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		
2.838	2.840	200	107.6	112.3
	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		
2.146	2.146	221	29.9	27.8
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		
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	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		
1.3104	1.3106	044	17.9	16.9
	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		

Table I cont.

d_{obs} [Å]	d_{calc} [Å]	*hkl*	I_{obs}	I_{calc}
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	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		
	1.2135	145		
1.2061	1.2073	154	20.8	14.6
	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	16.2	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	$a = 5.993(4)$ Å
	$b = 7.277(4)$ Å	$b = 7.819(6)$ Å
	$c = 7.559(4)$ 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.

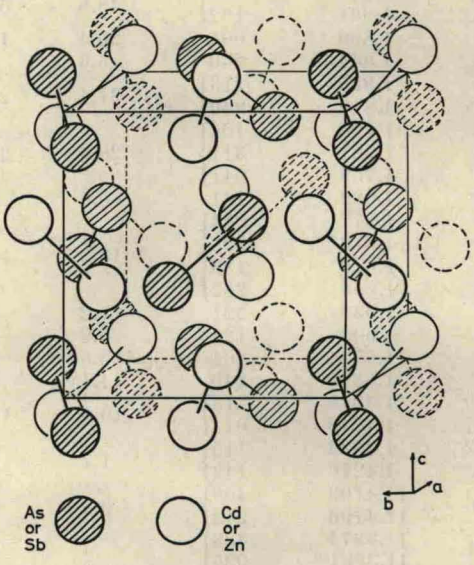

Fig. 1. Crystal structures of ZnAs and CdAs (The unit cell setting is that of l.c.[3] for comparison purposes).

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