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A Neutron Diffraction Study of the Nowotny Phase $Mo_{\le 5}Si_3C_{\le 1}$

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A neutron diffraction study of the Nowotny phase $Mo_{4\cdot8}Si_3C_{0\cdot6}$ combined with an X-ray diffraction analysis has been used to determine the C atom positions and to refine the other structure parameters. The compound crystallizes with a hexagonal unit cell with $a=7\cdot286\pm0\cdot001$, $c=5\cdot046\pm0\cdot002$ Å, in space group $P6_3/mcm$ (D_{6h}^3), six Mo atoms in position $6(g_{\rm I})$ with $x=0\cdot240$, only 3·6 Mo atoms in $4(d)$, six Si atoms in position $6(g_{\rm II})$ with $x=0\cdot60$ and 1·2 C atoms in $2(b)$. The carbon atoms occupy the octahedral voids formed by the Mo atoms in position $6(g_{\rm I})$.

It is shown that these carbon-centered transition metal octahedra are an important structural element not only of Nowotny phases but also of a whole group of complex transition metal carbides. From a knowledge of the tendency with which elements like to form T_6C octahedra, it is possible to predict the arrangement of the different atoms on the different structure sites of the complex ternary and quaternary carbides.

Introduction

For ten years American, Austrian, Swedish and Russian research groups have been actively engaged in the study of ternary phase diagrams containing as one component a high melting transition metal and having as second and third components meta- or non-metals like Si, Ge, Sn, B, C, N, P and others. One of the first systems investigated was the ternary system Mo–Si–C (Nowotny, Parthé, Kieffer & Benesovsky, 1954) which contains a ternary phase of composition $Mo_{\le 5}Si_3C_{\le 1}$ giving an X-ray diffraction pattern of the $D8_8(Mn_5Si_3)$ type. Many other isotypic ternary compounds have been found since then, most of them by Professor Nowotny and his co-workers (Kieffer & Benesovsky, 1963; Nowotny, 1963; Nowotny, Jeitschko & Benesovsky, 1964; Jeitschko, Nowotny & Benesovsky, 1964; Rieger, Nowotny & Benesovsky, 1965*a*). Appropriately, Kieffer, Benesovsky & Lux (1956) suggested that these ternary compounds be called Nowotny phases.

The *binary* $D8_8$ structure type as first reported for Mn_5Si_3 applies to a structure with space group $P6_3/mcm$ (D_{6h}^3) having a hexagonal unit cell with an axial ratio c/a of about 0·7. The point positions for Mn_5Si_3 originally given by Åmark, Boren & Westgren (1936) and later confirmed and refined by Aronsson (1960) are as follows:

6 Mn in $6(g_{\rm I})$ with $x_{\rm I}=0\cdot2358\pm0\cdot0006$

4 Mn in $4(d)$

6 Si in $6(g_{\rm II})$ with $x_{\rm II}=0\cdot5992\pm0\cdot0015$

All Nowotny phases give $D8_8$ type diffraction patterns, but the atomic arrangement in these phases, although principally similar to that in the binary compound Mn_5Si_3, has to have different characteristics. Since the first preparation of the ternary phase $Mo_{\le 5}Si_3C_{\le 1}$ efforts have been made to account for the positioning of the carbon atoms in the $D8_8$ structure and to explain the unusually wide homogeneity range which is characteristic of Nowotny phases. For $Mo_{\le 5}Si_3C_{\le 1}$ there have been published four different structure proposals which are given below:

(*a*) To account for the carbon content of $Mo_{\le 5}Si_3C_{\le 1}$ and the wide homogeneity range of the phase, it was assumed by Nowotny, Parthé, Kieffer & Benesovsky (1954) that the carbon atoms occupy partly silicon positions in $6(g_{\rm II})$ and silicon atoms, in turn, occupy former molybdenum positions on equipoint $4(d)$. This resulted in the following formula for the Nowotny phase:

$$Mo_6(Mo_{1-u},\quad Si_u)_4(Si_{1-v},\quad C_v)_6\,.$$

From the results of the phase diagram study, it was found that u could vary between 0·10 and 0·55 and v between 0·15 and 0·40.

(*b*) Brewer & Krikorian (1956) published another study on the same ternary phase and suggested a formula,

$$Mo_4CSi_3$$

with C atoms now occupying former Mo atom positions.

(*c*) Aronsson (1958) observed that the $D8_8$ structure contains octahedral holes which could easily accommodate the small carbon atoms interstitially. If the voids located at 000 and 00½ are completely filled, the formula of the Nowotny phase becomes:

$$Mo_5Si_3C$$

(*d*) Finally it was suggested by Parthé (1960) that the carbon atoms are located as above in the octahedral voids, but that a certain percentage of the available 4(*d*) positions remain unoccupied. The formula for this case is then:

$$Mo_6Mo_{4-x}Si_6C_{2-y}$$

which allows one to explain the broad homogeneity range by assuming variable filling of the 4(*d*) positions with Mo atoms and similarly, for C atoms in equipoint 2(*b*).

In view of the many suggestions about the position of the carbon atoms, it seemed that a neutron diffraction study would allow one to make more definite statements on the location of the carbon atoms.

Experimental

The sample which was used for this investigation had been hot-pressed from Mo, Si and C powders and annealed in a vacuum furnace at 1600°C for 12 hours in the research laboratory of the Metallwerk Plansee A.G. in Reutte, Austria.

The X-ray diffraction experiments were made with a conventional Philips diffractometer at the University of Pennsylvania. The neutron diffraction pattern of $Mo_{\leq 5}Si_3C_{\leq 1}$ has been obtained at the MIT experimental reactor in a manner described already in an earlier paper (Parthé & Sadagopan, 1962). Both the neutron and the X-ray diffraction patterns were obtained twice. The integrated intensity values used for the structure refinement were the average of the two independent measurements.

The structure of $Mo_{4,8}Si_3C_{0,6}$

The X-ray diffraction analysis of the sample gave a hexagonal unit cell with $a = 7{\cdot}286 \pm 0{\cdot}001$, $c = 5{\cdot}046 \pm 0{\cdot}002$ Å and $c/a = 0{\cdot}692_6$, which agrees with the published lattice constant values for the carbon-rich portion of the ternary phase (Nowotny, Parthé, Kieffer & Benesovsky, 1954). The X-ray diffraction pattern showed traces of Mo_2C lines and there was also a very small amount of free carbon in the sample (0·224 wt.%).* The exact amount of Mo_2C present was obtained by comparing calculated and observed relative intensities

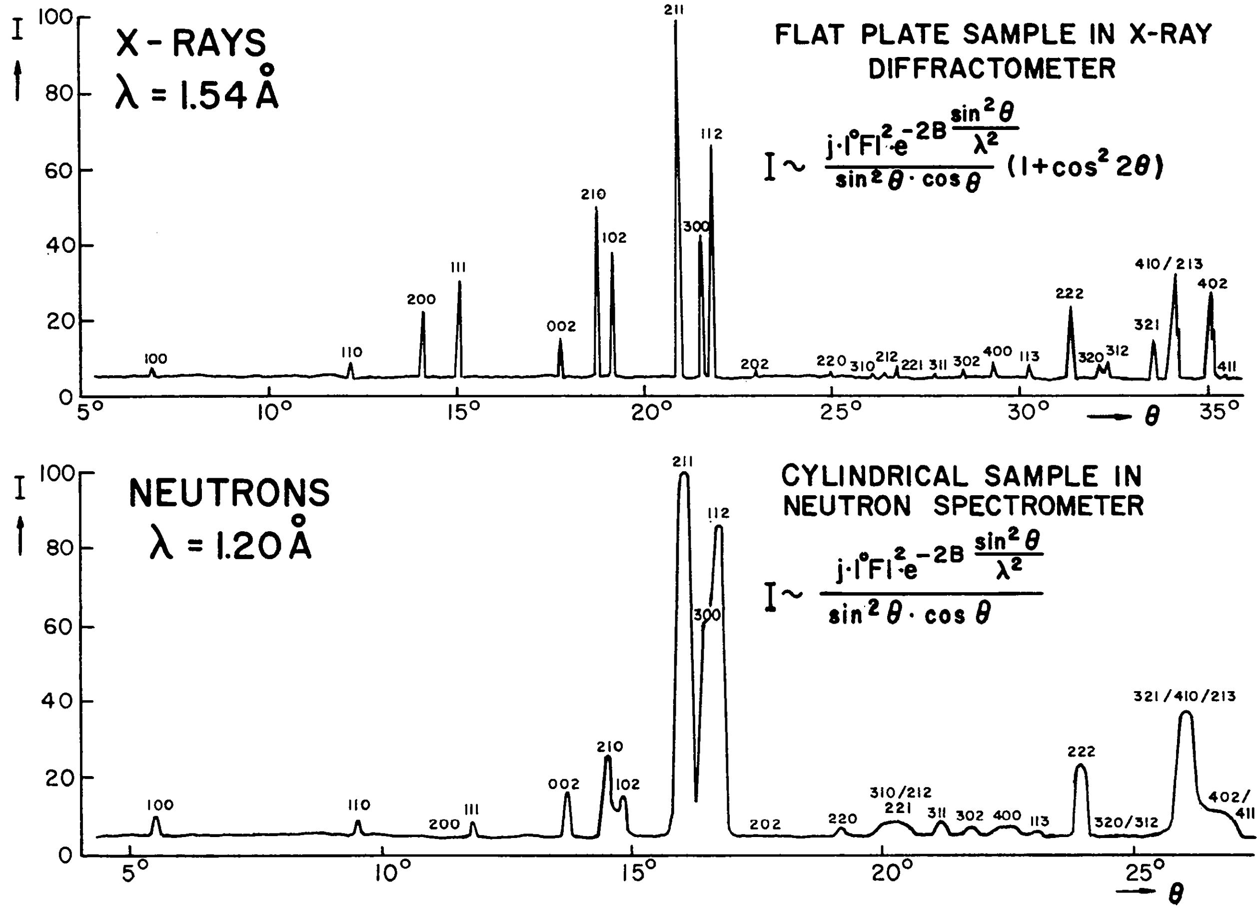

Fig. 1: X-ray and neutron diffraction pattern of the molybdenum carbosilicide.

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* At 1600°C the ternary phase is in equilibrium with Mo_2C and C. According to Rudy, Rudy & Benesovsky (1962) the molybdenum monocarbide MoC_{1-x} (more accurately probably Mo_3C_2) decomposes below 1800°C; however, the decomposition occurs extremely slowly.

of the $21\bar{3}1$ line of $\mathrm{Mo}_{\leq 5}\mathrm{Si}_3\mathrm{C}_{<1}$ with the 102/121 line of $\mathrm{Mo}_2\mathrm{C}$. The intensity of the $21\bar{3}1$ line of the ternary phase is independent of the atom occupation on equipoint $4(d)$ and the occupation of the interstitial sites. After correcting for $\mathrm{Mo}_2\mathrm{C}$ and free carbon, the composition of the ternary phase was determined from the average of three chemical analyses to be:

$$\mathrm{Mo}_{56\cdot 8\pm\cdot 4}\,\mathrm{Si}_{35\cdot 3\pm\cdot 3}\,\mathrm{C}_{7\cdot 9\pm\cdot 5} \text{ or } \mathrm{Mo}_{4\cdot 8}\mathrm{Si}_3\mathrm{C}_{0\cdot 6}\,.$$

It had been found by chemical analyses that a small amount of oxygen and nitrogen was present (in total less than $\frac{1}{2}$ at.%); however, for all further results it was not considered significant.

Fig. 1 shows the X-ray and neutron diffraction patterns for the molybdenum carbosilicide. The patterns have been drawn in such a way as to allow a good comparison between corresponding lines in the upper and lower diagram. For clarity, the weak impurity lines of $\mathrm{Mo}_2\mathrm{C}$ observed in the real diagrams have been omitted.

In order to interpret the neutron diffraction intensities with greater accuracy, it was found useful to refine the adjustable parameters of the ternary phase. Using the integrated X-ray intensities of the first 38 lines and shifting the adjustable parameters systematically (x_{I} from 0·23 to 0·25; x_{II} from 0·59 to 0·61) it was not possible to come to a perfect agreement between calculated and observed intensities unless one assumed a smaller scattering power of the atoms on the $4(d)$ position. The best agreement between observed and calculated intensities was obtained by using an isotropic temperature factor of $B=0\cdot 3\times 10^{-16}$ cm², the parameters $x_{\mathrm{I}}=0\cdot 240\pm 0\cdot 003$ for the Mo atoms in $6(g_{\mathrm{I}})$ and $x_{\mathrm{II}}=0\cdot 60\pm 0\cdot 01$ for the Si atoms in $6(g_{\mathrm{II}})$, and further the atomic scattering factor of strontium (4 electrons less than molybdenum) for the atoms on the $4(d)$ position. In consideration of the observed X-ray intensities, it was concluded that the $4(d)$ positions are either partly occupied by 3·6 molybdenum atoms, or by 3·2 Mo atoms and 0·8 Si atoms if one assumes that Si atoms substitute for Mo.

To verify one of the above given structure proposals for the Nowotny phase by utilizing the neutron diffraction data, one certainly has to incorporate the results obtained from X-ray and chemical analysis. As the formula of the available ternary phase was neither $\mathrm{Mo}_4\mathrm{CSi}_3$ nor $\mathrm{Mo}_5\mathrm{Si}_3\mathrm{C}$ only proposals (*a*) and (*d*) were available for the test. The task was thus to formulate formulae for proposals (*a*) and (*d*) which were consistent with the chemical and X-ray analysis, to calculate the neutron diffraction intensities, and to compare them with the observed data. The results are demonstrated in Table 1.

Proposal (*a*) involves a C–Si and Si–Mo substitution. The intensity calculation was performed using formula:

$$\begin{array}{ccc} \mathrm{Mo}_6 & (\mathrm{Mo}_{0\cdot 79}\mathrm{Si}_{0\cdot 21})_4 & (\mathrm{Si}_{0\cdot 80}\mathrm{C}_{0\cdot 20})_6 \\ 6(g_{\mathrm{I}}) & 4(d) & 6(g_{\mathrm{II}}) \\ x_{\mathrm{I}}=0\cdot 24 & & x_{\mathrm{II}}=0\cdot 60 \end{array}$$

Proposal (*d*) assumes that C atoms occupy interstitial positions and that the $4(d)$ positions are only partly occupied with Mo atoms. The following formula was used for the calculations:

Table 1. *Intensity calculation for* $\mathrm{Mo}_{4\cdot 8}\mathrm{Si}_3\mathrm{C}_{0\cdot 6}$

	Neutron diffraction ($\lambda=1\cdot 2$ Å)					X-ray diffraction ($\lambda=1\cdot 54$ Å)				
	$I_{\mathrm{calculated}}$					$I_{\mathrm{calculated}}$				
hkl	Proposal (*a*)		Proposal (*d*)		I_{obs}	Proposal (*a*)		Proposal (*d*)		I_{obs}
100		1·1		4·5	5·8		0·6		1·0	1·0
110		0·04		4·2	5·0		4·5		6·2	6·0
200		3·7		0·4	< 1		24·9		21·0	18·6
111		1·8		2·9	3·0		35·6		30·6	28·8
002		13·0		8·2	10·9		9·4		8·7	8·1
210	31·7	48·8	16·8	24·1	26·1		47·5		44·6	44·3
102	17·1		7·3				36·5		33·2	36·1
211		100·0		100·0	100·0		100·0		100·0	100·0
300	33·5	99·8	45·4	135·0	129·0		29·4		32·5	31·5
112	66·3		89·6				62·9		68·8	70·1
202		5·0		0·6	< 1		0·5		0·7	0·6
220		0·9		3·4	3·6		1·0		1·5	1·1
310	3·4	11·1	0·3	13·4	13·2		0·5		0·6	0·7
212	0·8		6·6				0·8		0·8	1·0
221	6·9		6·5				2·7		2·9	2·8
311		9·3		8·1	8·1		0·5		0·8	0·7
302		0·03		1·9	2·5		1·4		1·8	1·9
400		3·8		7·8	8·8		5·3		5·0	4·0
113		0·5		0·8	1		4·5		3·9	4·2
222		23·4		34·5	33·9		17·7		19·2	18·5
320	1·2	5·0	0·1	0·6	< 1		3·7		3·3	2·7
312	3·8		0·5				7·7		7·0	6·1
321	15·4	74·2	16·0	84·5	84·9		12·1		11·7	11·4
410	17·4		27·1			15·0	36·0	15·9	36·9	39·1
213	41·4		41·4			21·0		21·0		
402	25·6	25·8	18·5	18·7	17·3		21·3		20·3	20·3
411	0·2		0·2				0·1		0·1	0·3
	$R_{\mathrm{I}}=0\cdot 27$		$R_{\mathrm{I}}=0\cdot 04$			$R_{\mathrm{I}}=0\cdot 09$		$R_{\mathrm{I}}=0\cdot 04$		

$$Mo_6Mo_{3\cdot 6}Si_6C_{1\cdot 2}$$
$$6(g_{\mathrm{I}})\ 4(d)6(g_{\mathrm{II}})2(b)$$
$$x_{\mathrm{I}}=0{\cdot}24 \quad x_{\mathrm{II}}=0{\cdot}60$$

Table 1 combines neutron and X-ray diffraction data. The left-hand side shows observed neutron intensities and intensity values calculated for proposals (*a*) and (*d*), while on the right-hand side are listed the same data for the case of X-ray diffraction. At the bottom of the columns of Table 1 are given residual values which were calculated according to:

$$R_{\mathrm{I}} = \frac{\Sigma |I_{\mathrm{obs}}-I_{\mathrm{cal}}|}{\Sigma I_{\mathrm{obs}}}$$

Owing to the many coincidences, it was convenient not to use here the conventional R_F residuals based on structure factors. A study of the X-ray data does not allow us to draw a clear conclusion as to which of the proposals is the correct one. However, the neutron diffraction data indicate clearly that proposal (*d*) is the right one. Thus the carbon atoms do occupy interstitial positions and the 4(*d*) positions are only partly filled.

An additional method to decide between proposals (*a*) and (*d*) was found utilizing density considerations. One can calculate that the theoretical density for proposal (*a*) should be $7{\cdot}54_2$ g.cm^{-3} and for proposal (*d*) $7{\cdot}91_5$ g.cm^{-3}, while for a complete filling without defects according to proposal (*c*) the theoretical density amounts to $8{\cdot}26$ g.cm^{-3}. The experimental density, corrected for Mo_2C and C impurities was found to be $7{\cdot}86_2$ g.cm^{-3} which showed independently that proposal (*d*) is the correct one.

Several independent observations support the experimental result that the carbon atoms occupy the octahedral voids. Firstly, carbon atom centered transition metal octahedra are the characteristic construction elements of many transition metal carbides. This has been proven beyond doubt by neutron diffraction studies, for example, on TiC, (Ti, W)C (Sidhu, Heaton & Mueller, 1959) or Mo_2C (Parthé & Sadagopan, 1963). A further indication for an interstitial insertion of the C atoms is the increase of the unit-cell volume with an increase of the carbon content. In all measured cases, the *a* axis remains nearly constant, while the *c* axis increases noticeably. For example, with increasing carbon content, the *c*/*a* ratios change for $Mo_{\leq 5}Si_3C_{\leq 1}$ from $0{\cdot}68_7$ to $0{\cdot}69_5$ (Nowotny, Parthé, Kieffer & Benesovsky, 1954), for $Zr_5Si_3C_{<1}$ from $0{\cdot}702$ to $0{\cdot}705_5$, for $Nb_5Si_3C_{<1}$ from $0{\cdot}696$ to $0{\cdot}700$, (Nowotny, Lux & Kudielka, 1956), for $Mn_5Si_3C_{<1}$ from $0{\cdot}696_6$ to $0{\cdot}697_4$ (Jeitschko, 1964). It is possible that the last three examples have also defects in the occupation of the 4(*d*) metal positions; however, accurate data are not available.

Conclusions for Nowotny phases

The transition metal–carbon atom octahedra which were demonstrated above to exist in $Mo_{4\cdot 8}Si_3C_{0\cdot 6}$ seem to be an important construction element for Nowotny phases. It is known, for example, from the binary monocarbides that transition metals of the fourth group like Ti, Zr or Hf form much more stable transition metal–carbon octahedra than metals of the fifth group (V, Nb, Ta) or even metals of the sixth group (Cr, Mo, W) (Parthé, 1956). In WC, for example, the C atom is located in the center of a trigonal prism instead of an octahedron. This decreased tendency to form metal–carbon octahedra is probably one of the reasons why it is not possible to synthesize a Nowotny phase $W_{\leq 5}Si_3C_{\leq 1}$. However, tungsten can participate in mixed Nowotny phases. For example, Schachner, Cerwenka & Nowotny (1954) have investigated mixtures between Ti_5Si_3 with $D8_8$ structure and W_5Si_3 or Mo_5Si_3. Unfortunately these experiments were made many years ago, when the importance of small carbon contents was not yet recognized. However, the samples had been hot-pressed in carbon dies, and a small carbon content in the investigated samples seems very probable. It was found that Mo_5Si_3 – to a lesser degree also W_5Si_3 – can be dissolved into Ti_5Si_3, leading to an ordered $D8_8$ phase with Ti atoms remaining in equipoint $6(g_{\mathrm{I}})$ but Mo or W atoms substituting for the Ti atoms in 4(*d*). If transition metal–carbon octahedra are important for Nowotny phases such an ordering can be anticipated. Only the atoms in equipoint $6(g_{\mathrm{I}})$ participate in the formation of carbon centered octahedra and therefore one should find there those atoms which have a strong tendency to form octahedra. According to the sequence given above Ti atoms will form octahedra much easier than Mo or W. Thus Ti atoms should occupy equipoint $6(g_{\mathrm{I}})$, but Mo or W atoms position 4(*d*) just as reported. Fig. 2 shows a stereoscopic pair of drawings of the filled $D8_8$ structure clearly indicating which atoms participate in the formation of the C-atom centrered octahedra. Obviously not all interstitial positions need to be occupied by carbon atoms in order to stabilize the Nowotny phase. It seems that occasionally small amounts of stabilizer atoms are sufficient to bring about a structural change to the Nowotny phase.

Recently it has been observed that a structural analogy exists between the Nowotny phase and the apatite or $Ca_5(PO_4)_3F$ structure ($H5_7$type) (Schubert, 1964; Wondratschek, Merker & Schubert, 1964). If the PO_4 tetrahedra are considered as a structural unit the apatite structure becomes similar to the structure of the Nowotny phase with Ca atoms occupying $6(g_{\mathrm{I}})$ and 4(*d*) positions and PO_4 tetrahedra located on $6(g_{\mathrm{II}})$ positions .However, the compounds with the apatite structure are all normal valence compounds* (for example $Ca_2^{5+}(PO_4)_3^{3-}F^{1-}$) but the Nowotny phases are not. Further, Nowotny phases are non-stoichiometric and may have wide homogeneity ranges caused probably by a varying occupation of the 4(*d*) and 2(*b*) positions, but apatites are stoichiometric. Finally, the octahedron concept useful for Nowotny phases is not

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* For normal valence compounds the ratio $n_e/n_a=8$ where n_e is the total number of valence electrons and n_a is the total number of anions (Pearson, 1964).

Table 2. *Structure data of carbides and nitrides with* T_6X *octahedra*

Call name	Ideal formula	Examples	Space group Axial ratio	Point positions	Literature
(*a*) T:X=1:1. Every **T** atom belongs to six octahedra					
Monocarbides with *B*1 type	TX	$TiC_{\le 1}$	*Fm*3*m* (O_h^5)	T in 4(*a*) X in 4(*b*)	Sidhu, Heaton & Mueller, 1959
(*b*) T:X=2:1. Every **T** atom belongs to three octahedra					
Semi-carbides with Mo_2C or ζ-Fe_2N-type	T_2X	Mo_2C Fe_2N	*Pbcn* (D_{2h}^{14}) $b/a\sim 1{\cdot}28$ $c/b\sim\sqrt{3}/2$	T in 8(*d*) $x\sim\frac{1}{4}$ $y\sim\frac{1}{8}$, $z\sim\frac{1}{12}$ X in 4(*c*) $y\sim\frac{3}{8}$ or* T in 8(*d*) $x\sim\frac{1}{4}$ $y\sim\frac{1}{8}$, $z\sim\frac{11}{12}$ X in 4(*c*) $y\sim\frac{1}{8}$	Parthé & Sadagopan, 1963 Jack, 1948
***H*-phases** with Cr_2AlC type	T_2MX	Cr_2AlC	$P6_3/mmc$ (D_{6h}^4) $c/a\sim 4{\cdot}5$	T in 4(*f*) $x\sim 0{\cdot}08$ M in 2(*d*) X in 2(*a*)	Jeitschko, Nowotny & Benesovsky, 1964*b*
η-carbides with $E9_3$ type or filled Ti_2Ni type having **all** interstitial sites filled	$T_6^{I}T_2^{II}M_4X_2X_1$	$Nb_6Nb_2Zn_4C_3$ $\equiv Nb_8Zn_4C_3$	*Fd*3*m* (O_h^7) *International Tables*, p.340. Origin on $\bar{4}3m$	T^{I} in 48(*f*) $x\sim 0{\cdot}19$ T^{II} in 16(*d*) M in 32(*e*) $x\sim 0{\cdot}83$ X in 16(*c*) X in 8(*a*) or† T^{I} in 48(*f*) $x\sim 0{\cdot}31$ T^{II} in 16(*c*) M in 32(*e*) $x\sim 0{\cdot}91$ X in 16(*d*) X in 8(*b*)	Jeitschko, Holleck Nowotny & Benesovsky, 1964
(*c*) T:X=3:1. Every **T** atom belongs to two octahedra					
β-Mn carbides with filled, ordered A13 type	T_3M_2X	Mo_3Al_2C W_3Re_2C	$P4_132$ (O^7)	T in 12(*d*) $x\sim 0{\cdot}20$ M in 8(*c*) $x\sim 0{\cdot}08$ X in 4(*a*)	Jeitschko Nowotny & Benesovsky, 1963, 1964*c*
Perovskite carbides with $E2_1$ ($L'1_2$) type	T_3MX	$Mn_3AlC_{\le 1}$ Fe_3FeN $\equiv\gamma'$-Fe_4N Fe_3PtN	*Pm*3*m* (O_h^1)	T in 3(*c*) M in 1(*a*) X in 1(*b*) or† T in 3(*d*) M in 1(*b*) X in 1(*a*)	Stadelmaier, 1961 Jack, 1948 Wiener & Berger, 1955
Nowotny Phases with filled $D8_8$ structure	$T_3^{I}T_2^{II}M_3X$	$Ti_3Mo_2Si_3C$ $Mo_3Mo_{\le 2}Si_3C_{<1}$ $\equiv Mo_{\le 5}Si_3C_{<1}$	$P6_3/mcm$ (D_{6h}^3) $c/a\sim 0{\cdot}69$	T^{I} in 6(*g*) $x\sim 0{\cdot}24$ T^{II} in 4(*d*) M in 6(*g*) $x\sim 0{\cdot}61$ X in 2(*b*)	This work Schachner, Cerwenka & Nowotny 1954
η-carbides with $E9_3$ type or filled Ti_2Ni type having only **two-thirds** of the interstitial sites filled	$T_6^{I}T_2^{II}M_4X_2$	$W_6W_2Co_4C_2$ $\equiv W_4Co_2C$ $W_6Fe_2Fe_4C_2$ $\equiv W_3Fe_3C$ $Ti_6Ti_2Ni_4O_2$ $\equiv Ti_4Ni_2O$	*Fd*3*m* (O_h^7) *International Tables*, p.340 Origin on $\bar{4}3m$	T^{I} in 48(*f*) $x\sim 0{\cdot}19$ T^{II} in 16 (*d*) M in 32(*e*) $x\sim 0{\cdot}83$ X in 16(*c*) or† T^{I} in 48(*f*) $x\sim 0{\cdot}31$ T^{II} in 16(*c*) M in 32(*e*) $x\sim 0{\cdot}91$ X in 16(*d*)	Kislyakova, 1943 Kiessling, 1954 Westgren, 1933 Mueller & Knott, 1963
(*d*) T:X=6:1. Every **T** atom belongs to one octahedron.					
η-carbides with $E9_3$ type or filled Ti_2Ni type having only **one-third** of the interstitial sites filled	$T_6^{I}T_2^{II}M_4X_1$	$W_6Fe_2Fe_4C$ $\equiv W_6Fe_6C$	*Fd*3*m* (O_h^7) *International Tables*, p.340 Origin on $\bar{4}3m$	T^{I} in 48(*f*) $x\sim 0{\cdot}19$ T^{II} in 16(*d*) M in 32(*e*) $x\sim 0{\cdot}83$ X in 8(*a*) or† T^{I} in 48(*f*) $x\sim 0{\cdot}31$ T^{II} in 16(*c*) M in 32(*e*) $x\sim 0{\cdot}91$ X in 8(*b*)	Leciejewicz, 1964

* Assuming setting *Pbcn* and shifting origin for $\frac{1}{2}0\frac{1}{2}$ the structures of Mo_2C and ζ-Fe_2N become virtually identical.

† The η-carbide and the perovskite structure can be described in two ways which differ by a translation of $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Observe that for the η-carbide 16(*c*) will be interchanged with 16(*d*) and 8(*a*) with 8(*b*), further for 32(*e*) one obtains $\frac{3}{4}-x_{\text{Kiessling}}=x_{\text{Mueller and Knott}}$ and for 48(*f*) $\frac{1}{2}-x_{\text{Kiessling}}=x_{\text{Mueller and Knott}}$. The structures of W_4Co_2C and Ti_4Ni_2O are thus virtually identical.

of the same importance for apatites. It is generally assumed that the fluorine atoms in fluorapatite do not occupy the octahedral voids (2*b*):000, $00\frac{1}{2}$, but 'trigonal' voids instead (2*a*):$00\frac{1}{4}$,$00\frac{3}{4}$. A recent neutron diffraction analysis on hydroxyapatite (Kay, Young & Posner, 1964) has shown that the hydroxyl groups occupy actually a position half way between the octahedral and the 'trigonal' voids.

It is now appropriate to formulate a new definition for Nowotny phases which incorporates the new experimental results into earlier statements (Parthé, 1957):

Nowotny phases are quaternary or ternary metallic phases of composition $T^{I}_{3}T_{\leq 2}{}^{II}M_3X_{\leq 1}$ where T denotes a transition metal (group 3A to 8A), M denotes a metametal (group 3B to 5B, mostly Si and Ge) and X denotes a nonmetal like C, N, also B and O. The Nowotny phases crystallize with a hexagonal unit cell with *c*/*a* varying from 0·67 to 0·75. The space group and point positions are those given in Table 2. The Nowotny phases have wide homogeneity ranges. The change in composition, which is accompanied by a change of the axial ratio *c*/*a*, is presumably accomplished by varying the degree of atom occupation on equipoints 4(*d*) and 2(*b*). The formation of X-atom-centered T^I octahedra is of importance for the stabilization of Nowotny phases; however, it is not necessary that every available T^I octahedron is occupied by an X atom. In quaternary compounds where T^I and T^{II} are different transition metals T^I positions will be occupied by that element which has a greater tendency to form T_6X octahedra.

Other complex phases with T_6X octahedra

Recently a number of new complex ternary carbides, oxides and nitrides have been investigated which, like Nowotny phases, contain transition metals (T) and metametals (M) (Nowotny, Jeitschko & Benesovsky, 1964). Four different structure types have been found for these compounds; the *H*-phases of composition T_2MX have the Ti_2SC (Kudielka & Rohde, 1960) or Cr_2AlC structure, which is related to the known TiP structure type, the *β*-manganese carbides with formula T_3M_2X have a filled and ordered *A*13 structure type, the perovskite carbides T_3MX have the *E*2₁ structure and finally the *η*-carbide phases crystallize with the *E*9₃ structure type. Their structural data together with known examples are given in Table 2. All these structures contain octahedral voids, and it was assumed that the carbon or nitrogen atoms are positioned in the centers of these holes. This assumption is supported by the experimental verification of the T_6C octahedra in Nowotny phases. All these compounds belong to a group of complex structures where T_6X octahedra are an important construction element.

In each formula of Table 2 the particular elements which participate in the formation of the T_6X octahedra are printed with bold faced type; all others with normal type. According to the **T**:**X** ratio, one can distinguish four groups of compounds. With **T**:**X**=1:1 each **T** atom belongs to six octahedra. Only the monocarbides with *B*1 structure are known. For **T**:**X**=2:1, three structure types have been listed: Mo_2C carbides, *H*-phases and *η*-carbides with complete occupation of the octahedral voids by C atoms.* For **T**:**X**=3:1 are given the *β*-Mn phases, the perovskite carbides, the Nowotny phases and *η*-carbides with two thirds of the voids filled. Finally for **T**:**X**=6:1 one finds the third group of *η*-carbides with one third of the holes filled with C atoms.

If the tendency is known with which different elements like to form T_6X octahedra, it is possible to predict the ordering of the atoms on the different sites. An approximate measure of this tendency is the bonding energy of the transition metal mono-carbides, -nitrides and -oxides as given for example by Brewer & Krikorian (1956). The strongest bonds occur with transition metals of the fourth or fifth group and they become progressively weaker with increasing group number. The non-existence of binary carbide phases with most metametals is an indication that metametal–carbon bonds are very weak. Elements which have the biggest affinity to the interstitial elements will occupy the **T** sites printed with bold faced type; the other elements are to be found on the additional structure sites printed with normal type. One of such additional

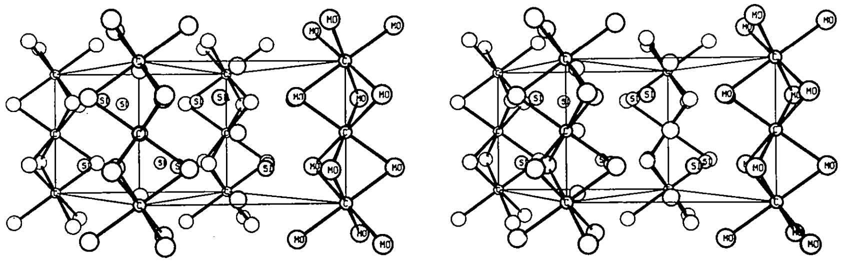

Fig. 2. A stereoscopic pair of drawings of the filled *D*8₈ structure demonstrating the position of the C-atom-centered transition-metal octahedra. (Courtesy of Dr C. K. Johnson from the Oak Ridge National Laboratory.)

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* Recently it has been shown (Jeitschko, Holleck, Nowotny & Benesovsky, 1964) that the ideal formula of *η*-carbides for complete filling of the interstitial sites is $T_8M_4C_3$ instead of T_4M_2C as previously assumed. With the occupation of the additional interstitial sites on the 8-fold positions as shown in Table 2, each bold type-T metal participates on three T_6X octahedra. In the cited paper the carbon positions given are in error. Table 2 contains now the corrected data for both settings.

structure sites each occurs with the *H*-, *β*-Mn and perovskite phases; two such sites are found with *η*-carbides and Nowotny phases. The elements which occupy these non-octahedron sites can be metametals or transition metals. For example, the *β*-Mn carbide structure is found with Mo_3Al_2C and W_3Re_2C (Kuzma, Lakh, Markiv, Stadnik & Gladyshevskii, 1963) or the *η*-carbide structure with $Nb_8Zn_4C_3$ and $W_8Co_4C_2$ or the perovskite structure with $Mn_3AlC_{\leq 1}$ and Fe_3PtN.

It is well known for the particular case of $TiC_{\leq 1}$ that the mono-carbide structure is still maintained even if 70% of the interstitial carbon atom sites are unoccupied. Considerable carbon, oxygen or nitrogen defects may occur also with some of the complex structures as for example in *η*-carbides and oxides, perovskites and Nowotny phases. It seems rather surprising that the T octahedra are not always completely filled and no good explanation can be given for this. However, even then the occupation of the different structure sites follows the rules developed above.

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