Coordination and Bonding in Representatives of the Fe_3P-, Ti_3P-, α-V_3S- and β-V_3S-Type Structures

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A survey of the atomic coordination in the compounds concerned is presented in the form of histograms showing the number and distribution of interatomic distances. This survey reveals certain systematic coordination trends. These are found to correspond to trends in the cohesive strength of the elemental transition metals. On this basis an empirical rule for phosphide representatives can be formulated as follows: the greater the cohesive strength of the parent metal, the smaller is the phosphorus coordination number in the corresponding phosphide. An attempt is made to rationalize this rule in terms of current theories for the chemical bonding in compounds between transition metals and nonmetals with unfilled p levels.

I. Introduction

The Fe_3P, Ti_3P, α-V_3S and β-V_3S types constitute a family of very closely related structures. Compounds belonging to this family are formed between transition metals and the nonmetals boron, silicon, germanium, phosphorus, arsenic, antimony and sulphur, with the majority of representatives among the Group 4 and 5 transition metal silicides, germanides, phosphides and arsenides. A list of representatives is given in Table I, together with appropriate references.

The geometric relationships between the four types of structure have been described and discussed in several articles (*1, 5, 8, 25–28*), and it has been hinted that the morphotropic transition from the Fe_3P to the

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Ti_3P type might be connected with size-factor effects (*25–27*).

Through X-ray single crystal structure refinements the interatomic distances are known rather accurately for a fair number of representatives. A closer analysis of the various interatomic distances reveals certain trends, which might indicate minor systematic changes in the chemical bonding, assuming that the gross overall bonding situation is largely the same for all members of the structure family.

The purpose of the present paper is to present a detailed comparison of interatomic distances for a number of compounds, to point out some interesting features revealed by the comparison, and, finally, to make an attempt to rationalize these observations in terms of current theories of the chemical bonding in compounds of the type under discussion.

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REPRESENTATIVES OF THE Fe_3P-, Ti_3P-, α-V_3S- AND β-V_3S-TYPE STRUCTURES

Fe_3P type	Ref.[a]	Ti_3P type	Ref.[a]
Ti_3Ge	(1)	Y_3Sb	(12)
Zr_3Sb	(2)	Ti_3Si	(2)
Hf_3Sb	(2)	Ti_3P	(13)
h-Ta_3Ge	(2)	Ti_3As	(14)
Cr_3P	(3)	Zr_3Si	(2)
Mn_3P	(4)	Zr_3Ge	(2)
Fe_3P	(5)	Zr_3P	(15)
$Co_3P_{1-x}B_x$	(5)	Zr_3As	(16)
$(x \sim 0.5)$			
Ni_3P	(6)	Hf_3P	(17)
Pd_3As	(7)	Hf_3Ge	(2)
		V_3P	(18)
		Nb_3Si	(19)
α-V_3S type		Nb_3P	(15)
		Nb_3As	(19)
α-V_3S	(8)	Ta_3Si	(1)
Mo_3P	(9)	l-Ta_3Ge	(2)
W_3P	(10)	α-Ta_3P	(20)
		$Fe_3P_{1-x}B_x$	
		$(0.5 < x < 1)$	(5)
		$Co_3P_{1-x}B_x$	
		$(x \sim 0.7)$	(5)
β-V_3S type		$Fe_{2.6}Mo_{0.4}B$	(21)
		$Fe_{2.6}Re_{0.4}B$	(22)
β-V_3S	(8)	$Fe_{2.6}Ru_{0.4}B$	(23)
β-Ta_3P	(11)	$(Co, Re)_3B$	(24)

[a] Only one reference has been selected for each phase. Reference is made either to the first report on the discovery of the phase, or, if a crystal structure refinement has been carried out, to the report on the structure determination.

II. General Description of the Four Structure Types

The four structures under consideration have tetragonal symmetries, with unit cell dimensions of approximately $a \sim 9$–11 Å, $c/a \sim 0.5$. The space groups are: for Fe_3P $I\bar{4}$; for Ti_3P $P4_2/n$; for α-V_3S $I\bar{4}2m$; and for β-V_2S $P4_2/nbc$. In each case, the atoms occupy four sets of eightfold positions, with z coordinates near or equal to 0, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$. Projections of the structures on the basal planes are shown in Fig. 1. The three

nonequivalent metal atom positions are denoted by $M(1)$, $M(2)$ and $M(3)$, and the nonmetal position by X.

The great similarities between the structures are evident from Fig. 1. The Fe_3P and Ti_3P structures can be regarded as distorted versions of the more symmetric α-V_3S and β-V_3S structures, respectively. The main difference between the body-centered Fe_3P and α-V_3S structures on the one hand, and the primitive Ti_3P and β-V_3S structures on the other hand, lies in the long-range configuration of the atoms. With respect to the near atomic environments, the Fe_3P and Ti_3P structures are quite similar, and this is also true for α-V_3S and β-V_3S.

III. Comparison of Interatomic Distances

The coordination of neighbors about the atoms in the structures is rather complex and irregular, and cannot always be presented in terms of well-defined coordination numbers or coordination polyhedra. For the purpose of the present discussion we have chosen a graphical presentation in the form of coordination histograms. Following a suggestion by Brunner (29), (see also 30), we have constructed the histograms on the basis of the reciprocals of the interatomic distances. The histograms in Figs. 2 and 3 thus indicate the number of M–X and M–M distances falling within given intervals of D/d, where D is a scale factor and d is the distance from a neighbor to the central atom. Each square in the diagrams corresponds to one interatomic distance. In order to facilitate comparison between different compounds we have chosen the scale factor D equal to twice the Goldschmidt radius for 12-coordination, $R(M)$, for the transition metal component in the case of M–M distances. For M–X distances, D has been chosen as the sum of $R(M)$ and one half of the shortest interatomic distance, $r(X)$, in the elemental X component. $r(X)$ corresponds exactly, or
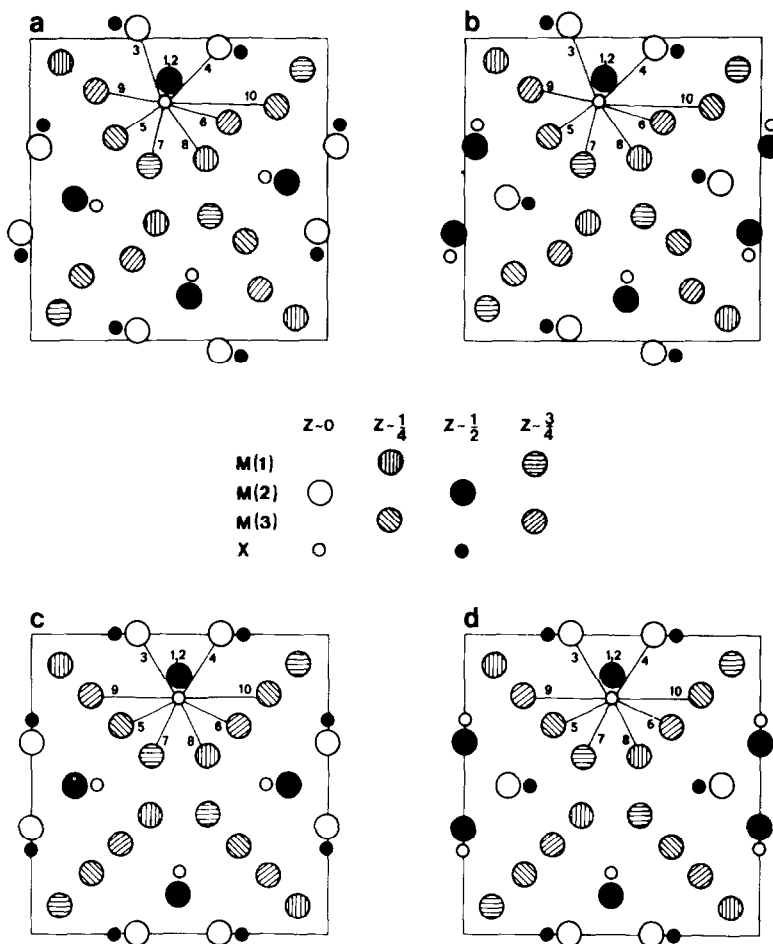
FIG. 1. The Fe_3P- (a), Ti_3P- (b), α-V_3S- (c) and β-V_3S- (d) type structures projected on the basal planes. Origin in the Fe_3P and α-V_3S types at $\bar{4}$, in the Ti_3P and β-V_3S types at 4_2. Metal (M) atom neighbors to the nonmetal (X) atoms are labelled 1–10.

very closely, to the covalent radius of X (31). The following values have been used: (Å units) $R(Ti) = 1.45$, $R(Zr) = 1.60$, $R(V) = 1.36$, $R(Nb) = 1.47$, $R(Ta) = 1.46$, $R(Cr) = 1.28$, $R(Mo) = 1.40$, $R(Mn) = 1.31$, $R(Fe) = 1.27$, $R(Ni) = 1.24$, $r(Si) = 1.17$, $r(P) = 1.10$, $r(S) = 1.04$, $r(As) = 1.18$. The histograms have been plotted in intervals of 0.02 in D/d, for values of D/d larger than 0.57 in the case of M–X distances and larger than 0.63 in the case of M–M distances. The interatomic distances have been calculated from data for those structures, where the

positional parameters have been determined from single crystal X-ray diffraction measurements (for references, see Table I). The accuracy varies considerably among the different structure determinations but suffices for the purposes of the present qualitative discussion.

It should be mentioned that the X–X distances in the structures are very large (P – P $\sim$ 3.44 Å in Ni_3P is the shortest X–X distance in the whole structure family), and X–X interaction is therefore entirely neglected in the following.
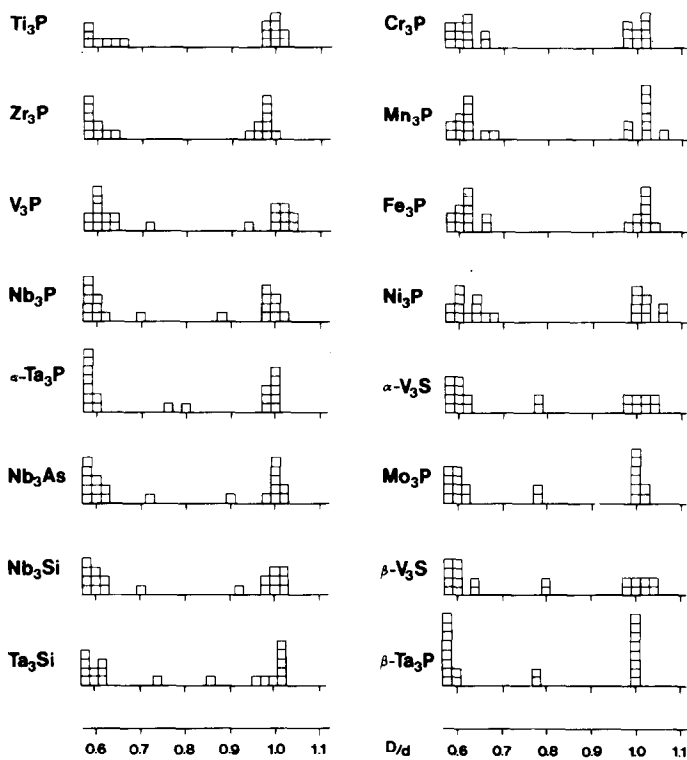
FIG. 2. Histographic representation of the coordination of metal (M) atoms about the nonmetal (X) atoms in structures of the Fe_3P, Ti_3P, α-V_3S and β-V_3S types. Each square corresponds to one interatomic distance. D is the sum of the Goldschmidt radius for the metal atom and the covalent radius for the nonmetal atom, and d is the M–X interatomic distance.

Histograms showing the distribution of M neighbors about the X atoms are presented in Fig. 2. The following observations can be made. In the α-V_3S and β-V_3S compounds, the X atoms have eight near metal neighbors (labelled 1–8 in Fig. 1). These are situated at the corners of a distorted Archimedian antiprism, with the X atom at the center. At considerably larger distances $(D/d < 0.80)$ there are two further metal atoms (labelled 9 and 10 in Fig. 1) situated outside the quadrilateral faces of the antiprism.

In the Fe_3P type phosphides the phosphorus atoms are nine-coordinated, with a gap in D/d of about 0.3 between the first and second coordination spheres. Describing the coordination polyhedron as an Archimedian antiprism with one additional neighbor is not

so appropriate, and it appears more convenient to describe it as a triangular prism, with one additional neighbor outside each of the quadrilateral faces (tetrakaidecahedral coordination (25)).

In Ti_3P and Zr_3P, the phosphorus atoms are nine-coordinated as in the Fe_3P-type phosphides. A tendency to eight-coordination observed earlier for Nb_3P (15) and V_3P (18), is clearly evident for the remaining Ti_3P-type compounds. In the sequence V_3P, Nb_3P, α-Ta_3P, metal atom No. 9 (see Fig. 1) moves successively farther away from the central phosphorus atom, while metal atom No. 10 moves closer. An analogous observation can be made for Nb_3Si and Ta_3Si, although here the effect is smaller than for the corresponding phosphides. The coor-
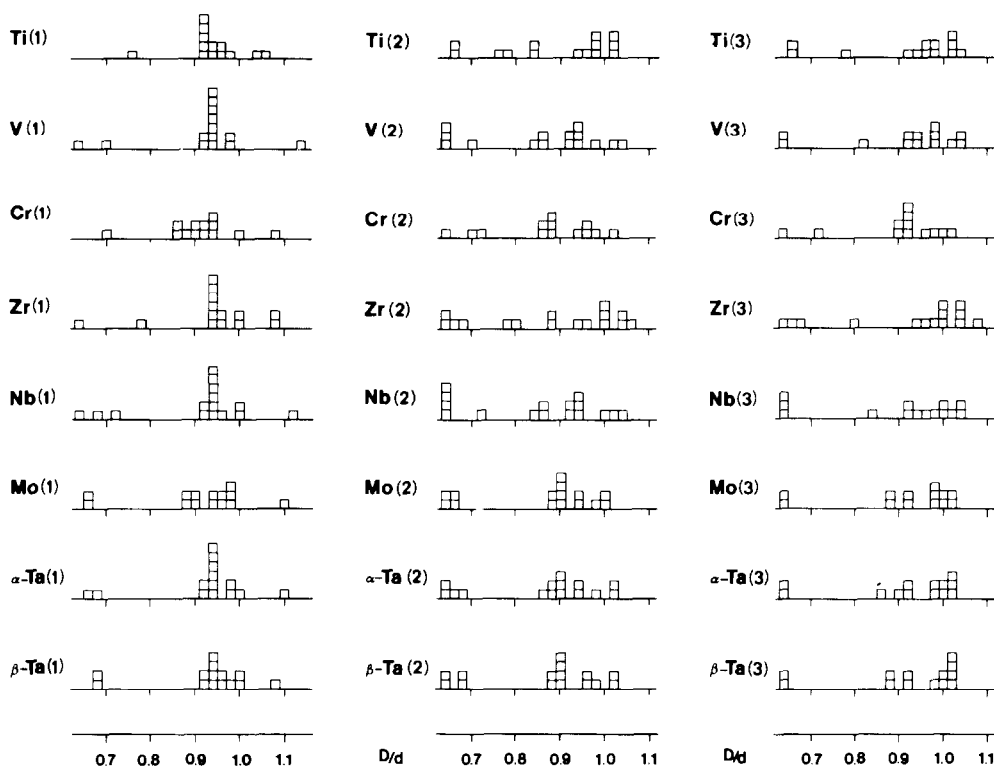
FIG. 3. Histographic representation of the coordination of metal (M) atoms about the metal atoms in phosphides of the Fe_3P-, Ti_3P-, α-V_3S- and β-V_3S-type structures. Each square corresponds to one interatomic distance. D is the Goldschmidt metal atom diameter, and d is the M–M interatomic distance.

dination in Nb_3As is very similar to that in Nb_3P.

While the coordination about the X atoms can be described in a fairly simple way, the coordination of neighbors about the M atoms is much more complex. In the present context the comparison is restricted to a selection of phosphides: Ti_3P, V_3P, Cr_3P, Zr_3P, Nb_3P, Mo_3P, α-Ta_3P and β-Ta_3P. The histograms, which include only M–M distances, are shown in Fig. 3. For all compounds in the whole structure family, M(1) has two near X neighbors, and M(2) has four. In the Fe_3P- and Ti_3P-type compounds, M(3) has three near X neighbors, one of which may be more or less distant as discussed in connection with Fig. 2. In the two V_3S types, M(3) has only two near X neighbors.

As is evident from Fig. 3, it is here very difficult to assign definite coordination numbers to the atoms in a clearcut way. This problem has been discussed by Brunner (*29*), who suggests the largest gap in D/d as the division line between nearest neighbors and the second coordination sphere. Without entering further into this problem, we can nevertheless note some interesting features displayed in Fig. 3.

In the series Ti_3P, V_3P, Cr_3P, the coordinations about the corresponding titanium and vanadium atoms are very similar, a tendency to higher coordination for vanadium being possibly discernible for the M(2) and M(3) atoms. The coordination for Cr(1) is not much different from that for Ti(1) or V(1), but for Cr(3), and particularly for Cr(2), a lower coordination than for the

corresponding titanium and vanadium atoms is clearly evident.

In the series Zr_3P, Nb_3P, Mo_3P, the situation is different. As in the previous series, the M(1) atoms have a rather similar coordination, but for M(2) and M(3) the coordination definitely tends to increase in the order Zr, Nb, Mo.

In the series V_3P, Nb_3P, α-Ta_3P and β-Ta_3P, finally, the coordinations for all corresponding metal atom sites are very similar.

IV. Discussion of Coordination and Bonding

The size-factor concept has often proved very useful in attempts to structurally systematize various classes of compound. As mentioned in the introduction, it has been suggested that the change from the Fe_3P- to the Ti_3P-type structure may depend on the radius ratio $r(X)/R(M)$: Ti_3P-type structures being formed at small radius ratios and Fe_3P-type structures at higher values. By inspection of the data presented in section III it is clear, however, that size-factor effects alone cannot explain the variations in coordination observed. Consider the series Zr_3P, Nb_3P, Mo_3P, as an example. Here, the phosphorus coordination numbers are 9, 8 (+1), and 8, respectively. This change is in the opposite direction to that expected from the change in radius ratio. The radius ratio increases monotonically in the series of compounds mentioned, which would rather favor an increase of the coordination number for phosphorus. In the subsequent discussion we leave the size-factor effects aside, and try to correlate the structural observations with simple qualitative pictures of the chemical bonding in the compounds concerned.

The variations in atomic coordination presented in section III may at first sight exhibit a rather confusing pattern. A certain order is revealed, however, if the variations in coordination are compared with variations

in the cohesive properties of the elemental transition metal components. The cohesive properties of the transition metals have been treated extensively in the literature. For simplicity, we refer only to a classical discussion by Hume-Rothery (32, 33), the principal observations made by him remaining essentially unchanged by more recent work (see, for instance, (34) and references therein).

From a survey of melting-points, heats of sublimation, compressibilities and interatomic distances for the transition elements, Hume-Rothery concluded that the strength of cohesion for the $4d$ and $5d$ elements increases to a maximum, when the group number in the periodic table increases from 3 to 6. For the $3d$ elements, the increasing trend is already broken at vanadium, and the cohesive strength is smaller for the remaining elements with higher group numbers. There is also a tendency to increasing strength of cohesion on passing from $3d$ to $4d$ and $5d$ elements within the same group.

The trends in cohesive strength for the transition metals are strikingly similar to the trends in coordination revealed in Fig. 2. The phosphides, which are well represented in the figure, provide a good illustration. The increasing cohesive strength in the series Zr, Nb, Mo is accompanied by a decreasing coordination number for phosphorus in the series Zr_3P, Nb_3P, Mo_3P. The series V_3P, Nb_3P, and Ta_3P, is a second analogous case. The increase in cohesion from Ti to V, followed by the decrease for Cr (and the remaining $3d$ metals) has a counterpart in the coordination number sequence 9, 8 (+1), 9 for phosphorus in Ti_3P, V_3P, Cr_3P (and Mn_3P, Fe_3P, Ni_3P). These observations suggest the following rule: The greater the cohesive strength of the parent metal, the smaller is the phosphorus coordination number in the corresponding phosphide.

An attempt to explain the connection between the properties of the parent metals and the M_3X compounds can be made as follows:

In the transition metals, $d-d$ bonding interaction provides the main contribution to the cohesive strength. As the group number increases, the bonding states in the d band are progressively filled. The cohesive strength rises to a maximum, when the d band is almost half-filled, which occurs near to group number 6. At larger group numbers, antibonding states of the d band become occupied, and the cohesion decreases (35).

In the M_3X compounds considered in the present paper, the great abundance of M–M atomic contacts as compared to M–X contacts in the structures makes it reasonable to assume that $d-d$ interactions should also here dominate the overall bonding situation. Regarding the M–X bonding interactions, electronic states formed by an admixture of metal d and nonmetal p orbitals are presumably involved (36). The radial parts of the silicon, phosphorus and sulphur $3p$ wavefunctions are indeed very similar in form to the radial parts of the zirconium, niobium and molybdenum $4d$ wavefunctions (37). The bonding situation in the M_3X compounds may thus be considered as an interplay between $d-d$ and $d-p$ interactions. The great structural similarities between the members of the structure family indicate that the gross features of the chemical bonding are largely the same for all members. However, the structural differences, that do exist, may well be connected with minor changes in the $d-d/d-p$ interplay, depending on the nature of the atomic species involved.

Returning to the phosphide series discussed above, the variations in coordination observed (Figs. 2 and 3), can be interpreted in the following way. The trends in $d-d$ interaction for the pure metals are retained in the M_3P compounds. For the two series Ti_3P, V_3P, Cr_3P; and Zr_3P, Nb_3P, Mo_3P, the changes in $d-d$ interaction are accompanied by corresponding changes in metal atom coordination: an increase in the occupation of bonding d states is followed by an increase in the number of metal neighbors surround-ing the metal atoms. In the series V_3P, Nb_3P, Ta_3P, the correlation between $d-d$ interaction and metal coordination number is less pronounced. The group number of the metal components is constant in this series, and the increase in $d-d$ bonding interaction may be due only to an increase in the effective overlap of the d orbitals involved. With increasing $d-d$ interaction, a smaller fraction of the d states is presumably available for $d-p$ interaction, leading to a decreasing metal atom coordination about the phosphorus atoms. This would explain the empirical "phosphide coordination rule" stated above.

The available structural information for the M_3X compounds containing p elements other than phosphorus is rather meagre. Comparison of Nb_3Si with Nb_3P, Ta_3Si with Ta_3P, and α-V_3S or β-V_3S with V_3P in Fig. 2 indicates, however, an increasing $d-p$ interaction on passing from sulphur to phosphorus to silicon. It can be mentioned that an analogous situation seems to prevail for oxygen, nitrogen and carbon according to band structure calculations made for the monoxides, mononitrides and monocarbides of titanium and vanadium (38). Observations of a similar nature have also been made by Franzen (39) in a more extensive survey of transition metal sulphide and phosphide structures.

V. Concluding Remarks

In the present paper we have focussed attention on differences in atomic coordination between individual members of the Fe_3P–Ti_3P–V_3S family of compounds. These differences are assumed to reflect variations in the chemical bonding, depending on the nature of the atomic species involved. Our analyses of the atomic coordination indicate that the bonding characteristics for the pure transition metal components are largely retained in the M_3X compounds, being modified to some extent by M–X interactions.

In our discussion of the relationships between coordination and bonding we have restricted the analysis to a very homogeneous family of compounds, and we feel that attempts to include other more remotely related structures within the same scheme will most likely fail. It would, for instance, be tempting to include the Cr_3Si (A 15 or β-W) type structure in the discussion (40). Where representatives for the structure family considered in the present paper are missing, Cr_3Si type structures (e.g., V_3Si, V_3As, Cr_3Si, Mo_3Si) often appear. Although there are certainly similarities between the present family of structures and the Cr_3Si type (1, 8, 28), the differences are probably very important, indicating major differences in bonding.

On the other hand, crystal structure refinements of a further number of representatives for the structure family discussed here would provide valuable tests of our tentative ideas. The monoclinic Ta_3As (41) and Hf_3As (42) structures may perhaps also be added to the structure family and provide interesting material for future discussion.

Acknowledgments

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