The Metal-Rich Sulfides and Phosphides of the Early Transition Metals

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INTRODUCTION

The sulfides and phosphides of the early transition metals have been studied extensively since the earliest days of solid-state chemistry, and their study has contributed significantly to our current understanding of the interrelation among structure, stability and electronic structure in solids. Today the study of structure and bonding of intermetallic compounds is an important and rapidly growing field of chemistry. This study evolved in part out of the early investigations of metal-rich compounds of the early transition elements with main-group elements above the Zintl line which revealed the existence of compounds with extensive metal bonding, i.e., with metallic clusters. In the early days of solid-state chemistry consideration of the cohesive energies of solid compounds was generally restricted to consideration of metal-nonmetal interactions, and chemists frequently restricted their exploration efforts to materials the stoichiometries of which could be rationalized on the basis of the stabilities of known or proposed oxidation states of the constituent elements.

The principal view that guided the synthesis efforts of chemists prior to the realization of the importance of homonuclear bonding was the Born-Haber cycle. Compounds that were projected to be stable were those for which the calculated or estimated Madelung energies could compensate for the energies required to prepare the appropriate gaseous ions from the elements in their stable forms. This mode of thinking interfered with the growth in understanding of the stabilizing effects that result from metal-metal or nonmetal-nonmetal bonding interactions. Today this view has been largely replaced by that in which the bonding is considered qualitatively, if not quantitatively, in terms of covalent interactions as revealed by band-structure calculations.

While there still do not exist theoretical frameworks that lead directly to the prediction of new structures and stoichiometries, it is now frequently the case that solid-state chemists thoughts are guided by band-theoretical concepts and are no longer circumscribed by ideas based upon the Born-Haber cycle and ions in unusual oxidation states. There has resulted a rich variety of metal-rich compounds with unexpected structures and stoichiometries a subset of which is comprised of the metal-rich sulfides and phosphides of the early transition metals (Table I).

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Table I. The binary and ternary metal-rich sulfides and phosphides of the early transition metals: chemical composition (column 1), lattice type and number of atoms per unit cell (column 2), number of independent metal-atom sites (column 3), space group symbol (column 4), percent of volume occupied (hard sphere model) (column 5), family (see text) (column 6), and reference (column 7).

Structure Type	Pearson Symbol	Sites	Space Group	% occ	Family	Ref
Hf ₂ S	hP6	1	6 ₃ /mmc	52.8	V	1
Nb _{0.95} Ta _{1.05} S	tP6	2	4/nmm	50.4	I	2
Ti ₅ P ₃	hP18	2	6 ₃ /mmc	60.0	V	3
Nb _{1.72} Ta _{3.28} S ₂	tI14	3	4/mmm	60.7	I	4
Hf ₃ P ₂	oP20	3	nma	61.6	I	5
V ₁₂ P ₇	hP26	3	6 ₃ /m	62.3	I	6
V ₃ S	tI32	3	$\bar{4}2m$	68.2	II	7
V ₃ S	tI32	3	4 ₂ /nbc	68.4	II	7
Ti ₃ P	tI32	3	4 ₂ /n	62.6	II	8
Zr ₉ Mo ₄ S	hP28	4	6 ₃ /mmc	69.9	IV	9
Ta _{4.75} V _{1.25} S	mC28	4	2/c	62.8	III	10
Ta ₂ S	oP36	4	bcm	62.0	III	11
Ta ₃ S ₂	oC40	4	bm2	52.0	III	12
Hf _{10.1} Ta _{2.9} S ₃	cI64	4	23	65.2	V	13
Zr _{6.45} Nb _{4.55} P ₄	oI30	5	mmm	64.3	I	14
Zr ₉ S ₂	tI88	5	4 ₁ /amd	65.1	II	15
Ta ₂ P	oP36	6	nma	68.4	I	16
Hf _{5.08} Mo _{0.92} P ₃	oP36	6	nm	66.3	I	17
Ta ₆ S	mC56	6	2/c	66.3	III	18
Nb ₂₁ S ₈	tI58	6	4/m	63.8	I	19
Ta ₆ S	aP14	7	$\bar{1}$	66.6	III	20
Mo ₈ P ₅	mP13	8	m	61.9	I	21

Table I - continued

Structure Type	Pearson Symbol	Sites	Space Group	% occ	Family	Ref
Nb ₇ P ₄	mC44	8	2/m	61.8	I	22
Mo ₄ P ₃	oP56	8	nma	63.6	I	23
Nb ₈ P ₅	oP54	9	bam	57.4	I	24
Nb ₅ P ₃	oP64	10	nma	61.2	I	25
Ta _{6.08} Nb _{4.92} S ₄	oP60	11	nma	62.8	I	26
Nb ₂ P	oP54	12	nma	62.5	I	27
Nb _{6.74} Ta _{5.26} S ₄	oP64	12	nma	64.3	I	28
Zr ₂ P	oC108	13	mmm	62.8	I	29
Nb ₁₄ S ₅	oP76	14	nma	64.9	I	30
Zr ₁₄ P ₉	oP92	15	nnm	60.5	I	31
Ti ₈ S ₃	mC88	16	2/m	61.7	I	32

The Binary Compounds, e.g., Ti₂S

For example, when the stability of Ti₂S, which prior to 1967 was a hypothetical compound, was initially considered, the consideration was based upon the packing of S⁻² ions and titanium ions in the usual oxidation state, Ti⁺. The resulting ionic structure was conceived to be one typical for the 2:1 stoichiometry with packing of anions about cations and vice versa, e.g., antifluorite, and was found to be highly unstable with respect to disproportionation. However, the experimental discovery of Ti₂S³³ by synthesis and structure determination showed that the basis for its existence was strikingly different from this view.

The structure of Ti₂S (Fig. 1) is heavily based upon *bcc* units of Ti and involves a substantial component of Ti-Ti bonding. Thus, the metal-rich compound, Ti₂S, which forms spontaneously from the reaction of well-known TiS(s) in the NiAs-type structure (Fig. 2) and Ti(s) at temperatures in the neighborhood of 1500 K, is stabilized by extensive metal-metal bonding. Discoveries of similar compounds with extensive metal-metal bonding such as those listed in Table 1 led to a change in the way chemical bonding in solids is viewed. Column one of the table lists examples of structure types that occur among the binary and ternary metal-rich phosphides and sulfides of the early transition metals, in column 2 the Pearson³⁴ symbols (a = triclinic, m = monoclinic, o = orthorhombic, h = hexagonal, t = tetragonal, c = cubic; P = primitive, I = body-centered, C = end

Fig. 1 The crystal structure of Ti_2S

Fig. 2 The NiAs-type structure of TiS

centered; the number gives the total number of atoms in a unit cell), are listed, in column 3 the numbers of symmetrically inequivalent metal sites are given, in column 4 the generating space group operations, in column 5 the percent of the cell volume occupied assuming Slater's covalent radii,³⁵ in column 6 the family types as discussed below are listed and, finally, column 7 gives the literature references for the structures.

A scan of the table shows that there is a considerable range of structural diversity and substantial structural complexity (low symmetry and large unit cells) exhibited by these compounds. It is apparent from column 6 that the compounds are rather densely packed, the percent volume occupied listed can be compared with the average value ($53.0 \pm 0.8\%$) calculated for the monophosphides and sulfides of the early transition metals.

The efficient packing arises out of the metal clustering that is found in the structures of the listed compounds. The clustering occurs in a number of ways that are broken down into families in the table. The largest family is I, the family to which Ti_2S (Fig. 1) and Nb_{21}S_8 (Fig. 3) belong. In the structures of this family the atoms all lie in mirror planes perpendicular to a short axis (ca. 3.5 Å) and the metal clustering is reminiscent of *bcc* with chains of body-centered cubes or substituted cubes running through the structure perpendicular to the short axis. These chains of cubes are not isolated – they are interconnected with other parallel chains in some cases forming columns of interpenetrating or face-sharing cubes.

In the compounds of family II the clusters are made up of two interpenetrating Kasper CN 14 polyhedra (with a common 6-ring consisting only of metal atoms and two additional 6-rings each containing two nonmetal atoms (either meta or para) form chains by corner or edge sharing and interpenetrate at right angles (hence the tetragonal symmetries)).

The compounds of family III (Fig. 4) are all based primarily upon Ta clustering. In the members of this family clusters of pentagonal antiprisms sharing pentagonal faces (and thus forming chains of interpenetrating icosahedra) are observed. These metallic clusters are decorated on the exterior by the nonmetal (sulfur) atoms, and form some intercluster metal-atom bridging. These robustly metallic materials have markedly refractory properties.

The compounds of family IV are exclusively kappa phase materials (Fig. 5) which, by virtue of the icosahedral metal atom clustering, could be placed in a family with the icosahedral Ta compounds, but which are differentiated because of the substantial differences in the connectivity of the icosahedra. In the kappa phase materials the icosahedra form triangles such as have recently been recognized as important building blocks in a wide variety of highly complex intermetallic compounds.³⁶

The fifth and final family contains all entries of the table that do not fall in the first four families and thus have exceptional structures. Included in this family are the unique filled γ -brass material $\text{Hf}_{10.1}\text{Ta}_{2.9}\text{S}_3$, the AbABcB layer material Hf_2S , and Ti_5P_3 with incompletely filled octahedral clusters of Ti that link chains of interpenetrating Kasper CN 14 polyhedra with 6-rings made up of 3 phosphorus atoms alternately with 3 titanium atoms.

The structurally based conclusions regarding the extents of metal-metal interactions in these metal-rich compounds have been quantified in the cases of several mono- and metal-rich compounds of early transition metals. Ab initio methods have been applied to TiS and VS ³⁷ and Extended-Hückel Tight Binding (EHTB) methods have been applied to a variety of metal-rich compounds.^{3,38,39}

Fig. 3 The crystal structure of Nb_{21}S_8

Fig. 4 The crystal structures of Ta_6S and Ta_3S_2

Fig. 5 The kappa-phase crystal structure

Band Theory Results

The ab initio results for TiS (Fig. 6) can be qualitatively described as follows: 1. there are six relatively low-lying bands (0.2 to 0.4 Ry below E_F) which correspond to states that are about 60% sulfur 3p-type in character, and the remaining 40% of these bands is principally a mixture of titanium 4p-type and 3d-type, indicating a polar covalent interaction between titanium and sulfur. Above these bands lie the bands that are made up principally of titanium 3-d type orbitals, and give rise to the titanium-titanium interactions contributing to the bonding in the solid. Turning to EHTB calculations for ease of computation, the ratio of the calculated Mullikan Overlap Populations (MOP's) (Ti-Ti MOP/Ti-S MOP) is 0.339. This result, in agreement with the ab initio results, confirms the intuitive view that while titanium-sulfur bonding plays a predominant role in stabilizing TiS, nonetheless titanium-titanium bonding is important as well.

The results of such calculations carried out for Ti(s), $Ti_2S(s)$ and TiS(s) are presented in Table II. The picture that emerges from such calculations is one of stoichiometries and structures competing for the most efficient use of the valence electrons. In comparing alternative structures and stoichiometries, those which provide the highest densities of low-lying states will be energetically stable with respect to disproportionation. E.g., Ti_2S is stable with respect to disproportionation into Ti and TiS because Ti_2S makes more efficient use of the valence electrons than does a mixture of Ti and TiS. The Ti-Ti interactions in Ti(s) and the strong Ti-S and relatively weaker Ti-Ti interactions in TiS lose out to the mixture of strong Ti-Ti and Ti-S

Fig. 6 Energy bands for TiS calculated by the KKR method

Table II. Ti-Ti and Ti-S Mullikan Overlap Populations for Ti, Ti₂S and TiS

	Ti-Ti MOP per Ti	Ti-S MOP per Ti
Ti(s)	1.635	
Ti ₂ S(s)	1.165	0.969
TiS(s)	0.510	1.504

interactions in Ti₂S. The ability of Ti to form Ti, Ti⁺ and Ti²⁺ in the gas phase has no direct relationship to the energetics of the reaction

which can instead be viewed as a trade-off of Ti-Ti bonding for Ti-S bonding in TiS(s), and a trade-off of Ti-S bonding for Ti-Ti bonding in Ti(s). The effectiveness of these trades is determined by the orbital overlaps as provided by the coordination polyhedra in Ti₂S. Looked at in this way it is readily understood that metal-rich sulfides other than Ti₂S could also form, and in fact Ti₈S₃ has been prepared and characterized.³²

The trade-off between metal-metal and metal-nonmetal bonding occurs within, as well as between, the metal-rich compounds. For example, in Ti₂S(s) there are six symmetrically inequivalent Ti atoms with six different coordination polyhedra (Fig. 7). In Fig. 7 Ti(1) is in the upper left, Ti(2) in the top middle and the numbering thus continues to Ti(6) in the lower right. The Ti to Ti and Ti to S CN's and MOP's for these six positions are given in Table III.

Fig. 7 The coordination polyhedra of the six symmetrically inequivalent titanium atoms in Ti_2S

Table III. Ti coordination numbers (to S and Ti) and Mullikan Overlap Populations in Ti_2S .

Ti	CN(to S)	CN(to Ti)	MOP(Ti-Ti)	MOP(Ti-S)	MOP(Total)
1	4	12	1.041	0.883	1.924
2	5	11	0.963	1.058	2.021
3	3	11	1.407	0.742	2.149
4	3	11	1.439	0.688	2.127
5	5	10	0.963	1.456	2.419
6	4	11	1.149	0.986	2.135

When the total MOP's for each site are compared with those for Ti in Ti(s) (1.635) and in TiS (2.014) it can be seen that in all sites titanium is more efficiently bonded than in Ti(s) and in sites 2 through 6 it is more efficiently bonded than in TiS(s) . In sites of Ti_2S for which the CN to sulfur (column 2) is less than five the Ti-Ti bonding outweighs the Ti-S bonding in importance, and even in the cases for which the CN to sulfur is five the Ti-Ti bonding makes a substantial contribution. The variety of coordination polyhedra shown in Fig. 7 demonstrates that Ti_2S is stable because the coordination polyhedra that result in efficient use of orbitals with differing amounts of Ti-Ti and

Ti-S bonding are structurally interrelated such that they can interpenetrate to form the observed structure (Fig. 1). This feature is common to all of the compounds in Family I.

Consider, as a second example, Nb_{21}S_8 .¹⁹ The CN's and MOP's are given in Table IV. The Nb-Ta-S system has been studied by high-temperature synthetic techniques.⁴⁰ Of special interest in this case are the facts that the structures of the metal-rich sulfides of Nb and Ta are in different families ($\text{Nb}_{14}\text{S}_5(\text{s})$ and $\text{Nb}_{21}\text{S}_8(\text{s})$ are in I; $\text{Ta}_3\text{S}_2(\text{s})$, $\text{Ta}_2\text{S}(\text{s})$ and $\text{Ta}_6\text{S}(\text{s})$ (two modifications) are in III) and Nb and Ta are very nearly the same size according to all tabulations of radii. It was found, for example, that $\text{Nb}_{21}\text{S}_8(\text{s})$ saturated with Ta yields a solid solution with different fractional site occupancies of the six symmetrically inequivalent sites (column 5 of Table IV gives the percent Ta occupation of the six metal-atom sites of Ta saturated $\text{Nb}_{21}\text{S}_8(\text{s})$). As shown in Fig. 8 there is a good correlation between the percent Ta occupation and the metal-metal MOP calculated for Nb_{21}S_8 . This correlation is expected based upon the DFSO (Differential Fractional Site Occupation) model⁴¹ in which it is proposed that the better metal-metal bonding element of a pair (e.g., Ta > Nb) preferentially occupies those sites with higher metal-metal MOP's in the binary compound.

Table IV. Nb coordination numbers (to S and Nb) and Nb-Nb Mullikan Overlap Populations in Nb_{21}S_8

Site	CN (to S)	CN (to Nb)	MOP (Nb-Nb)	% occ
1	4	10	2.48	14
2	1	13	3.53	61
3	3	9	2.54	25
4	2	12	3.05	46
5	4	10	2.27	11
6	4	11	2.17	8

Nb-Ta-S Compounds and DFSO

In 1991 it was discovered that DFSO could result in the stabilization of new ternary stoichiometries and structures.^{3,5,26,28} The initial discovery was the preparation and determination of structure of $\text{Ta}_{6.08}\text{Nb}_{4.92}\text{S}_4$ ²⁶ (Fig. 9) in a structure that is unknown in the S-Nb and S-Ta systems and has, in fact, not been found for any other combination of elements. Later $\text{Nb}_{0.95}\text{Ta}_{1.05}\text{S}$ (Fig. 10), $\text{Nb}_{1.72}\text{Ta}_{3.28}\text{S}_2$ (Fig. 11) and $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$ (Fig. 12) were also found, and only the $\text{Nb}_{0.95}\text{Ta}_{1.05}\text{S}$ structure had a precedent, i.e., it is known for Ta_2Se .⁴² These discoveries in the Nb-Ta-S system provided a clearcut case for the DFSO proposal because the radii of Nb and Ta are so nearly the same. Thus, the principal

Fig. 8 Percent Ta occupation of Ta saturated Nb_{21}S_8 versus Mullikan Overlap Population in Pure Nb_{21}S_8

Fig. 9 The crystal structure of $\text{Ta}_{6.08}\text{Nb}_{4.92}\text{S}_4$

energetic effect of substitution of niobium by tantalum is to replace 4d orbitals by 5d orbitals thereby increasing the bond overlaps. In the model the metal-metal bonding is emphasized over the metal-nonmetal bonding because: 1. metal-metal bonding is predominant in the metal-rich compounds, 2. the metal-nonmetal bonding is presumed to be saturated and therefore unaffected by the change. Table V gives the MOP's calculated for the hypothetical binary compounds³⁸ M_{11}S_4 and M_{12}S_4 with $\text{M} = \text{Nb}$ or Ta .

The MOP's listed for Ta in Table V are a factor of 1.10 ± 0.01 greater than the corresponding MOP's listed for Nb. The increase in the MOP calculated for elemental Ta(s) relative to elemental Nb(s) is 11% and the corresponding increase in enthalpy of

Fig. 10 The crystal structure of $\text{Nb}_{0.95}\text{Ta}_{1.05}\text{S}$

Fig. 11 The crystal structure of $\text{Nb}_{1.72}\text{Ta}_{3.28}\text{S}_2$

Fig. 12 The crystal structure of $\text{Nb}_{6.74}\text{Ta}_{5.26}\text{S}_4$

Table V. MOP's for Nb and Ta in hypothetical $M_{11}S_4$ ($M = Nb$ or Ta) and $M_{12}S_4$ ($M = Nb$ or Ta)

	$Nb_{11}S_4$	$Ta_{11}S_4$	$Nb_{12}S_4$	$Ta_{12}S_4$
1	3.57	3.93	3.81	4.18
2	3.43	3.79	3.39	3.75
3	3.03	3.36	3.44	3.79
4	3.57	3.94	3.03	3.36
5	3.10	3.43	3.00	3.33
6	2.57	2.83	2.49	2.74
7	2.55	2.80	2.71	3.02
8	2.48	2.73	2.45	2.70
9	2.58	2.83	2.28	2.53
10	2.52	2.78	2.17	2.42
11	1.76	1.95	1.98	2.21
12			2.04	2.27

vaporization is 9% suggesting a proportional relationship between bond energy and MOP at least to a first approximation.

If the bond energy is increased by a fixed percentage upon substitution of Nb by Ta and is similarly decreased upon substitution of Ta by Nb, the substitution of Nb for Ta into a more heavily metal-metal bonded structure will destabilize that structure to a greater extent than it will a less heavily metal-metal bonded structure, and similarly substitution of Ta for Nb into a less heavily metal-metal bonded solid will destabilize it relative to a more heavily metal-metal bonded material. The hypothetical materials, $Nb_{11}S_4$ and $Nb_{12}S_4$, are more heavily metal-metal bonded than the corresponding stoichiometric mixtures of $Nb_{21}S_8$ and $Nb_{14}S_5$, while the hypothetical materials $Ta_{11}S_4$ and $Ta_{12}S_4$ are less heavily metal-metal bonded than the corresponding stoichiometric mixtures of Ta_6S and Ta_2S . Thus, the ternary solid solutions $Ta_{6.08}Nb_{4.92}S_2$ and $Nb_{6.74}Ta_{5.26}S_4$, which are entropically stabilized relative to the pure binaries by configurational entropy, are energetically stabilized relative to solid solutions in the binary structures due to the stabilizing influence of Ta in the ternaries relative to the binary niobium sulfide solid solutions, and of Nb in the ternaries relative to its destabilizing effect in the solid solutions in the binary tantalum sulfides. Furthermore niobium and tantalum distribute over the 11 symmetrically inequivalent sites of $M_{11}S_4$ and over the 12 symmetrically inequivalent sites of $M_{12}S_4$ in a manner that minimizes the Gibbs free energy as determined by the bond energy (enthalpy) and site occupation (configurational entropy).

Ternary Phosphides

The DFSO principle does not apply as straightforwardly to most other ternary compounds as it does to mixed Nb-Ta compounds because size and valence differences complicate the interpretation. Nonetheless, some generalization appears to be valid, i.e., new ternary solids with structures that are unknown among the pure binaries occur in structures with a number of metal sites with significant and varied metal-metal bonding and mixed-metal occupancy. Several new ternary metal-rich phosphides have been prepared by high-temperature techniques. $\text{Zr}_{6.45}\text{Nb}_{4.55}\text{P}_4$ ¹⁴ (Fig. 13), for example occurs in a structure that is unknown for any other combination of elements and even the 11:4 stoichiometry is unknown among the binaries.

The compound $\text{Hf}_{5.08}\text{Mo}_{0.92}\text{P}_3$ (Fig. 14), a new structure type for the 2:1 stoichiometry, has also been prepared by high-temperature techniques.¹⁸ In this case Hf_2P with a different structure is known. Both structures have six independent metal-atom sites. The MOP's calculated for Hf_2P in the Hf_2P -type and $\text{Hf}_{5.08}\text{Mo}_{0.92}\text{P}_3$ -type structures are given in Table VI.

The values of Table VI show that overall there is increased metal-metal bonding in the new structure with partial Mo occupancy (site 5: 38% Mo; site 6: 54% Mo) and that the sites with Mo occupation are the two with the largest Hf-Hf MOP in the hypothetical binary with the same structure. This interpretation is, however, clouded by the fact that Mo is smaller than Hf (the ratio of the Slater radii is 1.07).

Fig. 13 The crystal structure of $\text{Zr}_{6.45}\text{Nb}_{4.55}\text{P}_4$

Fig. 14 The crystal structure of $\text{Hf}_{5.08}\text{Mo}_{0.92}\text{P}_3$.
Site 5 contains 38% Mo, site 6 contains 54% Mo.

Table VI. MOP for Hf in Hf_2P and hypothetical Hf_6P_3

Site	Hf_2P	$\text{Hf}_{5.08}\text{Mo}_{0.92}\text{P}_3$
1	2.04	2.12
2	2.07	2.22
3	2.11	2.32
4	2.21	2.38
5	2.27	2.46
6	<u>2.38</u>	2.62

Kappa-Phase Materials

Another structure type that yielded new examples when attempts were made to prepare new metal-rich sulfides with mixed early transition metals is the kappa-phase structure (Fig. 15), a structure type that is well-known for a wide variety of elements.³³ This structure forms with triangular clusters of metal-atom icosahedra, and these clusters provide the sites for DFSO by mixed early transition metal. Among these kappa phase materials one, $\text{Zr}_9\text{Nb}_4\text{S}_4$, has been shown to be a low-temperature superconductor.⁴³

Fig. 15 The filled gamma brass structure of $\text{Hf}_{10.1}\text{Ta}_{2.9}\text{S}_3$

An interesting feature of the kappa phase is the variability of occupation of the nonmetal positions. There are two different sites that are created by the packing of the icosahedra – a tricapped trigonal prismatic site of $\pm(1/3, 2/3, 3/4)$ and a distorted octahedral site at the group of positions equivalent to $1/2, 0, 0$. In many examples of the kappa phase the octahedral positions are occupied by first row main-group elements. In the DFSO sulfides these positions, as well as the trigonal prismatic ones are occupied (at least partially) by sulfur. This partial occupation of the octahedral sites by sulfur results in kappa phase structures with the largest known cell volumes. Partial occupation of the octahedral sites by oxygen as well as sulfur cannot be ruled out, and neutron diffraction results⁴⁴ indicate that the sites are partially occupied by S, partially occupied by O and partially vacant.

Filled Gamma Brass

The gamma-brass structure that plays a role in the Hume-Rothery electron concentration – phase stability rules was found in a new, filled variant for $\text{Hf}_{10.1}\text{Ta}_{2.9}\text{S}_3$ ¹³ (Fig. 15). This phase is unknown in either of the pure binary systems and thus is presumed to result from DMSO stabilization of the metal-atom cluster (inner tetrahedron, outer tetrahedron, octahedron, cuboctahedron). No technique was completely successful in establishing the site occupancies in this case, but a neutron diffraction study¹³ yielded 100% Ta on the inner tetrahedron, 39% Ta and 61%

Hf on the outer tetrahedron and 100% Hf on the remaining sites based upon the small difference in scattering lengths for Hf and Ta. These results are consistent with the DFSO concept in the sense that tantalum with a metallic valence of five is a better metal-metal bond former than hafnium and is found primarily in the inner tetrahedron and secondarily in the outer tetrahedron.

CONCLUSIONS

Early work on the preparation of refractory metal-rich compounds of the early transition metals resulted in the understanding that metal-metal bonding results in a structural variety that plays an important role in the high-temperature chemistry of these systems. The binary metal-rich systems have been thoroughly studied at high temperatures, and the structures of most, if not all, of the refractory sulfides and phosphides are known. More recently new ternary phases have been discovered, and these have been shown to result from distributed fractional site occupation of metal atom sites in complex structures. The extent of metal-metal bonding has been quantified by Extended-Hückel Tight-Bonding calculations using Mullikan Overlap Populations. Correlations of site occupancy with MOP based upon the DFSO model have been observed.

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