Acta Cryst. (1980). A**36**, 724–732

Dimensional Analysis of Interstitial Phases with the $AlCr_2C$ Structure

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(*Received* 6 *November* 1979; *accepted* 26 *February* 1980)

Abstract

A dimensional analysis is reported of interstitial phases with the hexagonal $AlCr_2C$, NM_2C, structure, which is based on examining the variation of the unit-cell parameters a and c as functions of D_M and D_N, the diameters of the M and N components for CN 12. The observed behaviour is uniquely different to that of phases with all other structures so examined, there being a drastic change of the D_N dependences of a and c in the region where $a \simeq D_N$. Nevertheless, equations are derived which reproduce the a and c dependences on D_M, D_N and the valency of the M component to better than 0·5% and which indicate the atomic arrays that control the cell dimensions. It is found that the M–M distances that do not lie in (0001) planes and which form half of the sides of the M octahedra surrounding the metalloid atoms, are an invariant feature of the structure for phases with the same M component. This invariant distance couples a, c and z, the atomic parameters of the M atoms, and it causes c dependences on $6{\cdot}5D_N$ ($a > D_N$) and $-1{\cdot}65D_N$ ($a < D_N$), which could not possibly arise through the intrinsic contacts of the N atoms. The electronic distribution from the M atoms to M–M and M–N contacts and also to bands derived from the metalloid $2p$ states and transition-metal d states, is further analysed to account for the apparent dependence of a and c on the M-atom valency. The cell dimensions of SnM_2C phases with the $AlCr_2C$ structure do not follow the systematic variations discussed above; reasons are advanced for this.

1. Introduction

True binary interstitial phases of the Hägg (1929, 1931) type can be referred to as those with the ratio of the radius of the metalloid to the radius of the transition metal, R_N/R_M, less than about 0·59. In their structures, the transition-metal atoms generally form a primitive or face-centred cubic lattice, or a simple hexagonal lattice, with the metalloid atoms occupying the centres of tetrahedra, octahedra or trigonal prisms in such lattices. Ternary phases satisfying the same radius ratio with metalloid atoms at the centres of similar polyhedra can also be regarded as true Hägg interstitial phases. One of the main features in the stability of such phases appears to be that the d levels of the transition-metal atoms overlap forming d bands. Interaction of the metalloid p orbitals with these d bands appears to be responsible for the particular physical properties of interstitial carbides and nitrides. Recent band-structure calculations, for example those of Neckel *et al.* (1976), confirm overlap of bands derived from the transition-metal $3d$ and metalloid $2p$ states in interstitial carbides and nitrides with the rock-salt structure.

A recently developed method of dimensional analysis of binary metallic phases (Pearson, 1979*a*,*b*) permits quantitative assessment of the dimensional changes in series of interstitial phases with a given structure, and particular interest attaches to non-cubic structures containing metalloids at the centres of transition-metal octahedra, which then become deformable in more than one mode. In the analyses, the unit-cell dimensions of phases, M_xN_y, with a given structure and the same N component, are examined as a function of D_M and of D_N at a constant D_M value, the atomic diameters being taken for coordination number (CN)12. In practically all cases, linear relationships are found between the cell dimensions and D_M or D_N. The analyses depend on assuming the validity of Pauling's (1947) equation, $R(1) - R(n) = 0{\cdot}30 \log n$, where n equals the atomic valency divided by the coordination number. With this assumption, it does not matter what the actual coordination numbers of the atoms in the structure examined are, since a change of diameter from CN 12 only results in the addition or subtraction of a constant term to the equations relating the cell dimensions and D_M or D_N for CN 12. The linear relationships between cell dimensions and D_M or D_N can be explicitly interpreted in terms of the atomic arrays that control the cell dimensions in the structure. Such explicit interpretation is rarely possible for relationships derived in terms of the conventional radius ratio, R_M/R_N, because of the properties of ratios.

The method of analysis also requires that two other conditions be satisfied (Pearson, 1980): (i) the valency and/or number of bonding orbitals on an atom in the structure examined must be the same as in its elemental structure from which its CN 12 diameter was derived;

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(ii) The distribution of the valence electrons from an atom to its surrounding neighbours must be in accord with the distances to these neighbours and Pauling's equation, referred to above. If either of these conditions is not satisfied, a 'valency effect' may be apparent in plots of cell dimensions *versus* D_M or D_N if the appropriate atomic arrays control the cell dimensions. That is to say, instead of all phases with a given structure and N component lying on a single line of a *versus* D_M, phases with M components of valency 1, 2, 3, ... will lie on a series of separate parallel lines. This is but an artefact of the method of analysis, and it does not invalidate the analyses; indeed, on the few occasions where valency effects have been observed, they could be quantitatively interpreted in terms of the valency states of the atoms existing in the alloys (Pearson, 1980).

In this paper the analysis is applied to phases with the hexagonal $AlCr_2C$ or H-phase structure, NM_2C (Jeitschko, Nowotny & Benesovsky, 1963), which show a different dimensional behaviour to that normally observed. Although these are ternary phases, the analysis can be extended to them, when the third component, there carbon, is the same for all phases, provided that any extra conditions that the third element introduces are taken into account.

The arrangement of the atoms in the $AlCr_2C$ structure is shown in Fig. 1. There are triangular networks of Cr atoms in (0001) planes located about 0 $\pm z$ and $\frac{1}{2} \pm z$, where z is the parameter of the Cr atoms along c. These layers create bands in (0001) planes of octahedra which share edges. Between these bands of octahedra, the Cr layers also create bands of contiguous trigonal prisms, alternate prisms being centred by Al atoms at fixed heights of $z = \pm\frac{1}{4}$. With the C or N atoms centering the octahedra of transition-metal atoms, phases with the $AlCr_2C$ structure can be regarded as true Hägg interstitial phases.

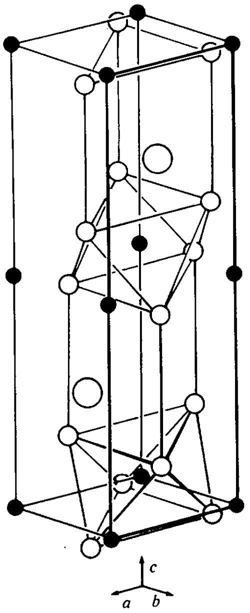

Fig. 1. Diagramatic view of the $AlCr_2C$ structure. Large circles Al; small circles Cr; filled circles C atoms. Two octahedra and two uncentred trigonal prisms are indicated.

The only variable parameters of the $AlCr_2C$ structure are the axial ratio of the unit cell and the z parameter of the M atoms, allowing their movement along [0001]. Unfortunately, accurate z values have been determined for very few phases. As the M and N atoms have fixed x and y positions at $\pm(\frac{1}{3},\frac{2}{3})$, constraining interatomic contacts in the (0001) plane are likely to be directly reflected by changes of the cell dimensions.

There are five arrays of interatomic contacts that may be important in accounting for the variations of a and c with D_M and D_N. The distances between the N atom at the centre of the trigonal prisms and the six M atoms in their corners are close to the appropriate radius sum. The M and N atoms in their triangular networks on (0001) planes may severally come into contact when $a \leq D_M$ or $a \leq D_N$. The condition $a \leq D_N$ is satisfied for all phases to the right of the broken line in Fig. 4. The condition $a \leq D_M$ would be satisfied for the Sn phases of Zr and Hf, if their lattice parameters adhered to the systematic variation with D_N of other phases with the $AlCr_2C$ structure, but they do not. Six of the M–M edges of the transition-metal octahedra form triangles in the (0001) planes and thus have a length a. The other six M–M edges join the corners of these two triangles, and therefore will generally have a length different from a. The length of these edges, which we shall refer to as M–M ($\neq a$), involves the z parameter and hence could also exercise control of the cell dimensions. Finally, the M–C–M distances along the diagonals of the octahedra are considerably shorter than the appropriate radius sums. These distances do not appear explicitly in the dimensional analysis because the ternary phases are treated as binary phases, NM_2, but the information must be included in all considerations.

Unit-cell dimensions of phases with the $AlCr_2C$ structure are taken from Pearson (1967) or later volumes of *Structure Reports* of the International Union of Crystallography. Diameters of the atoms for CN 12 are those of Teatum, Gschneidner & Waber (1960).

2. Dependence of unit-cell dimensions of $AlCr_2C$ phases on D_M and D_N

Figs. 2 and 3 show a and c as functions of D_M for carbide phases with the $AlCr_2C$ structure and the same N component, and Fig. 4 shows a and c as functions of D_N for carbide phases with the same M component.

The broken line in Fig. 4 separates the region where $a > D_N$, on the left, from that where $a < D_N$, on the right. Figs. 2 and 3 indicate a valency effect in respect of the M atoms, which is an artefact of the method of analysis as discussed in § 1.

The data shown in Figs. 2, 3 and 4 can be represented by the following equations.

When $a > D_N$

$$a = 0{\cdot}70D_M - 0{\cdot}65D_N + 0{\cdot}019S + 2{\cdot}814, \quad (1)$$

$$c = 3{\cdot}0D_M + 6{\cdot}5D_N + 0{\cdot}072S - 13{\cdot}870. \quad (2)$$

When $a < D_N$

$$a = 0{\cdot}70D_M + 0{\cdot}25D_N + 0{\cdot}019S + 0{\cdot}254, \quad (3)$$

$$c = 3{\cdot}0D_M - 1{\cdot}65D_N + 0{\cdot}072S + 10{\cdot}740, \quad (4)$$

where S represents the valency effect and has values of 1, 4 and 6 for Group IV, V and VI M components respectively. The values of S are selected to make the valency effect zero for the Group IV metals, as demonstrated in § 4. Equation (3) is obtained by adding $0{\cdot}9D_N - 2{\cdot}560$ to (1) and (4) is obtained by adding $-8{\cdot}15D_N + 24{\cdot}610$ to (2).

With the exception of the c values for the sulphur phases, these equations reproduce the a parameters of the 28 known carbide phases that do not have Sn as the N component, to within $|0{\cdot}015|$ Å (or 0·5%) of the observed values, and the c values to within $|0{\cdot}033|$ Å (or 0·25%) of the observed values, as shown in Table 1. The calculated c values of the three S phases differ by 0·20 to 0·29 Å from the observed values. The reason for this slight disagreement is understood and discussed in § 4.

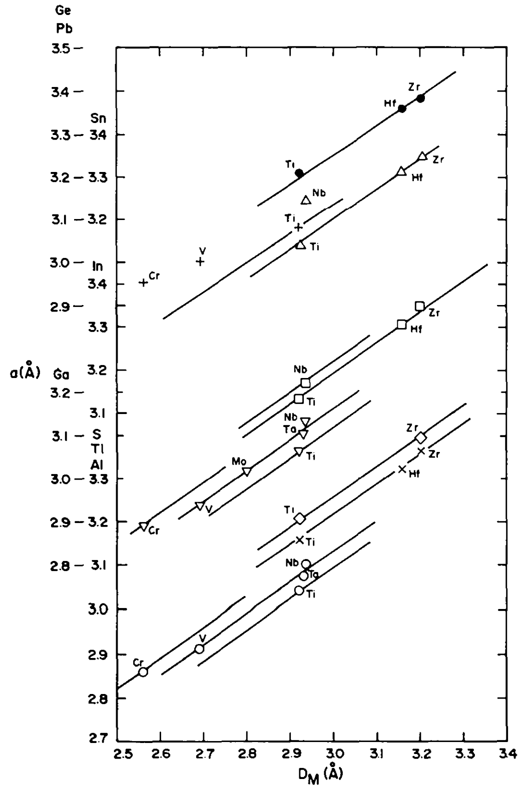

Fig. 2. Variation of a as a function of D_M for carbide phases with the AlCr$_2$C, NM_2C, structure and N components revealed by the symbols: + Ge; ● Pb; △ Sn; □ In; ▽ Ga; ◇ S; × Tl; ○ Al, and identified on the various scales. A valency effect is apparent for transition metals of valency 4, 5 and 6.

3. Explanation of the dimensional behaviour of phases with the AlCr$_2$C structure

Having accounted analytically for the observed dimensional behaviour, we must now explain its occurrence. In particular, we must account for: (i) the dramatic change of slope of a and c as functions of D_N in the region where a equals D_N; (ii) both the very high dependence of c on $6{\cdot}5D_N$ and the negative dependence on $-1{\cdot}65D_N$; (iii) the behaviour of the Sn phases which do not adhere to either of the systematic behaviour patterns of a and c *versus* D_N.

Accounting for the observed dependence of a on $0{\cdot}7D_M$ and c on $3{\cdot}0D_M$ (Figs. 2 and 3) presents no problems. Since the M–M separation in (0001) planes is always greater than D_M, the zig-zag arrays of atoms –M–N–M–M–N–M–, possibly with M–C–M replacing M–M, which run throughout the structure must be responsible for both dependences. Thus, in the a

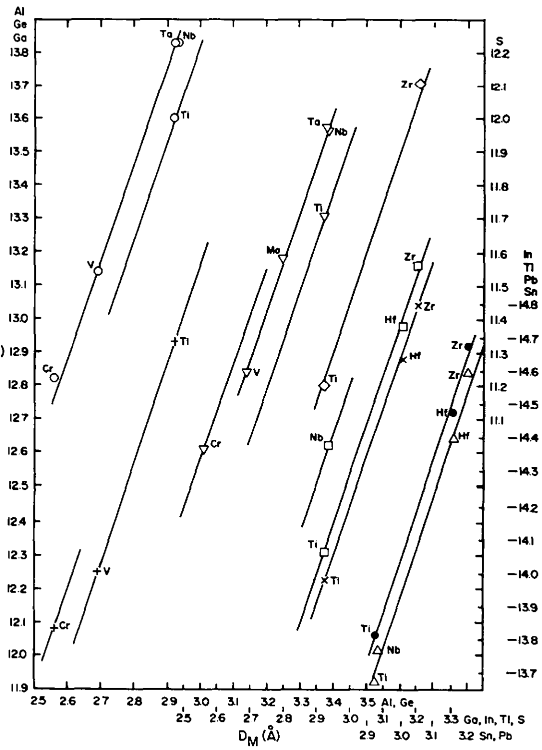

Fig. 3. Variation of c as a function of D_M; other comments are the same as in the caption to Fig. 2.

direction one M atom diameter is involved and in the c direction four M atom diameters are involved. Estimations of the resolved components of these proportionalities along a and c indicate that the observed a dependence on $0{\cdot}7D_M$ and c dependence on $3{\cdot}0D_M$ are very much to be expected on the basis that these arrays of atoms exercise dimensional control. The valency effect involving transition-metal M components of valency 4, 5 and 6 (Figs. 2 and 3) will be considered in § 4.

The change of dependence of a and c on D_N, which occurs in the region where $a = D_N$, results from the N–N distance (equal to a) in the triangular nets of N atoms in (0001) planes beginning to take control of the a dimension of the cell. This is apparent from the limiting slope of a *versus* D_N approaching 1·0 as D_N increases (Fig. 4), and from the required addition of $0{\cdot}9D_N$ to (1) to produce (3) which applies when $a < D_N$.

The large dependence of c on $6{\cdot}5D_N$ cannot arise directly from contacts with the N atoms. The only contacts with resolved components in the [0001] direction which involve the N atoms are the N–M contacts in the trigonal prisms. These would only be expected to contribute a c dependence of $2{\cdot}0D_N$ at the most. Therefore, the large dependence of c on D_N must result from a simultaneous dimensional adjustment in the structure which does not arise directly from the N atoms themselves.

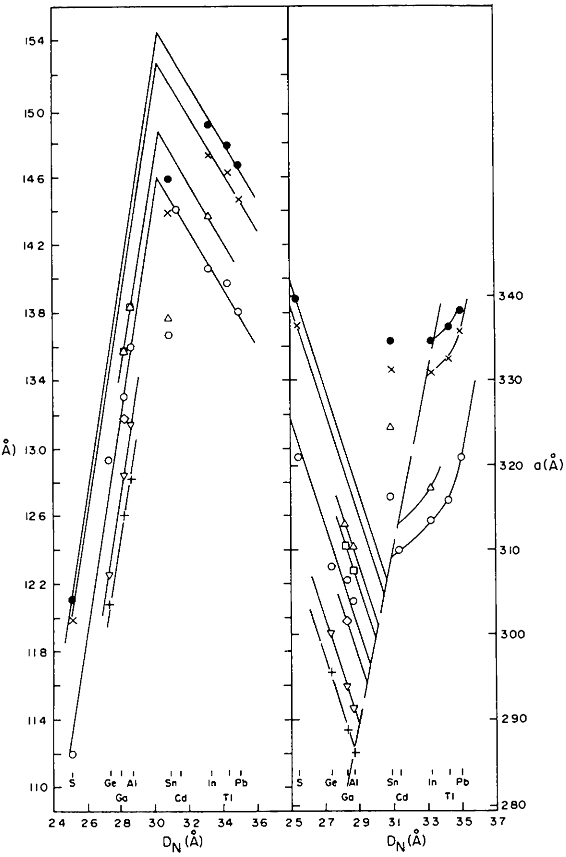

Fig. 4. Variation of a and c as a function of D_N for carbide phases with the $AlCr_2C$, NM_2C, structure. M components are revealed by the symbols: + Cr; ▽ V; ◇ Mo; ○ Ti; □ Ta; △ Nb; × Hf; ● Zr. The broken line in the right-hand diagram represents $a = D_N$.

Since there are very few phases with the $AlCr_2C$ structure whose z parameters have been determined accurately, if at all, we tried to explain the observed dimensional dependences on D_N on the basis of the unit-cell dimensions alone. Although it was possible to account quantitatively for the dependence of c on $6{\cdot}5D_N$ on this basis, it was not possible to obtain a driving mechanism whereby this dimensional behaviour would occur rather than the normal dependence on D_N, which would arise from direct contacts with the N atoms. It was therefore necessary to try to establish the variation of the z parameters of the M atoms with change of the N component, and the eight NTi_2C alloys were chosen as the most promising.

Of these NTi_2C phases, z values have been determined for the Ge, In and Pb phases from X-ray powder photographs, and a value of 0·099 ± 2 has been obtained for STi_2C from single-crystal X-ray

Table 1. *Observed and calculated lattice parameters of* $AlCr_2C$ *structure phases,* NM_2C

	a_{obs}	$a_{calc} - a_{obs}$	c_{obs}	$c_{calc} - c_{obs}$
$a > D_N$				
STi_2C	3·210	0·019	11·20	0·28
$GeTi_2C$	3·079	0·021	12·93	−0·16
$GaTi_2C$	3·064	−0·018	13·305	0·012
$AlTi_2C$	3·04	−0·022	13·60	−0·01
SHf_2C*	~3·365	0·029	~11·99	0·20
SZr_2C	3·396	0·029	12·121	0·21
GeV_2C	3·001	−0·007	12·25	0·04
GaV_2C	2·938	0·002	12·84	0
AlV_2C	2·913	−0·001	13·14	−0·03
$GaNb_2C$	3·131	−0·020	13·565	0·004
$AlNb_2C$	3·103	−0·020	13·83	0·01
$GaTa_2C$	3·104	0·006	13·57	−0·01
$AlTa_2C$	3·075	0·007	13·83	0·01
$GeCr_2C$	2·954	−0·011	12·08	−0·03
$GaCr_2C$	2·886	0·003	12·61	−0·01
$AlCr_2C$	2·860	0·001	12·82	0·05
$GaMo_2C$	3·017	0·037	13·18	+0·13
$a < D_N$				
$CdTi_2C$	3·099	0·005	14·41	0
$InTi_2C$	3·132	0·020	14·06	0·036
$TlTi_2C$	3·158	0·020	13·98	−0·059
$PbTi_2C$	3·209	−0·014	13·81	−0·001
$InZr_2C$	3·347	0·001	14·91	0·026
$TlZr_2C$	3·363	0·011	14·79	0·029
$PbZr_2C$	3·384	0·007	14·67	−0·021
$InHf_2V$	3·307	0·010	14·73	0·074
$TlHf_2C$	3·322	0·021	14·63	−0·001
$PbHf_2C$	3·358	0·002	14·47	0·047
$InNb_2C$	3·172	0·045	14·37	−0·02

* Actually $FeHf_2SC_2$.

photographs. These data, and an assumed value of $z = 0{\cdot}086$ for $AlTi_2C$ (the same as that accurately determined for $AlCr_2C$), are shown as functions of D_N in Fig. 5, together with the resulting calculated M–M ($\neq a$) and M–C–M distances. It seems that the relative self-consistency of the data can be greatly improved by changing z for $GeTi_2C$ to 0·089 and possibly changing z for $PbTi_2C$ to 0·082 – changes that appear well within the expected precision of the data.

There is now a smooth variation of the data in Fig. 5. z decreases monotonically with increasing D_N, probably attaining a constant value in the region where $a < D_N$. The M–M ($\neq a$) distances remain essentially constant and equal to $D_{Ti} = 2{\cdot}294$ Å CN 12, regardless of changes of z and D_N. The M–C–M distances probably go through a minimum value in the region where $a = D_N$, and are greatly compressed compared to $\frac{1}{2}(D_{Ti} + D_C)$.

There is little doubt from the data of Fig. 5 that the M–M ($\neq a$) distance is an invariant parameter of the $AlCr_2C$ structure. Therefore, when the interstitial octahedra are distorted it is at the expense of the M–M distance in (0001) planes and/or of the M–C–M lengths of the diagonals of the octahedra. Since the M–M ($\neq a$) distance is given by $d = (a^3/3 + 4z^2 c^2)^{1/2}$, it is seen that a change in the length of c, for example, must be compensated for by changes in a and/or z in order to keep d constant. Thus, for NTi_2C phases, a change from $D_N = 2{\cdot}96$ Å in the region where $a = D_N$ and (1) and (2) give $a = D_N = 2{\cdot}96$ and $c = 14{\cdot}214$ Å to $D_N = 2{\cdot}54$ Å of the STi_2C phase must be accompanied by a decrease in c, since z increases to 0·099 and a changes little. Indeed, putting the observed values of $d = 2{\cdot}89$, $a = 3{\cdot}21$ Å and $z = 0{\cdot}099$ for the STi_2C phase into the above expression for d, we must get the observed value of 11·20 Å for c, thus accounting quantitatively for the c dependence on $6{\cdot}5D_N$; it still does not explain why normal a and c dependences on D_N are not realized at the expense of z, while still maintaining the invariant M–M distances. This requires consideration also of M–N distances and unit-cell volumes. The M–N distances are also important in controlling the cell dimensions and these involve a, c and z, the latter being in a $(\frac{1}{4} - z)$ relationship, so that the effect of changing z is the opposite on M–N distances to that on M–M distances. Although the M–N distance changes appreciably with z, it varies relatively little as a and c (coupled) change widely at a constant z and M–M distance. For example, as c changes from 12 to 14 Å at $z = 0{\cdot}086$, the rate of change of a is 28 and c 80 times greater than the rate of change of the M–N distance. These facts introduce the situation illustrated in Fig. 6 for the $GaTi_2C$ phase (assumed $z = 0{\cdot}087$), which shows that although z is prescribed within fairly narrow limits, a and c can vary widely while still maintaining an invariant M–M distance and an acceptable M–N distance. However, in so doing the unit-cell volume also varies widely as Fig. 6 shows. Therefore, if the M–M and M–N distances have suitable values, it is ultimately the unit-cell volume which prescribes the acceptable a and c values.

Thus, the invariant M–M distance in coupling together a, c and z is primarily responsible for the dependence of c on D_N, which is far greater than that

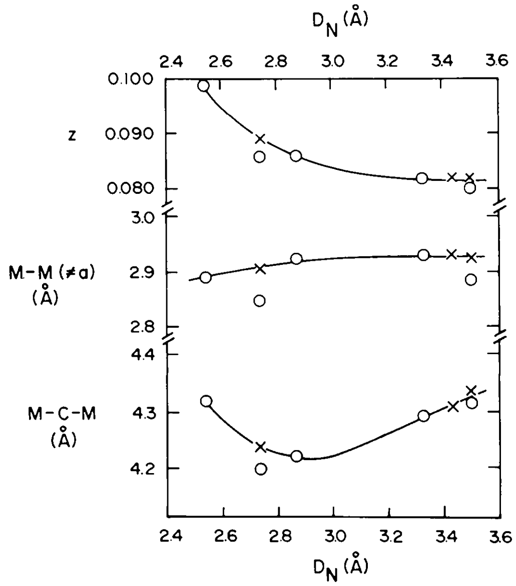

Fig. 5. NTi_2C phases with the $AlCr_2C$ structure. The z parameter of the M atoms and the calculated M–M ($\neq a$) and M–C–M distances *versus* D_N. O represents data of experimentally determined z values. × represents data of adjusted z values.

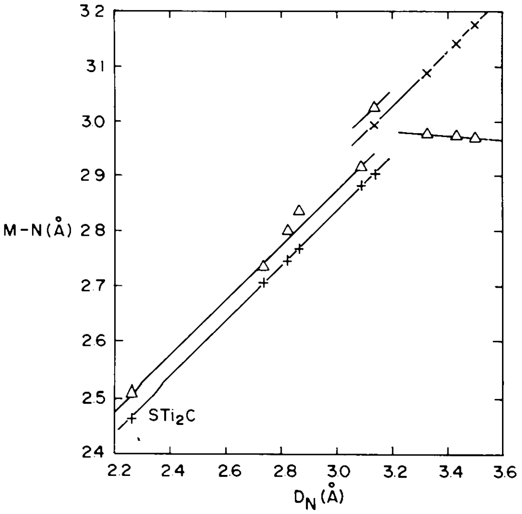

Fig. 6. Observed (△) and calculated (+,×) M–N distances of NTi_2C phases as a function of D_N. Observed distances are based on z values of 0·099, 0·089, 0·087, 0·086, 0·835, 0·080, 0·082, 0·082 and 0·082 for N components S, Ge, Ga, Al, Sn, Cd, In, Tl and Pb respectively. Calculated values are $\frac{1}{2}(D_M + D_N)$ with D_M for CN 9 and D_N for CN 6 except for Cd, In, Tl and Pb where D_N is for CN 12. The D_N value for S^{VI} is used.

which could arise intrinsically from contacts between the N atoms and their neighbours, and for the slight decrease of a with increasing D_N. Thereafter, it maintains suitable M–N distances, which also couple a, c and z, the latter in a $(\frac{1}{4} - z)$ relationship, and a suitable unit-cell volume, which couples a and c, to provide the driving force which results in the relationships observed. There is no reason why a cannot decrease with increasing D_N in this region, as both the N–N and M–M distances in the triangular networks of N and M atoms in (0001) planes are greater than D_N and D_M respectively.

In the region where $a < D_N$, the triangular networks of N atoms in (0001) planes in part control a, as the N–N distance is equal to a. z values appear to vary little, becoming constant at a value close to 0·082. As the M–M ($\neq a$) distance remains the invariant feature of the structure, equal in length to D_{Ti}, an increase of a with D_N causes a decrease in c as z is constant. The observed value of a for $\mathrm{PbTi_2C}$ at $D_N = 3{\cdot}50$ Å is 3·209 Å. Taking 2·925 Å as the M–M ($\neq a$) distance and $z = 0{\cdot}082$, we find that the calculated value of c is given by

$$2{\cdot}925^2 = 3{\cdot}209^2/3 + 4 \times 0{\cdot}082^2\, c^2,$$

whence $c = 13{\cdot}80$ Å, which agrees, as it must, with the observed value of 13·81 Å. Thus, the dependence of c on $-1{\cdot}65\ D_N$ in this region is quantitatively accounted for and arises from the constant value of the M–M ($\neq a$) distance which couples the a, c and z values, together with the maintenance of an equitable unit-cell volume for the phases.

The a parameters of the $\mathrm{Sn}M_2\mathrm{C}$ phases are too large and their c parameters are too small to follow the regular a and c dependence on D_N of other phases, although their cell volumes as a function of D_M or D_N appear to vary regularly with those of other phases. This does not seem to result from the phases lying in the region where $a = D_N$. Rather, it is because the distance a between the M atoms of the triangular networks on (0001) planes would be less than D_M for the Zr and Hf phases, and about equal to it for the Nb and Ti phases, if they followed the a and c dependences on D_N of the other phases. Thus, the expansion of a for the $\mathrm{Sn}M_2\mathrm{C}$ phases avoids the additional constraint on the M atoms in (0001) planes. The concomitant contraction of c maintains the systematic variation of cell volumes of the phases, there being no special reason to prevent a decrease of c when a increases. In no known phases, other than those of Sn, does the condition of a being smaller than D_M arise.

It is interesting to note that, if the condition that M–M ($\neq a$) is constant and equal to 2·925 Å holds for the $\mathrm{SnTi_2C}$ phase, the value of z calculated from the observed a and c values and 2·925 Å is 0·0835, which is exactly the value predicted for $D_N = 3{\cdot}09$ Å in Fig. 5.

Finally, the few nitride phases with the $\mathrm{AlCr_2C}$ structure appear to behave similarly to the carbides.

4. Observed valency effects

In the region where $a > D_N$, the M atoms each have 3 M, 3 N and 3 C contacts giving CN 9, and the N atoms have 6 M contacts for CN 6. Since the three M–M contacts [not in (0001) planes] are an invariant feature of the structure, the –M–N–M–M–N–M– arrays effectively control the cell dimensions. The M–C interstitial contacts within the octahedra, and the number of M electrons assigned to them, are initially assumed to have virtually no influence on the cell dimensions.

(i) *Sulphur in* $\mathrm{S}M_2\mathrm{C}$ *phases*

It is apparent from Fig. 7, which shows, as a function of D_N, M–N distances in $N\mathrm{Ti_2C}$ phases, together with $\frac{1}{2}(D_N + D_{\mathrm{Ti}})$ values with D_N for CN 6 and D_{Ti} for CN 9, that sulphur exhibits a valency effect. In $\mathrm{S}M_2\mathrm{C}$ phases its diameter corresponds to $\mathrm{S^{VI}}$ (2·26 Å for CN 12) which uses six bonding electrons, whereas the elemental D_M value for CN 12 which we have used is based on $\mathrm{S^{II}}$ with two bonding electrons. The effect is, however, scarcely apparent in Fig. 4 where a and c are plotted against D_N for CN 12, since neither a nor c are intrinsically dependent on the size of the N atom itself, as shown in § 3. Calculated c values based on $D_{\mathrm{S}} = 2{\cdot}54$ Å are slightly different from the observed values, as noted in § 2. Indeed, if $D_{\mathrm{S}} = 2{\cdot}51$ Å, the discrepancy of the c parameters is removed without spoiling the agreement of the a parameters.

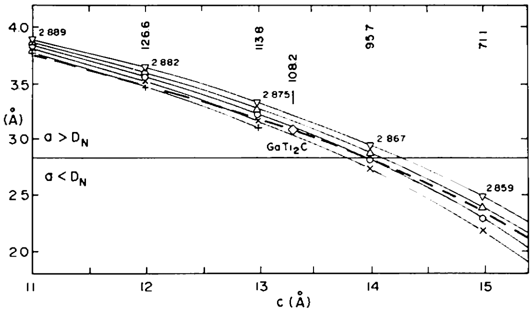

Fig. 7. Thin lines show values of a *versus* c for $N\mathrm{Ti_2C}$ phases, giving a constant M–M ($\neq a$) distance of 2·924 Å for constant z values; ▽ 0·085; △ 0·086; ○ 0·087; × 0·088; + 0·089. The thick broken line indicates a and c values that satisfy conditions of constant M–M ($\neq$) = 2·924 and constant M–N = 2·800 Å (calculated for the $\mathrm{GaTi_2C}$ phase with $z = 0{\cdot}087$). Numbers ranging from 2·859 to 2·889 indicate variation of the M–N distance with a and c for a constant M–M ($\neq a$) distance of 2·924 Å and a constant z of 0·085. The numbers at the top of the diagram which range from 126·6 to 71·1 indicate the unit-cell volume (Å^3) for c values of 12, 13, 14 and 15 Å, and for the $\mathrm{GaTi_2C}$ phase.

(ii) *The transition metals, M, in* $AlCr_2C$ *phases*

The obvious explanation of a valency effect that is greatest for transition metals of lowest valency, as arising from transference of electrons from the interstitial metalloid atoms to the transition metals, is quite untenable in view of the relative electronegativity values and because of known energy-band structures of interstitial carbides and nitrides with the rock-salt structure (*cf.* Neckel *et al.*, 1976). The valency effect can nevertheless be explained quantitatively on the basis of the number of electrons required to account for the distances between the atoms in the $-M-N-M-M-N-M-$ arrays which control the cell dimensions, calculated on the basis of Pauling's (1947) equation $R(1)-R(n) = 0{\cdot}3 \log n$. It is therefore assumed initially that the invariant $M-M$ distance in this array, rather than the alternate $M-C-M$ path, is dimension controlling, so that the number of M electrons involved in $M-C$ contacts or transferred to bands derived from the metalloid $2p$ states is unimportant. A second assumption, since the N atoms have only the six M neighbours in the region where $a > D_N$, is that the average difference in the $M-N$ distances from $\frac{1}{2}(D_M + D_N)$ with D_M for CN 9 and D_N for CN 6 (see *e.g.* Fig. 7), is to be attributed wholly to the number of electrons provided by the M atoms.

The results of these simple calculations for the four NTi_2C, three NV_2C and three NCr_2C phases in the region where $a > D_N$ are summarized in Table 2. The same z values are assumed for the V and Cr phases as for the corresponding Ti phases.

The calculated differences of CN 12 diameters in the NM_2C phases compared to the elemental structures, +0·004, +0·076 and +0·125 Å for the Ti, V and Cr phases respectively, indicate that in Figs. 2 and 3 the lines of a and c *versus* D_M for V and Cr phases should lie respectively at 0·072 and 0·121 Å lower D_M values than the lines for Ti phases. The average observed values in Figs. 2 and 3 are respectively 0·070 and 0·115 Å for the Al and Ga phases of these three M components. Similar calculations comparing Zr and Hf phases with Nb and Ta phases, although involving different electron numbers, give the same result that the Group V metal phases should lie 0·073 Å to lower D_M values than the Group IV metal phases.

In the region where $a < D_N$, there is only the $InNb_2C$ phase that can be compared with the NTi_2C phases. However, the valency effect appears to be no different from that in the region where $a > D_N$, even though now the CN of the N atoms should be considered as 12 due to the six $N-N$ interactions in the (0001) plane.

Fig. 8 confirms that the calculated electron distributions for the Ti, V and Cr phases are indeed sensible, since the number of transition-metal electrons assigned to carbon p bands and non-bonding in d bands extrapolates to zero for a hypothetical M component of valency two, which has no d electrons. Furthermore, the numbers of electrons assigned to the three $M-M$ and three $M-N$ contacts extrapolate to values that add

Table 2. *Results of calculations performed in the region* $a > D_N$

	Ti phases	V phases	Cr phases
Average observed $M-M$ ($\neq a$) distance minus D_M for CN 9 (Å)	0·077 (all phases)	0·186	0·262
Calculated number of electrons used in 3 $M-M$ bonds	0·992	0·816	0·732
Average of observed $M-N$ distances minus $\frac{1}{2}(D_M + D_N)$, D_M for CN 9, D_N for CN 6 (Å)	0·041	0·060	0·075
Calculated number of electrons used in 3 $M-N$ bonds	0·973	1·052	1·125
Total number of electrons used for 3 $M-M$ and 3 $M-N$ bonds	1·965	1·868	1·857
Number of electrons for carbon p bands, and non-bonding, per M atom	2·035	3·132	4·143
Average electrons per bond for 3 $M-M$ and 3 $M-N$ bonds in NM_2C phases	1·965/6 = 0·328	1·868/6 = 0·311	1·857/6 = 0·310
Number of electrons per bond in CN 12 element	4/12 = 0·333	5/12 = 0·417	6/12 = 0·500
Number of electrons per bond in NM_2C phases minus that for CN 12 element	−0·005	−0·106	−0·190
Corresponding difference in CN 12 D_M for NM_2C phases to CN 12 D_M for the elements (Å)	+0·004	+0·076	+0·125

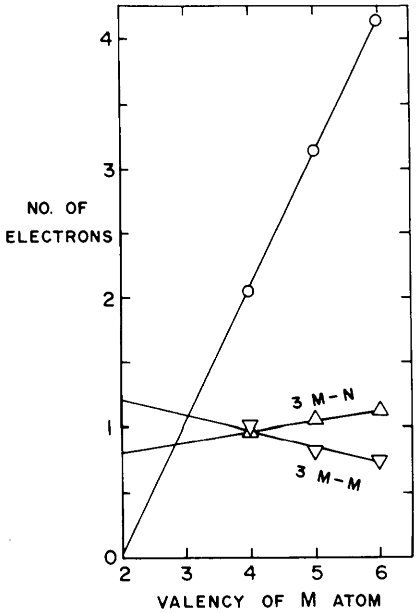

Fig. 8. Calculated average number of valency electrons involved in three $M-M$ bonds (▽), three $M-N$ bonds (△) and transferred to carbon $2p$ bands or in non-bonding d bands (○) *versus* M-atom valency for NTi_2C, NV_2C and NCr_2C phases in the region where $a > D_N$.

up to two electrons for an M component of valency two.

Thus the valency effect is shown to be the result of the arrays of atoms that control the cell dimensions $-M-N-M-M-N-M-$, using the numbers of valency electrons in their bonding that are commensurate with the distances between the atoms according to the Pauling equation. Furthermore, the reason for the valency effect being essentially zero for the Group IV M components, Ti, Zr and Hf, is that, in giving approximately two electrons per atom to the carbon p bands (assuming little overlap of these and the transition metal d bands), there are approximately two electrons left for the six M–M and M–N bonds that control the cell dimensions. This is the same ratio of electrons per bond as in the elemental structures from which D_M for CN 12 is calculated. Hence, D_M for CN 12 is the same in Ti, Zr and Hf phases with the $AlCr_2C$ structure as in their elemental structures. By the same token, since for $AlCr_2C$ phases of Group V and VI M components, some electrons are assigned to non-bonding d states, there are less electrons per bond controlling the cell dimensions; hence D_M for CN 12 is greater in these phases with the $AlCr_2C$ structure than in the elemental structures from which the D_M values for CN 12 were determined and so the valency effects are observed. These results account in the main for the data in Figs. 2, 3 and 4, although the lattice parameters of a few phases such as $GaMo_2C$ place them not quite in the right positions.

5. Discussion

In ternary interstitial phases with cubic structures, such as the perovskites, NTi_3C, the octahedra of Ti atoms surrounding the carbon atoms are regular and their edges, which equal $a/\sqrt{2}$, must expand as the cell edge expands. In contrast, the ternary hexagonal interstitial compounds with the $AlCr_2C$ and $SiTi_3C_2$ (Jeitschko & Nowotny, 1967) structures each have two degrees of freedom: the axial ratio c/a, and a z parameter allowing movement of the transition-metal atoms along the [0001] direction. As the relative sizes of the M and N atoms change in different phases, these two degrees of freedom could, for example, allow the octahedra to remain regular (condition $zc\sqrt{6} = a$ for the $AlCr_2C$ structure), allow their diagonals to maintain a fixed length equal to $(D_M + D_C)$, or allow the M–M edges of the octahedra that do not lie in (0001) planes to maintain some fixed length.

That the octahedral edges M–M which do not lie in (0001) planes have a fixed length, essentially equal to $D_{Ti} = 2.924$ Å in NTi_2C phases, is significant, since the M–M edges of the octahedra that lie in (0001) planes cannot have a fixed length of D_M, unless a is constant and equal to D_M in all phases, which is not the case. Thus, the M–M ($\neq a$) distances which vary between about 2.89 and 2.97 Å for NTi_2C phases (compared to interatomic distances of 2.89 and 2.95 Å in elemental hexagonal Ti) are responsible for maintaining the Ti d bands in these phases. That the transition-metal d bands are an important feature in the stability of the structures of Hägg interstitial phases has long seemed obvious, but here is a demonstration of it under conditions where the variable parameters of the hexagonal structure would have allowed almost any variation of interatomic distances. This condition that controls the cell dimensions is the only one which in all NTi_2C phases would maintain three-dimensional d bands between the Ti atoms within the layers of octahedra. Much the same situation occurs in the $SiTi_3C_2$ structure where the Ti–Ti distances that do not lie in (0001) planes are 2.971 Å and those that lie in (0001) planes are 3.068 Å.

$AlCr_2C$ phases with M components Ti, Zr, Hf, Nb and Ta are all true Hägg interstitial phases with $R_C/R_M < 0.59$, and the invariant M–M distances are equal to the elemental D_M values for CN 12 for the Ti, Zr and Hf phases and average just slightly larger (0.038 Å) for the Nb and Ta phases. However, for the V and Cr phases the M–M distances are distinctly larger (respectively 0.111 and 0.187 Å), but these are no longer true Hägg interstitial phases since for them $R_C/R_M > 0.59$. Thus it appears that the diameter of the carbon atom influences the invariant M–M distances through the M–C–M octahedron diagonals. Whether d bands are still formed between the transition-metal atoms under these conditions is uncertain.

Finally, there appear to be no reports of $AlCr_2C$ phases with an M component of valency three. Two possibilities therefore exist: either such phases cannot be stable, because, with approximately two electrons per M atom relegated to bands derived from carbon $2p$ states, the remaining electron per M atom is insufficient for the six M–M and M–N contacts to give a stable structure, or they have been insufficiently sought and when a phase is found its lattice parameters will be accurately given by (1) to (4) with a value of $S = -2$, there being approximately two electrons per M atom assigned to the M–M and M–N contacts.

6. Summary

(1) The study shows that it is possible to derive analytical expressions based on CN 12 atomic diameters which reproduce closely complex observed lattice-parameter variations in a series of phases with a given crystal structure – regardless of the actual coordination of the atoms in the structure, and regardless of the fact that the CN 12 diameters of atoms in the structure may differ from those in the

elemental structures from which standard CN 12 diameters are derived!

(2) It shows that an invariant parameter in a uniaxial crystal structure may couple the variable parameters of the structure, so as to produce apparent dependences of the cell edges on the diameter of a component atom, which could not possibly arise intrinsically through the direct contacts of the atom with its neighbours.

(3) The observed variations of the cell dimensions of phases with the $AlCr_2C$ structure lead to some interesting observations on the nature of the electronic interactions in true interstitial phases. Hopefully, these may stimulate band-structure calculations to confirm or reject the reliability of such analyses.

This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

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SHORT COMMUNICATIONS

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Acta Cryst. (1980). A**36**, 732–734

Weissenberg photographs: triclinic-cell parameters from one crystal setting.

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(*Received* 23 *January* 1980; *accepted* 18 *February* 1980)

Abstract

A simple method is given for deriving the triclinic-cell parameters from three general reflections by vertical or horizontal measurements on upper-level films.

Introduction

The problem of obtaining, with a Weissenberg camera, all unit-cell parameters from one crystal setting has been studied by different authors. In most methods, measurements on an upper-level photograph serve to determine the origin shift of this level relative to the true origin. Then, two direct angles can be calculated and the cell is completely defined, the four other cell parameters being provided by the oscillation and the zero-level photographs. Buerger (1942, pp. 377ff.) proposed a method of angular lag which requires the recording of both the zero and an upper level on the same film, and involves measurements of low-angle axial reflections. Hulme's (1966) method, easier and more accurate, enables one to determine the unknown angles from measurements of the angular distance between general reflections, either graphically or by iteration. More recently, Hebert (1978) has described a procedure for deriving these angles from measurements of distances between festoons representing either axes or r.l. lines parallel to the axes. A method, quite different from these, has also been reported by Alcock & Sheldrick (1967) where all reciprocal-cell parameters are calculated from the separations of the α_1–α_2 doublets and refined by least squares. In the following method, vertical or horizontal measurements involving three general reflections lead to an easy determination of the remaining reciprocal-cell parameters. These are accurate enough for preliminary work and may be refined later with a diffractometer.

Vertical measurements

Let us consider (Fig. 1) a crystal rotated about *c*. The r.l. point *P* has two components, ζ parallel to the rotation axis

0567-7394/80/040732-03$01.00