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ZrCuSiAs: A "Filled" PbFCl Type

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ZrCuSiAs is tetragonal, space group *P4/nmm*, $a = 3.6736$, $c = 9.5712$ Å, $Z = 2$. The structure is a "filled" PbFCl type, or it may alternatively be regarded as a tetragonally distorted $MnCu_2Al$ (Heusler) structure. HfCuSiAs is iso-structural. Bonding in PbFCl-related structures is discussed.

Introduction

In a previous paper (*1*) we discussed the crystal chemistry and valence compensation in ternary PbFCl-type chalcogenides and pnictides. These occur at compositions TMX where T is Zr, Hf, Nb, or Ta, M is Si or Ge, and X is a chalcogen (*2*) or pnicogen (*1*, *3*).

In particular, we suggested that the PbFCl structure may be regarded as cubic close-packed Pb atoms with Cl in the octahedral and F in one-half the tetrahedral voids in alternate layers. This arrangement leaves one-half the tetrahedral positions vacant. Silicon atoms in the tetrahedral position form layers perpendicular to *c* with close contacts within the layers. If we assume an intralayer valence of 2 for Si, then ZrSiS and NbSiAs may be formally regarded as $Zr^{4+}[Si]^{2-}S^{2-}$ and $Nb^{5+}[Si]^{2-}As^{3-}$, respectively. The brackets indicate intralayer bonding between Si atoms. This scheme readily rationalizes the fact that the silicochalcogenides occur with Zr, Hf, U, and Th and the silicopnictides with Nb and Ta.

Later we suspected that Nb^{5+} in NbSiAs could be valence-compensated with Zr^{4+} and another monovalent cation, e.g., Cu^{1+} which could occupy the vacant tetrahedral positions. The present paper reports the preparation and crystal structure of ZrCuSiAs and HfCuSiAs with this valence-compensated, "filled" PbFCl structure.

Experimental Procedures and Results

Sample Preparation

The elements[1] were used as starting materials. First, ZrSi and HfSi were prepared by arc melting under gettered argon on a water-cooled copper hearth. They were then crushed, ground to powder, and heated with stoichiometric amounts of As and freshly reduced Cu powder in evacuated and sealed silica tubes to 600°C over a 2-day period. The temperature was then raised to 900°C for 1 day, and the samples quenched. The products were ground, resealed in evacuated silica, and annealed at 750°C for 4 days. A final regrinding and annealing at 800°C for 4 days indicated equilibrium had been attained.

Cell Constants

Lattice parameters (Table I) were refined by a least-squares procedure from *d*-spacings recorded with a Hägg–Guinier powder diffraction camera. The photographs were read with a

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* Contribution No. 2102.

[1] Zr and Hf from ROC/RIC, Si from Texas Instruments, Cu from UMC and As from Asarco (all > 99.9% pure).

TABLE I

UNIT-CELL DIMENSIONS OF ZRCUSIAS AND HFCUSIAS[a]

	a(Å)	c(Å)	V(Å^3)	c/a
ZrCuSiAs	3.6736(2)	9.5712(9)	129.17(2)	2.605
HfCuSiAs	3.634(1)	9.601(1)	126.8(1)	2.642

[a] Standard deviation in last place are given in parentheses.

David–Mann film reader and calibrated internally with KCl($a = 6.2931$ Å).

Crystal Structure Refinement

The X-ray powder pattern of ZrCuSiAs showed similarity with the pattern of NbSiAs and was readily indexed with a corresponding tetragonal cell (Table I). The a axis of ZrCuSiAs is similar to that of NbSiAs while the c axis is longer by more than 1.6 Å. The similarity of the X-ray pattern and the correspondence in unit cell dimensions suggested that ZrCuSiAs indeed has the expected "filled" NbSiAs structure with Cu atoms filling the tetrahedral voids as discussed above.

The only observed systematic absences were hko reflections, which are missing if $h + k = 2n$. This leads to space groups $P4/n - C_{4h}^3$ and $P4/nmm - D_{4h}^7$ which offer identical positions for 2 formula units per cell. Therefore, the higher symmetry space group $P4/nmm - D_{4h}^7$ is the correct one.

The structure was refined from powder diffractometer data. They were recorded from 400-mesh powder with Cu$K\alpha$ radiation. Intensities were obtained by measuring the area under the peaks. Data from 2 different scans for different samples were scaled and averaged. A least-squares program which accounts for overlapping peaks (*4*) was used. Scattering factors for neutral atoms were taken from Cromer and Waber (*5*), corrected for anomalous dispersion (*6*). Initially 2 positional parameters, one overall thermal parameter, and the scale factor were refined. The resulting R value ($\sum|I_o - I_c|/I_o$) was 7.7% for 58 reflections. When occupancies were also refined, R decreased to 6.5%. Although the deviations from full occupancies are hardly significant, they are included in the list of final parameters (Table II). The evaluation of the Hägg–Guinier powder pattern and calculated and observed intensities of the diffractometer scans are shown in Table III.

TABLE II

STRUCTURAL DATA FOR ZRCUSIAS[a, b]

Atom	Position	x	y	z	Occupancy
Zr	2c	1/4	1/4	0.2246 ± 0.0006	1
Cu	2b	1/4	3/4	1/2	1.02 ± 0.03
Si	2a	1/4	3/4	0	1.08 ± 0.06
As	2c	1/4	1/4	0.6793 ± 0.0008	0.97 ± 0.02

[a] Space group $P4/nmm - D_{4h}^7$ $Z = 2$.

[b] Overall thermal parameter B = 0.6 ± 0.1 Å^2.

Discussion of the ZrCuSiAs Structure

ZrCuSiAs represents a new structural type. As was emphasized in the introduction, the structure was predicted and derived from PbFCl-type NbSiAs. Both structural types can be regarded as filled γ-TiCu (B11) type structures. In the PbFCl structure half the tetrahedral voids are filled; in ZrCuSiAs all are filled. TiCu is a tetragonally distorted NaCl structure. By filling half the tetrahedral voids in NaCl, the MgAgAs (ordered CaF_2) type structure is obtained; by filling all tetrahedral voids, one obtains the $MnCu_2Al$ (Heusler) structure. These relationships among the 6 structural types are emphasized in Fig. 1. The examples given for each type were chosen to illustrate chemical relationships as well. The B11 structure was originally described for more ionic compounds such as PbO and ZrS. Later, however, they turned out to have different structures or were really ternary compounds. Thus, the only representatives of the B11 structure are intermetallic phases.

Although the ZrCuSiAs structure was not observed before, the possibility of filling the tetrahedral position in the PbFCl-type structure was considered for the excess Li in $Li_{1.1}FeAs$ (*7*). Because of the small scattering

TABLE III

Calculated and Observed Intensities for ZrCuSiAs[a]

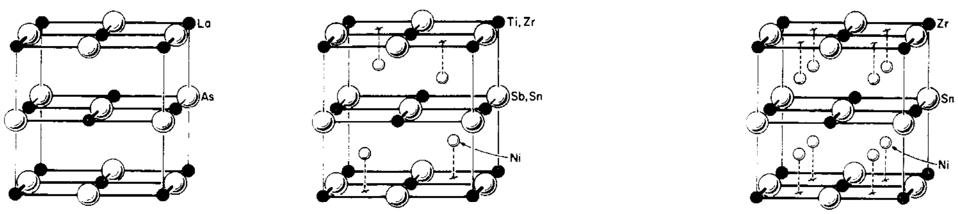
h k l	d_c	d_o	I_c	I_o
0 0 1	9.5712	9.5630	338	360
0 0 2	4.7856	4.7840	40	43
1 0 1	3.4297	3.4294	37	33
0 0 3	3.1904	—	<1	1
1 0 2	2.9140	2.9137	227	253
1 1 0	2.5976	2.5977	63	55
1 1 1	2.5069	—	7	9
1 0 3	2.4088	2.4086	91	223
0 0 4	2.3928	2.3932	131	
1 1 2	2.2830	2.2831	987	1000
1 1 3	2.0144	2.0137	47	258
1 0 4	2.0050	2.0053	197	
0 0 5	1.9142	—	2	5
2 0 0	1.8368	1.8371	312	282
2 0 1	1.8039	1.8045	21	26
1 1 4	1.7599	1.7596	10	10
2 0 2	1.7148	1.7133	11	14
1 0 5	1.6976	1.6977	82	86
2 1 1	1.6192	1.6186	8	8
0 0 6	1.5952	1.5951	16	18
2 0 3	1.5918	—	<1	
2 1 2	1.5539	1.5540	75	75
1 1 5	1.5410	—	8	11
1 0 6	1.4632	1.4633	49	186
2 1 3	1.4606	1.4605	34	
2 0 4	1.4570	1.4573	94	
0 0 7	1.3673	—	10	10
1 1 6	1.3593	—	21	135
2 1 4	1.3544	1.3544	98	
2 0 5	1.3253	—	1	2
2 2 0	1.2988	1.2988	87	91
2 2 1	1.2870	*	5	8
1 0 7	1.2814	*	32	36
2 2 2	1.2535	*	4	6
2 1 5	1.2467	*	54	54
3 0 1	1.2146	*	1	2
1 1 7	1.2099	*	6	29
2 0 6	1.2044	*	21	
2 2 3	1.2030	*	<1	
0 0 8	1.1964	*	1	2
3 0 2	1.1863	*	14	18
3 1 0	1.1617	*	10	16
3 1 1	1.1532	*	<1	2
2 1 6	1.1445	*	41	92
3 0 3	1.1432	*	7	
2 2 4	1.1415	*	38	
1 0 8	1.1376	*	6	
3 1 2	1.1289	*	165	153
2 0 7	1.0968	*	17	18
3 1 3	1.0916	*	8	50
3 0 4	1.0901	*	24	
1 1 8	1.0867	*	24	
2 2 5	1.0748	*	<1	2
0 0 9	1.0635	*	5	7
2 1 7	1.0510	*	34	33
3 1 4	1.0450	*	2	3
3 0 5	1.0315	*	15	11
1 0 9	1.0215	*	4	2
3 2 1	1.0131	*	2	2
2 2 6	1.0072	*	12	11
2 0 8	1.0025	*	3	2
3 2 2	.9965	*	17	15
3 1 5	.9931	*	3	2
1 1 9	.9842	*	34	29
3 0 6	.9713	*	14	33
3 2 3	.9706	*	10	
2 1 8	.9671	*	9	
0 0 10	.9571	*	3	2
2 2 7	.9417	*	13	60
3 1 6	.9391	*	14	
3 2 4	.9374	*	36	
1 0 10	.9262	*	1	2
2 0 9	.9203	*	18	64
4 0 0	.9184	*	36	
4 0 1	.9142	*	2	17
3 0 7	.9122	*	14	
4 0 2	.9019	*	3	39
3 2 5	.8994	*	27	
1 1 10	.8991	*	5	

[a] Intensities were obtained from powder diffractometer scans; d-spacings (Å) from Hägg–Guinier data. Cu$K\alpha$ radiation.

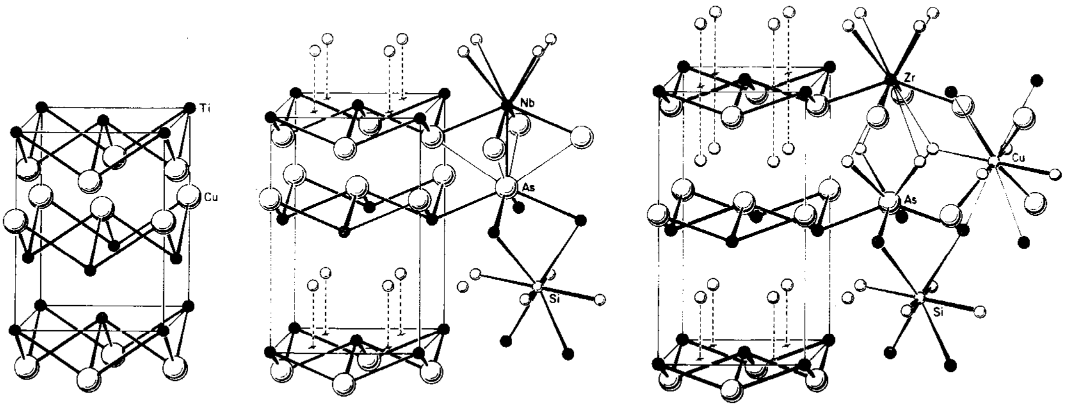
* Data not on Hägg–Guinier film.

power of Li, however, the occupancy of this site by 0.1 Li atoms is difficult to prove.

Near neighbor coordinations of ZrCuSiAs are shown in Fig. 1 and interatomic distances are listed in Table IV. It is interesting to compare the coordinations of the Cu and Si atoms. Both are of similar size and on equivalent crystallographic sites. The anion environment of the Cu atoms corresponds to the cation environment of the Si atoms. Nevertheless, bonding for Cu is more delocalized than for



LaAs (NaCl type) TiNiSb, ZrNiSn (MgAgAs type) $ZrNi_2Sn$ ($MnCu_2Al$ type)



TiCu (B11 type) NbSiAs (PbFCl type) ZrCuSiAs

FIG. 1. Crystal structure and near neighbour environment of ZrCuSiAs as compared to the structures of related compounds. The unit cells outlined for ZrCuSiAs, NbSiAs, and TiCu are twice as large as the ones normally given for these structures in order to emphasize the correspondence with the related cubic compounds.

TABLE IV

INTERATOMIC DISTANCES (Å) IN ZRCUSIAS[a]

Zr:	4 As	2.755	Cu:	4 As	2.514
	4 Si	2.827		4 Cu	2.598
	4 Cu	3.213		4 Zr	3.213
	4 Zr	3.674		4 Cu	3.674
Si:	4 Si	2.598	As:	4 Cu	2.514
	4 Zr	2.827		4 Zr	2.755
	4 As	3.577		4 Si	3.577
	4 Si	3.674		4 As	3.674

[a] All distances shorter than 4 Å are listed. Standard deviations are all 0.01 Å or less.

Si. The 12 nearest neighbors of Cu form an imperfect icosahedron, whereas the environment of the Si atoms is more irregular and the coordination better described as eightfold. The 4 Zr atoms closest to Si form a tetrahedron stretched along one twofold axis. This suggests some sp^3 character in the bonding of Si, although the population of these orbitals is probably less than unity since the interaction with the 4 close Si neighbors is certainly also bonding and only little participation of Si *d* orbitals is expected.

Bonding in PbFCl-Related Phases

Phases with PbFCl-related structures differ widely in both bonding and stoichiometry. To facilitate discussion we classify them broadly into normal valence compounds and ionic–covalent compounds.

Normal Valence Compounds

These occur at both compositions MXX′ and MM′X, where M and M′ are cations and X and X′ are anions. With rare exceptions (e.g., BiOF), the PbFCl structure is formed only with phases for which the radius ratio, $r(X)/r(X')$ or $r(M)/r(M')$ differs appreciably from one. The smaller ion occupies the tetrahedral $2a$ position, e.g., in PbFCl and BaMgSi, this position is occupied by F^{-1} and Mg^{2+}, respectively. These layer atoms do not bond with each other in these phases; this is presumably why the empirical criterion $r(X)/r(X')$ or $r(M)/r(M') > 1$ is important. Binaries cannot satisfy this condition; hence, the PbFCl structure would not be expected and has never been observed for binary compounds with normal valences.

Ionic–Covalent Compounds

Bonding in these phases is much less straightforward than in the more ionic phases discussed above; we therefore further divide these into 2 classes: metalloid-rich and metal-rich compounds.

Metalloid-rich compounds. The PbFCl structure is found for both binaries and ternaries when the electronegativity difference between metal and metalloid is small. Binary rare earth dichalcogenides and actinide dipnictides adopt the PbFCl structure. Examples are $LaTe_2$ and UP_2 (*8*). In these Te and P occupy both positions $2a$ and $2c$. If normal valences are assumed for La(III) and U(IV), then Te and P in the $2a$ position have formal oxidation number of −1. The lower oxidation number for these layer atoms is reasonable in view of the short Te–Te and P–P distances within the layers.

Large numbers of ternary metalloid-rich phases also adopt the PbFCl structure. Examples are ZrSiS, NbSiAs, USiS, LaAsSe, and UPS. As for the binary chalcogenides and pnictides, the atoms in the $2a$ layers form metalloid–metalloid bonds. The bond-order changes from group VI to IV. In $LaTe_2$, $2a$ Te forms 4 bonds of order 0.25; in UPS and LaAsSe the pnicogen forms 4 bonds of order 0.25 or 0.5; while Si in ZrSiS and NbSiAs also form 4 bonds of order 0.5.

Metal-rich compounds. For metal-rich metalloid compounds of transition metals, bonding is very poorly understood. In view of the systematics developed so far, we may speculate as to the electronic configurations of the atoms in metal-rich phases with the anti PbFCl or Cu_2Sb structure. We consider both binary and ternary phases.

Several binary arsenides and antimonides have the Cu_2Sb structure. Examples are Cu_2Sb and Cr_2As. In these the metal atoms occupy $2c$ and $2a$ sites. Magnetic properties of Cr_2As are consistent with the formulation $Cr^{2+}Cr^{1+}As^{3-}$ with the Cr^{1+} atoms occupying the tetrahedral layer sites (*9*). In these metallic phases the atoms in the tetrahedral layers undoubtedly form metal–metal bonds via the *d*-orbitals.

Several ternary metal-rich phases also have the anti-PbFCl structure. Among these are LnFeSi (*10*), MnAlGe (*11*) and ordered ternary phases based on the binary pnictides. In these Fe or Mn occupies the tetrahedral layer site with short interatomic distances suggestive of metal–metal bonding. MnAlGe is ferromagnetic with a moment of $<2\ \mu_B$, consistent with a somewhat delocalized low-spin, tetrahedral Mn^{1+}. Even these metallic phases may therefore be rationalized as formally $Ln^{3+}Fe^{1+}Si^{4-}$ and $Mn^{1+}Al^{3+}Ge^{4-}$, where the *d*-bands of the transition metal are sufficiently broadened by metal–metal and metal–metalloid interactions to give rise to metallic conductivity and a reduced effective magnetic moment.

Conclusion

Most PbFCl-related compounds can be usefully discussed in terms of formal valences, if intralayer bonding is assumed for the tetrahedral layer atoms in the covalent phases. The usefulness of this concept in combination with structural considerations is indicated by the successful prediction of the new compound ZrCuSiAs and its structure.

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