

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<sup>6</sup> 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 $x = 0.1003$ $y = 0.1003$ $z = 0.1003$  $\left(+\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$	8 Me in 8 c with $x = 0.10$ $y = 0.10$ $z = 0.10$ 8 X in 8 c with $x = 0.60$ $y = 0.60$ $z = 0.60$	8 As in 8 c with $x = 0.141$ $y = 0.076$ $z = 0.100$ 8 Zn in 8 c with $x = 0.530$ $y = 0.614$ $z = 0.639$	8 As in 8 c with $x = 0.141$ $y = 0.057$ $z = 0.098$ 8 Cd in 8 c with $x = 0.546$ $y = 0.631$ $z = 0.650$
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 mid-points 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 were 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.

One of us (CLARK) would like to thank the Alexander von Humboldt Foundation for a fellowship, which made this investigation possible. The Fonds der Chemischen Industrie supported our research. Calculations were carried out on the TR440 of the Leibniz-Computer Centre of the Bavarian Academy of Sciences.

Table VI. Guinier powder data for additional phases retained after quenching from above the melting curves of ZnAs and CdAs.

ZnAs		CdAs	
$d_{\text{obs}}$ [Å]	I [peak heights]	$d_{\text{obs}}$ [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

Table VI cont.

ZnAs		CdAs	
$d_{\text{obs}}$ [Å]	I [peak heights]	$d_{\text{obs}}$ [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	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	ZnAs cont.	
1.972	44	1.594	6
1.948	35	1.582	3
1.934	26	1.557	5
1.928	31	1.542	6
1.916	34	1.529	8
1.903	6	1.509	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	1.149	7

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

<sup>2</sup> P. M. DE WOLFF, *Acta Crystallogr.* **17**, 752 [1964].

<sup>3</sup> K. E. ALMIN, *Acta Chem. Scand.* **2**, 400 [1948].

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

<sup>5</sup> W. FISCHER, *Z. Kristallogr.* **138**, 129 [1973].

<sup>6</sup> J. NEUBÜSER and H. WONDRAUSCHEK, *Kristall u. Technik* **1**, 529 [1966].