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# PbFCl-type Pnictides of Niobium with Silicon or Germanium

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NbSiAs, NbGeAs, NbSiSb, and NbGeSb have been prepared with the tetragonal PbFCl structure. A powder refinement of the structure of NbSiAs shows Nb in 2c ($z = 0.256$), Si in 2a, and As in 2c ($z = 0.612$) of space group *P4/nmm*.

If atoms in the 2a position are assumed to form anion–anion bonds, the compositions for which PbFCl-type pnictides and chalcogenides exist can be rationalized.

## Introduction

Since the discovery of PbFCl-type ZrSiS by Jellinek and Hahn (*1*), several isotypic ternary chalcogenides have been reported (*2–9*). They usually occur at equiatomic compositions, TMX. In this formula X is the chalcogen. When T is Zr, Hf, U, or Th, M is Si, Ge, or Sn. When T is a rare earth, M is P, As, Sb, or Bi. Haneveld (*10*) has given a survey of these compounds.

We report here cell constants for the analogous new compounds NbSiAs, NbGeAs, NbSiSb, and NbGeSb, and the structure of NbSiAs refined from X-ray powder data. We also discuss atomic packing and valence compensation in these and similar phases.

## Experimental and Results

### Sample Preparation

The (<99.9% pure) elements were used as starting materials. Compositions NbSi and NbGe were first prepared by arc melting under gettered argon on a water-cooled copper hearth. These brittle materials were crushed, ground to powder, and heated with As (large pieces) or Sb (powder) in the appropriate stoichiometries in sealed silica tubes from 400 to 650°C over a 2-day period. The temperature was then raised to 750°C and held for 3 days. Samples were next cooled, ground, resealed in silica, heated to 800°C for 4 days, and quenched in water. Free-flowing powders resulted.

### Cell Constants

X-ray powder photographs were recorded with a Hägg–Guinier camera (Cu$K\alpha$ radiation) and *d*-spacings read with a David–Mann film reader. High-purity KCl ($a = 6.2931$ Å) was used for internal calibration. Lattice parameters were refined from these data by a computerized least-squares method. Standard deviations listed in Table I resulted from the refinements and do not include any compositional variation of the lattice constants.

### Refinement of NbSiAs

X-ray powder patterns of NbSiAs could be indexed with a tetragonal unit cell similar to that of ZrSiS previously known to have the PbFCl structure (*1*). Since that structure type has only two variable positional parameters the structure was refined from powder data. A Norelco diffractometer was used with 325-mesh powder and Ni-filtered Cu$K\alpha$ radiation. Intensities were determined from the area under each peak. Data from two different scans with different samples were scaled and averaged to yield the observed intensities. A least-squares program for powder intensities which accounts for overlapping peaks (*11*) was used. Scattering factors were taken from Cromer and Waber (*12*), corrected for anomalous dispersion (*13*). Two positional parameters—the overall thermal parameter, and one scale factor—were varied. The *R* value ($\sum |I_0 - I_c|/I_0$) was 13.6% for 52 reflections. When occupancies were allowed to vary also, *R* decreased to 13.0%;

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* Contribution No. 1911.

### TABLE I

### UNIT–CELL DIMENSIONS OF PbFCl-TYPE COMPOUNDS

| | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $c/a$ |
|---|---|---|---|---|
| NbSiAs | 3.4908(1) | 7.8992(2) | 96.26(1) | 2.263 |
| NbGeAs | 3.5519(2) | 7.9485(4) | 100.28(1) | 2.238 |
| NbSiSb | 3.6388(2) | 8.1794(5) | 108.30(1) | 2.248 |
| NbGeSb | 3.7035(2) | 8.2162(4) | 112.69(1) | 2.218 |

[a] Standard deviations in fourth place are given in parentheses.

### TABLE II

### STRUCTURAL DATA FOR NbSiAs–PbFCl TYPE [a, b]

| Atom | Position | $x$ | $y$ | $z$ | Occupancy |
|---|---|---|---|---|---|
| Nb | 2c | 1/4 | 1/4 | 0.2558 ± 0.0006 | 1.0 |
| Si | 2a | 3/4 | 1/4 | 0 | 1.03 ± 0.04 |
| As | 2c | 1/4 | 1/4 | 0.6117 ± 0.0007 | 0.97 ± 0.02 |

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

[b] Overall thermal parameter, $B = 0.6 \pm 0.2$ Å$^2$.

### TABLE III

### CALCULATED AND OBSERVED INTENSITIES FOR NbSiAs WITH PbFCl-TYPE STRUCTURE[a]

| $hkl$ | $d_c$ | $d_0$ | $I_c$ | $I_0$ | $hkl$ | $d_c$ | $d_0$ | $I_c$ | $I_0$ |
|---|---|---|---|---|---|---|---|---|---|
| 0 0 1 | 7.8992 | 7.8996 | 175 | 147 | 2 2 1 | 1.2194 | * | 4 | 7 |
| 0 0 2 | 3.9496 | 3.9483 | 113 | 112 | 2 2 2 | 1.1780 | * | 11 | 14 |
| 1 0 1 | 3.1929 | 3.1930 | 226 | 274 | 2 0 5 | 1.1713 | * | 27 | 23 |
| 0 0 3 | 2.6331 | 2.6332 | 350 | 334 | 1 1 6 | 1.1616 | * | 99 | 83 |
| 1 0 2 | 2.6156 | 2.6157 | | | 3 0 1 | 1.1512 | * | 8 | 12 |
| 1 1 0 | 2.4684 | 2.4685 | 485 | 641 | 0 0 7 | 1.1285 | * | 1 | 1 |
| 1 1 1 | 2.3560 | 2.3561 | 348 | 423 | 2 2 3 | 1.1175 | * | 35 | 44 |
| 1 0 3 | 2.1021 | 2.1022 | 1127 | 1000 | 3 0 2 | 1.1162 | * | | |
| 1 1 2 | 2.0932 | 2.0933 | | | 2 1 5 | 1.1104 | * | 94 | 95 |
| 0 0 4 | 1.9748 | 1.9749 | 17 | 12 | 3 1 0 | 1.1039 | * | 64 | 81 |
| 1 1 3 | 1.8008 | 1.8010 | 5 | 7 | 3 1 1 | 1.0933 | * | 51 | 60 |
| 2 0 0 | 1.7454 | 1.7454 | 320 | 322 | 1 0 7 | 1.0737 | * | 1 | 4 |
| 1 0 4 | 1.7188 | 1.7188 | 24 | 20 | 3 0 3 | 1.0643 | * | 150 | 168 |
| 2 0 1 | 1.7043 | 1.7043 | 15 | 15 | 3 1 2 | 1.0631 | * | | |
| 2 0 2 | 1.5965 | 1.5965 | 32 | 32 | 2 0 6 | 1.0511 | * | 30 | 28 |
| 0 0 5 | 1.5798 | 1.5799 | 20 | 14 | 2 2 4 | 1.0466 | * | 9 | 10 |
| 1 1 4 | 1.5420 | — | 0 | 2 | 1 1 7 | 1.0263 | * | 1 | 1 |
| 2 1 1 | 1.5315 | 1.5314 | 44 | 51 | 3 1 3 | 1.0180 | * | 1 | 1 |
| 2 0 3 | 1.4568 | 1.4547 | 124 | 121 | 2 1 6 | 1.0064 | * | 36 | 31 |
| 2 1 2 | 1.4518 | 1.4518 | | | 3 0 4 | 1.0025 | * | 4 | 5 |
| 1 0 5 | 1.4393 | 1.4394 | 113 | 86 | 0 0 8 | 0.9874 | * | 20 | 16 |
| 2 1 3 | 1.3429 | 1.3428 | 319 | 301 | 2 2 5 | 0.9726 | * | 17 | 17 |
| 1 1 5 | 1.3306 | 1.3307 | 4 | 2 | 3 1 4 | 0.9636 | * | 0 | 0 |
| 0 0 6 | 1.3165 | 1.3164 | 15 | 10 | 3 2 1 | 0.9610 | * | 12 | 18 |
| 2 0 4 | 1.3078 | 1.3078 | 16 | 14 | 1 0 8 | 0.9501 | * | 1 | 3 |
| 2 2 0 | 1.2342 | * | 124 | 129 | 2 0 7 | 0.9476 | * | 4 | 6 |
| 1 0 6 | 1.2318 | * | | | 3 2 2 | 0.9403 | * | 21 | 26 |
| 2 1 4 | 1.2247 | * | 14 | 15 | 3 0 5 | 0.9369 | * | 35 | 40 |

[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.

however, the deviations from full occupancy for the respective positions are hardly significant (Table II). It was noticed that all intensities for *hkl* with *l* large relative to *h* and *k* were measured too weak (Table III), indicating preferred orientation in the powdered sample. Since this effect is difficult to eliminate experimentally we assessed its influence on the structure refinement by excluding *hk*0 and *hk*1 reflections which are not important for the refinement of the positional parameters. This reduced *R* to 6.1% for 38 reflections but did not change the free parameters within the standard deviations. Preferred orientation is frequently observed for PbFCl-type structures (3, 8, 14).

## Discussion

The PbFCl-type structure is adopted by compounds with bonding varying from ionic to metallic (*15*). It may be regarded as cubic close-packed Pb atoms with Cl in octahedral and F in one-half the tetrahedral voids in alternate layers. This arrangement of Cl and Pb corresponds to NaCl if $c/a = \sqrt{2}$ and positional parameters, $z$, are 3/4 and 1/4 for Cl and Pb, respectively. In the PbFCl-type structure reported for LiFeP (*14*), Fe and P adopt the NaCl arrangement. However, in NbSiAs ($c/a = 2.263$), the NaCl arrangement of Nb ($z = 0.2558$) and As ($z = 0.6117$) is severely distorted (Fig. 1). This is also the case for Zr and S in ZrSiS (*3*).

In NbSiAs, the nearest-neighbor distances, Nb–As and Nb–Si (Table IV) are considerably shorter than the sum of the atomic radii indicating strong bonding between these elements. Si–Si and As–As distances are also only 5 and 18% longer than the corresponding covalent distances in the elements. No strong Nb–Nb or Si–As interactions occur. The short Si–Si distances suggest bonding within the Si layers; this will now be discussed.

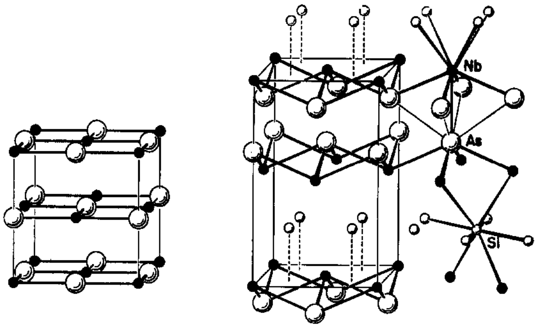

FIG. 1. Comparison of crystal structure of NbSiAs (right) with that of NaCl (left).

In the PbFCl structure, atoms in the tetrahedral position form layers perpendicular to *c* (Fig. 1) with short contacts within these layers. The ionic compounds such as PbFCl itself, the rare-earth oxyhalides, and uranium, thorium, and zirconium oxysulfides (*16*) conform to normal valence rules, hence the tetrahedral ions, $F^-$ and $O^{2-}$ can be regarded as nonbonding. On the other hand in the more covalent phases such as ZrSiS and UPS, the normal oxidation state of the group IV or V atoms, Si or P, is apparently reduced by intralayer bonding (*6*, *8*). If we assume intralayer valences of 2 for Si and 1 for P in these phases, then the oxidation states of Si with respect to Zr, and P with respect to U, are reduced to 2. These compounds may be represented by the formal valence formulas $Zr^{4+}[Si]^{2-}S^{2-}$ and $U^{4+}[P]^{2-}S^{2-}$, where the brackets indicate the intralayer bonding of the [Si] or [P] "complex".* If S in ZrSiS is

TABLE IV

INTERATOMIC DISTANCES (Å) IN NbSiAs[a]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Nb: | 4 As | 2.681 | | | | As: | 4 Nb | 2.681 |
| | 1 As | 2.811 | | | | | 1 Nb | 2.811 |
| | 4 Si | 2.670 | | | | | 4 As | 3.034 |
| | 4 Nb | 3.491 | | | | | 4 As | 3.491 |
| | | | | | | | 4 Si | 3.529 |
| | | | Si: | 4 Nb | 2.670 | | | |
| | | | | 4 Si | 2.468 | | | |
| | | | | 4 Si | 3.491 | | | |
| | | | | 4 As | 3.529 | | | |

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

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* The numbers 4+, 2−, etc., represent relative oxidation states and do not imply ionic bonding.

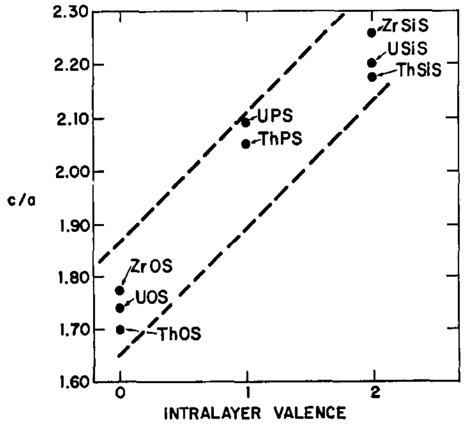

FIG. 2. Contraction of *a*-axis (normalized as *c*/*a*) vs intralayer valence in PbFCl-type phases.

replaced with a pnicogen, we might expect PbFCl phases to exist with pentavalent metal atoms. This is indeed the case since the Nb compounds reported here do have this structure. NbSiAs, for example, may be represented as $Nb^{5+}[Si]^{2-}As^{3-}$.

For the PbFCl-type phases with intralayer bonding (UPS, ZrSiS, etc.), the *a* axis contracts (*c*/*a* increases) relative to the normal valence compounds (ZrOS, etc.). This trend is not obvious for an arbitrary choice of PbFCl phases since the relative atomic sizes and other crystal-chemical properties also influence *c*/*a*. For compounds with atoms of similar sizes, however, *c*/*a* correlates with plausible intralayer valences (Fig. 2). There is a range of *c*/*a* values at a particular value of intralayer valence (Fig. 2), but the general increasing trend indicated by the dashed lines further justifies the assumption of intralayer bonding in the covalent phases.

Atoms within layers have neighbors of the same kind in a square-planar arrangement. Since Si and P seem to have intralayer valences of 2 and 1, respectively, the intralayer bonds must be of fractional order. Furthermore, Si–Si bonds should be of higher order than P–P bonds in their respective compounds. Observed Si–Si and P–P distances in ZrSiS, NbSiAs, and UPS are consistent with this rationalization.

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