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The structure of HfSn. By O. SCHOB and E. PARTHÉ, *School of Metallurgical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.*

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In the course of a study of compounds between fourth group transition metals and the 4B metals the compound HfSn has been synthesized. Hafnium hydride (Metal Hydrides, Inc., Beverly, Mass.) and tin powder have been thoroughly mixed, pressed and sintered under purified argon atmosphere in a tantalum-sheet-covered alumina crucible in a silicon carbide furnace at 1000 °C for 26 hr. It was found that the sintering temperature should not be higher or lower than 1000 °C to avoid the formation of other phases as for example, the Hf_5Sn_3 with D_{8h} structure (Boller, Nowotny & Wittmann, 1960; Bailey & Smith, 1961). It is not possible to synthesize HfSn by any melting process. Several samples prepared by arc melting or induction melting resulted in the formation of Hf_5Sn_3 . Similar results have been observed in the system Hf-Ge (Nowotny, Benesovsky & Schob, 1960).

The powder pattern could be indexed with a cubic unit cell with the lattice constant $a = 5.594 \text{ \AA}$. With four formula units HfSn per unit cell the X-ray density can be calculated to 11.27 g.cm^{-3} .

As the $h00$ reflections occur only for $h = 2n$ the space

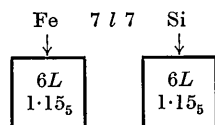
group of HfSn must be either $P2_13$ or $P4_232$. All existing twofold or fourfold positions in space group $P4_232$ (O^2) require additional special extinctions which have not been observed. The space group for HfSn is therefore $P2_13$ (T^4) with only one fourfold position having one adjustable parameter.

The best geometrical arrangement and good intensity agreement was found by placing 4Hf in equipoint $4(a)$ with $x_{\text{Hf}} = 0.155$ and 4Sn in $4(a)$ with $x_{\text{Sn}} = 0.845$. Table 1 shows the agreement between calculated and measured intensities. The 200 and 400 reflexes appeared with stronger intensities than calculated. This may be due partly to an orientation effect of the crystallites, partly to a coincidence with reflections from excess tin. Without consideration of temperature factor and diffraction lines with coincidences the residual factor can be calculated to be $R = 5.6\%$. The structure of HfSn belongs to the FeSi ($B20$) structure type.

The construction formula of the $B20$ structure type (Parthé, 1961) can be written as:

Table 1. *Intensity calculation for HfSn with FeSi ($B20$) structure type*
(Cu $K\alpha$ radiation)

hkl	d	$1000 \sin^2 \theta_c$	$1000 \sin^2 \theta_o$	I_c	I_o	Remarks
110	3.955 Å	37.92	37.7	4.7	3.9	
111	3.229	56.88	56.5	10.2	10.8	
200	2.797	75.84	76.0	15.4	45.0	Coincidence with Sn 101
210 } 120 }	2.501	94.80	94.5	98.3 } 1.7 }	100	100
211				2.284		
220	1.978	151.68	151.4	1.5	2.2	
221	1.865	170.64	170.0	11.4	10.0	
310 } 130 }	1.769	189.60	189.4	0.04 } 1.60 }	1.64	2.2
311				1.687		
222	1.615	227.52	227.0	0.8	1.4	
320 } 230 }	1.551	246.47	246.2	1.3 } 1.6 }	2.9	3.2
321				1.495		
231 }	1.398	303.35	303.0	7.8 }	7.3	11.6
400						
410 }	1.3185	341.27	340.9	0.5 }	4.84	4.3
140 }				322 }		
330 }	1.283	360.23	359.7	4.80 } 0.04 }	11.6	10.2
331				1.251		
420 }	1.2207	398.15	397.8	10.8 }	12.5	13.0
240 }				1.1926		
421 }	1.1188	473.99	473.8	0.75 }	0.75	≤ 1
241 }				1.142		
332 }	1.097	492.95	493.0	0.30 } 0.26 }	8.79	13.0
430 }				1.0766		
340 }	1.0766	511.91	512.2	8.00 }	7.8	8.0
431 }				1.097		
341 }	1.0766	511.91	512.2	0.18 }	7.8	8.0
510 }				1.0766		
150 }	1.0766	511.91	512.2	7.2 }	7.8	8.0
333 }				1.0766		
511 }	1.0766	511.91	512.2	0.6 }	7.8	8.0



From the symmetry of the construction formula it can be seen that HfSn has a structure with commutative partial structures (that means that from a geometrical standpoint, Hf and Sn sites are completely interchangeable). With the parameters which have been used for the intensity calculation, every atom, Hf and Sn, has seven equally distant neighbor atoms of the other kind at the ideal interatomic distance of 2.99 Å. The distance between atoms of the same kind can be calculated to 3.45₈ Å. The ideal parameter values are $x_{\text{Hf}} = -x_{\text{Sn}} = (\sqrt{5} - 1)/8 = 0.15_5$.

Exactly the same structure is obtained by using a different set of parameters (x_{Hf} , x_{Sn}) which are correlated in the following way:

$$\begin{aligned}
 (x)_{\text{Hf}} &= \frac{1}{4} - x_{\text{Hf}} = 0.095 \\
 (x)_{\text{Sn}} &= \frac{1}{4} - x_{\text{Sn}} = 0.405.
 \end{aligned}$$

The two settings differ only in the choice of the origin (shift for $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and the axes (Cullity, 1947).

It has been demonstrated by use of a space filling curve

Table 2. *Intermetallic compounds with FeSi (B20) structure type*

Silicides, germanides and stannides

Compound	a (Å)	r_T/r_B^*	Reference
HfSn	5.594	1.00	This work
CrSi	4.629	0.96	Pearson (1958), p. 562
CrGe	4.789	0.92	Pearson (1958), p. 539
MnSi	4.557	0.98	Pearson (1958), p. 746
TcSi	4.755	1.02	Darby (1964)
ReSi	4.775	1.04	Pearson (1958), p. 832
FeSi	4.488	0.96	Pearson (1958), p. 657
RuSi	4.703	1.01	Finnie (1962)
RuGe	4.846	0.97	Raub & Fritzsche (1962)
OsSi	4.729	1.02	Korst, Finnie & Searcy (1957)
CoSi	4.447	0.94	Pearson (1958), p. 523
RhSi	4.675	1.01	Pearson (1958), p. 833
RhSn	5.132	0.85	Pearson (1958), p. 834
NiSi	4.446	0.94	Existence of B20 type with the composition NiSi has been questioned. See Esslinger & Schubert (1957)

Aluminides and gallides

PdGa	4.89	0.91	Pearson (1958), p. 670
PtAl	4.864	0.97	Esslinger & Schubert (1957)
PtGa	4.91	0.915	Pearson (1958), p. 670

Compounds with elements of the second group of the P.S.

Pd(Au)Hg	5.22	0.94	Pearson (1958), p. 687
PtMg	4.863	0.87	Stadelmaier & Hardy (1961)
AuBe	4.668	1.25	Pearson (1958), p. 406

Ternary phases

Co ₄ GaGe ₃	4.64	} Esslinger & Schubert (1957)
Rh ₅ GaGe ₄	4.832	
Ni ₂ AlSi	4.56	
Ni ₅₀ Ga ₄₂ Ge ₈	4.65	
Pd ₄ Al ₃ Si	4.840	
Pd ₅₀ Al ₄₂ Ge ₈	4.87	

* The atomic radii have been calculated for a coordination number of 7.

(Parthé, 1961) that a contact between different kinds of atoms in the B20 structure is possible only in a restricted radius ratio range; namely,

$$0.731 < \epsilon = r_A/r_B < 1/0.731 = 1.365.$$

Table 2 gives a complete survey of all known compounds with B20 structure type. With the exception of AuBe, PtMg and RhSn the radius ratios of all compounds are within the relatively small range from 0.91 to 1.04. One obtains this good agreement if the radii are corrected for a 7-coordination according to Goldschmidt (1928).

The proper radius ratio is a necessary but not sufficient condition for the occurrence of a B20 structure type. All previously known compounds with the exception of AuBe contain transition metals of the sixth, seventh and eighth group. Silicides, germanides and stannides occur with Cr-, Mn-, Fe- and Co-group metals, while compounds containing Al, Ga and Mg — having one or two electrons less than Si — prefer metals of the Ni-group as partners. The existence of NiSi with B20 structure type has been questioned, but Esslinger & Schubert (1957) succeeded in preparing a ternary B20 type compound with Ni and part of Si replaced by Al.

Schubert (1963) has made a proposal for the spatial correlation of electrons which tries to explain the occurrence of the B20 structures with the previously known compounds.

HfSn is the first known B20 structure compound with a transition metal of the fourth group. Following Schubert's ideas one has to assume for HfSn a simple so-called '41-spatial correlation' with 32 electron sites per unit cell.

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References

- BAILEY, D. M. & SMITH, J. F. (1961). *Acta Cryst.* **14**, 57.
 BOLLE, H., NOWOTNY, H. & WITTMANN, A. (1960). *Mh. Chem.* **91**, 1174.
 CULLITY, B. D. (1947). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **171**, 396.
 DARBY, J. B. (1964). *J. Less-Common Metals*. In the press.
 ESSLINGER, P. & SCHUBERT, K. (1957). *Z. Metallk.* **48**, 126.
 FINNIE, L. N. (1962). *J. Less-Common Metals*, **4**, 24.
 GOLDSCHMIDT, V. M. (1928). *Z. Phys. Chem.* **133**, 397.
 KORST, W. L., FINNIE, L. N. & SEARCY, A. W. (1957). *J. Phys. Chem.* **61**, 1541.
 NOWOTNY, H., BENESOVSKY, F. & SCHOB, O. (1960). *Mh. Chem.* **91**, 270.
 PARTHÉ, E. (1961). *Z. Kristallogr.* **115**, 52.
 PEARSON, W. B. (1958). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*. London: Pergamon Press.
 RAUB, E. & FRITZSCHE, W. (1962). *Z. Metallk.* **53**, 779.
 SCHUBERT, K. (1963). *Kristallstrukturen zweikomponentiger Phasen*. Berlin: Springer.
 STADELMEIER, H. H. & HARDY, W. K. (1961). *Z. Metallk.* **52**, 391.