.4	22.1	1.1074	1.1072	441)		
3.277	3.278	021	2.9	2.8	1 1035	∫1.1035	352		
3.145	3.146	102	15.6	19.0	1.1000	1.1034	261	93 7	97 3
2.888	2.888	112]			1.0970	1.0970	136	20.1	41.0
0 0 0 0	(2.840	200}	107.6	112.3	1.0932	1.0928	063		
4.000	2.839	121			1.0871	1.0878	502		
2.495	2.497	211	36.1	29.1	1.0687	1.0683	254	3.8	3.0
2.380	2.380	122	10.1	8.3	1.0400	£1.0497	117)	45	00
2.271	2.270	202	1.0	1.0	1.0499	11.0490	353)	4.0	0.0
2.195	2.196	113	4.0	6.7	1.0404	1.0403	236)	7.0	10.1
2.169	2.167	212]			1.0281	1.0281	434)	1.9	10.1
2.146	2.146	221	29.9	27.8	1.0229	1.0229	443)	0.0	0.0
2.140	2.139	131			1.0137	1.0133	171)	9.0	8.9
1.945	1.946	123)	10.0	51.0					
1.921	1.921	132	48.8	51.2					
1.890	1.890	004	20.4	17.2					
1.844	1.844	230	5.6	5.6	Ta	ble II. Guinie	r powder o	lata for Cd	As.
1.824	1.825	213)	01.4	20.0			L		
1.819	1.819	040	31.4	28.6	dobs [Å]	deale [Å]	hkl	Iobs	Icale
1.793	1.793	104)				Cure L - J		005	cuic
1.779	1.781	311	28.0	25.9	4.092	4.090	111	2.0	1.1
1.769	1.769	041			3.908	3.909	020	10.0	16.1
1 689	1.689	141	6.5	6.9	3.517	3.513	021	39.9	38.6
1.677	1.677	024)	0.0	0.0	3.326	3.330	102	5.6	5.3
1.673	1 673	223			3.064	3.064	112)	0.0	0.0
1.670	1.670	133	13.2	14.1	3 031	3.031	121	183.0	169 1
1.657	1.658	232			2 996	2,996	200	100.0	100.1
1.629	1.630	2021	79	60	2.000	(2.798	210)		
1.600	1.608	194	0.9	1.1	2.798	2 798	022	4.7	4.4
1.573	1.573	204	26	27	2 642	2 641	211	49.0	49 5
1.5219	1 5318	204	4.1	3.6	2.042	2.041	192	111	15.5
1.4910	1 4919	212)	7.1	0.0	0 200	2.000	113	14.3	20.5
1.4010	1.4740	042	10.6	10.1	2.020	2.020	131)	11.0	20.0
1.4747	1 4999	115)			2.291	2.250	221	58.4	66.6
1.4004	1.4020	142	1.7	2.0	2.280	2.280	122)		
1.4210	(1 4100	400)			2.070	2.009	139	50.6	53.8
1.4196	1 4199	249	0.8	0.4	2.000	2.052	1521	99 9	99.0
	(1.4190	2421			1.055	1.055	040	10.0	22.0
1.3961	1 2061	025			1.900	1.999	919	10.9	91.5
1 9094	1 2026	410	8.3	7.5	1.954	1.994	213	20.2	21.0
1.3934	1.3930	410			1.899	11.900	104	11.3	10.3
1.3883	1.0001	332)	F 1	2.0	1.010	(1.599	041	4.1	
1.3000	1.0007	120	0.1	3.9	1.810	1.010	024)	4.1	0.0
1.3378	1.3373	304	0.5	0.8	1.781	11.701	1224	26.7	22.4
1.3207	1.3199	234			1 797	(1.781	1001	14.1	10.1
1.3104	11.3100	044	17.0	10.0	1.757	1.757	321	14.1	12.1
1 9000	(1.3089	243	17.9	10.9	1.000	1.000	204	5.5	4.0
1.3020	1.3029	421			1.057	1.037	240	8.4	11.5
1.2948	1.2901	2501	9.4	9.1	1.020	1.020	042)		
1.2705	1.2705	201	3.4	3.1	1.578	1.077	043	10.0	19.0
1.2531	1.2528	225	2.0	4.3	1.508	1.507	313	10.2	13.2
1.2394	1.2392	342	0.8	0.7	1.557	1.555	3311		
1.2254	1.2254	430	2.6	3.0	1.481	11.483	025	10.0	00 7
1.2128	1.2128	060	4.8	3.2	1 4 7 1	(1.480	323	19.9	22.7
1.1975	1.1974	061		0.0	1.471	1.471	410)		
1 1903	J1.1905	026}	6.7	6.3	1.4470	1.4472	411	4.1	4.6
1.1000	(1.1900	244 J			1.4387	1.4392	1255		2.00
1 1706	<i>§</i> 1.1712	334]	in the second second		1 4145	1.4155	152	3 5	54
1.1100	(1.1711	423 }	13.9	18.0	1.1110	(1.4143	304	0.0	0.1
1.1655	1.1661	315			1 3087	<i>∫</i> 1.3989	420]		
1 1590	(1.1519	253)	1 1	5.0	1.0007	1.3989	044 }	15.9	14.6
1.1520	1.1516	206	4.4	0.0	1.3860	1.3863	250		
1.1408	1.1406	351)	10.0	0.1	1.3296	1.3288	225)	14.0	17.0
1 1999	1 1916	1691	12.0	9.1	1 2100	1 2101	2491	14.0	17.2

dobs [Å]	d <sub>calc</sub> [Å]	khl	Iobs	Icale
Server 1 - 4	(1 9869	061)		
1.2857	1.2855	116	22.1	16.8
1.2671	1.2675	244	1000	- Parter
1.2340	1.2342	315)		1.1
1.2305	1.2304	253	7.4	4.4
1 0100	(1.2135	162)		
1.2150	11.2135	145		
1 9001	(1.2073	154}	20.8	14.6
1.2001	1.2050	216		
1.1973	1.1950	260		
1.1765	1.1770	352	11.4	13.0
1.1650	1.1656	136	4.6	3.5
1.1481	1.1482	502	16.9	99 3
1.1398	1.1399	254)	10.2	44.0
1.1129	1.1127	117	8.1	6.9

strongly deformed diamond structure<sup>3</sup>. Each atom was reported to have four nearest neighbours, one being of the same kind and the other three of the second kind. This structure was related to the highpressure Si III structure<sup>4</sup>, which was seen as a less distorted form of the diamond structure.

It is important to note that the CdSb-structure type can be thought of as an arrangement of Cd-Cd/Zn-Zn and Sb-Sb/As-As pairs. This is illustrated in Fig. 1 and supported by the fact that the intermetallic distances are very short, and in certain cases slightly shorter than in the corresponding pure metals.

Fig. 1. Crystal structures of ZnAs and CdAs (The unit cell setting is that of  $1.c.^3$  for comparison purposes).

The interatomic distances and bond angles show that ZnAs, CdAs, ZnSb and CdSb cannot be described as tetrahedral compounds. Table IV confirms that the coordination number for the CdSb-structure type is not 4. On the other hand, the structural relationship to the Si III structure with a coordination number 4 for Si (Table IV) is obvious. How should these structures be described ?

KASPER and RICHARDS<sup>4</sup> discussed the Si III structure as a distorted diamond structure, but no simple mechanism of transforming the diamond structure into this distorted form was found. Another viewpoint is obtained from FISCHER<sup>5</sup> who calculated the sphere-packing conditions for certain cubic lattices. For the space group Ia3, a dense

Table III. Cry	ystallographic	data for	ZnAs and	CdAs
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the second second	ZnAs	CdAs
Crystal system Space group Structure type	$egin{array}{c} { m Orthor}\ { m D}_{2h}^{15}-{ m F}\ { m Cd} \end{array}$	hombic Pbca Sb
Axes	a = 5.679(2)  Å b = 7.277(4)  Å c = 7.559(4)  Å	a = 5.993(4) Å b = 7.819(6) Å c = 8.011(6) Å
Unit cell volume Formula units/	$V = 312.4 \text{ Å}^3$	$V = 375.4 \text{ Å}^3$
unit cell	Z = 8	Z = 8
Density (exp.)	5.9 g $\cdot$ cm <sup>-3</sup>	- 6 62 g . am=3
Occupied positions	8 Zn/Cd	l in 8(c)
æ	0.530	0.546
y	0.614	0.631
z	0.639	0.650
	8 As i	n 8(c)
x	0.141	0.141
y	0.076	0.057
z	0.100	0.098

The compositions of the high-pressure phases ZnAs and CdAs were determined previously<sup>1</sup> using synthesis experiments at high pressures in the systems  $Zn_3As_2$ -As and  $Cd_3As_2$ -As. As a check, the occupancy factors for Zn, Cd and As were varied in the structural calculations. Significantly, any variation from the 1:1 composition produced a far worse R-value for both ZnAs and CdAs.

### Discussion

ZnAs and CdAs are isostructural with ZnSb and CdSb. The cell constants of ZnAs and CdAs are slightly smaller than those of ZnSb and CdSb, as would be expected for the smaller As atom. The structure of ZnSb and CdSb has been regarded as a

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sphere packing exists with 16 atoms in the 16(c) positions with x = 0.1035, and this arrangement bears no direct relationship to the diamond structure. Si III has the 16 Si atoms in the 16(c) positions with x = 0.1003, and Table IV confirms that this arrangement is a tetrahedral structure. This agreement suggests that the Si III structure is best described as a simple dense sphere packing. The CdSb-structure type can then be viewed as a distorted form of Si III which occurs when different-sized spheres are packed into the unit cell.

A possible route for lowering the symmetry of Ia3 into the symmetry of Pbca via maximal subgroups  $^{6}$  is Ia3 $\rightarrow$ Pa3 $\rightarrow$ Pbca.

The essential step for the adaptation of the Si IIIstructure for a binary 1:1 compound is the loss of centering (Ia3 $\rightarrow$ Pa3). However, from the present work it appears that an in-between structure type with space group Pa3 is not obtained. This can be understood if one tries to pack pairs of As and Cd/Zn atoms into a cube. Using a fixed As-As distance and the Si III coordinates a cell results in which the Cd-As and Zn-As distances have a value substantially larger than that found in the present work. It appears therefore that in order to obtain this shorter distance, the orthorhombic distortion occurs.

The distortion also increases the mean coordination number for both anions and cations to a value greater than four, and this is consistent with the average valence electron concentration VEC=3.5for ZnAs and CdAs, as compared to VEC=4 for Si III.

The orthorhombic distortion occurs with little changes in the atomic parameters and axial ratios (Table V). It should be emphasized, that this relatively small distortion of a dense sphere packing with high symmetry not only allows the adaptation for different sized spheres but also results in different coordination numbers.

Table IV. Interatomic distances (Å) for Si III, ZnSb, CdSb, ZnAs and CdAs.

Si III		ZnSb		CdSb		ZnAs	Nevet and	CdAs	
Si-Si	2.31 2.39 2.39 2.39 3.44	Zn–Zn Zn–Sb Zn–Zn Sb–Sb Sb–Zn	2.592.672.692.742.853.742.822.67	Cd–Sb Cd–Cd Sb–Sb Sb–Cd	2.81 2.81 2.91 3.08 2.99 3.85 2.81 2.81	Zn–As Zn–Zn As–As As–Zn	2.47 2.49 2.61 2.62 2.70 3.30 2.47 2.47	Cd–As Cd–Cd As–As As–Cd	$\begin{array}{r} 2.56\\ 2.72\\ 2.79\\ 2.87\\ 3.21\\ 3.40\\ 2.47\\ 2.56\end{array}$
			2.69 2.74 2.85 3.82		2.81 2.91 3.08 3.98		2.49 2.61 2.62 3.53		2.72 2.79 2.87 3.68

Table V. Comparison of structural data for Si-III, a hypothetical 1:1 compound, ZnAs and CdAs.

Compound	Si-III	Hypothetical 1:1 compound	ZnAs	CdAs
Space group	la 3	Pa 3	Pbca	Pbca
Position	16 Si in 16 c with	8 Me in 8 c with	8 As in 8 c with	8 As in 8 c with
	$\begin{array}{l} x = 0.1003 \\ y = 0.1003 \\ z = 0.1003 \end{array}$	x = 0.10 y = 0.10 z = 0.10 8 X  in  8 c with	x = 0.141 y = 0.076 z = 0.100 8 Zn in 8 c with	x = 0.141 y = 0.057 z = 0.098 8 Cd in 8 c with
	$\left(+\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$	x = 0.60 y = 0.60 z = 0.60	x = 0.530 y = 0.614 z = 0.639	x = 0.546 y = 0.631 z = 0.650
Axial ratios	1.1.1	1.1.1	0.780 • 1 • 1.039	0 766 . 1 . 1 025

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Finally, it will be noticed that the pairs of atoms in ZnAs and CdAs are arranged so that the midpoints of the pairs form a NaCl-like arrangement. This simple structural description would appear to be an extension of the pyrite structure. However, this picture gives very little information regarding space-filling and coordination of the CdSb-type structure. Therefore the use of the sphere-packing model is preferable.

## Appendix

Additional quenchable phases where found above the melting curves of ZnAs and CdAs<sup>1</sup>. The powder patterns of these two phases are listed in Table VI, but could not be indexed satisfactorily. The exact composition of these phases is not known, but is expected to be ZnAs and CdAs. However, it is also possible that the diffraction data presented represents a multiple phase mixture in each case. This is supported by the fact that a partial indexing of the data is possible.

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Table VI.	Guin	ier po	wder d	ata for	· addit	ional	phases
retained	after	quene	hing f	from a	bove	the 1	nelting
	CI	irves (	of ZnAs	s and C	dAs.		

Zı	nAs	CdAs			
d <sub>obs</sub> [Å]	I [peak heights]	dobs [Å]	I [peak heights]		
7.018	8	8.905	3		
6.170	12	6.291	3		
5.651	5	4.576	3		
4.634	20	4.068	7		
4.575	8	3.697	5		
4.360	15	3.487	3		
3.918	3	3.414	10		
3.869	5	3.188	100		
3.725	72	3,146	5		
3.587	12	3.051	11		
3,439	16	2,964	33		
3 340	69	2.844	54		
3 285	12	2 810	3		
3 193	36	2.706	10		
3 130	100	2 486	19		
2 0.96	26	2.100	5		
2.047	94	2.000	2		
2 020	40	2.200	97		
3.030	49	2.222	21		
2.844	8	2.180	0		
2.822	19	2.170	3		
2.784	92	2.087	4		
2.731	42	2.059	30		
2.678	9	2.052	shoulder		
2.632	7	2.032	5		

Table VI cont.						
Zr	nAs	CdAs				
dobs [Å]	I [peak heights]	dobs [Å]	I [peak heights]			
2.606	5	1.999	40			
2.574	12	1.988	shoulder			
2.552	12	1.963	2			
2.506	3	1.957	3			
2.480	30	1.869	8			
2.454	9	1.848	5			
2.396	shoulder	1.822	mile Contendent			
2.391	9	1.811	3			
2.381	6	1.786	2			
2.357	13	1.779	6			
2.346	shoulder	1.751	1			
2.336	22	1.722	2			
2.323	13	1.707	2			
2.312	23	1.686	3			
2 300	30	1.658	3			
2.290	6	1.593	2			
2.260	10	1.529	1			
2.225	3 m 1 m 1 m 1	1.523	2			
2.209	1	1.481	2			
2.196	9	1.431	1			
2.191	8	1.410	2			
2.178	23	1.392	3			
2.172	21	1.375	2			
2.140	1	1.324	3			
2.118	9	1.302	1			
2.071	12	1.282	4			
2.055	40	1.235	2			
2.015	10	1.070	3			
1.000	12	ZnAsco	nt			
1.999	11	1 504	<i>c</i>			
1.0/2	25	1.094	0			
1 034	26	1.567	5			
1 0 9 8	20	1.507	B			
1 016	34	1.542	0			
1 903	6	1.500	7			
1 881	35	1 469	7			
1.861	74	1 462	6			
1.847	30	1.452	2			
1.836	8	1.416	3			
1.829	2	1.413	5			
1.788	17	1.373	3			
1.763	6	1.362	7			
1.754	15	1.322	7			
1.751	20	1.319	3			
1.739	12	1.304	5			
1.729	2	1.286	3			
1.711	8	1.246	6			
1.705	8	1.239	6			
1.683	8	1.214	7			
1.654	7	1.195	10			
1.637	3	1.163	7			
1.626	6	1.157	9			
1 610	3	1 140	7			

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