JOURNAL OF SOLID STATE CHEMISTRY 2, 462–471 (1970)

Alloy Phases Crystallizing with Structures Which Occur with Non-metallic Compounds

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Received February 25, 1970

The wide occurrence of alloy phases having salt-like crystal structures will be emphasized. New examples within the complex carbides and related compounds can be derived. Some novel crystal structure types such as V_4P_2C and Ta_2S_2C prepared from the elements are to be described.

Introduction

In view of the unsatisfactory situation as far as the problem of the chemical bonding in intermetallic compounds is concerned, most information about stability is still related to the structural chemistry of alloy phases.[1] Crystal structure data, mainly based on X-ray diffraction analysis and sometimes supported by neutron or electron diffraction techniques, reflect a more or less averaged representation of an apparently homogenous fragment of the crystal under investigation.

More recently it has been shown that electron diffraction is occasionally a more effective method to differentiate between areas of a crystal which slightly change either in the mode of translation, domain–antidomain structure (shift structure) or in the true periodicity, e.g., intergrowth. Thus, electron microscopy was shown to be an essential tool for detecting the change of periodicity in small areas of some 10 Å or so.

There is a significantly wide variety of deviations with respect to an ideal macroscopic or even microscopic crystal; this fact will not be treated from the standpoint of general defect theories. However, some remarks should be made about the regular or extended defects which are widely discussed within the scope of nonstoichiometric compounds. There is evidence that numerous compounds exist which belong to so-called super-superstructures. This type of compound occurs with oxyfluorides of yttrium and rare earth (*1*), tellurides (*2*), silicides, germanides (*3*), etc., and with a number of alloy phases, particularly studied in the Ce–Cd system (*4*). In most cases one can attribute the compound to a precise formula, e.g., $V_{17}Ge_{31}$, and a great many phases or compounds are completely determined with respect to the atomic parameters on the assumption that all crystallographic positions are occupied. That is to say, $V_{17}Ge_{31}$ is not a nonstoichiometric compound, and a formulation as a defect digermanide, although practical as a rough approximation, is misleading. Because of the large cell parameter (either in one or, occasionally, in two dimensions) the question immediately arises as to the mechanism responsible for a specific arrangement repeating after about 100, 200, or 400 Å. A similar situation is well known for some varieties of polytypic structures such as ZnS or SiC; however, there are differences with respect to the structural principle. The super-superstructures such as the germanides and silicides are essentially characterized by a simple subcell of the metal atoms which form according to Parthé and Jeitschko (*5*) a white tin-like structure. In contrast, the other kind of atom forms an array which repeats only after a more or less large number, n, of the simple metal subcell. The nonmetal atoms are out of phase in one subcell. Moreover the super-superstructures differ in that a number of adjacent phases having different n occur. Thus, sometimes within very narrow regions of concentration, several compounds (phases) are observed, such as Mn_nSi_{2n-m} ($n = 11, 15, 26, 27$, $m = 3, 4, 7$) and it is very likely that others also exist. Similarly,

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[1] The term alloy phases implies a wider definition than intermetallic compounds because all phases exhibiting metallic character are included (e.g., metal–nonmetal combinations such as transition element borides, etc.).

as in the case with intergrowth, one has to expect quasicrystals consisting of domains which slightly differ with regard to the values of *n* and *m*; however, the reasons are not the same as seen from the viewpoint of structural elements. Nevertheless, the difference in energy of two neighboring compounds is small in both cases. Small portions of aggregates (*n* and *n*′) may result in an additional order or disorder which, e.g., for the so-called defect disilicide structures, would not affect the common partial lattice of the metal atoms. An indication of such an additional disorder can be recognized from the observation of sharp and diffuse reflections in single-crystal patterns (*6*).

Shifting to more metallic phases, there is a continuous evolution of the problem of order–disorder and clustering in solid solutions. It is well known, for example, that the treatment of a substitution solid solution assumes an invariant lattice and invariant symmetry, even though it is evident that the translation is distorted by the substituted atom (as usual, because of different radii of the solvent and the solute particles). The distortion can clearly be seen from experiments such as nmr which reflect the specific behavior of the solute atom in the field of the surrounding solvent atoms; integrating methods, such as X-ray diffraction, only reveal the distortion in a split of the intensity into a coherent part, corresponding to the average diffraction power, and an incoherent part.

It is of interest to mention the wide occurrence of random cation distributions in ionic crystals which also takes place within the intergrowth compounds. However, it may happen that under conditions of low-temperature equilibria a further ordering (long-range ordering of cations) is more stable, as is the case for $MgO \cdot Al_2O_3 \cdot xSiO_2$ (*7*). In general, some change in the type of bonding appears to be connected with ordering, in such a way that a stronger tendency to form covalent bonds, e.g., cation–cation bonds must be assumed. For the super-superstructure of the defect disilicide type, one can expect a misfit along the *c* axis between the orbitals of metal atoms and those of the Si or Ge atoms. The misfit appears to be compensated by a fluctuation of delocalized electrons. In fact, there is an interesting correlation between the mode of the super-superstructure and the valence electron concentration, as was shown by Parthé and Jeitschko (*5*) and Pearson (*8*).

Since the coordination number and type varies periodically along the *c* axis, one can assume sites preferentially occupied by valence electrons (spatial correlation of electrons); in other words, a periodicity of charge distribution along the *c* axis can also be expected. It is, however, not very likely that the wavelength corresponding to the long period is very important as seen from the energy band.

The Spatial Electron Correlation

To some extent, anions can be substituted by electrons and, although never proven, a preferential position for some electrons may be considered. Such an argument is nevertheless of interest for all cases where mixed types of chemical bonding are involved, e.g., for a great many alloy phases (*9*). The proposed substitution can take place in a geometrical sense only without the physical existence of a partial or continuous replacement. For instance, comparing silicon with the cubic SiO_2 modification,[2] the silicon atoms occupy essentially the positions (000, 1/4 1/4 1/4 + fcc) in both cases; the binding electrons between the silicon cores are localized at almost the same positions as are the oxygen anions in SiO_2.

Examples of alloy phases with so-called salt-like structures were earlier listed for AB, A_2B, ABC, and A_3B compounds (*11*). Many representatives of alloy phases such as LaBi (NaCl type), MgHg (CsCl type), etc., are characterized by a large difference in electronegativity of the participating atoms. Nevertheless, there are many other representatives which do not differ that much; furthermore there are representatives which obey the normal valence concept while others do not, e.g., SnAs (NaCl type). The latter compound is a typical alloy phase exhibiting a large domain of homogeneity and, as well, metallic conductivity. According to Pauling, the metallic valency of tin is between two and three; furthermore, the environment of white tin is not far away from an ideal six-coordination. Moreover, the three p-orbitals on the arsenic atom have the tendency to establish the same arrangement; this results in a NaCl-type structure which easily allows Sn/As substitution. A mesomeric bond system involving π-electrons appears to be more appropriate for a description of this system rather than the ionic picture which very likely fits for $R.E.^{3+}Te^{2-}e^{-}$ and other rare-earth chalcogenides. These compounds deviate from the normal valency concept. In a similar case, Krebs (*12*) has proposed a mesomeric bonding system for PbS which also crystallizes with the NaCl-structure type. One therefore can conclude that despite isotypic structures various compounds differ considerably in their detailed electronic distribution and in their

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[2] Very recently, however, indications were found for a fairly strong deviation of the face centered structure (*10*).

localized and delocalized bonding. Nevertheless, a stepwise or gradual change from one to the other bond mechanism is possible. Within the necessary volume conditions, the ability to form solid solutions (partial or complete) represents a measure as to whether the specific bond mechanism is similar or dissimilar. Thus, for example, one can not expect a strong tendency for mixing between nonmetallic SrS and PbS under normal pressure.

Ordered voids play a similar role for nonmixing, as was shown by Brauer for the series VO–NbO, which are apparently analogous from the chemical point of view, but do not mix. However, VO and NbO differ inasfar as the voids in NbO are ordered. One also can assert that NbO has a structure type differing from that of NaCl. By the overlap of d_ϵ orbitals (cation–cation bond) of the adjacent Nb-atoms, strong clustering, namely a $[Nb_6]$ group, occurs. Thus, the more detailed structure—the points of overlap form a cuboctahedron—certainly differs from a NaCl-type structure with randomly distributed cation and anion voids. There is almost no change of the Nb metal radius in the compound, especially if one considers a somewhat higher coordination than 8.

The Perovskite Structure Type

The largest number of binary alloy phases[3] of an average AB composition has been observed with the CsCl-type structure. Among these compounds, the ordered β-brass phase CuZn was an early subject of speculation (*13*) as to how the valence electrons could preferentially distribute according to a more detailed formula $Cu^+Zn^{++}e_3^-$. An extended discussion on the basis of the proposed spatial correlation by Bradley (*14*) has already been given (*15*). According to the principle of neutrality (Pauling), an accumulation of electrons at the positions around the Zn^{++} ion core at 000 is more likely than around the Cu^+ ion core at 1/2 1/2 1/2. Thus, at the positions 1/2 1/2 0, 1/2 0 1/2, 0 1/2 1/2 a higher electron density should result. In such a way, the total arrangement for $Cu^+Zn^{++}e^-_3$ compares with that of perovskite, e.g., the high-pressure form, $Cs^+Mn^{++}F_3^-$. The size of the participating particles is obviously a quantity which may also vary in a wide region for one and the same structure type. $Cr_{23}C_6$ or τ-phases can also be explained as a perovskite-array, namely, consisting of Cr_{13} and Cr_8 clusters. The first cluster is a filled cuboctahedron and the second a cube; one therefore gets a perovskite superstructure with $a' = 2a$. From the formula $[Cr_{13}][Cr_8]Cr_2C_6$, the correspondence to the perovskite can be seen.[4] There are a number of representatives, e.g., complex carbides and borides such as $[C_{13}][Cr_8]W_2C_6$ or $[Co_{13}][Co_8]Hf_2B_6$, which exhibit different transition element atoms within the clusters on the one hand and in the position (8c) on the other. In a more formal way, the nonmetal atoms boron and carbon act as electron acceptors, but nothing can be said about the degree of the metal–carbon transfer. Nevertheless, the above-mentioned carbides and borides display metallic behavior. This is even more pronounced for perovskite-carbides and nitrides which might better be described as an antiperovskite structure type; more than a hundred representatives such as Sc_3AlC, Ti_3AlC are known for these systems. They have extensively been described recently (*16*). The metallic character in these perovskite-carbides of formula T_3MX (T = transition element, M = transition or B-group element, X = nonmetal) is in agreement with the deviation of the nonmetal with respect to the ideal composition and with the occasionally observed gradual filling of the octahedral T_6 group, starting at the intermetallic T_3M.

Surprisingly different compounds belonging to the perovskite arrangement are listed as examples in Table I. The proposed charge is to be considered as an extreme ionic state only. One nevertheless can exploit the correspondence from one compound to another; thus, the octahedral group seems to be very uniform, representing a building element, such as $[MnF_6]$ or $[Sc_6C]$ octahedra. One also gets an indication for stronger bonding within such a group.

Structural Chemistry of Complex Carbides and Nitrides—Some Novel Structure Types

Investigations within ternary systems of the type, T (transition element)–M (another transition element, metametal or B group element)–X (nonmetal such as carbon or nitrogen) revealed the existence of a rather uniform class of compounds which are essentially characterized by octahedral or octahedral and trigonal prismatic $[T_6X]$ groups (*17*). The common features of these compounds with respect to composition and the mode of linking of the $[T_6X]$ groups may be seen from Table II. One must add that the amount of X is often less than mentioned above; in other words, the compounds are occasionally carbon and nitrogen deficient as is the case in many binary transition element carbides.

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[3] With respect to terminology, one should note that CsAu having CsCl-type is doubtless an intermetallic compound, although with semiconductor behavior.

[4] An analogous compound having the perovskite superstructure, $AgAuCs_2Cl_6$, has long been known!

TABLE I

EXAMPLES WITH PEROVSKITE ARRANGEMENT

Compound	Perovskite formula	a(Å)	Note
CuZn (β-brass)	$Cu^+Zn^{++}e_3^-$	2.95	
$CaTiO_3$	$Ca^{++}Ti^{4+}O_3^{2-}$	3.84	
Mn_4N	$MnNMn_3$	3.88_4	
$CsMnF_3$	$Cs^+Mn^{++}F_3{}^-$	4.33	high-pressure form
Sc_3AlC	$AlCSc_3$	4.48	
$Cr_{23}C_6$	$Cr[Cr_{13}]_{0.5}[Cr_8]_{0.5}C_3$	5.32	(= $a/2$, superstructure)
$Cs_2AgAuCl_6$	$Cs^+Au_{0.5}^{3+}Ag_{0.5}^+Cl_3{}^-$	5.50	(= $c/2$) tetragonal
		5.22	(= $a/\sqrt{2}$) superstructure

The Octahedral Building Group

The perfect correspondence of the octahedral groups $[MX_6]$ (M any metal and X = nonmetal) and $[T_6X]$ has already been discussed; it subsequently governs the wide occurrence of isotypic or antitypic compounds. Linking of these building elements by corners, as is the case for perovskites, also occurs with complex carbides and nitrides having filled β-Mn structure type. A salt-like compound which closely compares with a metallic compound as Mo_3Al_2C (filled β-Mn-type), obviously occurs with $RbAg_4I_5$ (*21*). The iodine positions split in a twelvefold position such as Mo and in a eightfold position such as Al in the carbide. The rubidium ion is octahedrally surrounded by iodine atoms at the twelvefold position which corresponds to the carbon position in Mo_3Al_2C. Sixteen silver ions, responsible for the high electrical conductivity (*21*), are randomly distributed over a large number of positions (72) representing the mobility of this kind of ion. Without going too far one can speculate that four electrons per formula Mo_3Al_2C are distributed in a way similar to the silver ions.

Other examples of linking of the octahedral building elements by corners include the K-carbide $W_9Co_3C_4$ and the hexagonal tungsten bronze M_xWO_3 ($M = Cs$, e.g., $0 < x < 0.33$), provided that the carbon position in 6g) are filled, as was already discussed earlier (*16*). Instead of the alkali metal atom, there can also be a more complex metal group consisting of transition elements and, occasionally, B-group elements such as aluminum.

Typical examples for the correspondence of octahedra linked by edges are Co_2C (metallic) and TiO_2 (rutile), as was emphasized by Goldschmidt (*22*); others include ζ-Fe_2N (or ζ-V_2C, ζ-Mo_2C, ζ-W_2C etc.) and the α-PbO_2-type or antitype. Sometimes, the correspondence between metallic

TABLE II

STRUCTURAL CHEMICAL SCHEME OF COMPLEX CARBIDES AND NITRIDES

Formula	Ratio (T + M)/X	Type	Structural element	Mode of linking	Example
T_5M_3X	8:1	Filled Mn_5Si_3	Octahedra	By planes	Mo_5Si_3C
T_3M_2X	5:1	Filled β-Mn	Octahedra	By corners	Mo_3Al_2C
T_3MX	4:1	Filled Cu_3Au (perovskite carbide)	Octahedra	By corners	Ti_3AlC
T_3MX	4:1	Filled U_3Si	Octahedra	By corners	Cr_3AsN(*18*)
T_3MX	4:1	Filled Re_3B	Octahedra + prism	By edges and corners	V_3AsC(*19*)
$T_8M_4X_3$	4:1	Filled Ti_2Ni	Octahedra	By planes	$Nb_8Zn_4C_3$
T_2MX	3:1	H phase	Octahedra	By edges	Cr_2AlC
T_3MX_2	2:1	Ti_3SiC_2	Octahedra	By edges	Ti_3SiC_2(*20*)

and nonmetallic type refers to the parent lattice only, as is the case for the parent lattice [Cr_2Al] of the H phase, e.g., Cr_2AlC and antitype compound MoS_2.[5] It is of interest to notice that an alkali metal atom pickup occurs in MoS_2 and related sulfides and selenides,[6] where the alkali metal ion can be accommodated in the octahedral voids as is the carbon atom in the T_6 octahedra. These compounds have often an alkali metal atom defect, as is also observed with the carbides (e.g., $Na_{0.6}MoS_2$). The wide occurrence of H phases with respect to the M component (from Cd to sulphur) as well as the substitution of carbon by phosphorus in the TiP structure reveals the importance of the structural elements as a common feature. According to the two different phosphorus positions, one can assume one trivalent trigonal (prism) and one pentavalent state (octahedron). Following the lines of complex carbide structures, another large group has already been discussed by Parthé and Rieger (*23*). Octahedra [T_6C] linked by planes are building elements in the filled Mn_5Si_3 structure such as Mo_5Si_3C as a correspondent structure to the well-known apatite structure type Ca_5^{++} $(PO_4)_3^{3-}Cl^-$.

Later on, it was found that octahedral filling can also be observed with small metal atoms provided an octahedron of sufficient size is available as in Hf_5Sn_3Cu, etc. (*24*). Further analogies, e.g., the deviation from the ideal composition, were also mentioned by the above cited authors. However no correspondence can be made with respect to charge distribution using normal ionic charges. Nevertheless the tetrahedral structural $[PO_4]^{3-}$ group which occupies the silicon position in Mo_5Si_3C demonstrates obviously the detailed shape of the silicon particle in the complex carbide. This means that electrons are forming an environment of a distorted trigonal prism for the molybdenum atoms in 4*d*). The electron environment, seen in the same way for the molybdenum atoms in 6**g**), differs significantly. It is of interest to notice that most of the Mn_5Si_3 and filled Mn_5Si_3 phases contain a IV B-group element (Si, etc.). The difference between the 4**d**) and 6**g**) positions can also be recognized from the partial substitution in one position only, as was shown, e.g., for $(Mn, Re)_5Si_3$ (*25*).

As is also demonstrated by Table II, there are metallic parent lattices, corresponding to relatively simple ordered structure types, which accommodate the X atoms in the octahedral or trigonal prismatic voids formed by the T atoms. For this reason, the complex carbides and related compounds can also be discussed within the concept of interstitial alloys. In fact, there are several examples known where the interstitial carbide can be formed starting from the binary intermetallic, such as in Mn_5Si_3C (*26*) or Nd_3InC, e.g. (*27*).

Deviations of the cubic symmetry are also well known for the perovskite structure type as is the case for the low-temperature form of $PbTiO_3$. Similar, although not isotypic, deviations were found for the filled U_3Si type and, more recently, for the Cr_3GeN-structure type (*28*) which is an intermediate between Cr_3GaN (perovskite type or antitype structure) and Cr_3AsN (filled U_3Si type) as can be seen in Fig. 1. The [T_6X] groups are somewhat turned around the *c* axis, either in one direction or alternating clockwise and anticlockwise. The deformation of the octahedral [T_6X] group generates a similarity to the white tin coordination which is obviously a link between octahedral and tetrahedral grouping. The C. N. of the B-elements Ga, Ge, and As continuously decreases from 12 to 10 to 8. It is very likely that some of the perovskite carbides, nitrides, etc., also deviate from the ideal cubic structure.

The occurrence of perovskite carbides and nitrides as well as the problem of bonding in this class of compounds has been discussed by Stadelmaier (*29*) who applied Häggs concept of the interstitial compounds. According to the above mentioned author, one must extend the critical radii ratio $r_{\text{nonmetal}}/r_{\text{transition element}}$ up to 0.62 or somewhat larger. An attempt was also made to correlate the carbon deficiency with the valence electron concentration; however, the valence of the B-group element does not exert a remarkable influence as can be seen from the series Fe_3ZnC, Fe_3GaC, Fe_3GeC. The regularity of the octahedral group appears to be dependent upon the degree of filling as can be seen from the fact that Fe_3GeN_{1-x} is of the filled U_3Si type structure and becomes the perovskite type at higher nitrogen deficiency.

Another explanation for the high stability of perovskite carbides has been proposed by Rosen and Sprang (*30*). These authors have emphasized a linear dependency between the relative change of lattice parameters and the relative change of the Goldschmidt radii for perovskite carbides and Cu_3Au-type phases (parent lattice). A strong contraction can be observed for the B-group elements In, Al, Sn, and Mg in order to meet the most favorable packing. Large atoms, e.g., rare-earth metals, will be diminished by the B-group element, while small transition element atoms, such as iron, will increase in average size. The lattice

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[5] Hexagonal form 2*s*-MoS_2, not rhombohedric modification.

[6] $NaCrSe_2$ ($NaHF_2$-type).

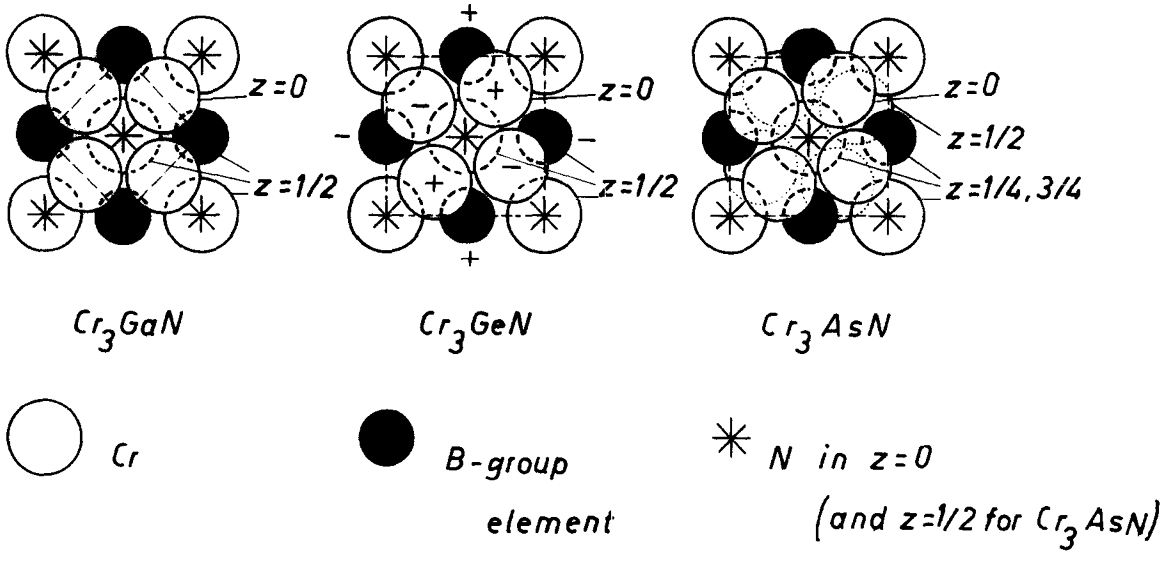

FIG. 1. The crystal structures of Cr_3GaN (perovskite nitride), Cr_3GeN and Cr_3AsN (filled U_3Si-type) viewed along the *c* axis.

parameters of Ti_3AlC, Ti_3InC, and Ti_3TlC, respectively, are therefore all alike; however, the precise amount of carbon is not known. Furthermore, a partial substitution of the transition element and B-group element occasionally occurs, a fact which is not sufficiently studied in detail.

Besides strong bonding between the transition element and the nonmetal atom there is, no doubt, some additional contribution in bonding by an interaction of the T metal and the B-group element atom. These interaction energies correspond to quantities which can be expected in disorder–order transitions. On the other hand, very likely, there is little or no bonding between the B-group element and the nonmetal atom, in agreement with the behavior of many binaries such as In–C, Tl–C, etc.

The nonbonding or weak bonding is also in agreement with the ionic representatives of the perovskite type, e.g., with the one- and two-valent cations such as Cs^+ and Mn^{++} in $CsMnF_3$, which certainly exert a repulsion. The so-called Goldschmidt relation is hardly applicable for the above mentioned perovskite carbides, inasfar as no radii of the participating atoms can clearly be defined. Because of the electron transfer in at least some cases (rare-earth metal containing perovskites), it does not appear useful to operate with metallic radii either.

Octahedral and Trigonal Prismatic Building Groups

There were quite a few structure types found more recently in which a combination of both of these building groups occur. The structural elements themselves are closely related in that the trigonal prism is generated by a rotation of 60° around the trigonal axis of the octahedron. For so-called interstitial compounds, it is well known that the switch from the one type to the other is related to the radii ratio; one can assume that the trigonal prismatic group can more flexibly accommodate larger atoms because of an easier adaptability provided by two different kinds of edges. With respect to "salt-like" structures, one must recall the competition between the NaCl (octahedral) type and NiAs (trigonal prismatic)-type. Combinations of both building elements occur with a large number of structure types, particularly for example in transition element chalcogenides and others and also within complex carbides such as the H phases or the filled Re_3B-type. For the H-phase V_2PC, one immediately can recognize the structural sum: VP (trigonal prism) + VC (octahedron) as is seen in Fig. 4. Furthermore, there is a continuous change in the packing principle, e.g., $Ti_2AlC = TiAl + TiC$, from the above mentioned V_2PC. For Ti_2AlC, the trigonal prismatic group is no longer so characteristic inasfar as six of the Al atoms also belong to the environment (hexagonal close packing). The intermediate position of V_2CrC_2 (octahedra + trigonal prism) $= 6VC_{2/3}$ (octahedra) + Cr_3C_2 (trigonal prism) represents another example of such a combination.

The Filled Re_3B-Type Structures

Although most of the phases of the filled-up Re_3B type—whose parent lattice is of the salt-like antitype, $PuBr_3$—contain phosphorus or arsenic as the B element, representatives have recently been found with germanium and gallium (Table III). Inspection of the ratio $a/\sqrt{bc}$, which is a measure of the contraction of the unit cell in the direction of the short axis, shows an interesting regularity: $a/\sqrt{bc}$ is roughly constant for all phases containing the same B element, while it decreases from group VA to IIIA (Fig. 2). A similar variation of the c/a ratio has been observed with the H phases. In the latter case, the effect is much stronger because six B–B neighbours are involved instead of two as in the Re_3B phases.

The compounds containing the small elements B, C, or N only, have also high $a/\sqrt{bc}$ ratios. In this case, the short axis is determined primarily by the T–T distances.

The occurrence of the various filled Re_3B-structure types can be seen from Table IV.

TABLE III

LATTICE PARAMETERS OF NEW COMPLEX CARBIDES AND NITRIDES HAVING THE FILLED Re_3B-TYPE STRUCTURE

Compound	a(Å)	b(Å)	c(Å)
V_3GaN	2.950	10.30	7.931
V_3GeN	3.010	10.30	7.793
V_3GeC	3.047	10.14	7.884
Cr_3GeC	2.899	10.34	7.724

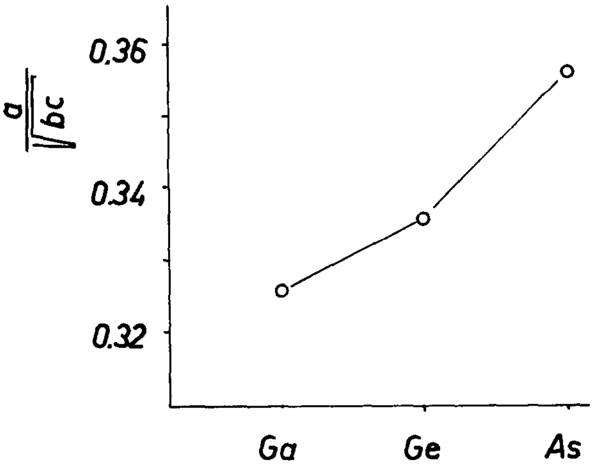

FIG. 2. The dependence of the $a/\sqrt{bc}$-ratio of filled up Re_3B-phases on the group number of the B element.

TABLE IV

OCCURRENCE OF THE FILLED Re_3B-STRUCTURE TYPE

T element	B element	Interstitial element
V	Ga, Ge, P, As	(C)[a] and N
V+ Cr	C	C
Cr	(B, C)[a] Ge, P, As	C and (N)[a]

[a] With elements in parentheses some of the possible Re_3B-phases have not been found.

V_4P_2C and Ta_2S_2C, New Complex Carbide Structures

Another representative of combined octahedral and trigonal prismatic building elements was recently found for V_4P_2C.[7] The ternary system vanadium–phosphorus–carbon is characterized by the occurrence of several complex carbides; these include V_5P_3C with the filled Mn_5Si_3-structure type, the above mentioned V_2PC (H phase), and V_3PC with filled Re_3B type. As is shown in Fig. 3, the crystal structure of V_4P_2C is built up by trigonal prisms (parallel and perpendicular to the c axis) and octahedra. It is of interest to notice the occurrence of a body-centered (irregular) cube. The same building elements without participation of octahedra have been observed with many complex transition metal pnictides, e.g., Nb_7P_4 or the U_3Si_2-type structure. The occurrence of B–B pairs in the latter structure type shows once more the increased tendency for additional bonding between the B elements of lower group number.

The crystal structures of the modifications of Ta_2S_2C are built up by a close packed stacking of hexagonal layers according to a sequence -S–Ta–C–Ta–S–. In the low-temperature hexagonal form the layers are stacked in a way that slabs with an arrangement like MoS_2 and TaC are combined, while the high-temperature rhombohedral modification of Ta_2S_2C is built up by $1s$-TaS_2 and TaC slabs.

The lattice parameters (*31*) were found to be

$1s$-Ta_2S_2C: $a = 3.26_5$ Å $c = 8.53_7$ Å

$3s$-Ta_2S_2C: $a_{hex} = 3.27_6$ Å $c_{hex} = 25.6_2$ Å

The latter structure type is another instructive example for the realization of a structural sum: $3s\text{-}Ta_2S_2C = 1s\text{-}TaS_2 + TaC$ (Fig. 4); this figure also shows the relationship to the H phase, for

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[7] The detailed structure determination of V_4P_2C and the phase relations in the ternary system will be published elsewhere.

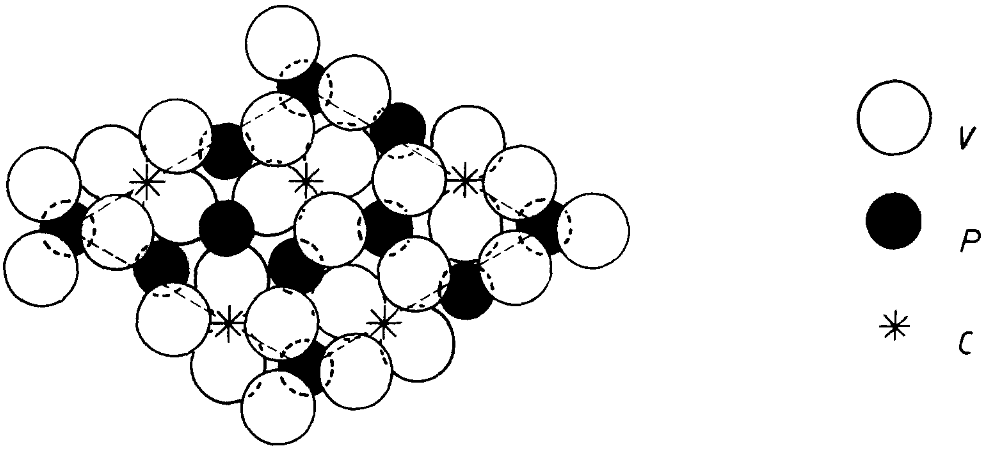

FIG. 3. The crystal structure of V_4P_2C viewed along the c axis.

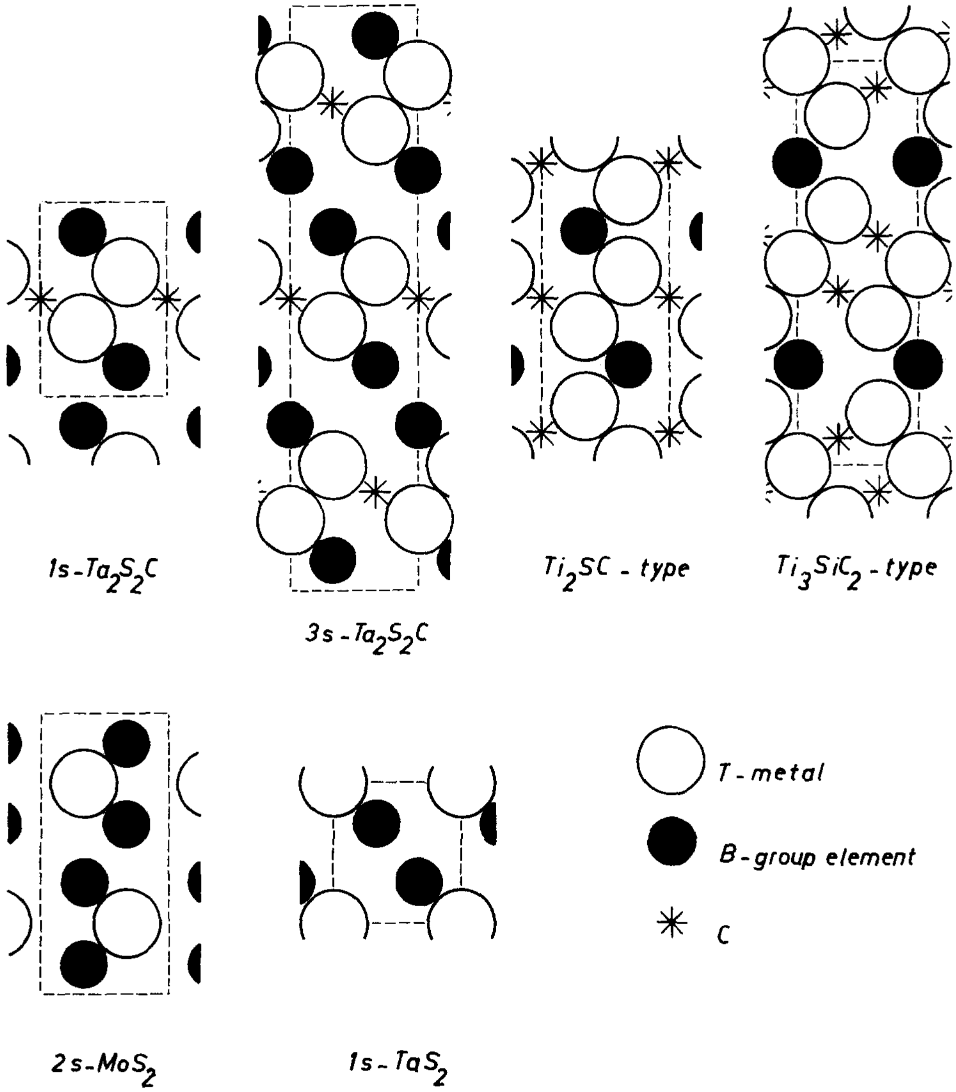

FIG. 4. Comparison of the different complex carbide layer structures [(110) plane of the hexagonal cell].

TABLE V

CORRESPONDENCE OF COMPLEX CARBIDE AND NITRIDE STRUCTURES WITH SALT-LIKE AND RELATED CRYSTAL STRUCTURES

Metallic	Intermediate	Ionic
Filled $Mn_5Si_3(Mo_5Si_3C)$		Apatite
Filled β-Mn(Mo_3Al_2C)		RbI_5 partial lattice in $RbAgI_5$
Filled Cu_3Au (perovskite carbide)		Perovskite
Filled Re_3B		$PuBr_3\square$[a]
K-carbide ($W_9Co_3C_4$)	Linking of octahedra like in hexagonal tungsten bronze $M^b_xWO_3$	
H phase (Ti_2SC)	$M^b_xMoS_2$	
Mg_3As_2	1s-Ta_2S_2C U_2N_3, U_2N_2X, $Th(N,O)_2X$ (X = P, S, As, Se)	La_2O_3, Ce_2O_2S
	3s-Ta_2S_2C	Bi_2Te_2S

[a] □ void.

[b] Alkali metal.

instance to Nb_2SC which has the hexagonal layer sequence -Nb-C-Nb-S- and Ti_3SiC_2. Since the chemical bonding between adjacent sulphur layers is very weak, Ta_2S_2C exhibits stacking faults, which depend strongly on heat and mechanical treatment.

The antitype of 1*s*-Ta_2S_2C is known for Mg_3Sb_2 and some isostructural phases. A similar arrangement is also found in the Ce_2O_2S-type compounds (Table V). In these compounds, however, the coordination around the oxygen (or its analog) differs mainly because of the smaller c/a ratio. Oxides of this type were recently discussed from the standpoint of building elements having oxygen as a coordination center (*32*). The same layer stacking as in 3*s*-Ta_2S_2C is also found in some salt-like chalcogenides like Bi_2Te_2S.

A short survey concerning the correspondance of complex carbides and nitrides with salt-like and related crystal structures is given in Table V.

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