Crystal Structures of the High Pressure Phases ZnAs and CdAs

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Zinc Arsenide, Cadmium Arsenide, High Pressure Phases, Crystal Structures

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 $ZnAs_2$ and $CdAs_2$ or by high-pressure synthesis from Me_3As_2–As mixtures[1]. 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 $ZnAs_2$ and $CdAs_2$ yielded further quenchable phases whose stability and exact composition are not known[1]. 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[1]. ZnAs could be synthesized practically without impurities, while CdAs still had fair amounts of Cd_3As_2 and As present. However, the diffraction lines due to the impurities were not as sharp, and thus were easy to recognize and remove. The 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 $CuK_{\alpha 1}$ ($\lambda = 1{,}5405$ 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[2], 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 $g \cdot cm^{-3}$, the unit cell must contain 16 atoms. The experimentally determined density of CdAs was less accurate due to the presence of Cd_3As_2 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[3]. Using the published data for CdSb as a starting model, the structural parameters could be calculated and refined (Table III). The I_{obs} and I_{calc} 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.

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Table 1. Guinier powder data for ZnAs.

d_{obs} [Å]	d_{calc} [Å]	*hkl*	I_{obs}	I_{calc}
3.852	3.852	111	0.6	0.1
3.781	3.779	002	1.0	1.1
3.638	3.638	020	23.4	22.1
3.277	3.278	021	2.9	2.8
3.145	3.146	102	15.6	19.0
2.888	2.888	112	107.6	112.3
2.838	2.840	200		
	2.839	121		
2.495	2.497	211	36.1	29.1
2.380	2.380	122	10.1	8.3
2.271	2.270	202	1.0	1.0
2.195	2.196	113	4.0	6.7
2.169	2.167	212	29.9	27.8
2.146	2.146	221		
2.140	2.139	131		
1.945	1.946	123	48.8	51.2
1.921	1.921	132		
1.890	1.890	004	20.4	17.2
1.844	1.844	230	5.6	5.6
1.824	1.825	213	31.4	28.6
1.819	1.819	040		
1.793	1.793	104	28.0	25.9
1.779	1.781	311		
1.769	1.769	041		
1.689	1.689	141	6.5	6.9
1.677	1.677	024	13.2	14.1
1.673	1.673	223		
1.670	1.670	133		
1.657	1.658	232		
1.638	1.639	321	7.2	6.0
1.609	1.608	124	0.9	1.1
1.573	1.573	204	2.6	2.7
1.5318	1.5318	240	4.1	3.6
1.4810	1.4818	313	10.6	10.1
1.4747	1.4749	043		
1.4332	1.4323	115	1.7	2.0
1.4275	1.4276	143		
1.4196	1.4199	400	0.8	0.4
	1.4196	242		
1.3961	1.3974	323	8.3	7.5
	1.3961	025		
1.3934	1.3936	410		
1.3883	1.3881	332		
1.3553	1.3557	125	5.1	3.9
1.3378	1.3375	304	0.5	0.8
1.3207	1.3199	234	17.9	16.9
1.3104	1.3106	044		
	1.3089	243		
1.3020	1.3029	421		
1.2948	1.2951	250		
1.2765	1.2765	251	3.4	3.1
1.2531	1.2528	225	2.6	4.3
1.2394	1.2392	342	0.8	0.7
1.2254	1.2254	430	2.6	3.0
1.2128	1.2128	060	4.8	3.2
1.1975	1.1974	061	6.7	6.3
1.1903	1.1905	026		
	1.1900	244		
1.1706	1.1712	334	13.9	18.0
	1.1711	423		
1.1655	1.1661	315		
1.1520	1.1519	253	4.4	5.9
	1.1516	206		
1.1408	1.1406	351	12.0	9.1
1.1322	1.1316	162		
1.1241	1.1236	325	3.8	3.8
1.1217	1.1216	414		
1.1074	1.1072	441	23.7	27.3
1.1035	1.1035	352		
	1.1034	261		
1.0970	1.0970	136		
1.0932	1.0928	063		
1.0871	1.0878	502		
1.0687	1.0683	254	3.8	3.0
1.0499	1.0497	117	4.5	8.8
	1.0490	353		
1.0404	1.0403	236	7.9	10.1
1.0281	1.0281	434		
1.0229	1.0229	443	9.6	8.9
1.0137	1.0133	171		

Table II. Guinier powder data for CdAs.

d_{obs} [Å]	d_{calc} [Å]	*hkl*	I_{obs}	I_{calc}
4.092	4.090	111	2.0	1.1
3.908	3.909	020	10.0	16.1
3.517	3.513	021	39.9	38.6
3.326	3.330	102	5.6	5.3
3.064	3.064	112	183.0	169.1
3.031	3.031	121		
2.996	2.996	200		
2.798	2.798	210	4.7	4.4
	2.798	022		
2.642	2.641	211	49.0	49.5
2.535	2.535	122	11.1	15.5
2.328	2.329	113	14.3	20.5
2.291	2.290	131	58.4	66.6
2.280	2.280	221		
2.070	2.069	123	50.6	53.8
2.053	2.052	132		
2.002	2.003	004	22.2	22.0
1.955	1.955	040	10.9	9.2
1.932	1.932	213	23.2	21.5
1.899	1.900	104	11.3	10.3
	1.899	041		
1.810	1.810	141	4.1	5.5
1.781	1.783	024	26.7	22.4
	1.781	133		
1.737	1.737	321	14.1	12.1
1.665	1.665	204	5.5	4.6
1.637	1.637	240	8.4	11.5
1.626	1.626	322		
1.578	1.577	043	16.2	13.2
1.568	1.567	313		
1.557	1.555	331		
1.481	1.483	025	19.9	22.7
	1.480	323		
1.471	1.471	410		
1.4470	1.4472	411	4.1	4.6
1.4387	1.4392	125		
1.4145	1.4155	152	3.5	5.4
	1.4143	304		
1.3987	1.3989	420	15.9	14.6
	1.3989	044		
1.3860	1.3863	250		
1.3296	1.3288	225	14.0	17.2
1.3182	1.3191	342		

Table II cont.

d_{obs} [Å]	d_{calc} [Å]	*khl*	I_{obs}	I_{calc}
1.2857	1.2862 1.2855	061 116	22.1	16.8
1.2671	1.2675	244		
1.2340	1.2342	315	7.4	4.4
1.2305	1.2304	253		
1.2130	1.2135 1.2135	162 145	20.8	14.6
1.2061	1.2073 1.2050	154 216		
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	16.2	22.3
1.1398	1.1399	254		
1.1129	1.1127	117	8.1	6.9

Table III. Crystallographic data for ZnAs and CdAs.

	ZnAs	CdAs
Crystal system	Orthorhombic	
Space group	D_{2h}^{15}–Pbca	
Structure type	CdSb	
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	$V = 312.4$ Å^3	$V = 375.4$ Å^3
Formula units/ unit cell	$Z = 8$	$Z = 8$
Density (exp.)	5.9 g · cm^{-3}	–
Density (calc.)	5.96 g · cm^{-3}	6.63 g · cm^{-3}
Occupied positions	8 Zn/Cd in 8 (*c*)	
x	0.530	0.546
y	0.614	0.631
z	0.639	0.650
	8 As in 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[1] 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 strongly deformed diamond structure[3]. 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 high-pressure Si III structure[4], 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.

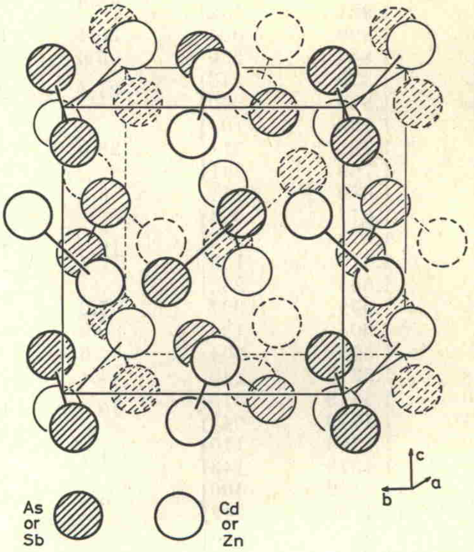

Fig. 1. Crystal structures of ZnAs and CdAs (The unit cell setting is that of l.c.[3] for comparison purposes).

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[4] 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[5] who calculated the sphere-packing conditions for certain cubic lattices. For the space group Ia3, a dense 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 → Pa3 → Pbca.

The essential step for the adaptation of the Si III-structure for a binary 1:1 compound is the loss of centering (Ia3 → 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 = 3.5 for 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		CdAs	
Si–Si	2.31	Zn–Zn	2.59	Cd–Sb	2.81	Zn–As	2.47	Cd–As	2.56
	2.39	Zn–Sb	2.67		2.81		2.49		2.72
	2.39		2.69		2.91		2.61		2.79
	2.39		2.74		3.08		2.62		2.87
	3.44		2.85	Cd–Cd	2.99	Zn–Zn	2.70	Cd–Cd	3.21
		Zn–Zn	3.74		3.85		3.30		3.40
		Sb–Sb	2.82	Sb–Sb	2.81	As–As	2.47	As–As	2.47
		Sb–Zn	2.67	Sb–Cd	2.81	As–Zn	2.47	As–Cd	2.56
			2.69		2.81		2.49		2.72
			2.74		2.91		2.61		2.79
			2.85		3.08		2.62		2.87
			3.82		3.98		3.53		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	Ia 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
	$x = 0.1003$	$x = 0.10$	$x = 0.141$	$x = 0.141$
	$y = 0.1003$	$y = 0.10$	$y = 0.076$	$y = 0.057$
	$z = 0.1003$	$z = 0.10$	$z = 0.100$	$z = 0.098$
		8 X in 8 *c* with	8 Zn in 8 *c* with	8 Cd in 8 *c* with
	$\left(+\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$	$x = 0.60$	$x = 0.530$	$x = 0.546$
		$y = 0.60$	$y = 0.614$	$y = 0.631$
		$z = 0.60$	$z = 0.639$	$z = 0.650$
Axial ratios $a:b:c$	1 : 1 : 1	1 : 1 : 1	0.780 : 1 : 1.039	0.766 : 1 : 1.025

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[1]. 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. Guinier powder data for additional phases retained after quenching from above the melting curves of ZnAs and CdAs.

ZnAs		CdAs	
d_{obs} [Å]	I [peak heights]	d_{obs} [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
3.139	100	2.486	18
3.086	36	2.395	5
3.047	84	2.286	3
3.030	49	2.222	27
2.844	8	2.180	5
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
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	1
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	1.523	2
2.209	7	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
2.146	7	1.324	3
2.118	9	1.302	7
2.071	12	1.282	4
2.055	40	1.235	2
2.013	13	1.070	3
2.007	12		
1.999	6		
1.972	44		
1.948	35		
1.934	26		
1.928	31		
1.916	34		
1.903	6		
1.881	35		
1.861	74		
1.847	30		
1.836	8		
1.829	2		
1.788	17		
1.763	6		
1.754	15		
1.751	20		
1.739	12		
1.729	2		
1.711	8		
1.705	8		
1.683	8		
1.654	7		
1.637	3		
1.626	6		
1.610	3		
1.594	6		
1.582	3		
1.557	5		
1.542	6		
1.529	8		
1.509	7		
1.469	7		
1.462	6		
1.452	2		
1.416	3		
1.413	5		
1.373	3		
1.362	7		
1.322	7		
1.319	3		
1.304	5		
1.286	3		
1.246	6		
1.239	6		
1.214	7		
1.195	10		
1.163	7		
1.157	9		
1.149	7		

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[1] J. B. CLARK and K.-J. RANGE, Z. Naturforsch. **30b**, 688 [1975].

[2] P. M. DE WOLFF, Acta Crystallogr. **17**, 752 [1964].

[3] K. E. ALMIN, Acta Chem. Scand. **2**, 400 [1948].

[4] J. S. KASPER and S. M. RICHARDS, Acta Crystallogr. **17**, 752 [1964].

[5] W. FISCHER, Z. Kristallogr. **138**, 129 [1973].

[6] J. NEUBÜSER and H. WONDRATSCHEK, Kristall u. Technik **1**, 529 [1966].