Research on the Structure of Matter, University of Pennsylvania, supported by the Advanced Research Projects Agency, Office of the Secretary of Defense. The authors would like to express their great gratitude to Dr Benesovsky at the Metallwerk Plansee A.G. in Reutte, Austria, who kindly supplied the vanadium-, niobium- and tantalum carbide samples. The authors would also like to acknowledge the fruitful discussions they had with Professor H. Nowotny.

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On the Crystal Chemistry of the Close Packed Transition Metal Carbides. II. A Proposal for the Notation of the Different Crystal Structures*

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To counteract the prevailing confusion in the notation of the close packed transition metal carbides a notation is proposed which is based on the structural features of the carbide phases. It consists of the Jagodzinski–Wyckoff symbol for the stacking sequence of the close packed metal atom layers followed by the space group of the compound to distinguish between different arrangements of the carbon atoms on the octahedral interstices. The known close packed carbide types are reviewed and their new notation is given. It is found that in the case of the NaCl defect structures there exist two different structure types which although not homometric yet give rise to identical powder diffraction patterns. A distinction between both types in principle is possible only with single-crystal diffraction data.
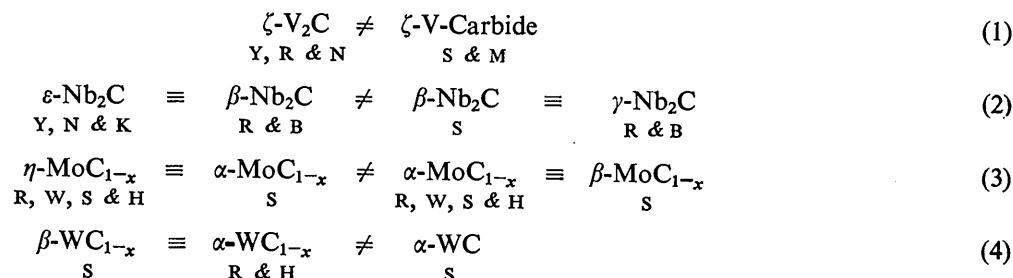
Introduction

During the last fifteen years, the structures and phase relationships of the refractory transition metal carbides have been studied quite intensively (for review see Kieffer & Benesovsky, 1963; Storms, 1967; Goldschmidt, 1967; Nowotny & Benesovsky, 1968). Nearly all occurring carbide structures have already been solved. For the most part they are simple structures consisting of an arrangement of close-packed transition metal atoms with carbon atoms positioned in the octahedral interstices. Quite often not all of the available octahedral interstices are occupied and the remaining carbon atoms can then have ordered arrangements which may require unit cells which are a multiple of the earlier assumed repetitive units. The ordering of the carbon atoms leads to superstructure lines. These may be seen in X-ray diffraction patterns of Sc, Ti and V carbides but not at all in the X-ray patterns of carbides with heavier transition metals. In the latter case, only neutron and electron diffraction experiments will permit the determination of the supercell and the C atom arrangement. Certain carbides, depending on temperature and carbon content, show a variety of ordered carbide structures, with some of the phase changes occurring at very high temperature as indi-

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* Part I, Yvon & Parthé (1970). Acta Cryst. B25, 149.

cated from high-temperature thermal analysis experiments.

No guide lines have ever been given on how to denote the different close packed carbide phases. The various notations used by different authors are confusing at least, but more probably misleading. The notation problem has become now even more serious because we have not only to distinguish between different carbon atom arrangements for one particular metal layer stacking but following the structure determination of the ζ carbides (Yvon & Parthé, 1970) we have to discern between different metal layer stackings as well. The customary use of the Greek prefixes does not lend itself to any reasonable distinction between the structures and has resulted in contradictory phase notations. Examples from recent publications have been used to formulate the following notation inequalities:

As is well known for close packed element structures a convenient method of presenting the stacking sequence graphically is to describe all structures with hexagonal unit cells and then to show the atom arrangement in the $(11\bar{2}0)$ plane. In Fig. 1 are shown the five known stacking arrangements of the metal atoms (big open circles) in the close packed transition metal carbides. The stacking sequence of the hexagonal metal layers can be described by the Jagodzinski–Wyckoff symbols: h for T_2C, hcc and hhc for T_3C_2, $hhcc$ for T_4C_3 and c for TC. These Jagodzinski symbols printed in bold face will form the first part of our proposed notation. As shown before (Jagodzinski, 1954a, b; see also Parthé, 1964) there exists a simple relationship between the number of letters in the Jagodzinski–Wyckoff symbol and the number of close packed layers in the unit cell.*

It is known from the studies of Gunnar Hägg that the carbon atoms occupy the octahedral interstices

$$\zeta\text{-}V_2C \quad \neq \quad \zeta\text{-V-Carbide} \tag{1}$$
$$\text{Y, R \& N} \qquad \text{S \& M}$$

$$\varepsilon\text{-}Nb_2C \quad \equiv \quad \beta\text{-}Nb_2C \quad \neq \quad \beta\text{-}Nb_2C \quad \equiv \quad \gamma\text{-}Nb_2C \tag{2}$$
$$\text{Y, N \& K} \qquad \text{R \& B} \qquad\qquad \text{S} \qquad\qquad \text{R \& B}$$

$$\eta\text{-}MoC_{1-x} \quad \equiv \quad \alpha\text{-}MoC_{1-x} \quad \neq \quad \alpha\text{-}MoC_{1-x} \quad \equiv \quad \beta\text{-}MoC_{1-x} \tag{3}$$
$$\text{R, W, S \& H} \qquad \text{S} \qquad\qquad \text{R, W, S \& H} \qquad\qquad \text{S}$$

$$\beta\text{-}WC_{1-x} \quad \equiv \quad \alpha\text{-}WC_{1-x} \quad \neq \quad \alpha\text{-WC} \tag{4}$$
$$\text{S} \qquad\qquad \text{R \& H} \qquad\qquad \text{S}$$

R & B: Rudy & Brukl (1967)
R & H: Rudy & Hoffman (1967)
R, W, S & H: Rudy, Windisch, Stosick & Hoffman (1967)
S: Storms (1967)
S & M: Storms & McNeal (1962)
Y, N & K: Yvon, Nowotny & Kieffer (1967)
Y, R & N: Yvon, Rieger & Nowotny (1966)

It should be obvious that any effort to devise a new, more logical notation would be welcomed by anyone interested in the close packed transition metal carbides. We decided to propose a new notation which would relate to the structural features and be based on a simple logical principle which will allow one to apply it to new structures not yet known, and still be concise, unambiguous, and easy to remember.

The metal atom layer stacking

As mentioned before, X-ray diffraction experiments will always permit one to determine the metal layer stacking in the carbides while the determination of the carbon atom arrangement is more difficult. Consequently, the first part of our proposed notation contains a symbol for the stacking sequence of the metal atom layers which can be given for every close packed carbide without difficulty.

We can distinguish five different stacking variations of transition metal atoms in the close packed carbides.

between the close packed metal atoms. The number of octahedral interstices in any close packed structure is equal to the number of atoms and is independent of the way the hexagonal metal layers are stacked. Thus one might expect that the theoretical composition of all transition metal carbides with close packed metal layers is TC. This is however not the case. It was found that only in carbides with metal layer stacking c is it possible for the carbon atoms to occupy all available octahedral interstices.† Phase diagram studies have shown that in carbides with metal layer stacking h, hcc, hhc and $hhcc$ not all the interstitial sites are occupied,

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* In a nutshell: if the sum of symbols h in the total symbol is odd then the structure has twice as many layers as symbols. If the sum is even then the structure has three times as many layers as symbols, except for special cases where there are as many layers as symbols.

† The upper limit TC is reached only in certain carbides, for example TaC. Others like 'VC' for reasons not understood come close but don't reach it quite (composition of upper limit is $VC_{0.89}$).

the compositions for maximum carbon content being T_2C, T_3C_2, T_3C_2 and T_4C_3 respectively.

These compositions can be explained if we assume that there exists a restriction on the occupation of the octahedral interstices by carbon atoms which depends on the particular stacking of the metal atom layers. If two interstices are located directly above each other in the (11$\bar{2}$0) plane (which happens with every h stacking of the metal layers) only one site will be occupied by a carbon atom, the other remains empty. All neutron diffraction studies on close packed transition metal carbides show that this rule is fulfilled without exception.* One can use this rule to calculate the compositions of hypothetical close packed carbide phases assuming different metal atom layer stackings. In Table 1 are listed all possible metal layer stackings with a maximum of six h,c symbols and the corresponding carbide compositions. We find that the carbide compositions for metal atom stackings h, hcc, hhc, $hhcc$ and c should be T_2C, T_3C_2, T_3C_2, T_4C_3 and TC respectively in agreement with the experimentally found results. Thus the stacking symbol gives not only information on the particular arrangement of the metal layers but indicates also the highest possible carbon content.

The carbon atom arrangement

The second part of the proposed notation is the Schoen-

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* If the metal layers are not close packed, this rule does not apply as demonstrated on WC (Parthé & Sadagopan, 1962).

flies space group symbol.* For a given metal layer stacking and given carbon content different structures can be formed depending on the ordering of the carbon atoms in the available octahedral interstices.

In the first part of Table 2 are listed the six different carbide structures with hexagonal close packed metal atoms. Two structure types, one ordered and one with random C atom arrangement, have small hexagonal cells. Four other ordered structure types have supercells of the same height as the small hexagonal cells, but with longer translational periods within the hexagonal base plane. On the left hand side is shown the carbon atom arrangement in these structures by means of a projection on the hexagonal base plane. For clarity the transition metal atoms have been omitted. The notation we propose for these six types is $h(D_{6h}^4)$, $h(D_{3d}^3)$, $h(D_{3d}^1)$, $h(D_{2h}^{12})$, $h(D_{2h}^{14})$ and $h(D_{2h}^{16})$.

The order of the carbon atoms in Mo_3C_2 and $(Ta_2V)C_2$ has not yet been determined. Therefore only hcc and hhc can be listed for their structure. The notation for the structure type of the ζ-phase is $hhcc$. Here is a case where the space group for the ordered structure is identical with the space group for the not ordered structure. For the structure notation one can use $hhcc$

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* In the case of an orthorhombic structure different settings are possible which lead to different Hermann—Mauguin notations. In order to avoid any possible confusion for persons less experienced in crystallography the preference was given here to the Schoenflies notation.

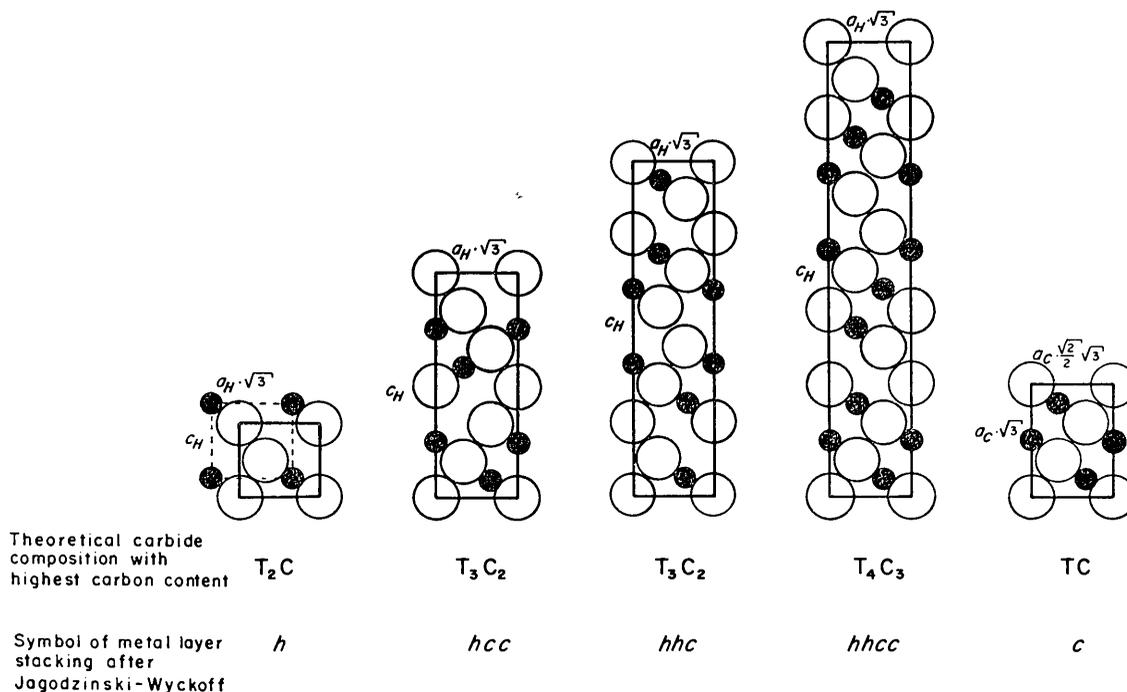| Theoretical carbide composition with highest carbon content	T_2C	T_3C_2	T_3C_2	T_4C_3	TC
Symbol of metal layer stacking after Jagodzinski-Wyckoff	h	hcc	hhc	$hhcc$	c

Fig. 1. Stacking variations of the hexagonal metal atom layers in the close packed transition metal carbides. Metal atoms (big open circles) are shown in their arrangement in the (11$\bar{2}$0) plane of corresponding hexagonal unit cells. The ordered arrangement of the carbon atoms (small black circles) on the octahedral interstices is only schematic and has not necessarily been found in nature.

(ord.) and **hhcc** (disord.) or if the C atom order is not known, simply **hhcc**.

In the case of metal stacking **c** with all the octahedral interstices occupied only one structure type is possible, the NaCl (*B*1) type. Most carbides with cubic close packed metal atoms are, however, carbon deficient. Until the present time four NaCl-defect types are known with ordered carbon atom vacancies. For a comparison of the different NaCl-defect structures it is convenient to describe the structures using hexagonal unit cells. The carbon atoms are found to be arranged in hexagonal layers similar to the arrangements shown for the **h** structures except that the stacking is now different. One such carbon layer is shown in each of the drawings for the **c** structures listed in the last part of Table 2. In the NaCl structure type there are no carbon defects and all sites are occupied. In NaCl-defect types some layer sites are empty and are indicated by a square. It can be shown that in most NaCl-defect structures the defects occur only in alternative carbon layers, the layers in between being completely occupied by carbon atoms. For the proper comparison of the different structures it is therefore sufficient to show only that one layer where not all sites are occupied. The experimental study of the carbides with NaCl-defect structures has only recently been started and more data on new structure types can be expected. We have therefore included in the Table a few extra types which have not yet been observed experimentally with carbides. The proposed structure type notation is listed in the second column of Table 2. The type notation consists here of the overall formula of the defect carbide, the letter **c** to indicate cubic stacking of the metal atom layers followed by the space group in parentheses.

Structure problems with T_2C, c phases

Two NaCl-defect structure types listed in Table 2, T_2C, **c** (O_h^7) and T_2C, **c**(D_{3d}^5) with $(c/a)_{hex} = 2\sqrt{6}$, deserve special mention because it is impossible in principle to distinguish between them by powder techniques. The structures are not homometric according to the common usage of the term, yet they produce identical powder diffraction patterns as the combined intensities of all coinciding reflections have the same values. To facilitate the comparison both structures have been described below with hexagonal cells of equal size and equal number of atoms per cell. That means as compared with the data given in Table 2, the *a* axis of T_2C, **c**(D_{3d}^5) is doubled and T_2C, **c**(O_h^7) is described with a triple hexagonal cell. The space group and the point positions of the atoms in the new cell are given by

T_2C, **c**(D_{3d}^5) $c/a = \sqrt{6}$ T_2C, **c**(O_h^7)

Space group $R\bar{3}m$ Space group $R\bar{3}m$

18 T in 18(h) with $x=\frac{1}{2}, z=\frac{1}{4}$ 18 T in 18(h) with $x=\frac{1}{2}, z=\frac{1}{4}$

6 T in 6(c) with $z=\frac{1}{4}$ 6 T in 6(c) with $z=\frac{1}{4}$

9 C in 9(d)   9 C in 9(d)

3 C in 3(b)   3 C in 3(a)

The identical powder diffraction intensities for both structures have been demonstrated by us out to $\sin^2\theta/(\sin^2\theta$ of $100_{NaCl}) = 14$ where $\sin^2\theta$ of 100_{NaCl} indicates the $\sin^2\theta$ values of the (unobservable) 100 reflection of the cubic NaCl-type substructure common to both structures. One example each for a superstructure line (normalized $\sin^2\theta = 2\frac{3}{4}$) and a fundamental line (normalized $\sin^2\theta = 3$) are given below, where we have listed the product: multiplicity factor times square of the structure factor. The sum of the $p.F^2$ values for a given θ is the same for both structures.

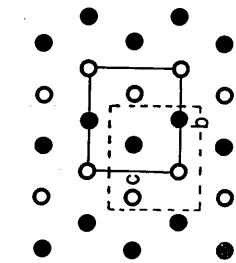| $\dfrac{\sin^2\theta}{\sin^2\theta \text{ of } 100_{NaCl}}$	hkl for big hexagonal cell with $c/a=\sqrt{6}$	hkl for cubic NaCl subcell	T_2C, c(D_{3d}^5) $p.F^2$		T_2C, c(O_h^7) $p.F^2$	
$2\frac{3}{4}$	015		0		$6(+6f_C)^2$	
$2\frac{3}{4}$	021	—	$6(-12f_C)^2$	$864f_C^2$	$6(-6f_C)^2$	$864f_C^2$
$2\frac{3}{4}$	113		0		$12(+6f_C^2)$	
3	006	111	$2(-24f_T+12f_C)^2$		$2(-24f_T+12f_C)^2$	
3	202		$6(-24f_T+12f_C)^2$		$6(-24f_T+12f_C)^2$	

Table 1. *Ideal formulae and maximum carbon content for some hypothetical carbides with differently stacked close packed metal atom layers*

Stackings of known carbide phases are printed in bold face.

T_2C	33·3 at% C:	**h(2H)**, **hc(4H)**, $h_3c(8H)$, $h_5c(12H)$, $h_3chc(6H')$
T_5C_3	37·5 at% C:	$h_3c_2(10H)$, $h_2chc(10H)$, $hc_2hc(15R)$, $h_4c(15R)$
T_3C_2	40·0 at% C:	**$hc_2(6H)$**, **$h_2c(9R)$**, $h_3c_3(12H)$, $h_2chc_2(12H)$, $h_2c_2hc(12H)$, $h_4c_2(18R)$, $hc_3hc(18R)$
T_4C_3	42·8 at% C:	$hc_3(8H)$, **$h_2c_2(12R)$**
T_5C_4	44·4 at% C:	$h_2c_3(5T)$, $hc_4(10H)$
T_6C_5	45·5 at% C:	$hc_5(12H)$, $h_2c_4(18R)$
TC	50·0 at% C:	$c(3C)$

The stacking variations of the metal layers are denoted by the Jagodzinski–Wyckoff notation (Jagodzinski, 1954a,b). Behind each stacking formula is given in parenthesis the corresponding Ramsdell notation (Ramsdell, 1947) consisting of a number and a letter. The number indicates the number of hexagonal metal layers in the hexagonal unit cell. The letter *H*, *H'*, *R*, *T* or *C* denotes if the symmetry of the metal atom arrangement is hexagonal ($P6_3/mmc-D_{6h}^4$), hexagonal with lower symmetry ($P\bar{6}m2-D_{3h}^1$), rhombohedral ($R\bar{3}m-D_{3d}^5$), trigonal primitive ($P\bar{3}m1-D_{3d}^3$) or cubic ($Fm3m-O_h^5$). If the carbon atoms are ordered in general lower symmetries will occur.

Table 2. *A summary of all the known structure types of the transition metal carbides with close packed metal atom layers*

METAL LAYER STACKING **h** (2 close packed layers per cell)

C atom arrangement Open circles: C at 0 or $\frac{1}{4}$ Full circles: C at $\frac{1}{2}$ or $\frac{3}{4}$	Notation of structure type	Space group and unit-cell dimensions	Atom positions	Examples Data obtained by neutron diffraction experiments are printed in bold face
	h(D_{6h}^4) L'3-type	$P6_3/mmc(D_{6h}^4)$ a_H, c_H $c_H/a_{II} \sim 2 \cdot \frac{\sqrt{2}}{\sqrt{3}}$	2 T in 2(c) 1 C in 2(a) randomly distributed	**β-V₂C:** Bowman, Wallace, Yarnell Wenzel & Storms (1965) γ-Nb₂C: Rudy, Windisch & Brukl (1968) β-Ta₂C: see Storms (1967) β-Mo₂C: Rudy, Windisch, Stosick & Hoffman (1967) **β-W₂C:** Yvon, Nowotny & Benesovsky (1968)
	h(D_{3d}^3) C6-type or CdI₂-antitype	$P\bar{3}m1(D_{3d}^3)$ Unit-cell dimensions as above	2 T in 2(d) with z~$\frac{1}{4}$ 1 C in 1(a)	**α-Ta₂C:** Bowman, Wallace, Yarnell, Wenzel & Storms (1965) α-W₂C: Butorina & Pinsker (1960)
	h(D_{3d}^1) ε-Fe₂N-type	$P\bar{3}1m (D_{3d}^1)$ $a \sim a_H\sqrt{3}$ $c \sim c_{II}$	6 T in 6(k) with x~$\frac{1}{3}$, z~$\frac{1}{4}$ 2 C in 2(d) 1 C in 1(a)	ε-V₂C: Yvon, Nowotny & Kieffer (1967) **ε-Nb₂C:** Terao (1964); Yvon, Nowotny & Kieffer (1967) **ε-W₂C:** Yvon, Nowotny & Benesovsky (1968)
	ht(D_{2h}^{12}) C35-type or CaCl₂-antitype	$Pnnm(D_{2h}^{12})$ $a \sim a_H\sqrt{3}$ $b \sim c_H$ $c \sim a_H$	4 T in 4(g) with x~$\frac{1}{3}$, y~$\frac{1}{4}$ 2 C in 2(a)	Co₂C: Clarke & Jack (1951)

Table 2 (cont.)

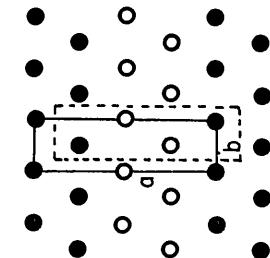| Structure type	Space group / lattice	Atom positions	References / Notes
h(D_{2h}^{14}) ζ-Fe₂N-type	Pbcn(D_{2h}^{14}) $a \sim c_H$ $b \sim 2a_H$ $c \sim a_H/3$	8 T in 8(d) with $x \sim \frac{1}{4}$, $y \sim \frac{1}{4}$, $z \sim \frac{1}{12}$ 4 C in 4(c) with $y \sim \frac{3}{8}$	ζ-V₂C: Yvon, Rieger & Nowotny (1966); Yvon, Nowotny & Kieffer (1967) α-Mo₂C: Parthé & Sadagopan (1963) W₂C: Rudy & Windisch (1967) however there are misprints in the atom positions Telegus, Gladyshevskii & Kripyakevich (1968)
h(D_{2h}^{16}) ξ-Nb₂C-type	Pnma(D_{2h}^{16}) $a \sim 2\sqrt{3}a_H$ $b \sim a_H$ $c \sim c_H$	4 T in 4(c) with $x \sim \frac{1}{24}$, $z \sim \frac{3}{4}$ 4 T in 4(c) with $x \sim \frac{5}{24}$, $z \sim \frac{1}{4}$ 4 C in 4(c) with $x \sim \frac{3}{8}$, $z \sim 0$	ξ-Nb₂C: Yvon, Nowotny & Kieffer (1967) Note: space group given here is different from that one listed in the original publication. With setting Pnma which corresponds to the setting given in *International Tables for X-ray Crystallography* (1952) the lattice parameters of ξ-Nb₂C are: $a=10\cdot92_0$, $b=3\cdot09_0$ and $c=4\cdot97_4$ Å. (Y,N & K) or $a=10\cdot906_0$, $b=3\cdot096_0$ and $c=4\cdot968$ Å (Storms, 1967)

METAL LAYER STACKING hcc (6 close packed layers per cell)

Structure type	Space group / lattice	Atom positions	References / Notes
hcc(D_{6h}^{4}) Mo₃C₂-type, not ordered	P6₃/mmc(D_{6h}^{4}) a_H, c_H $c_H/a_H \sim 6 \cdot \frac{\sqrt{2}}{\sqrt{3}}$	4 T in 4(f) with $z \sim \frac{1}{12}$ 2 T in 2(b) 4 Carbon atoms randomly distributed over 4(f) with $z \sim \frac{2}{3}$ and 2(a)	Mo₃C₂: Nowotny, Parthé, Kieffer & Benesovsky (1954) Note: composition was originally given as MoC, but phase diagram studies by Rudy, Windisch, Stosick & Hoffman (1967) indicate that the true composition is Mo₃C₂. Phase is denoted there as η-MoC₁₋ₓ.
hcc(C_{6v}^{4}) Mo₃C₂-type, ordered	P6₃mc(C_{6v}^{4}) unit-cell dimensions as above	2 T in 2(b) with $z \sim \frac{1}{12}$ 2 T in 2(b) with $z \sim \frac{5}{12}$ 2 T in 2(a) with $z \sim \frac{1}{4}$ 2 C in 2(b) with $z \sim \frac{10}{12}$ 2 C in 2(a) with $z \sim 0$ 2 ☐ in 2(b) with $z \sim \frac{8}{12}$	As neutron diffraction experiments have not yet been done it remains undecided whether or not Mo₃C₂ has an ordered C atom arrangement

METAL LAYER STACKING hhc (9 close packed layers per cell)

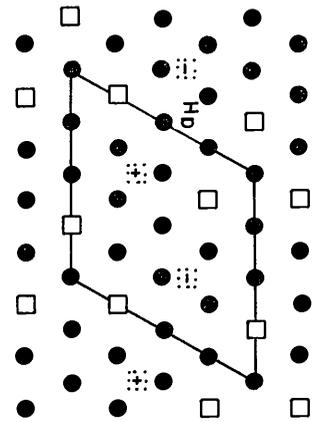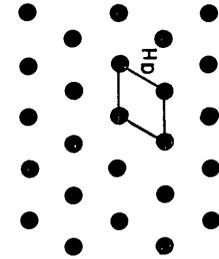| Structure type	Space group / lattice	Atom positions	References / Notes
hhc (D_{3d}^{5}) Ta₂VC₂-type	$R\bar{3}m$(D_{3d}^{5}) a_H, c_H $c_H/a_H \sim 9 \cdot \frac{\sqrt{2}}{\sqrt{3}}$ Same if C atoms are not ordered	6T in 6(c) with $z \sim \frac{2}{9}$ 3T in 3(a) 6C in 6(c) with $z \sim \frac{7}{18}$ 3 ☐ in 3(b)	(Ta₂V)C₂: Rudy (1969)

Carbon atom vacancies not ordered

Carbon atom vacancies ordered

Table 2 (cont.)

METAL LAYER STACKING hhcc (12 close packed layers per cell)

hhcc(D_{3d}^5)	$R\bar{3}m(D_{3d}^5)$		
ζ-phase structure	a_H, c_H	6T in 6(c) with $z \sim \frac{3}{24}$	V$_4$C$_3$, Nb$_4$C$_3$, Ta$_4$C$_3$: Yvon & Parthé (1969)
Sn$_4$P$_3$-type	$c_H/a_H \sim 12 \cdot \sqrt{2}/\sqrt{3}$	6T in 6(c) with $z \sim \frac{7}{24}$	In the V$_4$C$_{3-x}$ samples investigated
	same if C atoms	6C in 6(c) with $z \sim \frac{10}{24}$	no carbon atom order was found.
	are not ordered	3C in 3(a)	X-ray data do not permit us to
		3□ in 3(b)	make conclusions on the C atom
			order in Nb$_4$C$_3$ and Ta$_4$C$_3$
			Sn$_4$P$_3$, Sn$_4$As$_3$: Olofsson (1967)

METAL LAYER STACKING c

Carbon atom site occupied } refers only to alternative carbon atom layers. If not indicated otherwise carbon atom layers in between are completely occupied
Carbon atom site not occupied } by carbon atoms.
Site in neighboring carbon atom layer either above or below the reference layer not occupied. This is the irregular case as defects occur normally only in alternative carbon atom layers.
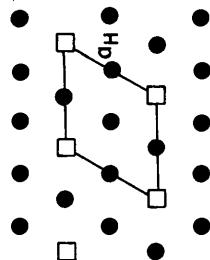
● □ ⊕ or ⊟

NaCl or B_1-type	$Fm3m(O_h^5)$		
	a_{B1}	4T in 4(a)	TiC: Gorbunov, Shishakov, Sadikov & Babad-Zakhryapin (1961)
	$a_H = a_{B1}\sqrt{2}/2$	4C in 4(b)	
	$c_H = a_{B1}\sqrt{3}$	Note: many of these phases	ZrC
	$c_H/a_H = 3 \cdot \sqrt{2}/\sqrt{3}$	deviate considerably from the	HfC
		ideal composition and for the	VC
		most part the arrangement of	NbC
		the C defects is not known.	TaC
			βMoC$_{1-x}$ } Notation of phases
			βWC$_{1-x}$ } after Storms (1967)

| T$_8$C$_7$,c(O^6)	$P4_332(O^6)$		
V$_8$C$_7$-type	$a_C = 2a_{B1}$	24T in 24(e) with $x \sim \frac{1}{8}$,	V$_8$C$_7$: Kordes (1968),
	$a_H = a_C\sqrt{2} = 2\sqrt{2}a_{B1}$	$y \sim \frac{3}{8}, z \sim \frac{1}{8}$	De Novion, Lorenzelli & Costa (1966),
	$c_H = a_C\sqrt{3} = 2\sqrt{3}a_{B1}$	8T in 8(c) with $x \sim \frac{3}{8}$	Froidevaux & Rossier (1967)
	$c_H/a_H = \frac{3}{2} \cdot \sqrt{2}/\sqrt{3}$	12C in 12(d) with $x \sim \frac{5}{8}$	
		12C in 12(d) with $x \sim \frac{3}{8}$	
		4C in 4(a)	

Table 2 (cont.)

T₈C₇, c(O_h^5) Mg₆MnO₈-antitype

$Fm3m(O_h^5)$
$a_C = 2a_{B1}$
$a_H = a_C \dfrac{\sqrt{2}}{2} = a_{B1}\sqrt{2}$
$c_H = a_C\sqrt{3} = a_{B1}2\sqrt{3}$

24T in 24(e) with $x \sim \frac{1}{4}$
8T in 8(c)
24C in 24(d)
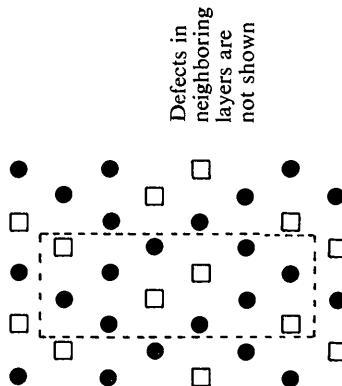4C in 4(a)
4□ in 4(b)

For Mg₆MnO₈ see Kasper & Prener (1954)
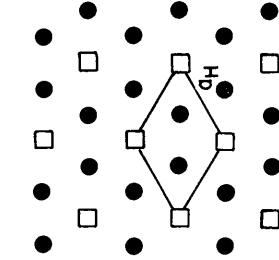
T₆C₅, c(C_3^2) V₆C₅-type

$P3_1(C_3^2)$
$a_H \sim a_{B1}\dfrac{\sqrt{2}}{2}\sqrt{3}$
$c_H \sim 2\sqrt{3}a_{B1}$
$c_H/a_H \sim 2 \cdot \sqrt{2}$

All atoms in 3(a)
T: $x \sim \frac{4}{9},\ y \sim \frac{8}{9},\ z \sim \frac{1}{4}$
T: $x \sim \frac{7}{9},\ y \sim \frac{5}{9},\ z \sim \frac{1}{4}$
T: $x \sim \frac{1}{9},\ y \sim \frac{2}{9},\ z \sim \frac{1}{4}$
T: $x \sim \frac{7}{9},\ y \sim \frac{8}{9},\ z \sim \frac{1}{12}$
T: $x \sim \frac{4}{9},\ y \sim \frac{2}{9},\ z \sim \frac{1}{12}$
T: $x \sim \frac{1}{9},\ y \sim \frac{5}{9},\ z \sim \frac{1}{12}$
C: $x \sim \frac{5}{9},\ y \sim \frac{5}{9},\ z \sim \frac{1}{3}$
C: $x \sim \frac{7}{9},\ y \sim \frac{5}{9},\ z \sim \frac{1}{3}$
C: $x \sim \frac{4}{9},\ y \sim \frac{2}{9},\ z \sim \frac{1}{3}$
C: $x \sim \frac{7}{9},\ y \sim \frac{2}{9},\ z \sim \frac{1}{6}$
C: $x \sim \frac{4}{9},\ y \sim \frac{5}{9},\ z \sim \frac{1}{6}$
□: $x \sim \frac{1}{9},\ y \sim \frac{8}{9},\ z \sim \frac{1}{6}$
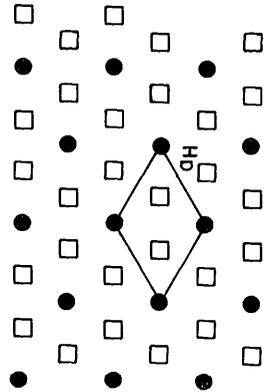
V₆C₅: Venables, Kahn & Lye (1968)

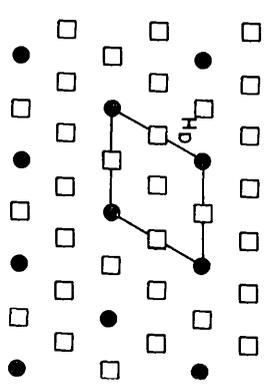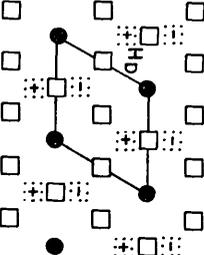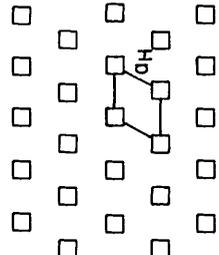**T₃C₂, c(D_{2h}^{24}) Sc₂S₃-antitype**

$Fddd(D_{2h}^{24})$
$a \sim 2a_{B1}$
$b \sim \sqrt{2}a_{B1}$
$c \sim 3\sqrt{2}a_{B1}$

32 T in 32(h) with
    $x \sim \frac{1}{8},\ y \sim \frac{1}{8},\ z \sim \frac{11}{24}$
16 T in 16(f) with $y \sim \frac{3}{8}$
16 C in 16(g) with $z \sim \frac{1}{24}$
16 C in 16(g) with $z \sim \frac{7}{24}$
16□ in 16(g) with $z \sim \frac{13}{24}$
Symmetry center at origin

For Sc₂S₃ see Dismukes & White (1965)

Defects in neighboring layers are not shown

Table 2 (cont.)

T_3C_2, $\mathbf{c}(C_3^2)$	$P3_1(C_3^2)$ $a_H \sim a_{B1}\frac{\sqrt{2}}{2}\sqrt{3}$ $c_H \sim 2\sqrt{3}a_{B1}$ $c_H/a_H \sim 2 \cdot \sqrt{2}$	All atoms in $3(a)$ T: $x \sim \frac{4}{9}, y \sim \frac{8}{9}, z \sim \frac{1}{4}$ T: $x \sim \frac{5}{9}, y \sim \frac{5}{9}, z \sim \frac{1}{4}$ T: $x \sim \frac{1}{9}, y \sim \frac{2}{9}, z \sim \frac{1}{4}$ T: $x \sim \frac{7}{9}, y \sim \frac{6}{9}, z \sim \frac{1}{12}$ T: $x \sim \frac{4}{9}, y \sim \frac{8}{9}, z \sim \frac{1}{12}$ T: $x \sim \frac{1}{9}, y \sim \frac{1}{9}, z \sim \frac{1}{12}$ C: $x \sim \frac{7}{9}, y \sim \frac{5}{9}, z \sim \frac{1}{3}$ C: $x \sim \frac{8}{9}, y \sim \frac{8}{9}, z \sim \frac{1}{3}$ C: $x \sim \frac{4}{9}, y \sim \frac{2}{9}, z \sim \frac{1}{3}$ C: $x \sim \frac{7}{9}, y \sim \frac{8}{9}, z \sim \frac{1}{6}$ □: $x \sim \frac{2}{9}, y \sim \frac{2}{9}, z \sim \frac{1}{6}$ □: $x \sim \frac{7}{9}, y \sim \frac{4}{9}, z \sim \frac{1}{6}$ □: $x \sim \frac{5}{9}, y \sim \frac{5}{9}, z \sim \frac{1}{6}$	
T_8C_5, $\mathbf{c}(C_{3v}^5)$	$R3m(C_{3v}^5)$ $a_H \sim a_{B1} \cdot \sqrt{2}$ $c_H \sim a_{B1} \cdot 2\sqrt{3}$ $c_H/a_H \sim 3 \cdot \frac{\sqrt{2}}{\sqrt{3}}$	9 T in $9(b)$ with $x \sim \frac{5}{6}, z \sim \frac{1}{12}$ 9 T in $9(b)$ with $x \sim \frac{1}{2}, z \sim \frac{1}{4}$ 3 T in $3(a)$ with $z \sim \frac{5}{12}$ 9 C in $9(b)$ with $x \sim \frac{1}{6}, z \sim \frac{1}{6}$ 3 C in $3(a)$ with $z \sim \frac{10}{12}$ 3 C in $3(a)$ with $z \sim 0$ 9□ in $9(b)$ with $x \sim \frac{1}{2}, z \sim 0$	
T_2C, $\mathbf{c}(O_h^7)$ Ti$_2$C-type	$Fd3m(O_h^7)$ $a_C \sim 2a_{B1}$ $a_H = a_C\frac{\sqrt{2}}{2} = a_{B1}\sqrt{2}$ $c_H = a_C\sqrt{3} = a_{B1}2\sqrt{3}$	32 T in $32(e)$ with $x \sim \frac{1}{4}$ 16 C in $16(c)$ } can be inter- 16□ in $16(d)$ } changed Symmetry center at origin	Sc$_2$C: Rassaerts, Nowotny, Vinek & Benesovsky (1967) Ti$_2$C: Goretzki (1967) Zr$_2$C: Goretzki (1967) See text.
T_2C, $\mathbf{c}(D_{3d}^5)$ CdCl$_2$-antitype or C19-type	$R\bar{3}m(D_{3d}^5)$ $a_H \sim a_{B1} \cdot \frac{\sqrt{2}}{2}$ $c_H \sim a_{B1}2 \cdot \sqrt{3}$ $c_H/a_H \sim 6 \cdot \frac{\sqrt{2}}{\sqrt{3}}$	6 T in $6(c)$ with $x \sim \frac{1}{4}$ 3 C in $3(a)$ 3□ in $3(b)$	Ho$_2$C: Bacchella, Mériel, Pinot & Lallement (1966) Y$_2$C Gd$_2$C } Dean, Lallement, Dy$_2$C } Lorenzelli & Pascard Er$_2$C } (1964) See text.

We recognize that the agreement of the powder intensities has nothing to do with the small scattering factor of carbon, but depends only on the particular geometrical relationship between these two types. Thus also neutron diffraction data can not resolve the problem. This is in principle possible only with single-crystal diffraction data. As single crystals were not available for the structure determination of any of the compounds listed in the row for T_2C, $c(O_h^7)$ and T_2C, $c(D_{3d}^5)$ it can not be stated which of the two carbon atom arrangements actually does occur in these sub-carbides.

The compound Ho_2C was reported to crystallize with the T_2C, $c(D_{3d}^5)$ type but with a c/a ratio which deviates slightly from the ideal value. In this case formerly coinciding diffraction lines become separated. The separation and the intensities of the NaCl *sub*-structure lines ($\sin^2 \theta/\sin^2 \theta_{100B1}$ values 3, 4, 8, ...) are the same for the $c(D_{3d}^5)$ and a rhombohedrally deformed $c(O_h^7)$ structure, however from the different separation of the NaCl *super*structure lines it should be in principle possible to distinguish between both structure types. As the intensities of the NaCl superstructure lines depend only on the scattering factor of carbon the superstructure lines in X-ray powder patterns of Ho_2C are to weak to permit the observation of the type of line separation (see footnote to Table 1 in the paper by Dean, Lallement, Lorenzelli & Pascard, 1964). The superstructure lines are strong enough in neutron diffraction patterns, but the wave length resolution is here so much smaller that separate lines appear to coincide (see Fig. 1 in the paper by Bacchella, Mériel, Pinot & Lallement, 1966). Thus it is still not possible to make a decision here although the c/a ratio deviates from the ideal value.
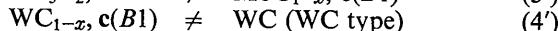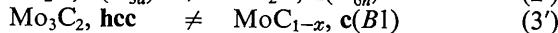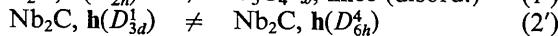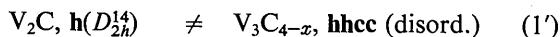
As is well known two structures belonging to a homometric set have identical F^2 values and consequently lead to the same Patterson map. From

$$F(hkl) \cdot F(\bar{h}\bar{k}\bar{l}) = \sum_j \sum_g f_j \cdot f_g \cdot \exp 2\pi i[h \cdot (x_j - x_g)$$
$$+ k \cdot (y_j - y_g) + l \cdot (z_j - z_g)]$$

one sees that equal F^2 values mean equal components of interatomic vectors or in other words equal interatomic vectors, characterized by magnitude and direction. The two carbide structures under discussion don't have equal interatomic vectors, but equal interatomic distances which means only equal magnitudes of the interatomic vectors. This was proved for all interatomic distances within a sphere of radius corresponding to four times the shortest C—C distance. As only the magnitudes but not the directions of the interatomic vectors are equal, the individual F^2 values in general will not be the same and the two structures cannot be called homometric (at least in the conventional usage of the word). However, two structures with equal interatomic distances must give identical powder diffraction patterns. This one can conclude from the Debye scattering equation for powder patterns (see Guinier, 1963; Warren, 1969). The interference function for a powder pattern depends on the *absolute values* of the interatomic vectors in the structure. Thus, although the individual F^2 values are different, the combined intensity of all coinciding diffraction lines for a particular θ value will be the same for both structures.

In conclusion we will rewrite the earlier given inequalities using the proposed notation:

V_2C, $h(D_{2h}^{14})$	$\neq$	V_3C_{4-x}, **hhcc** (disord.)	(1')
Nb_2C, $h(D_{3d}^1)$	$\neq$	Nb_2C, $h(D_{6h}^4)$	(2')
Mo_3C_2, **hcc**	$\neq$	MoC_{1-x}, $c(B1)$	(3')
WC_{1-x}, $c(B1)$	$\neq$	WC (WC type)	(4')

No space group is given for Mo_3C_2 because the C atom order has not yet been determined.*

Naturally no guarantee can be given that the proposed notation will always be applicable without ambiguity. But it is hoped that at the present it might help to dam the evergrowing confusion.

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* *Note added in proof:* — According to a personal communication by Dr A. L. Bowman neutron diffraction studies on Mo_3C_2 did not reveal ordering of the carbon atoms. Thus the structure of Mo_3C_2 can be denoted by hcc (D_{6h}^4).

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The Crystal and Molecular Structure of Platycodigenin Bromolactone

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The crystal structure of the bromolactone of platycodigenin, $C_{30}H_{47}O_7Br$, has been determined in order to elucidate the molecular structure and the absolute configuration of platycodigenin, $C_{30}H_{48}O_7$, one of the sapogenins of *Platycodon grandiflorum* A. DC. The bromolactone of platycodigenin was prepared by the action of Br_2–NaOAc in acetic acid; it crystallized in a structure with space group $P2_1$ and unit-cell dimensions $a=16\cdot81$, $b=7\cdot49$, $c=13\cdot52$ Å, $\beta=103\cdot3°$; $Z=2$. The crystal structure was solved by the heavy-atom method and refined by the method of least squares. The final R value for 2205 observed reflexions was $0\cdot09$. The molecular structure of platycodigenin was determined by the present study to be $2\beta,3\beta,16\alpha,23,24$-pentahydroxyolean-12-en-28-oic acid, which is the first example of the naturally occurring triterpenes having geminal hydroxymethyl groups at C(4) of the A ring.

Introduction

Platycodigenin (Fig. 1, II), $C_{30}H_{48}O_7$, (Tsujimoto, 1940) is one of the sapogenins isolated from the roots of *Platycodon grandiflorum* A. DC. Later Kubota & Kitatani (1968) and Akiyama, Tanaka & Shibata (1968) isolated this sapogenin together with polygalacic acid (II) from the same plant. The structure of the latter compound was proposed by Rondest & Polonsky (1963). However, the configuration of the C(16) hydroxy group has recently been revised to α. Structural studies of platycodigenin by chemical and spectral methods have been carried out for several years past. Comparative studies on the corresponding derivatives of platycodigenin and polygalacic acid suggest that platycodigenin can be represented by one of the three possible structures; $2\beta,3\beta,16\alpha,23,24$-; $2\beta,3\beta,16\alpha,23,25$- and $2\beta,3\beta,16\alpha,24,25$-pentahydroxyolean-12-en-28-oic acids (Akiyama, Tanaka & Shibata, 1968).

In order to determine the chemical structure and the stereochemistry of platycodigenin, we carried out an X-ray study of the bromolactone of this substance (III) which showed the molecular structure of platycodigenin, including its absolute configuration, to be (II). A preliminary short note on this work has already been published (Akiyama, Iitaka & Tanaka, 1968).

Experimental

As in the case of the known olean-12-en-28-oic acid type triterpenes, platycodigenin yielded bromolactone (III) by the action of Br_2–NaAc in acetic acid. Crystallization of (III) was tried from various solvents in order to obtain a crystal of a suitable size for X-ray analysis; crystals grown from a mixed solvent of ethyl acetate and benzene were found to be of an appropriate size. They were colourless needles elongated along the b axis. During the refinement of the crystal structure it was found that the crystal contains one equivalent mole of benzene as a solvent of crystallization. The density was measured by the flotation method in a mixture of benzene and carbon tetrachloride. The cell