

A New Interpretation of Interstitial Compounds—Metallic Carbides, Nitrides and Oxides of Composition MX^*

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Evidence is cited to show that interstitial monocarbides, mononitrides and a few monoxides tend to have the sodium chloride structure irrespective of metal structure and metal radius. The need for important metal–non-metal bonds to explain the physical properties of the interstitial phases is pointed out.

Interstitial phases are regarded as electron-deficient structures, where the non-metal forms more bonds than it has bond orbitals. It is suggested that hybrid sp -orbitals combined with p -orbitals are used by the non-metal in bonds to metal. A single p -orbital is used to form two bonds at 180° , but the two bonds or half-bonds contain only one electron pair. Resonance of sp and p bonds leads to octahedral bonding by the non-metal.

The concept of half-bonds is used to explain the structure, hardness, brittleness, conductivity and high melting-points of interstitial phases with the sodium chloride-type structure, and a few other interstitial types. The bond distances are consistent with this picture.

The conditions for forming half-bonds are discussed, and it is concluded that they may be formed between the non-metals H, B, C, N and possibly O and the less electropositive A -group metals. Only in the case of C, N and O is octahedral bonding and the sodium chloride-type structure to be expected on the basis of the proposal. The proposal also accounts for the limitation of metallic MX compounds with the sodium chloride structure to the third, fourth and fifth group A -metals.

The metal–non-metal distances in the interstitial phases agree well with predicted distances for $\frac{2}{3}$ or $\frac{1}{2}$ bonds, as given by Pauling's rule.

Introduction

A large number of metals form metal-like phases with hydrogen, boron, carbon, nitrogen, and occasionally oxygen. The metallic properties of these compounds or phases include electronic conductivity, high thermal conductivity, metallic luster, but do not include ductility and malleability.

There exists, largely due to Hägg (1929, 1930*a, b*, 1931), a large body of information concerning the properties and structures of these phases. Following suggestions of Hägg, these phases are generally regarded as interstitial solutions of the small, light elements in the metals.

The following points are usually cited in support of the interstitial solution theory:

(1) Relative metal positions are not appreciably changed by the formation of interstitial phases from metals.

(2) Metals retain all or much of their electrical conductivity upon formation of interstitial phases.

(3) The compositions of interstitial phases are generally not definite, but have a wide range of stability. The light elements can be introduced in amounts varying from little to the amount necessary to fill inter-

stices of a given sort in the metal. The ultimate composition of the phase is determined by the ratio of metal atoms to interstices of the kind occupied by the light element.

(4) The type of interstices available to the light atom is determined by the ratio of metal radius to light atom radius.

The metallic compounds of formula MX are among the most commonly cited examples of interstitial phases. In this paper, the above points in favor of the interstitial solution theory will be examined for these compounds. (Compounds MX of clearly ionic character will be excluded from the discussion.)

Since there are very few borides of formula M_2B , and since the ones whose structures are known appear to be unrelated structurally to the other interstitial phases (generally borides seem to contain important boron–boron bonds), borides will not be included in the present discussion. Hydrides, too, seem to be a special case, and are dealt with in other papers (Rundle, 1947*b*; Rundle & Wilson, to be submitted for publication). Consequently, the discussion here will be limited to carbides, nitrides and certain metallic oxides.

Relation of metal to compound structure

In Table 1 an extensive list of structures of metallic carbides, nitrides and oxides of formula MX is compared with the structures of the corresponding metals.

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We believe this list contains all monocarbides, mononitrides and monoxides which have metallic character and whose structure is known. A notable point in Table 1 is that nearly all the compounds have the sodium chloride structure (B1 in the *Strukturbericht* designation), and this structure is preferred, no matter what the structure or the radius of the metal. Indeed, it is the exception rather than the rule that the metal-atom arrangement is the same in metal and interstitial phase. Thus, aside from the rare earths, only one metal (thorium) in Table 1 has the cubic closest-packed structure, identical with the metal arrangement in the sodium chloride structure. On the other hand, all the metallic monocarbides and all the reliably known metallic mononitrides and monoxides, of third, fourth and fifth group metals, have the sodium chloride structure. The sixth group metals, the last to form metallic monocarbides and mononitrides, generally give different structures, but this is probably due to an extra large number of electrons used in metallic bond formation (see below).

Table 1. *Structure of metals and of interstitial phases, MX^{a, b}*

	Metal	Carbide	Nitride	Oxide
Sc	A1	—	B1	—
La	A1	—	B1	—
Ce	A1	—	B1	—
Pr	A3	—	B1	—
Nd	A3	—	B1	—
Ti	A3	B1	B1	B1
Zr	A3	B1	B1	B1
Hf	A2, A3	B1	—	—
Th	A1	B1 ^c	B1 ^c	B1 ^c
V	A2	B1	B1	B1 ^d
Cb	A2	B1	B1 ^e	B1 (distorted) ^d
Ta	A2	B1	— ^e	—
Cr	A2	Hex. ?	Hex. (& B1 ?)	—
Mo	A2, A3	Hex.	Hex.	—
W	A2	Hex.	Hex. ?	—
U	A2, A20	B1 ^c	B1 ^c	B1 ^c

(a) Data taken from *Strukturbericht* unless otherwise designated.

(b) Symbols used are those of *Strukturbericht*: A1, cubic closest-packed; A2, body-centered cubic; A3, hexagonal closest-packed; B1, sodium chloride type.

(c) From data obtained at Ames, for Manhattan project, to be published.

(d) See reference in Table 2.

(e) Hexagonal phases with the wurtzite structures have been reported for CbN and TaN, but these have lattice parameters very close to those for Ta₂C, and are too small for the mononitrides. In our experience, the hexagonal tantalum nitride contains considerably less nitrogen than required for the mononitride. We suggest that the reported hexagonal CbN and TaN are Cb₂N and Ta₂N.

From Table 1 we conclude that points (1) and (4), above, are not generally valid for interstitial compounds *MC*, *MN* and *MO*. Something beyond the interstitial solution theory seems to be required to explain the great preference for the sodium chloride structure by these interstitial compounds. It seems probable that rearrangement of the metal positions occurs to provide octahedral 'interstices' for the non-metal.

Electronic structure of the metal

It is to be noted that Table 1 includes only metals of the so-called *A*-subgroups, and all of these are contained in Table 1 for periodic groups III, IV, V and VI, except for occasional metals of such rarity that their chemistry has not been thoroughly studied. Over this large range electronegativities and radii vary widely and overlap values of many of the *B*-subgroup metals.

The important difference between *A*- and *B*-subgroup metals is in the number of stable orbitals available for bond formation. The *A*-group metals all have only partially filled *d*-orbitals below the valence shell, so that as a minimum the six *d²sp³*-orbitals are available for bond formation. On the other hand, the *B*-group metals have completed *d*-subshells below the valence shell, so that as a *maximum* they have available for bond formation only four low-energy orbitals, one *s*- and three *p*-orbitals. Of course, low energy is a relative term, and these elements occasionally use more than four orbitals in bond formation, e.g. tin in SnCl₄. However, the *d*-levels above the valence shell are relatively unstable, and apparently are never stable enough to cause electron-deficient bonding. As we shall see below, only in case of an excess of low-energy orbitals can we expect an electron-deficient bonding of the type proposed in this paper.

Range of composition of the phases

Though many of the compounds of Table 1 have variable compositions, some do not, e.g., UC, UN, and UO (Rundle, Baenziger, Wilson & McDonald, 1948). Some of the reported variability in composition seems to arise from the fact that carbon, nitrogen and oxygen can frequently replace each other in all proportions in these compounds. It would be interesting to have much more complete analytical data on this point. At any rate, variable composition does not set these compounds apart from others. Often 'normal' chemical compounds have somewhat variable compositions in the solid phase, and this property is not important evidence favoring the interstitial solution theory.

Metal-to-metal bond distances

In Table 2 metal-metal bond distances are compared in metal structures and in the corresponding monocarbides, nitrides and metallic oxides. The differences between the distances in the metals and corresponding interstitial phases vary widely for these compounds. For example, there is apparently no increase in the metal-metal distance in going from certain rare-earth metals to the mononitride of the metal. On the other hand, in almost all cases, and very notably in uranium, there is a large increase in the metal-metal distance on going to the interstitial phase. In the case of uranium the increase in volume accompanying the increased metal distances in the carbide is about 33%.

In accordance with the view of metal structures due to Pauling (1939, ch. 11; 1947), increased metal distances mean that the metal bonds are of lower bond number, or that electrons have even drained out of the metal-metal bonds. In effect, the metal valence electrons must be drawn away from metal-metal bonds to form metal-non-metal bonds.

Table 2. *Metal-metal distances in metals and interstitial phases, MX^a*

	Distance ^b in Angström units in			
	Metal	Carbide	Nitride	Oxide
Sc	3.20	—	3.14, 1	—
La	3.75	—	3.73, 5	—
Ce	3.64	—	3.54, 5	—
Pr	3.64	—	3.65, 5	—
Nd	3.64	—	3.64, 5	—
Ti	2.93	3.05, 4	2.99, 7	2.99
Zr	3.19	3.32, 3	3.27 ^h	—
Hf	3.16	(3.15), 4	—	—
Th	3.59	3.75 ^h	3.68 ^h	3.71(?) ^h
V	2.63 ^c	3.03, 2	2.920 ^k	2.91 ^f
Cb	2.85 ^e	3.16 ^j	3.12, 1	2.96 ^g
Ta	2.85 ^e	3.14, 4	—	—
Cr	2.71	—	{Hex. 2.75 ⁱ {(B1 2.93 ?)	—
Mo	2.72 ^c	2.90 ⁱ , 2	2.86 ⁱ , 2	—
W	2.74 ^c	2.91 ⁱ , 2	3.03 ⁱ	—
U	2.97 ^c ; 2.80; 3.27 ^d	3.50 ^e	3.45 ^e	3.47 ^e

(a) Data taken from *Strukturbericht* unless otherwise indicated. Bold numeral after distance indicates vol. Distances from vol. 1 may be in error by ± 0.1 A.

(b) For co-ordination number 12 unless specified. An average distance is given in case of hexagonal closest-packing.

(c) Co-ordination number 8 (usually body-centered cubic).

(d) Co-ordination number 12 with 4 shorter and 8 longer distances.

(e) Rundle, Baenziger, Wilson & McDonald (1948).

(f) Klemm & Grimm (1942).

(g) Brauer (1941).

(h) Rundle, Baenziger, Wilson, McDonald & Chiotti (unpublished data).

(i) Co-ordination number 8, simple hexagonal.

(j) Umanskii (1940).

(k) Epelbaum & Breger (1940).

Interstitial compounds of the type listed in Table 1 have exceedingly high melting-points, among the highest known for any substance. Even for those compounds where metal-to-metal bonding has been weakened, i.e. where metal-metal distances have been lengthened, the interstitial compound still melts at a higher temperature, usually far higher, than the metal itself. For example, uranium monocarbide melts fully 1000° C. higher than uranium metal (Snow, to be published), even though the volume increase on forming the carbide is very large. A high melting-point cannot be understood, especially in cases where metal bonds are weakened, unless the structure is strengthened by strong metal-to-non-metal bonding. Even where metal-metal bonds are not changed, some rather important non-metal bonding is necessary to explain the extraordinary melting-points of interstitial compounds. In view of the apparent strength of the metal-non-metal bonds it appears likely that an octahedral configuration is preferred by the non-metal because of favorable

bonding in that configuration. (It is to be noted that octahedral interstices have to be created by rearrangement of the metal atoms in most of the cases of Table 1.)

In this respect we can inquire as to how metal-metal bonds should be influenced in different cases by the removal of valence electrons to metal-non-metal bonds. By use of Pauling's recently suggested formula relating bond length to bond number, we can see that, if the metal valence (as defined by Pauling) is low, then the bond number in the metal, where co-ordination numbers are large, is already very low. Further reduction in the bond number now makes very little increase in the metal-metal bond length. On the other hand, a metal with a large valence and approximately the same co-ordination number will have a relatively high bond number for the bonds in the metal, and the reduction of this bond number by the removal of electrons will play an important role in increasing bond length.

From Table 2 we discover that the least increase in metal-metal distances (here it is within the experimental error of no increase at all, or even a decrease in some instances) is in the third group metals, with valence 3. It is greatest for uranium, which has a valence, as given by Pauling, of 5.78-6. In general, the increase in metal-metal distance in forming interstitial compounds correlates well with the metal valence of Pauling.

Brittleness and conductivity

Another general property of interstitial compounds is brittleness. Upon formation of interstitial phases even very ductile metals become exceedingly hard and brittle. Like high melting-points, brittleness and hardness cannot be understood on the basis of a solution theory, particularly in those cases where metal-to-metal bonds are weakened. Brittleness seldom is coupled with electronic conductivity. The combination of these two properties is one of the interesting characteristics of interstitial phases.

In accordance with modern theories of metals the conductivity of metal phases may be ascribed to essentially free electrons. In metals these electrons may be thought of as the bonding electrons of the metal; they are not, however, restricted to particular, directed orbitals, but rather to levels characteristic of the metal aggregate. For metals there are many more stable electronic levels than electron pairs to fill them. Pauling (1939, ch. 11; 1947) describes the bonding in a metal as due to the resonance of the electrons among the large excess of bond positions. In general, where the number of stable bond orbitals considerably exceeds the number of bonding electrons, distortions in structure would still lead to satisfactory bond direction, so the directional properties of bonds are lost. Metals are therefore ductile.

To explain both the brittle character and the conductivity of interstitial phases it seems necessary to

retain essentially free electrons, but also to provide for directional properties in the bonding. The situation of the electrons in an interstitial phase must more nearly parallel the situation in graphite than in a metal. In graphite there is a resonating system of bonds which gives considerable freedom to the electrons. At the same time the bonding is directional. Graphite is brittle, but still an electronic conductor.

Proposed nature of the bonding in interstitial phases, MX

The considerations of the preceding sections lead to certain requirements for any satisfactory theory of interstitial compounds of formula MX . Important points which the theory must explain are:

- (1) Preference for the sodium chloride structure of the compound, irrespective of metal structure.
- (2) High melting-point and hardness in spite of decreased metal binding in the interstitial phase.
- (3) Brittle character of the interstitial phases in spite of decreased metal bonding.
- (4) Conductivity.

The first three points seem to require metal-non-metal bonds of considerable strength. The third point seems to require directional bonds; the first that the direction of the bonds be octahedral; and the fourth, though the bonds be directed, that they be not localized.

Though the presence of covalent bonding between metal and non-metal in interstitial compounds has been assumed before, no very extensive consideration of the nature of this bonding seems to have been made. Such discussions of the bonding as have been made have not attempted to discuss directional properties (Pauling, 1939, ch. 11; 1940, pp. 420-1; 1947).

Though in essence the picture of electron-deficient bonding used in this and previous papers (Rundle, 1947*b*, submitted for publication) is similar to that used by Pauling, Pauling has adopted a point of view which would, perhaps, exaggerate the non-specific nature of the bonding in the case of structures where the electron deficiency is small (he was not particularly interested in this case), and, though he is thereby able to discuss more general types of bonds, directional properties are lost sight of. To understand directional properties we have perhaps over-emphasized the localized picture of the bonding, and this is a good approximation only where the electron deficiency is low. Consequently we shall generally be unable to understand the directional properties of bonds in interstitial compounds where the metal: non-metal ratio is high and the electron deficiency correspondingly large.

In interstitial compounds a first-row element apparently forms six bonds. These bonds must be essentially covalent, since these compounds do not have the properties of ionic compounds. Moreover, the electronegativity difference of metal and non-metal would

lead, for most carbides and nitrides of Table 1, to estimated ionic characters of less than 20-40% for the metal-to-non-metal bonds (Pauling, 1940, ch. 11). (Because of the greater ionic character of oxygen-metal bonds, no great emphasis will be placed on the oxides in the discussion.)

Since first-row elements have but four stable bond orbitals, the formation of six bonds is abnormal. One might suppose, as has been done (Pauling, 1939, 1947), that four electron pairs resonate among the six bonds, but without further specification of the type of bonding one can understand neither the brittleness of the structure nor the preference for octahedral bonds to the light element.

If we assume that preference for octahedral bonding of the first-row element and brittleness are indications of directed valence in interstitial compounds, the problem of the nature of the bonding resolves itself into the choosing of appropriate stable orbitals for the bonding. It is clear from the number of bonds that the first-row element is sharing its bond orbitals with more than one bond. Under these circumstances the natural orbitals to choose for bonding are the three $2p$ -orbitals of the light element. These orbitals are mutually perpendicular, and each orbital has equal concentration in two directions at 180° . (For a description of these orbitals see Pauling (1940) or an elementary quantum mechanics text.) It would seem perfectly possible to form six bonds with the three $2p$ -orbitals. Of course these six bonds could possess but three electron pairs.

In the case of interstitial compounds, better bonding with the same directional properties can be achieved by the use of two hybrid sp -orbitals and the two remaining p -orbitals. The two sp -orbitals are directed oppositely, leading to bond angle of 180° , and the other two p -orbitals are at right angles to each other and to the hybrid sp -orbitals. This type of bonding would permit two of the six bonds formed by the light element to be ordinary, electron-pair bonds. Resonance would make all six bonds equivalent.

In a formal way we could say that, when one orbital is used with one electron pair to form two bonds, each bond is a half-bond or has bond number $\frac{1}{2}$. Since the bonds in the interstitial compounds discussed here would be one-third electron pair bonds and two-thirds half-bonds, the electron density in the bond would be two-thirds that of an ordinary single bond, or the bond number would be two-thirds in Pauling's nomenclature.

It may well be that, depending on the electronegativities of metal and non-metal, either p -orbitals alone, or sp -orbitals and p -orbitals may be used by the non-metal in bond formation. If only p -orbitals were used in bond formation, presumably the $2s$ -orbital of the non-metal would be occupied by an electron pair. This would be expected if the non-metal were quite electronegative, as in the suboxides, or in the case of the nitrides and the more electropositive metals. Evidence

as to which type of bonding is employed can be obtained from bond distances (see below).

In any case, certain formal charges may be introduced by the bonding. For an example let us consider a carbide of a metal which has four electrons to contribute to the bonding. If two of the six bonds to carbon are ordinary single bonds, and four are half-bonds, then the formal charge on both metal and carbon is zero. If, however, only p -orbitals are used by carbon, and the $2s$ -orbital of carbon is occupied by an electron pair, then the formal charge will be negative for carbon and positive for the metal. The formal charge for nitrogen in similar bonding will be one unit more positive, and for oxygen, two units more positive, than for carbon. It would seem unlikely that oxygen would ever use more than its p -orbitals in bond formation for this reason.

There can, of course, be considerable ionic character to the covalent bonds, and this will vary with electronegativity of metal and non-metal. As the ionic character of the bonds increases, 'interstitial', i.e. metallic, properties such as electronic conductivity, luster, etc., should decrease, since the electrons would be tied more closely to the non-metal. For a given metal the carbide should be a better conductor than the nitride and the nitride better than the oxide. (This appears to be true (Emelús & Anderson, 1945, p. 452).) If the metal is sufficiently electropositive, metallic conduction should just about disappear, and the classification of the compound as 'interstitial' (or metallic) would become difficult. This is no doubt true of some of the compounds of Table 1.

Conditions for forming half-bonds in interstitial compounds

Bonds of the type described above are a type of electron-deficient bond. Indeed, the bonding is probably very similar to that involved in such electron-deficient molecules as the boron hydrides, alkyl-aluminum dimers, etc.* Electron-deficient bonding is the rule rather than the exception whenever 'normal', electron-pair bond structures would leave stable bond orbitals unused. In this case several atomic orbitals may be combined to form one bond orbital of lowest energy. This combined orbital may contain only one electron-pair, but may effectively bond together more than two atoms. Except in metals, the resulting structures may usually be explained in terms of half-bonds.*

The conditions for forming half-bonds have been discussed previously; they are: (1) One element, A , must have more stable bond orbitals than valence electrons. A will, therefore, generally be a metal. (2) Another element, B , must have relatively few bond orbitals. Consequently B will generally be a non-metal, and will generally be limited to H and the first row non-

metals. (If all elements are metallic, falling in class A , the bonding will be electron-deficient, leading to true metal structure. These cannot be understood in terms of a localized bond, such as a half-bond. In this case no one has yet been able to discuss directional properties of the resultant bonds, though Pauling (1940, 1947) has discussed other points connected with bonds of low number.) (3) The electronegativities of A and B must not differ so much that the bond is essentially ionic.

If the above conditions are met, compounds of A and B may be formed such that not all the bond orbitals of A are used in bond formation unless B uses some orbital for more than one bond. Generally it will be better for B to form two half-bonds instead of one single bond.

As a result of the above conditions the non-metals which may form interstitial compounds MX with the sodium chloride structure are carbon, nitrogen and occasionally oxygen. Fluorine will be too electronegative and oxygen will frequently be too electronegative. Boron has more stable orbitals than valence electrons. Hence boron falls in class A , and so may be expected to behave differently. Hydrogen has only one orbital and presumably will form only bridge bonds (Rundle, 1947*a*). (It is possible that some second row non-metals which follow the octet rule may form half-bonds of the type described.)

Only metals having more than four stable bond orbitals will require carbon, nitrogen and oxygen to use a single orbital for more than one bond. These are the so-called A -group metals, since the d -levels below the valence shell of the B -group metals are filled. (For example, Ga, In and Tl have only the four sp^3 tetrahedral orbitals and form perfectly normal mononitrides, with both nitrogen and metal bonded tetrahedrally to four atoms of the opposite kind at distances equal to those expected for single, electron pair bonds.) Of the A -group metals, the alkali and alkaline earth metals will generally be too electropositive to form bonds of considerable covalent character with C, N and O. Hence the metals expected to form compounds MX with the sodium chloride structure should begin at about the third A -group, and should contain the other A -metals. Actually, only A -metals in the third, fourth and fifth groups form interstitial compounds, MX , with the sodium chloride structure. From the sixth group onwards, the structures are different or the compounds do not have this composition. It is noteworthy that the sixth, seventh and eighth group metals use nearly six electrons (5.78) in metallic bond formation (Pauling, 1939, 1947). In forming interstitial compounds this would leave a significant number of electrons for metal-metal bonds. The failure of sixth group metals to form interstitial compounds with the sodium chloride structure can be understood in terms of the metal-to-metal bonding (see below). Aside from this latter point all metals expected to form interstitial compounds with

* For a discussion of electron-deficient bonding in these molecules, see Rundle (1947*b*, submitted for publication).

the sodium chloride structure do so (Table 1). We conclude that there are no other serious limitations on the formation of half-bonds of the type described.

Metal-non-metal distances

In accordance with the above proposal the bonding in the carbides, nitrides and suboxides of Tables 1 and 2 should be through bonds of number $\frac{2}{3}$ or $\frac{1}{2}$, depending on whether the non-metal uses its $2s$ -orbital in bond formation or to hold an unshared pair. In either case Pauling's rule relating bond length to order should apply, and using this in conjunction with his metallic radii one may check the bond number. In Table 3 this has been done. The expected Δ (increase in bond length over sum of covalent radii) is 0.10 and 0.18 Å, respectively for $\frac{2}{3}$ and $\frac{1}{2}$ bonds.

Table 3. *Determination of bond number in interstitial phases, MX*

Bond	Distance ^a	$\Sigma R(1)^b$	Δ^c	Probable bond no.
Ti-C	2.158	2.095	0.063	$\frac{2}{3}$
Zr-C	2.344	2.225	0.219	$\frac{1}{2}$
Hf-C	(2.229) ^d	2.213	(0.016)	($\frac{2}{3}$)
Th-C	2.645	2.423	0.222	$\frac{1}{2}$
V-C	2.068	1.995	0.073	$\frac{2}{3}$
Cb-C	2.231	2.112	0.119	$\frac{2}{3}$
Ta-C	2.223	2.114	0.109	$\frac{2}{3}$
Mo-C ^d	2.17	2.06	0.11	$\frac{2}{3}$
W-C ^d	2.20	2.07	0.13	$\frac{2}{3}$
U-C	2.476	2.192	0.274	$\frac{1}{2}$ or less
La-N	2.64	2.39	0.25	$\frac{1}{2}$ or less
Ce-N	2.506	2.346	0.16	$\frac{2}{3}$
Pr-N	2.578	2.348	0.23	$\frac{1}{2}$
Nd-N	2.571	2.342	0.23	$\frac{1}{2}$
Ti-N	2.11	2.02	0.09	$\frac{2}{3}$
Zr-N	2.315	2.15	0.165	$\frac{1}{2}$
Th-N	2.60	2.35	0.25	$\frac{1}{2}$ or less
V-N	2.065	1.925	0.14	$\frac{1}{2}$
Mo-N ^d	2.165	1.999	0.166	$\frac{1}{2}$
U-N	2.44	2.12	0.32	$\frac{1}{2}$ or less
Ti-O	2.11	1.98	0.13	$\frac{1}{2}$?
Th-O	(2.62)	2.31	0.31	or less
V-O	2.06	1.88	0.18	$\frac{1}{2}$
Cb-O	2.09	2.00	0.09	?
U-O	2.45	2.08	0.33	$\frac{1}{2}$ or less

(a) Data obtained from sources listed in Table 2.

(b) Pauling's metallic radii for bond number of unity.

(c) Increase in distance over single-bond distance.

(d) Simple hexagonal structure, trigonal prism of metals about non-metal.

(e) The expected Hf-C distance is the same as that for Zr-C, and the literature value is certainly incorrect.

It is seen that quite generally the increase in bond distance over that expected for a single bond is the correct order of magnitude for bonds of number $\frac{2}{3}$ or $\frac{1}{2}$. The differences from the ideal values may be largely experimental, since many lattice constants listed were doubtful and phase composition uncertain. If the lattice constant of the compound was listed only in the first volume of *Strukturbericht*, we have not used the data in Table 3, since fairly accurate distances are necessary in determining bond number and early determinations of lattice constants seem unreliable. In a few cases we have obtained supplementary data at Ames.

It is gratifying to note that the more electropositive metals form interstitial compounds with bonds of order $\frac{1}{2}$, since we might expect the non-metal to keep its $2s$ -level filled with an unused pair in this case. Moreover, with nitrogen the tendency to fill the $2s$ -level with an unshared pair is greater than for carbon, as is to be expected.

It is surprising that in the case of CbO and possibly TiO a bond number of $\frac{2}{3}$ is suggested by the distances. It may well be that some errors exist in these data, or that the ionic character of the bonds predominate. Certainly one must expect oxygen to share fewer of its electrons in covalent bond formation than either nitrogen or carbon.

It would be interesting to have more reliable data, so that one could see if bonding by six or eight electrons in the six bonds is continuous or discontinuous. The present data seem to indicate that the bond increments tend to fall in two fairly well-separated groups, one fairly small corresponding to $\frac{2}{3}$ bonds, the other much larger and of the right order of magnitude for $\frac{1}{2}$ bonds. It seems possible that better data might separate them into bond numbers of $\frac{1}{2}$ and $\frac{2}{3}$, with none of intermediate bond number, although uranium and thorium, the most electropositive elements in the table with the exception of the rare earths, do generally have distances so large as to suggest bonds of lower number than $\frac{1}{2}$.

Importance of metal-metal bonds in determining structure

In the case of III A-group nitrides and IV A-group carbides the electron density of the metal-non-metal bonds accounts for the total number of valence electrons of both metal and non-metal. One could, of course, calculate an electron density or bond number of the metal-metal bonds in these compounds using Pauling's rule, and the bond density would turn out to be far from negligible. Indeed, by strict application of Pauling's rule one would have to assign a valence of about 7.4 to Sc in ScN, and similar unsatisfactory, large values to other third and fourth group metals (Table 4, last column). It seems much more logical to use the usual metallic valence of Pauling, and to assume that in these compounds the metal-metal distances are dictated entirely by the strong metal-non-metal bonds. Since one may expect the metal-non-metal bonds to be stronger, and hence to acquire electrons preferentially, this is not an unreasonable procedure.

For fourth group nitrides and for fifth group carbides there is one electron per metal atom available for metal-metal bonds, and the metal-metal bonds will then have bond number $\frac{1}{2}$ in the sodium chloride structure, where each metal atom has 12 nearest metal neighbors. Again in this case the metal-metal distances are shorter than would be predicted by Pauling's rule, and may be assumed to be determined by the strong metal-non-metal bonds.

Fifth group nitrides and sixth group carbides have two electrons per metal atom for metal-metal bonds, again assuming the metal-non-metal bonds are saturated. In the sodium chloride structure the bond number of the metal-metal bonds should be $\frac{1}{2}$, and this provides for strong enough metal-metal bonds that the situation becomes critical with respect to the stability of the sodium chloride structure. This is illustrated by Table 4.

Table 4. Influence of metal-metal bonding on structure

$\sqrt{2}(M-X)^a$	$(M-M)^b$ calc.	Bond no. expected ^c	Bond no. calc. ^d	Pseudo- valence of metal ^e
LaN 3.74	—	0	0.25	6.0
CeN 3.55	—	0.1 ^f	0.37	7.4
PrN 3.65	—	0	0.38	7.6
NdN 3.64	—	0	0.38	7.6
TiC 3.05	—	0	0.22	6.6
ZrC 3.32	—	0	0.21	6.5
ThC 3.74	—	0	0.19	6.2
TiN 2.98	3.30	$\frac{1}{2}$	0.28	6.4
ZrN 3.28	3.56	$\frac{1}{2}$	0.24	5.9
ThN 3.68	3.96	$\frac{1}{2}$	0.23	5.8
VC 2.93	3.09	$\frac{1}{2}$	0.16	5.9
CbC 3.16	3.33	$\frac{1}{2}$	0.16	5.9
TaC 3.14	3.33	$\frac{1}{2}$	0.18	6.1
VN 2.92	2.91	$\frac{1}{2}$	0.17	5.0
CbN (3.04) ^g	3.15	$\frac{1}{2}$	—	—
TaN (3.04) ^g	3.15	$\frac{1}{2}$	—	—
TaN (3.14) ^g	3.15	$\frac{1}{2}$	—	—
CoC (2.90) ^g	2.84	0.148 ^j	—	—
MoC 3.07 ^h	3.07	0.148 ^j	—	—
WC 3.11 ^h	3.09	0.148 ^j	—	—
UC 3.50	(3.31)	0.148 ^j	0.08	4.9
CrN (2.79) ^g	2.72	0.232 ^j	—	—
MoN 3.04 ^h	2.96	0.232 ^j	—	—
WN (3.08) ^g	2.98	0.232 ^j	—	—
UN 3.46	(3.20)	(0.232) ⁱ	0.09	4.1

(a) This is the required $M-M$ distance for the NaCl structure, and is equal to the observed $M-M$ distance for those compounds which have the NaCl structure.

(b) These distances are calculated using the rule of Pauling (1939, 1947), assuming that the $M-X$ bonds are saturated and only remaining valence electrons are used in $M-M$ bonds. If this distance is larger than or equal to $\sqrt{2}(M-X)$, the NaCl structure should be stable.

(c) Assuming $M-X$ bonds are saturated, and only excess electrons are used in $M-M$ bonds.

(d) Calculated by applying Pauling's rule to the observed distance. (It is our thesis that this is not legitimate and leads to too great a metal valence.)

(e) This is the sum of electrons furnished by metal in $M-X$ and $M-M$ bonds, applying Pauling's rule to all observed bond lengths, and assigning normal valences for the non-metals.

(f) Pauling assigns a valence of 3.2 to Ce in metallic compounds.

(g) Distance has not been observed, but is calculated assuming Pauling's rule and the indicated bond number. (In the case of CbN, a rough value is available from *Strukturbericht*, 1.)

(h) Calculated from the observed $M-X$ distance in the hexagonal compound.

(i) Uranium has been assumed here to have a valence of 5.78 in metal compounds, but lower valences are possible, and would be sufficient to explain this apparent anomaly.

(j) The valence of sixth group metals is 5.78, according to Pauling.

In the sodium chloride arrangement the shortest $M-M$ distances are $\sqrt{2}$ times the shortest $M-X$ distances, which, as we have seen, are structure-determining when the $M-M$ bonding is weak. As soon as the

number of electrons available for metal-metal bonding is sufficient to make the $M-M$ distances less than that required for the sodium chloride structure we might expect a new structure to allow for better metal-metal bonding. In other words, the number in the second column should be equal to or less than that in the third for a stable sodium chloride structure. This is exactly the case (Table 4). Pauling (1947) has given a similar explanation of the fact that AuSn has the nickel arsenide rather than the sodium chloride structure.

In Table 4 the second column gives the expected $M-M$ distance for the sodium chloride structure. In the third, the bond distance expected on the basis of Pauling's rule is given, assuming that the $M-X$ bonds are saturated and only the remaining electrons are used in $M-M$ bonds. The next column gives the bond number of the $M-M$ bonds on this basis if the coordination number is 12. The next two columns are interesting only in that they illustrate that it must be assumed that the $M-M$ distances, especially for the lower-valent metals, are determined completely by the strong $M-X$ bonds, since otherwise the calculated or pseudo-valence of the metal becomes ridiculously high.

It is seen that fifth group nitrides should have the sodium chloride structure if the $M-X$ bonds are $\frac{2}{3}$ bonds. If, however, the $M-X$ bonds are longer, corresponding to $\frac{1}{2}$ bonds, as might be expected for the more electropositive members of the series, then the sodium chloride structure is just stable (see the case of TaN in Table 4). Actually the fifth group nitrides have the sodium chloride structure with the possible exception of TaN, which is probably unknown (see footnote in Table 1).

The sodium chloride structure is definitely unstable for sixth group carbides, and even more so for sixth group nitrides. These are known to have simple hexagonal structures, where metal-metal distances can be much reduced. Uranium is exceptional, but may not be hexavalent in these compounds.

Our proposal thus explains the occurrence of this large body of interstitial compounds with the sodium chloride structure, and even permits us to understand rather precisely its limitation to the III, IV and V group A -metals. At least at present, however, where both metal-metal bonds and metal-non-metal bonds compete to determine structure, it does not explain why a particular hexagonal structure predominates in the region where the sodium chloride structure is unstable. The hexagonal structure does, of course, permit shorter metal bonds, but only at the sacrifice of what must be better directional properties for the metal-non-metal bonds. (It is interesting to note that the carbides of the sixth group metals are thermally less stable than those having the sodium chloride structure.)

In the hexagonal monocarbides and mononitrides the non-metal still forms six bonds, which must mean that the metal-non-metal bonds are still $\frac{2}{3}$ or $\frac{1}{2}$ bonds (see Table 3). The metal arrangement in the hexagonal

interstitial compounds is not that of the metals, and must be dictated in this case by the best combination of both metal-metal and metal-non-metal bonds, and not by the metal alone.

Physical properties and half-bonds

The bonding suggested here for the interstitial phase with the sodium chloride structure provides for the equivalent of two electron-pair bonds plus four half-bonds, or in other cases six half-bonds, to each metal and non-metal atom. This bonding is probably considerably stronger than an equivalent number of single bonds. Moreover, it provides for directed-valence bonds and a continuous structure. Consequently, as far as melting-points, hardness and brittleness are concerned, these compounds should resemble what Seitz (1940, p. 2) classifies as 'valence crystals', e.g. diamond and carborundum. In these particular properties the interstitial compounds do indeed resemble diamond and carborundum and are frequently used for similar purposes where great hardness and stability are required.

Unlike most 'valence crystals', the interstitial compounds are electronic conductors and possess metallic luster. The structure suggested here provides for a resonating system of bonds, much as in a metal, except that in the interstitial structure, owing to the non-metal, the bonds are directed. Consequently, one should expect for interstitial compounds electronic conductivity, high polarizability and metallic luster. These metallic properties should vary with the difference in electronegativity of metal and non-metal, a situation which, as we have already seen, probably prevails.

Finally, we have seen that in the case of a first row element the tendency to form two bonds with one orbital should lead to the use of p -orbitals, since p -orbitals are ideally oriented for this purpose. The use of p -orbitals leads to octahedral bonding, which is also in accord with nearly all the interstitial compounds capable of forming half-bonds of the type described.

Application of half-bonds to other carbide and nitride phases

There are a number of carbides and nitrides of the type represented by Fe_4N in which the metal atoms are cubic closest-packed, and the non-metal is in one of the octahedral interstices. Compounds of this type include Fe_4N and $(Fe, Cr)_4C$, whose structures are described in the various volumes of the *Strukturbericht*. It seems likely that the metal-non-metal bonds in these compounds are like those in the sodium chloride-type

structures discussed above. In this case, however, metal-metal bonding must also be quite important.

Another class of interstitial compounds has the cementite (Fe_3C) structure. In this structure the light element atoms are in trigonal pyramidal interstices similar to those in WC, MoC, etc. It is interesting to note the Fe-N distance for the octahedral nitrogen in Fe_4N is 1.89 Å., while the Fe-C distance for the trigonal carbon in Fe_3C is 2.01 Å. This difference in distance is greater than the difference in radii of C and N by a significant amount. It appears that the bonding is better in the case of the octahedral light atom, and it is probable that the trigonal pyramidal configuration is not ideal for any arrangement of orbitals of a first row element. The formation of the six bonds in this arrangement probably involves the general type of bonding described above, but without optimum use of orbitals. (Pauling (1939, 1947) has already interpreted the bonding to carbon in cementite in terms of $\frac{2}{3}$ bonds.) In the case of trigonal pyramidal bonding of the light element, metal-metal bonding must be the structure-determining feature. Compounds having the cementite structure are Fe_3C , Co_3C , Ni_3C , $(Fe, Mn)_3C$ and Fe_2MnC .

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