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The Crystal Structure of Hf_3As

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Hf_3As has a monoclinic unit cell of dimensions $a = 15.3898(14)$ Å, $b = 5.3795(5)$ Å, $c = 15.3330(14)$ Å, $\beta = 90.291(6)°$. A structure proposal based on space group $C2/c$ (No. 15) has been refined by the least-squares method using a Rietveld-type fullprofile analysis of Guinier–Hägg X-ray powder film intensity data. The Hf_3As structure is an intermediate between the Fe_3P and the Ti_3P types. The atomic coordination follows rules formulated earlier for representatives of the Fe_3P–Ti_3P–V_3S family of structures.

Introduction

In a brief note on the Hf–As system, Rundqvist and Carlsson (*1*) reported the occurrence of a phase of composition Hf_3As. X-Ray Weissenberg photographs recorded for crystalline Hf_3As fragments invariably indicated twinning such that neither the Weissenberg films nor the powder diffraction patterns could be interpreted satisfactorily. In a later study a similar situation was encountered for Ta_3As (*2*).

Recently, Murray *et al.* (*3*) found that Ta_3As crystallizes with a monoclinic symmetry. With this information at hand, we have reexamined the X-ray diffraction data for Hf_3As. As a result we have found that Hf_3As crystallizes with a monoclinic unit cell of dimensions similar to those of Ta_3As. The two compounds are most probably isostructural. Further analysis of the diffraction data suggested a structure proposal for Hf_3As which subsequently refined successfully (see below).

Crystal Structure Analysis

The Hf_3As powder diffraction patterns recorded originally (*1*), using Guinier–Hägg-type focusing cameras with $CrK\alpha_1$ radiation and silicon ($a = 5.431065$ Å) (*4*) as the internal calibration standard, were tentatively indexed on the basis of a monoclinic unit cell of dimensions similar to those reported for Ta_3As (*3*). A least-squares refinement using the local program CELNE (*5*) gave the following values and standard deviations (Å): $a = 15.3898(14)$, $b = 5.3795(5)$, $c = 15{,}3330(14)$, $\beta = 90.291(6)°$.

On reexamination of the rotation and Weissenberg films recorded earlier (*1*), we found that the data could be interpreted in terms of monoclinic twins with a pseudo-tetragonal symmetry about the monoclinic axis. The intensity data were compatible with *Cc* or $C2/c$ space group symmetry, in agreement with the results for Ta_3As. Furthermore, the unit cell dimensions and the intensity data indicated a close structural relationship to the Fe_3P–Ti_3P–V_3S family of tetragonal structures (*6*). The members of this family have approximate unit cell

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dimensions of $a = 9-11$ Å, $c/a = 0.5$. For Hf_3As and Ta_3As, the monoclinic (pseudotetragonal) axes are approximately equal to the tetragonal axes in the Fe_3P–Ti_3P–V_3S structures, and the monoclinic angles are very close to 90°. The a and c axes are nearly equal and are approximately $2^{1/2}$ times larger than the a axes for the Fe_3P–Ti_3P–V_3S compounds.

Consideration of the various possibilities for adapting the structural theme in Fe_3P and Ti_3P to the lower symmetry of Hf_3As eventually led to a structure proposal based on the space group $C2/c$. It involved six eightfold hafnium positions and two eightfold arsenic positions. Intensity calculations based on x and z positional parameters derived from the Zr_3P structure (*7*) and y parameters approximating to multiples of $\frac{1}{4}$ strongly supported the assumptions made. Refinement of the structure model was accordingly started using the method for profile analysis of powder film intensity data developed by Malmros and Thomas (*8*).

The intensity profile data were obtained using a SAAB automatic film scanner (*9, 10*) connected to an IBM 1800 computer. The powder films recorded earlier were too strongly exposed to be suitable for intensity measurements. New powder films were therefore recorded in a Philips XDC-700 camera using $CrK\alpha_1$ radiation. The original sample contained small amounts of hafnium metal in addition to Hf_3As. Storage in air for more than 10 years had also led to some oxidation, so that additional faint HfO_2 lines were visible on the powder photographs. The three hafnium lines present on the films were removed from the profile data without serious loss of intensity information for Hf_3As, while the HfO_2 reflections were included in the subsequent refinements by employing the multiphase refinement program described by Werner *et al.* (*11*).

Structure data for HfO_2 were calculated using lattice parameters from Ref. *12* and the same positional parameters as those reported for ZrO_2 (*13*). The refinement converged in a very satisfactory manner considering the numerous overlaps among the diffraction lines. The final agreement factors obtained (for definitions, see Ref. *8*) were $R_I = 0.057$, $R_F = 0.063$, $R_p = 0.128$, and $R_{wp} = 0.193$. A list of observed and calculated intensities, corrected for Lp and geometrical factors (*8*), is given in Table I. Final structure data are presented in Table II. The following parameters were refined: *profile parameters*—halfwidth (3), asymmetry (1), and 2θ-zero point (1); *structure parameters*—overall scale factor (1); for HfO_2, "occupancy parameter" (1); for Hf_3As, lattice parameters (4), positional parameters (24), and "overall temperature factor" (1). Scattering factors, corrected for the real part of the anomalous dispersion, were interpolated from values given in the "International Tables" (*14*). The occupancy parameter common for all atoms in HfO_2 permits refinement of the HfO_2/Hf_3As relative proportion in the sample. No attempt was made to correct for absorption. This means that the "overall isotropic temperature factor" as obtained from the refinement (3.5(2) Å^2) includes absorption effects and thus provides no meaningful information on thermal vibrations.

Discussion of the Hf_3As Structure

Interatomic distances calculated for Hf_3As are given in Table III. The relationship between the three structure types Fe_3P, Ti_3P, and Hf_3As is described with reference to Fig. 1, which shows the structures in projection on the basal planes.

In the Fe_3P- and Ti_3P-type structures, the metal atoms occupy three eightfold positions, denoted $M(1)$, $M(2)$, and $M(3)$, and the nonmetal atoms, X, occupy a fourth eightfold position. The $M(1)$ and $M(3)$ atoms form an infinite three-dimensional network common to both types of structures. The $M(2)$ and X atoms are situated in chan-

TABLE I

OBSERVED[a] AND CALCULATED POWDER DIFFRACTION INTENSITY DATA FOR Hf_3As

$h\,k\,l$	I_{calc}	I_{obs}[b]	$h\,k\,l$	I_{calc}	I_{obs}[b]	$h\,k\,l$	I_{calc}	I_{obs}[b]	$h\,k\,l$	I_{calc}	I_{obs}[b]
2 0 0	3	[c]	2 2 0	18,017	18,848	0 2 5	95	101	−4 2 5	235	233
0 0 2	2	[c]	0 2 2	17,559	18,205	4 2 3	538	575	1 1 8	198	196
−2 0 2	3	[c]	−5 1 2	5,922	6,231	−5 1 5	5	6	4 2 5	1,380	1,331
2 0 2	8	[c]	5 1 2	3,135	3,134	−7 1 1	33	43	1 3 0	44	97
1 1 0	14	[c]	−2 2 1	390	439	7 1 1	76	114	−1 3 1	888	1,052
−1 1 1	17	[c]	2 2 1	765	816	−1 1 7	229	306	1 3 1	316	414
1 1 1	33	[c]	−6 0 2	189	[d]	1 1 7	1 1 7	206	−6 2 3	413	20
−1 1 2	71	99	−2 0 6	14,570	[d]	5 1 5	67	116	6 2 3	145	8
1 1 2	456	454	6 0 2	13,007	[d]	−7 1 2	1,378	1,497	−1 3 2	4	3
4 0 0	260	319	2 0 6	131	[d]	7 1 2	128	247	1 3 2	295	255
0 0 4	59	108	−2 2 2	5,966	[d]	−2 2 5	1	4	−8 0 4	98	112
3 1 0	36	13	2 2 2	5,182	[d]	2 2 5	95	91	−4 0 8	2,373	2,244
−3 1 1	256	201	0 2 3	769	[d]	8 0 0	364	614	8 0 4	2,579	2,682
−1 1 3	40	33	−5 1 3	21,672	21,115	0 0 8	92	99	4 0 8	118	195
3 1 1	17	14	−3 1 5	5,322	5,096	−4 2 4	2,021	2,059	−3 1 8	526	889
1 1 3	117	97	5 1 3	6,104	5,962	4 2 4	2,176	2,021	3 1 8	10	11
−4 0 2	147	92	3 1 5	19,462	19,452	−7 1 3	891	[d]	−7 1 5	7,691	8,033
−2 0 4	77	43	−1 1 6	140	199	−3 1 7	3	[d]	0 2 7	238	246
4 0 2	177	83	1 1 6	1,981	2,220	7 1 3	4	[d]	−5 1 7	2,261	2,297
2 0 4	150	58	−2 2 3	3,647	3,741	3 1 7	533	[d]	3 3 0	772	828
−3 1 2	1,740	1,388	2 2 3	1,540	1,765	−8 0 2	94	270	7 1 5	1,606	1,704
3 1 2	142	120	4 2 0	10,069	10,261	8 0 2	1,187	1,417	5 1 7	8,480	8,454
−1 1 4	0	2	0 2 4	11,905	11,771	−2 0 8	633	653	−3 3 1	0	0
1 1 4	721	783	−5 1 4	2,769	2,959	2 0 8	248	209	−1 3 3	207	326
−3 1 3	1,130	1,152	5 1 4	3,383	3,608	6 2 0	1,170	1,009	3 3 1	558	876
3 1 3	1,630	1,525	−4 2 1	2,306	2,513	0 2 6	833	794	1 3 3	2	4
−4 0 4	176	13	4 2 1	428	499	−5 1 6	415	409	−6 2 4	57	60
4 0 4	378	14	−6 0 4	9,154	9,535	−6 2 1	20	22	−4 2 6	520	505
0 2 0	1,299	1,433	−4 0 6	4	4	5 1 6	262	265	6 2 4	449	394
−3 1 4	4,976	4,757	6 0 4	90	110	6 2 1	269	262	4 2 6	169	129
5 1 0	1,111	1,063	4 0 6	8,438	9,053	−6 0 6	4	53	−2 2 7	3	2
3 1 4	7,756	7,713	−4 2 2	5	5	6 0 6	360	348	2 2 7	292	221
0 2 1	78	268	−2 2 4	9,827	10,262	−6 2 2	156	150	−3 3 2	244	218
−5 1 1	10,269	10,881	4 2 2	11,067	11,612	−2 2 6	758	758	3 3 2	2,988	2,740
5 1 1	15,689	16,099	2 2 4	225	232	6 2 2	327	326	9 1 0	289	242
−1 1 5	18,657	18,464	−3 1 6	3,711	3,949	−7 1 4	986	1,008	−9 1 1	76	5
1 1 5	10,544	10,019	3 1 6	3,960	4,599	2 2 6	11	11	9 1 1	460	18
6 0 0	12,061	11,728	7 1 0	1,061	981	−1 1 8	156	155			
0 0 6	13,517	15,275	−4 2 3	37	43	7 1 4	246	245			

[a] Recorded in a Philips XDC-700 focusing camera with CrK_{α_1} radiation, and measured by a SAAB automatic film scanner.

[b] I_{obs} for overlapping reflections decomposed into individual components by the profile analysis program.

[c] Cut off by scanner slit system.

[d] Overlapped by hafnium line.

nels in the $M(1)$–$M(3)$ network. The two structures appear almost identical when viewed in projection on the basal plane. The major difference between them lies in the disposition of the $M(2)$ and X atoms in the direction of the tetragonal axis. The $M(2)$ atoms are situated at the corners of slightly distorted tetrahedra. By sharing edges, the

TABLE II

STRUCTURE DATA FOR Hf_3As[a]

Atom[b]	x[c]	y[c]	z[c]
Hf(11)	7367(5)	7895(12)	4026(6)
Hf(12)	1570(5)	7231(15)	5100(5)
Hf(21)	9415(5)	4802(15)	1669(5)
Hf(22)	0808(5)	9664(14)	6899(5)
Hf(31)	7362(5)	2672(13)	3021(5)
Hf(32)	9487(5)	7556(14)	4835(5)
As(11)	9161(9)	9916(35)	1317(10)
As(12)	1214(9)	4602(31)	6627(12)

[a] Space group $C2/c$ (No. 15), lattice parameters (Å): $a = 15.3898(14)$, $b = 5.3795(5)$, $c = 15.3330(14)$, $\beta = 90.291(6)°$.

[b] All atoms in 8f.

[c] Positional parameters × 10^4; estimated standard deviations referring to the least significant digits in parentheses.

TABLE III

INTERATOMIC DISTANCES IN Hf_3As (Å)[a,b]

Hf(11)-As(12)	2.76(2)	Hf(12)-As(12)	2.79(2)
As(11)	2.89(2)	As(11)	2.84(2)
Hf(31)	3.00(1)	Hf(12)	2.90(2)
Hf(11)	3.04(2)	Hf(32)	3.05(1)
Hf(12)	3.11(1)	Hf(32)	3.23(1)
Hf(21)	3.11(1)	Hf(32)	3.24(1)
Hf(31)	3.17(1)	Hf(22)	3.28(1)
Hf(31)	3.21(1)	Hf(31)	3.31(1)
Hf(32)	3.36(1)	Hf(21)	3.36(1)
Hf(12)	3.37(1)	Hf(31)	3.43(1)
Hf(22)	3.42(1)		
Hf(12)	3.47(1)		
Hf(32)	3.49(1)		
Hf(12)	3.68(1)		
Hf(21)-As(11)	2.71(2)	Hf(22)-As(11)	2.69(2)
As(12)	2.79(2)	As(11)	2.75(2)
As(12)	2.81(2)	As(12)	2.76(2)
As(11)	2.83(2)	As(12)	2.83(2)
Hf(32)	3.09(1)	Hf(32)	3.08(1)
Hf(21)	3.11(2)	Hf(31)	3.09(1)
Hf(31)	3.18(1)	Hf(22)	3.10(2)
Hf(32)	3.23(1)	Hf(31)	3.27(1)
Hf(22)	3.24(1)	Hf(32)	3.92(1)
Hf(22)	3.27(1)		
Hf(22)	3.68(1)		
Hf(22)	3.72(1)		
Hf(31)	3.96(1)		
Hf(31)-As(12)	2.69(2)	Hf(32)-As(11)	2.70(2)
As(11)	2.83(2)	As(12)	2.74(2)
As(12)	3.02(2)	As(11)	3.02(2)
2Hf(31)	3.16(1)	Hf(32)	3.11(2)
		Hf(32)	3.21(2)

[a] Distances shorter than 4 Å included.

[b] Estimated standard deviations referring to the least significant digit in parentheses.

tetrahedra form infinite chains extending in the direction of the tetragonal axis. The nonmetal atoms are at the corners of larger, distorted tetrahedra enclosing the $M(2)$ tetrahedra. In the Fe_3P-type structure, the $M(2)$ and X tetrahedra in one channel are translated a distance of approximately one-half of the tetragonal axis with respect to the tetrahedra with equal orientation in the four adjacent channels. In contrast, the $M(2)$ and X tetrahedra of equal orientation are situated at approximately the same level in all channels in the Ti_3P-type structure.

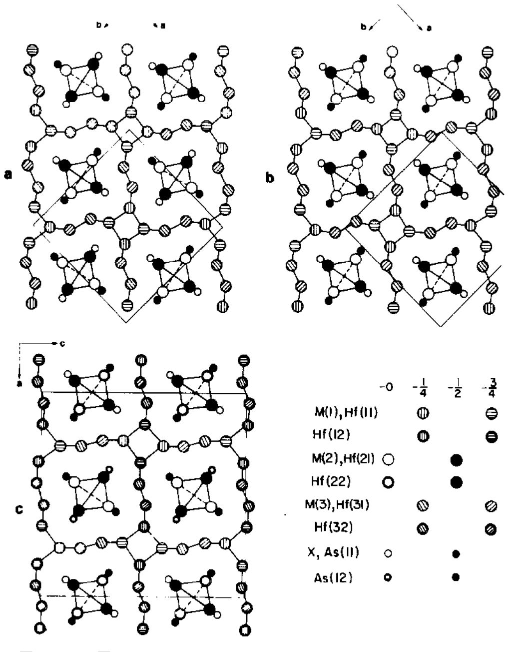

FIG. 1. The structures of (a) Fe_3P, (b) Ti_3P and (c) Hf_3As projected on the basal planes.

In Hf_3As, the six nonequivalent hafnium positions and the two arsenic positions correspond pairwise to the atomic positions in Fe_3P and Ti_3P: Hf(11) and Hf(12) to $M(1)$, Hf(21) and Hf(22) to *M*(2), etc. The *M*(1)–*M*(3) network in Fe_3P and Ti_3P has a nearly identical counterpart in the Hf(11)–Hf(12)–Hf(31)–Hf(32) network of Hf_3As. Likewise, the Hf(21), Hf(22), As(11), and As(12) atoms form chains of tetrahedra similar to those formed by *M*(2) and *X*. With respect to one particular Hf_4 (or As_4) tetrahedron in one channel, the tetrahedra of equal orientation in two of the adjacent channels lie at approximately the same *y* level, while they are translated a distance of approximately *b*/2 in the remaining two channels. This feature reduces the symmetry from fourfold to twofold and represents the major structural distinction of Hf_3As from the Fe_3P and Ti_3P types. The Hf_3As structure can accordingly be regarded as an intermediate step in the morphotropic transition from Fe_3P to Ti_3P.

Coordination and bonding in compounds of the Fe_3P–Ti_3P–V_3S family have been discussed qualitatively in a recent article (*6*). Analysis of the interatomic distances indicated certain coordination trends which appeared to be associated with trends in the cohesive properties of the transition metal components. For the phosphide representatives, an empirical rule was formulated as follows: The greater the cohesive strength of the parent metal, the smaller is the phosphorus coordination number in the corresponding phosphide. For arsenide representatives, accurate structure data are available only for Nb_3As. Its coordination closely resembles that for Nb_3P.

The present results for Hf_3As show that this compound can be regarded as a new type among the members of the Fe_3P–Ti_3P–V_3S family of structures. It might then be expected that the coordination in Hf_3As should follow the same trend as that exhibited by the other representatives. The increasing cohesive strength in the series Ti–Zr–Hf suggests that the coordination for the nonmetal atoms in Hf_3P and Hf_3As should tend to be smaller than that in the corresponding compounds with titanium and zirconium. A histographic representation of the phosphorus atom coordination in Ti_3P and Zr_3P (*6*) shows that the phosphorus atoms have a fairly even nine-coordination of metal neighbors in these compounds. An analogous histographic representation of the coordination about As(11) and As(12) in Hf_3As is shown in Fig. 2. The histograms indicate the number of Hf–As distances falling within given intervals of *D*/*d* where *D* is a scale factor equal to the sum of the Goldschmidt radius for 12-coordination for hafnium (1.58 Å) and the covalent radius for arsenic (1.18 Å), and *d* is the distance from a central arsenic atom to a hafnium neighbor. For further details of the histographic representation, see Ref. *6*.

The moderate accuracy of the Hf_3As interatomic distances as obtained in the present study precludes any more detailed conclusions. It appears from Fig. 2, however, that there is indeed a tendency toward an eight-coordination for arsenic, the ninth hafnium neighbor being situated at an appreciably greater distance from As(12) than the remaining eight. No structure data are yet available for Hf_3P.

An even stronger tendency toward eight-coordination for the arsenic atoms would be expected for Ta_3As, considering the greater cohesive strength of tantalum metal compared with hafnium. It is interesting to observe that the powder line intensities reported for Ta_3As (*3*) are, in many cases, quite different from those of corresponding lines in the Hf_3As pattern, in spite of the small difference in X-ray scattering power between hafnium and tantalum. We interpret the differences in intensity in terms of

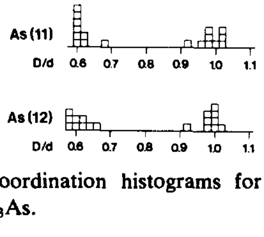

FIG. 2. Coordination histograms for As(11) and As(12) in Hf_3As.

small, systematic shifts of the atomic positional parameters in such a way that the ninth metal neighbor is farther removed from the arsenic atoms in Ta_3As than in Hf_3As.[1]

We finally conclude that Hf_3As represents a new member of the Fe_3P–Ti_3P–V_3S family of structures. The observed distribution of interatomic distances in Hf_3As supports the tentative coordination rules proposed for the class of compounds as a whole.

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[1] *Note added in proof:* A crystal structure refinement of Ta_3As was recently reported by Yu Wang, L. D. Calvert, E. J. Gabe, and J. B. Taylor, *Acta Crystallogr.* **B35**, 1447 (1979). The results are in full agreement with our predictions.