Synthesis, Crystal Structure, and Properties of HfM'P (M' = Fe, Co, Ni) in Comparison to ZrNiP

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Received April 8th, 1996.

Abstract. The new phosphides HfM'P (M' = Fe, Co, Ni) have been synthesized by arc melting of HfP and the corresponding 3 d metal, and subsequent annealing at 1400 °C. The lattice constants vary from a = 6.247(2) Å, b = 3.7177(6) Å, c =7.137(2) Å, V = 165.74(8) Å³ for HfFeP, a = 6.295(3) Å, b = 3.668(2) Å, c = 7.175(4) Å, V = 165.7(2) Å³ for HfCoP to a = 6.240(3) Å, b = 3.716(2) Å, c = 7.135(2) Å, V =165.4(2) Å³ (HfNiP) in the orthorhombic space group Pnma. Although ZrNiP occurs only in the Ni₂In structure type, all three Hf phosphides crystallize in the Co_2Si structure type, isotypic to ZrFeP and ZrCoP. The structural differences between HfNiP and ZrNiP can be explained by the preference of Hf for structures with more metal-metal bonds rather than by size effects.

Keywords: Hafnium Iron (Cobalt, Nickel) Phosphide; Preparation; Crystal Structure

Synthese, Kristallstruktur und Eigenschaften von HfM'P (M' = Fe, Co, Ni) im Vergleich mit ZrNiP

Inhaltsübersicht. Die neuen Phosphide HfM'P (M' = Fe, Co, Ni) wurden durch Aufschmelzen von HfP und dem entsprechenden 3d Metall im Lichtbogen und anschließendem Tempern bei 1400 °C hergestellt. Die Zellkonstanten variieren von a = 6.247(2) Å, b = 3.7177(6) Å, c = 7.137(2) Å, V = 165.74(8) Å³ für HfFeP, a = 6.295(3) Å, b = 3.668(2) Å, c = 7.175(4) Å, V = 165.7(2) Å³ für HfCoP bis a = 6.240(3) Å, b = 3.716(2) Å, c = 7.135(2) Å, V = 165.4(2) Å³ (HfNiP) in

Introduction

During the last decades, a number of metal-rich compounds with interesting structural and physical properties has been discovered. In our group the interest has focused on phosphides, oxides, sulphides and selenides of the electron-poor transition metals zirconium, hafnium, niobium, and tantalum [1-20]. The metal-rich compounds of Zr and Hf often possess striking differences in their composition, structure and properties, which is also true for Nb and Ta compounds. I.e., the sulphides Nb₂₁S₈ [3], Nb₁₄S₅ [7] and Zr₂S [6, 9] form structures containing in part b.c.c. arrangements of the metal atoms, whereas the structures of the Ta sulphides Ta₂S [4] and Ta₆S (in both modifications) [5, 21] consist of chains of Ta-centered pentagonal antiprisms of Ta atoms, and the unique Hf₂S [1] crystallizes in the anti-NbS₂ der orthorhombischen Raumgruppe Pnma. Obwohl ZrNiP nur im Ni₂In-Strukturtyp auftritt, kristallisieren alle drei Hafniumphosphide im Co₂Si-Strukturtyp, isotyp zu ZrFeP und ZrCoP. Die strukturellen Unterschiede zwischen HfNiP und ZrNiP lassen sich eher auf die Vorliebe des Hf für Strukturen mit mehr Metall-Metall-Bindungen zurückführen, als auf die unterschiedlichen Radien von Zr und Hf.

structure type. The recently found Hf_2Se_3 [22], Hf_3Te_2 [23], Ta_3S_2 [24, 25], Ta_2Se [26], Ta_2Te_3 [27] and Ta_6Te_5 [28] all have no counterpart among the compounds of the corresponding 4d metal. In addition, none of the 5d metal atom phosphides analogues to Zr_2P [29], Zr_7P_4 [30], $Zr_{14}P_9$ [31], Nb_2P [32], Nb_8P_5 [33] and Nb_7P_4 [34] had been found until most recently, we could synthesize and characterize Hf_7P_4 [35], which is isostructural to Zr_7P_4 , indicating that the above mentioned compounds might have their analogous as well. On the other hand, many compounds with the same stoichiometry such as Zr_2P and Hf_2P [36], Nb_2P and Ta_2P [37], as well as Nb_2Te_3 [38] and Ta_2Te_3 , crystallize in different structure types.

The structural differences between the metal-rich sulphides of Nb and Ta, as well as Zr and Hf, can be related to the tendency of the 5d metals to form structures which contain more metal-metal bonds [39]. The same preference causes the site preferences of Ta in the ternary Nb/Ta sulphides [10-13] and tellurides [40].

Previous research on the ternary systems (Zr, Hf)/(Fe, Co, Ni)/P was concentrated on the iron-group-metal-rich regions [41-46]. A possibly different behavior of the Zr and Hf phosphides in these systems, as is expected to occur in the more early-transition-metal-rich region, has not been investigated so far. The recently found $Zr_9M_2P_4$ (M' = Co, Ni) [47], $Zr_2Ni_{0.48}P$ [48] and $Hf_5Co_{1+x}P_{3-x}$ [49] could not be prepared with the other homologous group IV metal, whereas $M_4M'P$ (M = Zr, Hf; M' = Fe, Co, Ni) [50] exists with Zr and Hf, and both ZrP and HfP are able to intercalate nickel [44, 51].

During our systematic investigations of the (Zr, Hf)/(Fe, Co, Ni)/P systems we were able to prepare a new series of ternary Hf phosphides: HfM'P with M' = Fe, Co, Ni. These phosphides are isostructural to ZrFeP [52] and ZrCoP [53] (Co₂Si structure type), whereas ZrNiP crystallizes in a different structure type (Ni₂In) [54]. Our investigations show that the occupations of the atomic positions of ZrNiP, as reported in the literature, need to be corrected, however, we did confirm the structure type. Here we report about the synthesis, crystal structure and properties of these phosphides, as well as about the similarities and differences with the Zr phosphides with the same compositions.

Experimental

Since phosphorous cannot be used in an arc-melter in its elemental form, the monophosphides ZrP and HfP were synthesized by a reaction of the elemental metal (Zr: Alfa, powder, -20 + 60 mesh, purity 99.7% (including 2-3.5% Hf), Hf: Alfa, powder, -325 mesh, purity 99.6% (2-3.5% Zr)) with phosphorous (Alfa, powder, -100 mesh, red amorphous, 99%) in an evacuated sealed silica tube at a reaction temperature of 800 °C. ZrNiP and HfM'P (M' = Fe, Co, Ni) were prepared by arc melting of ZrP or HfP, respectively, with an equimolar amount of the corresponding iron-group-metal (Fe: Alfa, 99.999%; powder. -22 mesh, Co: Alfa, powder, -50 + 150 mesh, 99.9%; Ni: Fisher, powder, purified). To obtain a higher homogeneity, these samples were pressed into pellets under a pressure of 10000 psi, and then arc melted twice for 20s under an argon atmosphere. All four samples were annealed in an induction furnace at a temperature of 1400 °C for a period of six hours.

All samples were partially ground to obtain samples to produce the experimental powder diagrams. In order to identify the reaction products, the powder patterns of (theoretical) HfM'P were calculated under the assumption of the Co₂Si and the Ni₂In structure types. None of the diagrams obtained from the ternary Hf phosphides showed the reflections of the Ni₂In type; in all these cases diffraction from the Co₂Si type predominated in the powder pattern.

On the other hand, the experimentally obtained powder diagram of ZrNiP consisted more or less of the expected lines, as calculated from the cell and atomic parameters given by *Kuz'ma* and *Pivan* [54]. Interchanging the postulated positions of Ni and Zr, however, led to a better conformity of observed

and calculated powder diagram (table 1) and more reasonable metal-phosphorous distances: the reported Zr—P distance of 2.18 Å would correspond to an unlikely bond order greater than 4, whereas Ni—P bond lengths of 2.18 have been observed previously. Nonetheless, the reflections could be indexed on the basis of the hexagonal Ni₂In type, resulting in cell dimensions of a = 3.7672(6) Å, c = 7.167(2) Å, V = 88.09(4) Å³, using nine strong reflections. The atomic parameters of ZrNiP are given in table 2. The powder diagrams of HfFeP and HfCoP were indexed under the assumption of orthorhombic symmetry (corresponding to the Co₂Si structure) to yield a = 6.247(2) Å, b = 3.7177(6) Å, c = 7.137(2) Å, V = 165.74(8) Å³, and a = 6.295(3) Å, b = 3.668(2) Å, c = 7.175(4) Å, V = 165.7(2) Å³, respectively, using 15 reflections.

Table 1 Observed and calculated intensities for ZrNiP

hkl	\mathbf{I}_{obs}	I_{calc} ^a)	I _{calc} ^b)	
100	20	12	1	
101	1	7	32	
102	100	100	100	
110	50	44	54	
200	6	2	0	
104	10	3	0	
202	50	25	25	
114	50	32	33	
210	7	2	0	

a) ZrNiP with atomic coordinates as given in table 2
 b) ZrNiP with atomic coordinates as given in ref. [54]

 Table 2
 Atomic coordinates for ZrNiP

Atom	site	x	У	Z
Zr	2a	0	0	0
Ni	2 c	1/3	2/3	1/4
Р	2 d	1/3	2/3	3/4

A needle-like single crystal of the sample with the initial composition "HfNiP" with the dimensions 0.05 mm×0.003 mm× 0.003 mm was mounted on a glass fiber to be used to collect data to determine its structure. The data collection was performed on an automatic four-circle-diffractometer with a rotating anode (RIGAKU AFC6R). The cell constants were calculated from least-squares refinement using the setting angles of 17 carefully centered reflections in the range of $11.40^{\circ} < 2\theta < 22.02^{\circ}$ yielding a = 6.240(3) Å, b = 3.716(2) Å, c = 7.135(2) Å, V = 165.4(2) Å³. Four octants were measured using the ω - 2θ technique to 60° , using Mo-K α radiation, and were later merged. The data were corrected for Lorentz and polarization effects. The absorption correction was made using a ψ -scan, followed by DIFABS [55].

The systematic extinctions of k + 1 = 2n + 1 for all 0kl and h = 2n + 1 for all hk0 reflections restricted the possible space groups to Pnma and Pna2₁. Since the intensity distribution pointed to centrosymmetry, the structure solution and refinements were performed successfully in the centric space group Pnma (No. 62), corresponding to the Co₂Si structure type. Refinements of the structure model ultimately obtained in the acentric space group Pna2₁ neither lead to any significant changes nor to an improvement of the residual values.

The structure was solved using the direct method (program SHELXS [56]). The three atomic positions, as taken from the emap, were identified as Hf, Ni and P sites, respectively. The subsequent calculations were performed using the TEXSAN program package [57]. The refinements with anisotropic temperature factors for the metal atom sites converged to R = 0.033, $R_w = 0.028$, GOF = 1.16. The unusual high temperature factor for the Ni position (more than twice of the Hf temperature factor) led to the supposition of a partially occupied site. Refinements of a split position of Ni, which would correspond to the high U_{22} value, did not yield in a reliable structure model. The possibility of a mixed Ni/P occupation could be excluded because of the short Ni-P distances of HfNiP: replacement of Ni by P would lead to most unlikely short P-P distances. Refinements of the model of a disordered Ni position resulted in an occupation of 90(2)% Ni on this site

Table 3 Crystallographic data for HfNi_{1-x}P

Empirical formula Molecular weight Temperature of data collection Crystal dimensions Space group Unit cell dimensions	HfNi _{0.90(2)} P 262.29 g/mol 295 K 0.05 mm×0.003 mm×0.003 mm Pnma (No. 62) $a = 6.240(2) \text{ Å}, b = 3.716(2) \text{ Å}, c = 7.135(2) \text{ Å}, V = 165.4(2) \text{ Å}^{3}$
Number of formula units	4
Calculated density	10.530 g/cm ³
Absorption coefficient	72.86 mm ⁻¹
F(000)	448
Scan mode, scan width	ω -2 θ , $(1.50 + 0.34 \tan\theta)^{\circ}$
Scan speed	4.0°/min (in ω , 3 rescans)
Range of 2θ	4°-60°
No. of measured reflections	1382
No. of independent reflections	$324 (R_{int} = 0.128)$
No. of observed reflections	187
$(I > 3\sigma(I))$	
No. of parameters refined	18
R^{a}), R_{w}^{b}), goodness of fit	0.031, 0.026, 1.07
(GOF [*]))	1 100 - 10 - 6
Extinction coefficient	$1.488 \times 10^{\circ}$
diff man	$2.9967 A^{\circ}$,
Abcomption connection	- 3.200 / A ²
Min., max. transmission	ψ scan, followed by DIFABS 0.82 – 1.18
•	

^a) $\mathbf{R} = \Sigma ||\mathbf{F}_{o}| - |\mathbf{F}_{c}|| / \Sigma |\mathbf{F}_{o}|$ ^b) $\mathbf{R} = [\Sigma \mathbf{w}(|\mathbf{F}_{o}| - |\mathbf{F}_{c}|)^{2} / \Sigma \mathbf{w} |\mathbf{F}_{o}|^{2}]^{1/2}; \mathbf{w} = 1/\sigma^{2}(|\mathbf{F}_{o}|)$

^c) GOF = $\Sigma(||F_o| - |F_c||\sigma_i)/(N_{obs} - N_{parameters})$

and significantly lower residual values: R = 0.031, $R_w = 0.026$, GOF = 1.07. According to the results of the Hamilton test, we can reject the hypothesis of a fully occupied Ni site at the 0.005 level [58]. Therefore, the empirical formula was determined to be HfNi_{1-x}P with x = 0.10(2). The refined occupancy factor is independent of the use of DIFABS as well as the inclusion of unobserved reflections: residual factors without using DIFABS: R = 0.036, R_w = 0.028, GOF = 1.22, x = 0.10(2); without using DIFABS and including all reflections: R = 0.075, R_w = 0.034, GOF = 1.23, x = 0.10(2). Crystallographic data for HfNi_{0.90}P can be found in table 3. Atomic positions and temperature factors are listed in table 4.¹)

Results and Discussion

The new phosphides HfM'P (with M' = Fe, Co, Ni) all crystallize in the Co₂Si structure type with complete ordering on the metal sites. The structure of HfNiP contains only three different crystallographic sites: one Hf, one Ni and one P position. As often observed in metalrich phosphides, the P atom is situated in a three-capped trigonal prism of the metal sublattice. The Hf atoms build four corners of the prism and one cap, whereas the Ni atoms form the two remaining corners and the two other caps. These prisms are interconnected by common opposite triangular faces to form chains running parallel [010], and by common edges to form zigzag chains parallel [100], resulting in puckered sheets perpendicular to the c axis. Through the a-glide-plane perpendicular to the c axis the neighboring sheet along the c axis is shifted and converted, and the caps of one layer correspond to the corners of the next layer. Figure 1 emphasizes the zigzag chains of trigonal prisms parallel to the a axis in a projection along [010].

Altogether, a three-dimensional network of the prisms results in short metal-metal bonds along all directions: the Hf—Hf bond length within the triangular faces of the trigonal prism is 3.269(2) Å, the Hf—Hf bond between the prisms at 3.200(2) Å is even shorter, and the Hf—Ni bonds within the prisms vary from 2.825(3) Å to 2.909(3) Å, whereas the Hf—Ni separations between the prisms of 2.903(3) Å are in the same range. In addition,

¹) Further details of the crystal structure determination can be ordered from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, under the depository number CSD-405289

Table 4	Atomic positions and	temperature factors	[Ų]	for	HfNi _{0.90(2)} P *	ľ)
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Atom	Х	Z	B _{eq} ^b)	\mathbf{U}_{11}	U ₂₂	U ₃₃	U_{13}	
Hf	0.0218(1) 0.1480(5)	0.8184(1) 0.4381(4)	0.30(3)	0.0032(4)	0.0060(4)	0.0020(3)	0.0003(4)	
P	0.2769(8)	0.1185(7)	0.31(7)	0.003(1)	0.009(1)	0.002(1)	-0.0013(9)	

^a) All atoms on Wyckoff position 4c, y = 1/4, $U_{12} = U_{23} = 0$

^b) $\mathbf{B}_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j\mathbf{U}_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$

°) Occupancy factor = 0.90(2)

Compound	Space group	a/Å	b∕ Å	c/ Å	V∕ų	z	V/z/ų	reference
ZrFeP	Pnma	6.3088(4)	3.7401(2)	7.1717(4)	169.22	4	42.31	[52]
ZrCoP	Pnma	6.332(1)	3.698(1)	7.160(1)	167.66	4	41.92	[53]
ZrNiP	P6 ₃ /mmc	3.7672(6)	3.7672(6)	7.167(2)	88.09(4)	2	44.05	this work
HfFeP	Pnma	6.247(2)	3.7177(6)	7.137(2)	165.74(8)	4	41.44	this work
HfCoP	Pnma	6.295(3)	3.668(2)	7.175(4)	165.7(2)	4	44.43	this work
HfNiP	Pnma	6.240(3)	3.716(3)	7.135(2)	165.4(2)	4	41.35	this work
ZrNi _x P	P6 ₃ /mmc	3.745	3.745	12.791	155.4	4	38.85	[44]
HfNi _x P	P6 ₃ /mmc	3.737(1)	3.737(1)	12.666(2)	153.21(7)	4	38.30	[51]

Table 5 Comparison of the cell dimensions of the MM'P series



Fig. 1 Structure of HfNiP in a projection along [010]. Small, white circles: P; medium, black circles: Ni; large, white circles: Hf atoms

short Ni—Ni distances (2.764(5) Å) occur between the zigzag chains of prisms. All these distances indicate that the interactions between the prisms are probably as strong as within the prisms. The metal-metal interactions in the prisms along [010] correspond to the length of the *b* axis (3.716(2) Å) and have therefore only weak or non-bonding character.

From another point of view, the structure of HfNiP consists of square pyramidal HfP₅ prisms and NiP₄ tetrahedra in which the Hf—P bonds vary from 2.658(4) Å to 2.670(4) Å and the Ni—P bonds from 2.308(4) Å to 2.418(7) Å. An additional P atom at the longer distance of 3.471(5) Å completes the Hf coordination to a distorted octahedron. Considering the different metal-phosphorous bonds, it becomes clear that the metal sites have to be completely ordered for steric reasons: Hf—P bonds of 2.308(4) Å are much too short,

compared to the sum of Pauling radii of $r_{Hf} + r_P = 1.442 \text{ Å} + 1.10 \text{ Å} = 2.542 \text{ Å}$: this would correspond to a Pauling bond order of 2.45 (calculated using the Pauling's equation $d(n) = d(1) - 0.6 \log n$ [59]).

Surprisingly, no significant trend of the lattice dimensions from HfFeP over HfCoP to HfNiP is observed (table 5), although the radii of the iron-group decrease from $r_{Fe} = 1.170 \text{ Å}$ over $r_{Co} = 1.162 \text{ Å}$ to $r_{Ni} = 1.154 \text{ Å}$. Therefore, electronic reasons must be responsible for the occurrence of almost identical volumes of the unit cells, whereas the b axis of HfCoP is remarkably short. In order to determine and understand the differences among the isotypic compounds, we calculated the interatomic distances, the Pauling bond orders (PBO) and Mulliken overlap populations (MOP), as obtained by band structure calculations using the Extended Hückel approximation [60-62]. The atomic positions for HfFeP and HfCoP were taken from the related Zr compounds [52, 53], the parameters for the metal atoms from charge iterations [63, 64] as listed in table 6, and for P from standard sources [65]. The results of these calculations are listed in table 7.

Table 6 Used parameters of the EH calculations

Orbital	H_{ii}/eV	ζ_1	C ₁	ζ_2	c ₂
Zr, 5s	-8.76	1.82			
Zr, 5p	-5.07	1.78			
Zr, 4d	-9.07	3.84	0.6213	1.505	0.5798
Hf, 6s	-8.12	2.210			
Hf, 6p	-4.50	2.170			
Hf, 5d	-8.14	4.360	0.7145	1.709	0.5458
Fe, 4s	-8.29	1.90			
Fe, 4p	-4.27	1.90			
Fe, 3d	-10.25	5.55	0.5411	1.800	0.6734
Co, 4s	-8.14	2.00			
Co, 4p	-3.33	2.00			
Co, 3d	- 10.00	5.55	0.5679	2.100	0.6059
Ni, 4s	-7.77	1.925			
Ni, 4p	-3.66	1.925			
Ni, 3 d	- 9.86	5.750	0.5862	2.200	0.5845
P, 3s	-18.60	1.880			
P, 3 p	- 12.50	1.630			

		-										
Bond		no.	HfNiP length∕ Å	PBO	MOP	HfCoP length	PBO	MOP	HfFeP length	PBO	MOP	
Hf	Hf	$2 \times$	3.200(2)	0.30	0.098	3.217	0.28	0.069	3.216	0.28	0.075	
Hf	Hf	$2 \times$	3.269(2)	0.23	0.105	3.290	0.21	0.063	3.267	0.23	0.055	
Hf	Hf	$2 \times$	3.716(3)	0.04	0.033	3.668	0.05	0.021	3.718	0.04	0.022	
Hf	Hf		sum:	1.14	0.472	sum:	1.08	0.306	sum:	1.10	0.304	
Hf	М'	$2 \times$	2.815(2)	0.43	0.052	2.779	0.49	0.062	2.804	0.45	0.099	
Hf	М'	$1 \times$	2.825(3)	0.41	0.049	2.820	0.42	0.066	2.815	0.43	0.109	
Hf	M′	$2 \times$	2.903(3)	0.31	0.050	2.947	0.26	0.049	2.923	0.29	0.104	
Hf	М'	1×	2.909(3)	0.30	0.036	2.972	0.24	0.033	2.912	0.30	0.091	
Hf	M′		sum:	2.19	0.289	sum:	2.16	0.321	sum:	2.21	0.606	
Hf	Р	2×	2.658(2)	0.64	0.266	2.676	0.60	0.258	2.665	0.62	0.216	
Hf	Р	$1 \times$	2.668(5)	0.62	0.278	2.664	0.63	0.284	2.674	0.60	0.189	
Hf	Р	$2 \times$	2.670(4)	0.61	0.210	2.642	0.68	0.230	2.675	0.60	0.245	
Hf	Р	1 ×	3.471(5)	0.03	0.009	3.474	0.03	0.009	3.439	0.03	0.005	
Hf	Р		sum:	3.15	1.239	sum:	3.22	1 .269	sum:	3.07	1.116	
M′	M′	$2 \times$	2.764(5)	0.17	0.000	2.696	0.23	0.005	2.755	0.18	0.017	
M′	М′	$2 \times$	3.716(3)	0.00	002	3.668	0.01	004	3.718	0.00	011	
M′	M′		sum:	0.34	004	sum:	0.48	0.002	sum:	0.36	0.012	
M′	Р	$2 \times$	2.308(4)	0.80	0.129	2.301	0.84	0.125	2.298	0.85	0.190	
M′	Р	$1 \times$	2.351(6)	0.68	0.138	2.351	0.69	0.127	2.335	0.73	0.207	
M′	Р	1×	2.418(7)	0.54	0.142	2.458	0.46	0.120	2.444	0.48	0.235	
M′	Р		sum:	2.82	0.538	sum:	2.83	0.497	sum:	2.9 1	0.822	

Table 7 Comparison of the structures of HfNiP, HfCoP and HfFeP

To a first approximation, apart from the different sizes of the iron-group-metal atom, two different trends cause the differences in the bonding in the HfM'P series: first, the number of valence electrons decreases from HfFeP to HfNiP, and second, the electronegativity of M' increases from HfFeP to HfCoP. In order to get a qualitative picture of the dependence on the electron count, we calculated the density of states for HfNiP. As can be seen in figure 2, the Hf 5d states predominate at the Fermi level of HfNiP, whereas the Ni 3d states are located in a small region ca. 1 eV well below the Fermi level. Decreasing the number of valence electrons leads to a lower Fermi level. and therefore to a partial oxidation of the irongroup-metal as well as of hafnium. As expected by considering the extended metal network in the structure of HfM'P, all three phosphides show some density of states at the Fermi level. The Fermi level of HfCoP corresponds to a minimum, whereas HfFeP and HfNiP have significantly more states at their Fermi level. Therefore, we expect metallic conductivity for all three HfM'P, decreasing from HfFeP to HfNiP to HfCoP.

Since the Hf—Hf interactions have bonding nature in the region around the Fermi level (figure 3), they are strongest in case of the Ni compound (MOP_{Hf-Hf} = 0.472 vs. 0.304 (HfFeP)). In contrast, the Hf—M' bonds are most bonding in the structure of HfFeP (0.606 vs. 0.289 for HfNiP) for two reasons: first, the lower valence electron concentration comes along with fewer antibonding Hf—M' interactions, and second the lower electronegativity leads to a more covalent Hf—M' bonding character. The M'—M' interactions are more or less antibonding in all three Hf phosphides discussed, but the most bonding character occurs in HfFeP, because fewer antibonding states are filled.

The Hf—P overlap populations in HfFeP, HfCoP and HfNiP are almost equal, which can be explained by two opposite trends: the lower VEC in case of HfFeP decreases the number of Hf states available for the Hf—P bonds, whereas the more covalent Hf—Fe bonds lead to more covalent Hf—P bonds by lowering the energy of the Hf orbitals. The lower energy of the Fe states is responsible for the stronger M'—P bonds, compared to HfCoP and HfNiP, because the number of available states is independent of the VEC: the M'—P bonding states lie well below the Fermi level of HfFeP as well as HfNiP.

The above discussed differences in the Mulliken







Fig. 3 Selected Crystal Orbital Overlap Populations (COOP) for HfNiP

Overlap Populations (MOP) are accompanied by different Pauling Bond orders (PBO) and bond lengths, resulting in approximately identical cell volumes for all HfM'P compounds despite the differences in radii, electronegativities and number of d electrons of the irongroup-metal atoms.



Fig. 4 Structure of ZrNiP in a projection along [010]. Small, white circles: P; medium, black circles: Ni; large, white circles: Zr atoms

At the first glance, it might be surprising to find ZrNiP crystallizing in a different structure type. ZrNiP crystallizes in the Ni₂In structure type, although all HfM'P with M' = Fe, Co, Ni and ZrM'P with M' = Fe, Co apparently occur only in the Co₂Si structure type. The structure of ZrNiP consists of eclipsed layers of Zr atoms, the P and Ni atoms occupying all trigonal prismatic voids of the Zr sublattice in an alternating fashion (figure 4). Therefore, each P atom is surrounded by six Zr atoms at a distance of 2.818 Å and three Ni atoms at a distance of 2.175 Å, which cap all rectangular faces of the prisms. Both triangular faces of the Zr_6P prism are capped by Ni atoms at the longer distance of 3.583 Å. The faces of the Zr_6Ni prisms are capped by three close P atoms ($d_{Ni-P} = 2.175$ Å) and two more distant P atoms at 3.583 Å. The Zr—P distances, equal to the Zr—Ni distances, are significantly longer than the Hf—P distances in HfNiP (2.818 Å vs. from 2.658(2) Å to 2.670(4) Å), whereas the Ni—P distances are much shorter (2.175 Å vs. from 2.815(2) Å to 2.909(3) Å). The shortness of the Ni—P bond apparently prohibits the formation of ZrFeP and ZrCoP in this structure type for steric reasons.

Table 8 Interatomic interactions in the structure of ZrNiP^a)

Bond		length∕ Å	no.	PBO	MOP	
Zr	Zr	3.583	$2 \times$	0.07	.038	
Zr	Zr	3.7672	6×	0.04	.050	
Zr	Zr	sum:		0.38	0.376	
				(1.14)	(0.472)	
Zr	Ni	2.818	6×	0.45	0.070	
Zr	Ni	sum:		2.70	0.420	
				(2.19)	(0.289)	
Zr	Р	2.818	6×	0.36	0.184	
Zr	Р	sum:		2.16	1.104	
				(3.15)	(1.239)	
Ni	Ni	3.7672	6×	0.00	002	
Ni	Ni	sum:		0.00	012	
				(0.34)	(004)	
Ni	Р	2.175	$3 \times$	1.35	0.178	
Ni	Р	sum:		4.05	0.534	
				(2.82)	(0.538)	

^a) Corresponding values for HfNiP in brackets

As depicted in table 8, large differences in the Pauling bond orders arise from the differences in the bond lengths: The total PBO for the M-P bonds is 2.16 in ZrNiP and 3.15 in HfNiP, and the opposite trend is found for the Ni-P bond orders: 4.05 vs. 2.82. However, the calculated Mulliken overlap populations are comparable for the metal-nonmetal interactions (M-P: 1.104vs. 1.239; Ni-P: 0.534vs. 0.538), indicating that the differences in these interactions are smaller than expected on basis of the bond lengths. More significant are the differences in the metal-metal bonds of ZrNiP and HfNiP: the shortest Zr-Zr bond of 3.583 Å is much longer than the shortest Hf—Hf bond of 3.200(2) Å, whereas the Zr-Ni distance of 2.818 Å is shorter than the average Hf—Ni distance of 2.862 Å. Correspondingly, the Mulliken overlap populations are different as well: the total Hf-Hf overlap population of 0.472 is about 26% higher than the Zr—Zr overlap population of 0.376. whereas the Ni-Ni MOP in HfNiP is ca. 31% lower than that in ZrNiP (0.289vs. 0.420).

It might be expected that HfNiP would appear in a different structure than ZrNiP for steric reasons, because the already short Ni—P distance of 2.175 Å in the structure of ZrNiP would be even shorter in a hypothetical isoelectronic HfNiP, but shorter distances are possible as shown by the structure solution of HfNi_xP (x = 0.426) [51] with $d_{Ni-P} = 2.1578(7)$ Å, occurring in the same coordination sphere. We suggest that the main driving force for the different structures of ZrNiP and HfNiP lies in the tendency of Hf to form structures with higher metal-metal bond order. The tendency of Hf to form more metal-metal bonds, as also observed in solid solutions (Zr, Hf)₂S [15], can be explained with the larger extension of the 5d orbitals, which of course has greater influence on the M-M than on the M-Ni interactions. That the latter bonds are even stronger in ZrNiP can be related to the distribution of the same total number of valence electrons, with more electrons available for M-Ni bonds because fewer electrons are located in M-M bonds. It is interesting that the tendency of Hf to form stronger metal-metal bonds becomes clear in the case of the MNiP compounds even though the metalnonmetal ratio is not very high.

Altogether, the differences within the MM'P series as discussed here have to be explained with steric reasons as well as electronical reasons. The formation of the Ni₂In structure type with Fe or Co is sterically inhibited, whereas the Hf compounds in general prefer structures with more metal-metal interactions, compared to the Zr compounds, leading to the crystallization of HfNiP in the Co₂Si structure type.

H. K. thanks the Deutsche Forschungsgemeinschaft for financial support of this work. The Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was also supported by the Office of the Basic Energy Sciences, Materials Science Division, Department of Energy.

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