

Table I. Guinier powder data for ZnAs.

$d_{\text{obs}} [\text{\AA}]$	$d_{\text{calc}} [\text{\AA}]$	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		
2.838	{2.840 2.839}	{200 121}	107.6	112.3
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		
2.146	2.146	221	29.9	27.8
2.140	2.139	131		
1.945	1.946	123		
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
1.824	1.825	213		
1.819	1.819	040	31.4	28.6
1.793	1.793	104		
1.779	1.781	311	28.0	25.9
1.769	1.769	041		
1.689	1.689	141	6.5	6.9
1.677	1.677	024		
1.673	1.673	223	13.2	14.1
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		
1.4747	1.4749	043	10.6	10.1
1.4332	1.4323	115		
1.4275	1.4276	143	1.7	2.0
1.4196	{1.4199 1.4196}	{400 242}	0.8	0.4
1.3961	{1.3974 1.3961}	{323 025}		
1.3934	1.3936	410	8.3	7.5
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		
1.3104	{1.3106 1.3089}	{044 243}		
1.3020	1.3029	421	17.9	16.9
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		
1.1903	{1.1905 1.1900}	{026 244}	6.7	6.3
1.1706	{1.1712 1.1711}	{334 423}	13.9	18.0
1.1655	1.1661	315		
1.1520	{1.1519 1.1516}	{253 206}	4.4	5.9
1.1408	1.1406	351		
1.1322	1.1316	162	12.0	9.1

Table I cont.

$d_{\text{obs}} [\text{\AA}]$	$d_{\text{calc}} [\text{\AA}]$	hkl	I_{obs}	I_{calc}
1.1241	1.1236	325		
1.1217	1.1216	414	3.8	3.8
1.1074	1.1072	441		
1.1035	{1.1035 1.1034}	{352 261}		
1.0970	1.0970	136	23.7	27.3
1.0932	1.0928	063		
1.0871	1.0878	502		
1.0687	1.0683	254	3.8	3.0
1.0499	{1.0497 1.0490}	{117 353}	4.5	8.8
1.0404	1.0403	236		
1.0281	1.0281	434	7.9	10.1
1.0229	1.0229	443		
1.0137	1.0133	171	9.6	8.9

Table II. Guinier powder data for CdAs.

$d_{\text{obs}} [\text{\AA}]$	$d_{\text{calc}} [\text{\AA}]$	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		
3.031	3.031	121	183.0	169.1
2.996	2.996	200		
2.798	{2.798 2.798}	{210 022}	4.7	4.4
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		
2.280	2.280	221	58.4	66.6
2.070	2.069	123		
2.053	2.052	132	50.6	53.8
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 1.899}	{104 041}	11.3	10.3
1.810	1.810	141	4.1	5.5
1.781	{1.783 1.781}	{024 133}	26.7	22.4
1.737	1.737	321	14.1	12.1
1.665	1.665	204	5.5	4.6
1.637	1.637	240		
1.626	1.626	322	8.4	11.5
1.578	1.577	043		
1.568	1.567	313	16.2	13.2
1.557	1.555	331		
1.481	{1.483 1.480}	{025 323}		
1.471	1.471	410	19.9	22.7
1.4470	1.4472	411		
1.4387	1.4392	125	4.1	4.6
1.4145	{1.4155 1.4143}	{152 304}	3.5	5.4
1.3987	{1.3989 1.3989}	{420 044}		
1.3860	1.3863	250	15.9	14.6
1.3296	1.3288	225		
1.3182	1.3191	342	14.0	17.2

Table II cont.

$d_{\text{obs}} [\text{\AA}]$	$d_{\text{calc}} [\text{\AA}]$	hkl	I_{obs}	I_{calc}
1.2857	{1.2862	{061}	22.1	16.8
	1.2855	116}		
1.2671	1.2675	244}		
1.2340	1.2342	315}	7.4	4.4
1.2305	1.2304	253}		
1.2130	{1.2135	{162}	20.8	14.6
	1.2135	145}		
1.2061	{1.2073	{154}		
	1.2050	216}		
1.1973	1.1950	260}	11.4	13.0
1.1765	1.1770	352}		
1.1650	1.1656	136}		
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	$a = 5.679(2) \text{\AA}$ $b = 7.277(4) \text{\AA}$ $c = 7.559(4) \text{\AA}$ $V = 312.4 \text{\AA}^3$	$a = 5.993(4) \text{\AA}$ $b = 7.819(6) \text{\AA}$ $c = 8.011(6) \text{\AA}$ $V = 375.4 \text{\AA}^3$
Unit cell volume	$Z = 8$	$Z = 8$
Formula units/unit cell	$5.9 \text{ g} \cdot \text{cm}^{-3}$	$-$
Density (exp.)	$5.96 \text{ g} \cdot \text{cm}^{-3}$	$6.63 \text{ g} \cdot \text{cm}^{-3}$
Density (calc.)	8 Zn/Cd in 8(c)	
Occupied positions	8 As in 8(c)	
x	0.530	0.546
y	0.614	0.631
z	0.639	0.650
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 previously¹ 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 structure³. 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 structure⁴, 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.

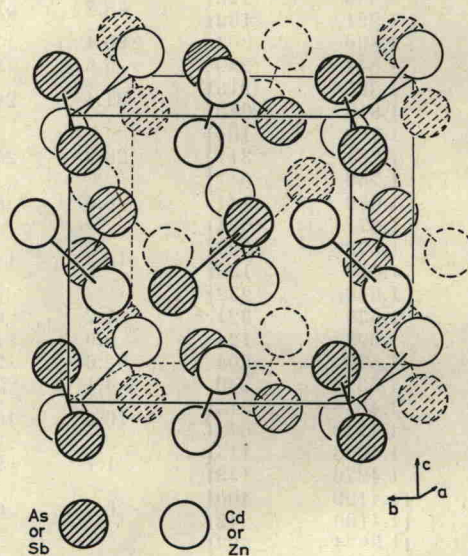


Fig. 1. Crystal structures of ZnAs and CdAs (The unit cell setting is that of I.c.³ for comparison purposes).

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 RICHARDS⁴ 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 FISCHER⁵ who calculated the sphere-packing conditions for certain cubic lattices. For the space group $Ia\bar{3}$, a dense