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Electronic structure and pairwise interactions in substoichiometric transition metal carbides and nitrides

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Résumé. — Dans les carbures et nitrures sous-stoechiométriques de métaux de transition de structure NaCl, les lacunes qui apparaissent sur le sous-réseau FCC occupé par les atomes de carbone (azote) peuvent s'ordonner sous certaines conditions. Les phases ordonnées observées sont les mêmes que celles que prévoient, pour les alliages FCC de substitution, des calculs théoriques utilisant des interactions de paires limitées aux premiers et seconds voisins (V_1 , V_2). Nous montrons ici que l'énergie d'ordre de ces composés peut s'exprimer comme une somme d'interactions de paires, calculées à partir de la structure électronique de l'état désordonné, et limitées aux premiers et seconds voisins. Nous en déduisons un diagramme (V_1 , V_2) calculé, dans lequel les domaines d'existence des carbures et nitrures sont bien séparés : plus précisément les carbures existent dans la région ($V_2 > 0$, $V_2 \gg V_1$) tandis qu'on trouve les nitrures pour ($V_1 \gtrsim V_2$, $V_1 > 0$) en bon accord avec les observations expérimentales.

Abstract. — In substoichiometric transition metal carbides and nitrides crystallizing with the NaCl structure, the vacancies, which appear on the metalloid FCC lattice only, may order under some conditions. The corresponding long range ordered phases are analogous to those predicted, for FCC substitutional alloys, by theoretical calculations using pair interactions limited to first and second neighbours (V_1 , V_2). We show here that the ordering energy of these compounds can be expanded in terms of pairwise interactions calculated from the electronic structure of the disordered state and that this expansion can be limited to a good accuracy to first and second neighbours. From these calculated pair interactions we then derive a theoretical (V_1 , V_2) diagram in which the domains of existence of ordered carbides and nitrides are well separated ; more precisely carbides exist in the region ($V_2 > 0$, $V_2 \gg V_1$) whereas nitrides are found for ($V_1 \gtrsim V_2$, $V_1 > 0$), in fair agreement with experiments.

1. Introduction.

This paper is devoted to the study of the ordering processes in substoichiometric transition metal carbides and nitrides, $MX_{1-\alpha}$, which crystallize with the NaCl structure (the transition metal atoms, M, occupying one FCC sublattice whereas the carbon or nitrogen atoms, X, occupy the other one, referred to as « interstitial »). In most of these compounds, vacancies appear on the interstitial FCC lattice only [1, 2].

Under certain conditions (annealing temperature and duration) these vacancies may order [3]. Most of the long range ordered phases observed in this case (on the interstitial sublattice) are analogous to those predicted, for FCC substitutional alloys, by theoretical calculations using an Ising model with pair

interactions limited to first and second neighbours (V_1 , V_2) [4-6]. An appealing particularity of the ordered structures observed in the case of carbides and nitrides is that some of them have never been observed in the substitutional alloys. These observations strongly suggest, firstly that an analysis in terms of pair interactions of the ordering processes between vacancies is likely to be valid for substoichiometric NaCl carbides and nitrides, and secondly that the characteristics of these pair interactions must differ from those found in the case of FCC substitutional alloys. More precisely, one expects a (V_1 , V_2) diagram to be relevant for the interstitial compounds knowing that it was not for the corresponding substitutional alloys [6].

Our purpose here is to show that starting from the electronic structure of the disordered state, one

can calculate such pairwise interactions, by extending the generalized perturbation method previously developed for the case of substitutional transition metal alloys [7-9] to the interstitial case. After a short review of the observed structures and of their classification (§ 2), we first describe the electronic structure model used to calculate densities of states for ordered and disordered interstitial compounds (§ 3). Then (§ 4), we check the validity of a pairwise interaction expansion of the ordering energy and we will study the variation of the calculated pair interactions with the vacancy concentration and the chemical nature of the metalloid ($X = C, N$). Finally, (§ 5), we derive from this calculation a theoretical (V_1, V_2) diagram in which the domains of existence of ordered carbides and nitrides are well separated, in fair agreement with experiments.

2. Description and classification of the ordered structures.

We deal here with non-stoichiometric carbides and nitrides $MX_{1-\alpha}$, where M can be either a transition metal belonging to columns III to VI of the periodic table (see table I), or some rare earth or actinide which will be considered here as a transition metal having three d electrons. As already mentioned, the vacancies on the interstitial lattice can order. The corresponding ordered structures are generally described as a stacking of one or several types of metalloid octahedra surrounding a metal atom [3]. This type of description has been used by Sauvage and Parthé [66] to analyse the shapes of diffuse intensity surfaces for carbides and nitrides when only short range order is present. This, however, is only one aspect of a more general description of vacancy ordering that we will describe below.

Actually, the ordering processes in interstitial compounds of the NaCl type such as the carbides or nitrides of interest here, can be treated as a lattice gas problem, i.e. in terms of an Ising model on the partially occupied carbon (or nitrogen) sublattice [67-68]. From this point of view, the metal sublattice is ignored in the atomic description of the model (it will, of course, reenter the problem in the calculation of the electronic structure). In this Ising model, the configurational part of the energy [9, 69-71] can be written, up to a constant :

$$U \simeq \frac{1}{2} \sum_R q_R V_R \quad (1)$$

where V_R is the pair interaction between metalloid atoms separated by a distance R on the interstitial FCC sublattice and q_R the corresponding number of carbon (nitrogen) atom pairs. The search for the most stable ordered structure at $T = 0$ K for a finite set of interaction parameters and a given concentration, reduces to the problem of finding the ground

state of this Ising model. This problem can be solved exactly in some cases : for example, the case of substitutional binary alloys A_cB_{1-c} has been treated using pair interactions up to the 4th neighbour on the FCC lattice [72] and up to the fifth neighbour on the BCC one [73]. The corresponding ground states can be described as periodic stackings of a set of clusters (tetrahedra, octahedra, ...) having a given configuration (i.e. with given positions for A and B atoms). For example, the so-called AB-CuPt type structure (which includes not only the CuPt phase but also the degenerate one : Fd3m) is built with only one type of octahedra in a given orientation (R3m structure).

The most stable ordered structures observed in substoichiometric NaCl carbides and nitrides can then be analysed phenomenologically in terms of the various stackings which account for the ground states of the FCC substitutional alloys. Some of these structures may be degenerate (i.e. may have the same energy U) when only octahedra are considered (M_2C compounds [74]). This degeneracy is lifted when tetrahedra are taken into account. In figure 1 we have illustrated some of these structures by drawing only the FCC metalloid sublattice. In this sense, the ordered structure with space group $R\bar{3}m$ observed in Ti_2C , for instance, can be referred to as a CuPt-type structure for C and vacancy, neglecting Ti, i.e. : $Ti(C_{0.5} \square_{0.5})$ ($\square$: vacancy).

In this framework, the originality of these interstitial compounds, compared to the substitutional ones,

Fig. 1. — (1) Ground states of the Ising model with first and second neighbour interactions on a FCC A_cB_{1-c} alloy [4-5]. The notations are those of De Fontaine [6].

Region I : AB (CuPt), A_2B , A_3B (observed structures in carbides are underlined); note that the « CuPt type » denomination applies as well to the Fd3m structure.

Region II : A_2B_2 (also called 40 by Kanamori and Kakehashi [72], A_2B , A_3B (DO_{22}), A_5B (observed structures in nitrides are underlined)

Region III : AB (CuAu), A_3B (Cu_3Au)

Region IV : AB (CuPt) (observed structure in carbides)

Region V : Segregation.

(2) The corresponding ordered structures for $\alpha = 1/2(M_2X)$. The metal atoms are not shown : (a) CuAu, (b) A_2B_2 , (c) CuPt, (d) segregation.

results from the fact that most of the observed ordered structures are well displayed in a (V_1, V_2) map (note however that a few structures such as V_8C_7 or Ti_8C_5 would require further interactions, $V_R, R > 2$). Structures such as CuPt, A_5B and A_2B_2 are encountered in substoichiometric carbides or nitrides (see Fig. 1) whereas they are not (except in one case CuPt for the CuPt type) in transition metal alloys [6, 67]. It means that, contrary to what occurs for substitutional alloys, a (V_1, V_2) map is meaningful for these interstitial compounds. Such a map (which was, at first, established by Kanamori [4] and Allen and Cahn [5] for substitutional FCC alloys) is shown in figure 1 : it gives for each value of V_2/V_1 , the sequence of predicted stable ordered structures with a definite composition (A, AB, A_2B , ...). For intermediate compositions, the most stable structure is obtained as a mixture of these ordered phases. It is clear from the domains of existence of the CuPt, A_2B and A_5B phases that the second neighbour interaction V_2 is relevant here, whereas it is not for transition metal substitutional alloys for which the observed structures suggest that $|V_1| \gg |V_2|$ and consequently that other interactions (V_3, V_4) are required to stabilize the ordered structures [72] (as Ni_4Mo for example) which are not found in a (V_1, V_2) map.

Moreover, there is a clear separation in this map between the domains of existence of ordered carbides and nitrides. The carbides exist in a region where V_1 is very small and V_2 large and positive (the sign of V_1 does not matter since the most frequently observed structure is AB-CuPt type which occurs on both sides of the V_2 axis). The nitrides, however, are found (essentially with A_2B_2 and A_3B type structures) for small positive values of V_2 and larger positive values of V_1 . To summarize, most of the observed structures for these interstitial compounds appear in the (V_1, V_2) map of figure 1 (in regions I or IV for carbides and II for nitrides) while for substitutional alloys only a few of those encountered can be found in this figure and they belong to region III.

3. Electronic structure and densities of states of carbides and nitrides.

3.1 STOICHIOMETRIC COMPOUNDS : ELECTRONIC STRUCTURE PARAMETERS. — A first necessary step, before going to the more complicated case of a vacancy ordered or disordered compound, is to have a good description of the electronic structure of a stoichiometric MX NaCl carbide or nitride. Since we deal here with transition metal interstitial compounds, it is justified to use a tight-binding formalism, the Hamiltonian of which can be written (in the stoichiometric case) :

$$H = \sum_n \sum_i \sum_{\lambda_i} p_n^i |n, \lambda_i\rangle \varepsilon_i^{\lambda_i} \langle n, \lambda_i| + \sum_{n,m} \sum_{i,j} \sum_{\lambda_i, \mu_j} p_{nm}^{i,j} |n, \lambda_i\rangle \beta_{nm}^{\lambda_i \mu_j} \langle m, \mu_j| p_m^j \quad (2)$$

where the indices i, j label the chemical nature of the atoms : $i, j = M(X)$ for the transition metal (metal-loid) atoms. p_n^i is an atomic occupation number ; $p_n^i = 1$ if the site n is occupied by an atom of type i and $p_n^i = 0$ otherwise. $|n, \lambda_i\rangle$ is the atomic orbital λ_i (2p or 2s if $i = X$ and 3d, 4d or 5d if $i = M$) centred on site n . $\varepsilon_i^{\lambda_i}$ is the atomic energy level corresponding to the orbital λ_i at site n . Since here we have a cubic symmetry, only four different values of $\varepsilon_i^{\lambda_i}$ have to be considered : $\varepsilon_X^s, \varepsilon_X^p, \varepsilon_M^{xy}$ (or ε^{t2g}) and $\varepsilon_M^{x^2-y^2}$ (ε^{eg}). Finally, $\beta_{nm}^{\lambda_i \mu_j}$ is the hopping integral between the λ_i orbital at site n and the μ_j orbital at site m . Since $\beta_{nm}^{\lambda_i \mu_j}$ decreases very rapidly with the distance between sites n and m , we will consider three types of hopping orbitals only, corresponding to first ($\beta_{MX}^{\lambda_M \mu_X}$) and second ($\beta_{MM}^{\lambda_M \mu_M}$ and $\beta_{XX}^{\lambda_X \mu_X}$) neighbour distances. As usual, these hopping integrals can be expressed in terms of two centre integrals : $\{dd\sigma, dd\pi, dd\delta\}$ for β_{MM} ; $\{pp\sigma, pp\pi, ss\sigma, sp\sigma\}$ for β_{XX} and $\{sd\sigma, pd\sigma, pd\pi\}$ for β_{MX} . All these parameters can be deduced from self consistent APW band structure calculations — if available — using interpolation schemes.

From this Hamiltonian H (Eq. (2)) it is then easy to calculate the partial density of states of symmetry λ at site 0, $n_0^\lambda(E)$, as the imaginary part of the projection, on the atomic orbital $|0, \lambda\rangle$, of the Green function $G(E)$

$$\left. \begin{aligned} G(E) &= (E - H)^{-1} \\ n_0^\lambda(E) &= -\frac{\text{Im}}{\pi} \langle 0, \lambda | G(E + i0) | 0, \lambda \rangle \end{aligned} \right\} \quad (3)$$

$n_0^\lambda(E)$ can be calculated either in reciprocal space by inverting $(E - H)$ or in direct space as a continued fraction, the coefficients of which will be computed within the recursion method [75].

3.1.1 Stoichiometric carbides. — We shall use here the standard Slater-Koster parameters deduced by Schwarz [76] from his APW band structure calculation for NbC, with the previous simplification of keeping only the first (metal-carbon, which couples the two sublattices) and second (metal-metal and carbon-carbon, on each sublattice) nearest neighbour hopping integrals. This simplification is supported by the following observation : for the integrals associated with further neighbours, only very small values have been found in his fitting procedure. Besides these ten hopping parameters, we have to consider three atomic levels : ε^s and ε^p for the s and p orbitals on a C atom and ε^d for a M atom (in view of the small difference between ε_M^s and ε_M^{t2g} , we will neglect here the crystal field effects). The corresponding numerical values are given in table II. These parameters will be used without modification for other transition metals and rare earth or actinide carbides ; they define then a standard carbide density of states. Therefore the various compounds will only differ by the number of d electrons of the metal involved. These effective d band fillings N_d

Table I. — Domains of existence, ordered phases, parameters and critical temperatures of substoichiometric NaCl carbides and nitrides of transition metals, rare earths and actinides. The notation [n] (ref. [i]), with $n = 1, 2, 3$, means : reference (i) of the article referred to as n in the present paper.

Compound	Existence domain of the disordered phase (maximum)	Parameter (Å)	Ordered phases	Distortion of the ordered phases	T_c	References
ScC	0.3-0.5	ScC _{0.3} 4.67	Sc ₂ C (I)			[3] (ref. [39]), [10]
YC	0.3-1.0 ⁽²⁾	ScC _{0.5} 4.72	Y ₂ C (I)		$\leq 980^\circ\text{C}$	[3] (ref. [40]), [11, 12]
TiC	0.47-1.00	YC _{0.4} 5.10 TiC _{0.5} 4.299	Ti ₂ C (I)		TiC _{0.58} : 759 °C	[1], [2], [3] (refs. [31, 32, 33]), [13, 27-29, 31]
		TiC _{1.00} 4.327	Ti ₂ C-Fd3m ⁽³⁾ Ti ₈ C ₅ -R3m		TiC _{0.63} : 783 °C	
ZrC	0.58-0.97	ZrC _{0.58} 4.691	Zr ₂ C (I)		$\sim 860^\circ\text{C}$	[3] (ref. [31, 34]), [14]
HfC	0.52-0.99	ZrC _{0.97} 4.698 HfC _{0.61} 4.619 HfC _{0.99} 4.640	Zr ₄ C ₃ (?)		—	[1]
VC	0.6-0.9	VC _{0.73} 4.131	V ₆ C ₅ - $\begin{matrix} P3_1 \\ P3_2 \end{matrix}$ (I)	90.12° (Rhomb. compression) ~ 0	1 260 °C	[2] (ref. [16], chap. 2 and ref. [24], chap. 3)
		VC _{0.88} 4.166	V ₆ C ₅ -B2/m (I) V ₈ C ₇ - $\begin{matrix} P4_132 \\ P4_332 \end{matrix}$		1 120 °C	[3] (ref. [8, 12-18, 29]) [13, 15-24]
NbC	0.5-0.99	NbC _{0.70} 4.432	Nb ₆ C ₅ - $\begin{matrix} P3_1 \\ P3_2 \end{matrix}$ (I)	90.08° (Rhomb. compression)	1 025 °C	[2] (ref. [19], chap. 3), [3] (refs. [20, 21]), [13, 25, 26, 28-30, 65]
TaC	0.6-0.99	NbC _{0.99} 4.471 TaC _{0.70} 4.410 TaC _{0.99} 4.455	Ta ₆ C ₅ (I)		< 1 000 °C	[1], [3] (ref. [20])
MoC	0.69-0.75	MoC _{0.69} 4.266 MoC _{0.75} 4.281 WC _{0.61} 4.220				[2]
WC	0.6-0.7					[2]
RC, R = Sm → Yb	$\sim 0.4-0.6$		R ₂ C (I) R = Gd, Dy, Ho, Er			[3] (ref. [40, 41]), [32-34]
ThC	0-1 ⁽²⁾	ThC _{0.67} 5.304 ThC _{0.96} 5.342 UC _{1.00} 4.960 NpC _{0.96} 5.006 PuC _{0.89} 4.972	Th ₄ C ₃ (I) (?)			[3] (ref. [35, 38]), [35-40]
U Np Pu	UC : 0.9-1 ⁽²⁾ NpC : 0.82-0.96 PuC : 0.65-0.9					[3] (ref. [6, 54]), [41-49]
Sc Y La rare earths actinides	~ 1	ScN 4.450-4.499 YN 4.87-4.88 LaN ~ 5.30 ThN 5.159 UN 4.889 TiN _{0.45} 4.218	Ti ₂ N-I4 ₁ /amd (II)			[3] (ref. [3]), [50-56]
TiN	$\sim 0.42-1$ ⁽²⁾					
ZrN	$\sim 0.55-1$ ⁽²⁾	ZrN _{0.55} 4.584				[2] (ref. [22], chap. 1), [3] (ref. [2, 49, 50]), [13, 50, 57-59]
HfN	$\sim 0.7-1$ ⁽²⁾	HfN _{0.72} 4.526				[2] (ref. [31] and [46], chap. 3), [60]
VN	$\sim 0.7-1$	VN _{0.72} 4.066	V ₃₂ N ₂₆ (?)			[2] (ref. [46] and [48], chap. 3)
NbN	$\sim 0.75-0.93$	NbN _{0.87} 4.382	Nb ₄ N ₃ -I4/mmm (II)			[2] (ref. [50], chap. 3), [61]
						[2] (ref. [7] and [8], chap. 3), [25, 31, 62, 63]
CrN	$\sim 0.98-0.99$	CrN ~ 4.149				[64]
MoN	0.38-0.48	MoN _{0.43} 4.157	Mo ₂ N (II)			[2] (ref. [67 and 68], chap. 3)
WN	~ 0.5	WN _{0.5} 4.13				[2] (ref. [68], chap. 3)

⁽¹⁾ The Roman numbers in parenthesis correspond to the notation of figure 1 for the ordered phases

⁽²⁾ When the existence domain of the disordered NaCl phase extends in the non-metal rich region $\left(\frac{C \text{ or } N}{M} > 1\right)$, there are also metal vacancies or

C₂ molecules in the interstitial sites.

⁽³⁾ The 2 ordered structures reported for Ti₂C have exactly the same pair correlations q_i (see text) for all neighbour distance r_i . They are therefore degenerate on the $(V_1, \bar{V}_2)$ map of figure 1.

Table II. — *Electronic structure parameters used in the present study for carbides and nitrides (in rydbergs), taken from an LCAO fit of NbC [76]. ϵ_M^d is the origin of energies.*

	Energy levels			Carbon-metal bonds			Metal-metal bonds			Carbon-carbon bonds			
	ϵ_X^s	ϵ_X^p	ϵ_M^d	$sd\sigma$	$pd\sigma$	$pd\pi$	$dd\sigma$	$dd\pi$	$dd\delta$	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$
• carbide	-0.7	-0.1134	0	-0.1701	-0.1705	0.096	-0.0732	0.025	0.0022	-0.0203		0.0453	-0.0088
• nitride		-0.25	0		-0.1705	0.096	-0.0732	0.025	0.0022				

Table III. — *Effective d band fillings (N_d) of transition metals, rare earths and actinides in carbides and nitrides, $MX_{1-\alpha}$. The corresponding total fillings (N_e) and Fermi levels (E_F) in the stoichiometric compounds are derived according to (9).*

	Column III (Sc, Y, La) + rare earths actinides	Column IV (Ti, Zr, Hf)	Column V (V, Nb, Ta)	Column VI (Cr, Mo, W)
N_d	3	4	5	6
N_e (carbide)	0.31 ($\alpha = 1/2$)	0.38 ($\alpha = 1/2$)	0.45 ($\alpha = 1/4$ $\alpha = 1/6$)	
N_e (nitride)		0.42 ($\alpha = 1/2$)	0.50 ($\alpha = 1/2$ $\alpha = 1/4$ $\alpha = 1/6$)	0.58 ($\alpha = 1/2$)
E_F (carbide) $\alpha = 1/2$	- 0.12 ryd	- 0.08 ryd		

(taking into account the s valence electrons of the metal) can be found in table III.

In figure 2 we show this standard density of states, typical of a stoichiometric NaCl carbide, calculated with a continued fraction exact up to the 14th level (28 exact moments). The full calculation including the 2s orbitals of the carbon (broken curve) is in good agreement with the results of Schwarz [76] and others [77, 78]. It is clear from the partial p and d densities of states of figure 2 that the well separated minority band which can be seen below the majority one is essentially of 2s character. This « 2s » band contains about 2 electrons and can be omitted when interested in cohesive properties, in which case we set : $ss\sigma = sp\sigma = sd\sigma = 0$.

Fig. 2. — Density of states of NbC with 28 exact moments (electronic parameters defined in table II) : — without the s band (normalized to 8/9); - - - - with the s band (normalized to unity); (a) p orbital, (b) d orbital, (c) total density of states. Note that very similar curves would be obtained with only 14 exact moments.

The corresponding results are shown in figure 2 (full line). A comparison between the p and d partial densities of states calculated with and without the s contribution shows that the latter contribution does not affect them significantly (note that the full density of states is normalized to 18 electrons whereas the other is normalized to 16). The small differences between both calculations are completely negligible when we study integrated quantities such as the energies of interest here.

3.1.2 From carbides to nitrides. — Having a satisfactory description of the electronic structure for a stoichiometric carbide, we are now faced with the problem of finding a similar description for a stoichiometric nitride. Two solutions can be chosen.

The first one is to use a similar scheme as for NbC, namely to take the corresponding values for NbN available from the LCAO fit to the band structure calculation of Schwarz [76]. This procedure presents two major drawbacks. First, from a practical point of view, there is no clear cut-off in distance for the hopping integrals (the value of $dd\sigma$ between Nb atoms second neighbours on the FCC lattice, for instance, is rather large) so that it is no longer justified to keep only first and second neighbour hopping integrals. Let us recall that an interpolation scheme is nothing but a fitting procedure and that the resulting values depend on the number of parameters used for the fit. Therefore, using a limited number of these parameters if the others are not negligible is not equivalent to using values deduced from an interpolation scheme where only these parameters are taken into account. Furthermore, changing the interpolated values for carbides into a completely different set of values fitted to nitrides would not give us a simple physical insight into the origin of the different behaviours of these two types of compounds.

The second choice is to use the same interpolation scheme as for carbides and to vary only a few relevant parameters, i.e. the physical parameters that make a nitride differ from a carbide. It is then easier to relate the different behaviours to the variations of these few parameters and then to the physics of the problem.

We have chosen the second procedure, i.e. we have kept the same parameters as for carbides (NbC) except for a few parameters that we have identified as responsible for the difference between a carbide and a nitride. These parameters are the following :

i) due to the increasing ionic character when going from carbides to nitrides (and oxides), the p level ε_p^X should be deeper below the d level ε_d in the latter than in the former

ii) in relation with this more ionic character, the crystal field effects should be stronger in nitrides; hence, an enhanced difference between the $\varepsilon_d^{e_g}$ and $\varepsilon_d^{t_{2g}}$ levels

iii) the lattice parameter is roughly the same for carbides and nitrides whereas the size of the nitrogen atom is smaller than that of the carbon atom (the atomic size decreases along a series when the nuclear

charge increases). This suggests that the direct coupling ($pp\sigma$ and $pp\pi$) between metalloid atoms is smaller in nitrides than in carbides.

One can largely confirm these three statements by comparing the LCAO interpolation parameters of NbC and NbN [76]. In practice, we will limit this set of parameters by assuming that only two of them (ε_X^p , X-X coupling) are relevant, but we neglect argument ii) above, since the crystal field effect is more difficult to characterize.

In conclusion we will describe the electronic structure of a standard stoichiometric NaCl nitride by using the same parameters as for the corresponding carbide (§ 2.1.1) except for the ε_p level ($|\varepsilon_N^p - \varepsilon_M^d| > |\varepsilon_C^p - \varepsilon_M^d|$) and the hopping integrals between metalloid atoms ($\{|pp\sigma|, |pp\pi|\}_N < \{|pp\sigma|, |pp\pi|\}_C$). This choice of a « physical » procedure to derive the nitride parameters from the carbide ones is probably not suited to an accurate determination of the density of states for a given nitride (in fact, we have verified that the overall agreement with Schwarz' density of states for NbN is quite reasonable), but it will give us all the trends followed by quantities, such as the band energy, when going from carbides to nitrides.

3.2 SUBSTOICHIOMETRIC COMPOUNDS. — The Hamiltonian of substoichiometric compounds can be formally written as in equation (2) except that is now describes a ternary alloy $M(X_{1-\alpha}\square_\alpha)$, [68, 79-80] i.e. indices i, j can take three values corresponding to metal ($i = M$) and metalloid ($i = X$) atoms as well as to vacancies ($i = \square$).

We will assume that the existence of vacancies does not modify the values of the electronic parameters for metal and metalloid atoms, i.e. we will keep constant the energy levels and hopping integrals defined in the previous paragraph. The only additional parameters are those associated with the vacancies. In practice, there are two equivalent ways to replace a metalloid atom by a vacancy, on a given site. The first one, which is well suited to the case of ordered vacancies [68], consists in breaking all the bonds with neighbouring sites, i.e. in setting $\beta_{\square-i} = 0$. In the second procedure, which is more convenient when the vacancies are disordered [79-80], we set an infinite energy level $\varepsilon_\square = +\infty$ on the vacant site. Both cases will be studied in detail now, in the case of carbides.

3.2.1 Vacancy-ordered compounds. — Setting $\beta_{\square-i} = 0$, we are reduced to a true binary alloy $(M_\beta X; \beta = \frac{1}{1-\alpha})$ problem. Then, using the parameters defined in § 2.1 one can use the recursion method to calculate the densities of states per FCC site, $n_i^{OSn}(E)$

$$n_i^{OSn}(E) = 2 \sum_{\lambda_M=1,5} n_M^{\lambda_M, OSn}(E) + 2(1-\alpha) \sum_{\lambda_X=1,3} n_X^{\lambda_X, OSn}(E) \quad (4)$$

corresponding to any of the ordered structures, OS_n , predicted by an Ising model limited to 1st and 2nd neighbour interactions on an FCC lattice (see Fig. 1). This calculation has been performed for a vacancy concentration $\alpha = 50\%$ on the interstitial sublattice in the case of carbides (M_2C , see Fig. 1) with continued fractions exact up to the 7th level. The only difference with the stoichiometric case (MX) comes from the reduced basis of atomic orbitals (the whole band contains now 13 electrons). The resulting densities of states of the four AB-type ordered structures are displayed in figure 3. There is a strong similarity between the densities of states of the segregated, CuAu and A_2B_2 type structures (smooth shape and broad pseudo-gap) but a very different shape is obtained for the CuPt-type structure (high densities of states at the bottom and at the top of the band and a well pronounced pseudo-gap).

Fig. 3. — : densities of states of the ordered structures shown in figures 1-2, with 14 exact moments : (a) CuPt, (b) segregation, (c) CuAu, (d) « A_2B_2 »; ----- density of states of disordered M_2C . Note that the curves are normalized to unity ($n(E) = 1/13 n_1(E)$).

3.2.2 Vacancy-disordered compounds. — Let us now come back to our ternary alloy $M(X_{1-\alpha}\square_\alpha)$. For all atoms of the metal sublattice, the energy level is ε_M^d whereas, on the interstitial sublattice, ε_X^p and $\varepsilon_\square = \infty$ are distributed randomly when the vacancies are disordered. The simplest way to treat such a problem is to use the coherent potential approximation (CPA) which replaces the levels ε_X^p and $\varepsilon_\square$ on each site of the metalloid sublattice, by an average energy dependent complex potential $\Sigma(z)$ which has to be determined self consistently from the equation

$$(1 - \alpha) \frac{\varepsilon_X^p - \Sigma(E^+)}{1 - (\varepsilon_X^p - \Sigma(E^+)) \bar{G}_X(E^+)} - \frac{\alpha}{\bar{G}_X(E^+)} = 0 \quad (5)$$

in which $\bar{G}_X$ is the projection on the interstitial sublattice of the average Green function :

$$\left. \begin{aligned} \bar{G}_X(z) &= \frac{1}{3} \sum_{\lambda_X=1,2,3} \langle n_X, \lambda_X | \bar{G}(z) | n_X, \lambda_X \rangle \\ \bar{G}(z) &= (z - \bar{H})^{-1} \end{aligned} \right\} \quad (6)$$

where n_X is a site of the metalloid sublattice and $\bar{H}$ the average Hamiltonian derived from H (Eq. (2)) by changing ε_X^p and $\varepsilon_\square = \infty$ into $\Sigma(z)$. The problem is now that, due to the presence of metal atoms with unchanged levels ε_M^d on the « frozen » metal lattice, this projection cannot in any way be written as a continued fraction (contrary to the simple case of binary substitutional atoms for which $\bar{G}(z) = G(z - \Sigma(z))$).

The only solution is then to inverse the function $(z - \bar{H})$ on the whole basis (including both sublattices). We have to work in the reciprocal space and calculate the average Green function $\bar{G}(z, k) = (z - \bar{H}_k)^{-1}$ for each value of k before summing over the whole Brillouin zone (this is exactly the procedure used by Klima [79] and Faulkner [80]). This summation can be easily performed by using special points in this Brillouin zone [81]. We have thus calculated $\bar{G}$ and then $\bar{G}_X$ and Σ , by summing over ten special k points of $(1/48)$ th of the FCC Brillouin zone, having checked that using a larger number of k points (60) does not significantly improve the accuracy of the calculation. The resulting total density of states per FCC site

$$\bar{n}(E) = -\frac{\text{Im}}{\pi} \sum_{i=M,X} \sum_{\lambda_i} \langle n_i, \lambda_i | \sum_k \alpha_k \bar{G}(E^+, k) | n_i, \lambda_i \rangle \quad (7)$$

(where n_i is a site of the i -sublattice, λ_i the corresponding orbital and α_k the weight of the special point k) is shown in figure 3 (dotted curve) for M_2C ($X = C$, $\alpha = \frac{1}{2}$). The most striking result is that, in spite of completely different calculations (in direct and reciprocal spaces), the ordered and disordered densities of states are very similar. In particular, close to the Fermi level (the energy position of which is given in table III) these densities are almost indistinguishable, a fact which suggests that the specific heat coefficient γ should not differ significantly when going from the ordered to the disordered compound. This statement is indeed confirmed by electronic specific heat measurements [82] performed on ordered (CuPt type) and disordered $TiC_{0.625}$ samples. In both cases, the same value of $n_i^{os}(E_F) \simeq \bar{n}(E_F) \simeq 38$ states/ryd, is obtained if the electron-phonon enhancement is not taken into account.

Note that due to the properties of CPA, the whole band exactly contains 13 electrons, as it should (3p states being rejected at infinity).

4. Stability of ordered phases in terms of effective pair interactions.

4.1 RELATIVE STABILITIES OF ORDERED PHASES OF CARBIDES : « EXACT » CALCULATION. — Here it is not intended to calculate a phase diagram at finite temperature but rather to find the most stable ordered structure at 0 K. The most direct — if not the most convenient — method consists in considering *all* possible existing ordered structures, for a given vacancy concentration and comparing their band energies. As usual, we assume that the main contribution to the cohesive energy of the transition metal compound comes from the valence d electrons of the transition metal and from the valence p electrons of the metalloid (in § 2.1.3 we have shown that valence s electrons could be omitted). The band energy per FCC site for a given ordered structure OS_n is then given by :

$$E_b^{OS_n} = \int_{-\infty}^{E_f^{OS_n}} E n_t^{OS_n}(E) dE \quad (8)$$

where $n_t^{OS_n}(E)$ is the density of states defined in equation (4) and $E_f^{OS_n}$ is the corresponding Fermi level, which is directly related to the filling of the p-d band, N_e^t :

$$N_e^t = \int_{-\infty}^{E_f^{OS_n}} n_t^{OS_n}(E) dE \quad (9)$$

as can be seen in table III. (In the following, we use a band filling normalized to unity, i.e. :

$$N_e = N_e^t / \{ 10 + 6(1 - \alpha) \}.$$

We have then to calculate the stability energies per FCC site :

$$\Delta E_{stab}^{n-m} = E_b^{OS_n} - E_b^{OS_m} \quad (10)$$

for *all* the ordered structures of a (V_1, V_2) Ising model, for a given vacancy concentration, on an FCC sublattice (see Fig. 1). For a concentration $\alpha = 0.5$ (M_2X), there are four such ordered structures ($OS_1 = \text{« CuPt »}$, $OS_2 = \text{« CuAu »}$, $OS_3 = A_2B_2$, $OS_4 = \text{segregation}$) the densities of which have been described in the previous section (see Fig. 3) for carbides ($X = C$). The stability energies ΔE_{stab}^{1-n} ($n = 2 - 4$) which are derived from these densities of states are shown in figure 4 (see also Ref. [68]). The main result is that for small and large band fillings, the most stable structure is the segregated phase while for N_e between 0.22 and 0.51 (which, according to table III, corresponds to the case of carbides), OS_1 (« CuPt ») is preferred. That vacancies should order according to a CuPt type structure in M_2C carbides is indeed confirmed by experiments (see Table I and Fig. 1).

In spite of these satisfactory results, this method present two major drawbacks. First, it is easily realized from figure 4 that the order of magnitude of the stability energies is about one hundredth that of the band

Fig. 4.— Stability energies : $\Delta E_{stab}^{1-n}(1/2, N_e)$

* exact calculation for $n = 2$ CuPt-CuAu (c)
(Eq. (10)) $n = 3$ CuPt- A_2B_2 (a)

(—) $n = 4$ CuPt-segregation (b)

* pairwise interactions

(-----) (Eq. (14))

(c) $(V_1 - 3V_2 + 2V_3)/2$

(a) $V_1/2 - V_2 - V_3 + 2V_4$

(b) $-3V_1 - 3V_2 - 6V_3$.

energies from which they are derived. This means that the required accuracy on these band energies is very high. However, previous calculations have shown that, in the case where $n_t^{OS_n}(E)$ is obtained by a continued fraction technique, the knowledge of 7-8 exact levels is really sufficient to ensure this accuracy [70]. More cumbersome is the necessary exhaustivity in terms of structures. Actually we have to calculate, for *each* concentration, the densities of states of *all* possible ordered structures. This is why it is preferable to try to write directly the stability energies in terms of pair interactions.

4.2 EFFECTIVE PAIR INTERACTIONS.

4.2.1 Formalism. — Although the total energy of a transition alloy cannot be written in terms of pair interactions, it has been shown, in several recent works [7-9, 69-71] that the configurational part of this energy can be written in this way, i.e. as a sum of effec-

tive pair interactions. The idea is that the energy of any ordered alloy can be obtained by a perturbation expansion from the disordered medium (chosen as a reference medium in order to ensure a rapid convergence of the expansion). This so-called « generalized perturbation method » allows us to define cluster interactions which, in most cases, decrease when the size of the cluster increases [83]. It has been checked that, for substitutional transition metal alloys, ordering on simple (FCC [9, 70], ...) or complex (A15 [84])

lattices, this expansion could be, to a good accuracy, limited to pairwise interactions and that these pair interactions could be used to determine the most stable ordered structures at $T = 0$ K.

This generalized perturbation method can easily be extended to the case of transition metal carbides or nitrides, by expanding the energy per FCC site of a compound $MX_{1-\alpha}$ with the ordered structure OS_n (characterized by the set of occupation numbers $\{p_i^{j=X}\}$, see Eq. (2)) in the following way :

$$E_b^{OS_n}(\{p_i^X\}, N_e) = E_b^{dis}(\alpha, N_e) + \frac{1}{2} \sum_{i,i'} \{p_i^X - (1 - \alpha)\} \{p_{i'}^X - (1 - \alpha)\} V_{ii'}^{XX}(\alpha, N_e) \quad (11a)$$

or equivalently

$$E_b^{OS_n}(\{q_R^n\}, N_e) = E_b^{dis}(\alpha, N_e) + \frac{1}{2} \sum_R \{q_R^{(n)} - (1 - \alpha)^2 Z_R\} V_R(\alpha, N_e) \quad (11b)$$

where Z_R and $q_R^{(n)}$ are respectively the number of FCC sites and the mean number of X atoms (in the ordered structure OS_n) at a distance $R = |l - l'|$ of a given X atom. E_b^{dis} is the energy of the disordered state treated within the CPA

$$E_b^{dis}(\alpha, N_e) = \int_{E_f^{dis}}^{E_f^{dis}} E \bar{n}(E, \alpha) dE \quad (\bar{n}(E, \alpha) \text{ given by equation (6)}) \quad (12)$$

and $V_R = V_{ii'}^{XX}$ is the effective pair interaction between metalloid atoms separated by the distance R

$$V_R(\alpha, N_e) = V_{ii'}^{XX}(\alpha, N_e) = -2 \frac{\text{Im}}{\pi} \int_{E_f^{dis}}^{E_f^{dis}} dE \left\{ \frac{1}{\bar{G}_X(1 - \bar{G}_X[\epsilon_p - \Sigma])} \right\}^2 \times$$

$$\sum_{\lambda_X \mu_X} \sum_{k, k'} \langle l_X \lambda_X | \bar{G}(E, k) \bar{G}^*(E, k') e^{i(k-k')R} | l'_X \mu_X \rangle \quad (13)$$

where all the quantities have been defined in § 2. The only (practical) difference with the numerical calculation of the disordered density of states comes from the double summation over k and k' which prevents us from summing in 1/48th of the Brillouin zone only.

It is clear from formulae (11)-(13) that, if such an extension is valid, the corresponding pair interactions only depend on the neighbouring distance, the vacancy concentration and the band filling. This means that for a given vacancy concentration and neighbour distance, only the knowledge of the disordered density of states is required. In particular, the stability energies are obtained directly, without resorting to differences between large quantities, since, from equation (11b)

$$\Delta E_{stab}^{n-m}(\alpha, N_e) = \frac{1}{2} \sum_R (q_R^{(n)} - q_R^{(m)}) V_R(\alpha, N_e). \quad (14)$$

Thus, all accuracy problems disappear.

Having all these advantages in mind we want to justify the generalized perturbation expansion, limited to pair interactions, from a numerical point of view.

4.2.2 Application to carbides : justification of the method. — The pair interactions $V_R(\alpha, N_e)$ are given by equation (13) and have been calculated in the case of carbides for three vacancy concentrations ($\alpha = 1/2, 1/4, 1/6$) and eight neighbouring distances ($R =$ first, second, ... eighth nearest neighbour distance). The results are plotted as a function of the band filling N_e in figure 5 for $\alpha = 1/2$ and $\alpha = 1/6$. The most striking feature is the importance of the second neighbour pair interaction V_2 compared to $V_1, V_3, \dots, V_5$ ($V_{R>5}$ is too small to be visible on this figure). Moreover, V_2 presents two zeros (in addition to those that necessarily occur at $N_e = 0$ and 1) whereas V_1 is always negative and the other interactions either are much smaller or present more oscillations. These results are very different from those obtained for substitutional FCC alloys ($V_1 \gg V_2, V_3, V_4, \dots$; two zeros for V_1 and three or more for the others [9]) which can be understood from arguments based on the moments μ_p of the density of states [67]

$$\mu_p^{OS_n} = \int dE E^p n_i^{OS_n}(E). \quad (15)$$

Fig. 5. — Calculated pairwise interactions for $\alpha = 1/2$ (a) and $\alpha = 1/6$ (b) in the case of carbides $MC_{1-\alpha}$

----- V_1 ; — V_2 ; V_3 ; $\times \times \times$ V_4 .

In insert is shown V_5 ($V_{n>5}$ is indistinguishable on this scale).

Actually, the relative orders of magnitude and numbers of zeros of these interactions can be related, at least qualitatively, to the topology of the lattice and to the anisotropy of the d-d and p-d orbitals. In the case of carbides, the most important hopping integrals are those linking a metal atom to another metal atom or to a carbon atom (see Table II). For simplicity, we can forget — in a first step — the hopping integrals between carbon atoms. In this case, the first moment which depends on the C-configuration (it must at least include two distinct C sites) is the fourth moment (μ_4) which involves four p-d hoppings. Then, for a given concentration, all the ordered (and the disordered) structures have the same μ_0 , μ_1 , μ_2 and μ_3 and the differences in energy $\Delta E_{\text{stab}}^{n-m}$ between these structures can be written [85]

$$\Delta E_{\text{stab}}^{n-m}(N_e) \sim \sum_{i \geq 4} \varphi_i(N_e) \delta \mu_i^{n-m} \quad (16)$$

$$\delta \mu_i^{n-m} = \mu_i^{\text{OS}_n} - \mu_i^{\text{OS}_m}$$

where $\varphi_i(N_e)$ is an oscillating function of the band filling N_e , independent of the ordered structures $n-m$; more precisely, $\varphi_i(N_e)$ presents at least $(i-2)$ zeros (for N_e within the interval $]0, 1[$). Then, if we limit the expansion (14) to the fourth moment μ_4 , it is easy to predict the qualitative trends of the first and second neighbour pair interactions. Actually, $\delta \mu_4$ induces first ($\{4-5-6-5-4\}$ and $\{4-5-6-7-4\}$ paths in figure 6a) and second ($\{1-2-3-2-1\}$ path) pair interactions, V_1 , V_2 , between carbon sites. It is known [67, 86-87, 83] that in general the contribution of open paths such as $\{4-5-6-7-4\}$ is smaller than that of self-retracing ones such as $\{1-2-3-2-1\}$ or $\{4-5-6-5-4\}$. Moreover in the latter case, this $\delta \mu_4$ -contribution is positive and maximum for straight

Fig. 6. — (a) path contributions to μ_4 inducing first $\{4-6\}$ and second $\{1-3\}$ neighbour interactions on the interstitial sublattice. Full and empty circles denote metallic and interstitial sites respectively. (b) Schematic $\delta \mu_4$ - (and $\delta \mu_2$ -) contribution to V_1 and V_2 with $(X-X \neq 0)$ and without $(X-X = 0)$ direct metalloid-metalloid coupling. The dotted lines correspond to the ratio $pd\pi/pd\sigma = -0.56$ deduced from parameters of table II whereas the full lines should be obtained for any ratio slightly different from this critical value (e.g. $pd\pi/pd\sigma \approx -0.3$).

paths (the sign is not well defined for open paths). In our present case this means that

$$|\mu_4^{\{1-2-3-2-1\}}| \gg |\mu_4^{\{4-5-6-5-4\}}| > |\mu_4^{\{4-5-6-7-4\}}|.$$

A more detailed analysis shows that $\mu_4^{\{4-5-6-5-4\}}$ and $\mu_4^{\{4-5-6-7-4\}}$ are of opposite signs, so that $|V_2| \gg |V_1|$. Since $\varphi_4(N_e)$ exhibits two zeros for $0 < N_e < 1$, we understand the shape and magnitude of V_2 qualitatively (compare Figs. 5 and 6b). As for the shape of V_1 , the absence of zeros in figure 6b comes from the contribution of C-C hopping integrals that we have neglected in our qualitative arguments. These integrals introduce a $\delta \mu_2$ contribution ($\{4-6-4\}$ path) which is not negligible compared to the small $\delta \mu_4$ contribution to V_1 and presents no oscillation ($\varphi_2(N_e)$ has no zero). This leads to the schematic results of figure 6b which are fairly well reproduced by our calculations.

Another important information given by figure 5 is the influence of vacancy concentration on these

pair interactions. From the curves for $\alpha = 1/2$ and $\alpha = 1/6$ (the curves for $\alpha = 1/4$ are just intermediate between them), it appears that the deformation of V_R with α is not very important, the main effect being a reduction of the domain (measured on the N_e axis) where V_2 is positive when the number of vacancies decreases.

The problem now is to justify the pair interaction expansion of the energy in equation (11), i.e. to verify that the difference in energy ΔE^{n-d} per FCC site :

$$\Delta E^{n-d} = E_b^{OS_n} - E_b^{DS} \quad (17)$$

between any ordered structure (OS_n) and the disordered structure (DS) can be reconstructed, to a good approximation, by a sum of pair interactions

$$\Delta E^{n-d} \simeq \frac{1}{2} \sum_R (q_R^{(n)} - (1 - \alpha)^2 Z_R) V_R(\alpha, N_e). \quad (18)$$

This has been checked for two ordered structures (CuPt and CuAu type) and a given vacancy concentration ($\alpha = 1/2$). The results plotted in figure 7 (where the summation in Eq. (18) has been truncated to the fourth neighbour) show that the agreement between the « exact » calculation (Eq. (17)) and the

Fig. 7. — Ordering energy ΔE^{n-d} (see Eqs. (17)-(18)) as a function of the band filling N_e for $n = 1$ (CuPt-Fig. 7a) and $n = 2$ (CuAu-Fig. 7b)

— full calculation (Eq. (17))

$$\Delta E^{1-d} = E^{OS_1} - E^{DS}$$

$$\Delta E^{2-d} = E^{OS_2} - E^{DS}$$

----- pair interactions (Eq. (18))

$$\Delta E^{1-d} = -3/4 V_2 + 3/2 V_4$$

$$\Delta E^{2-d} = -V_1/2 + 3 V_2/4 - V_3 + 3 V_4/2$$

generalized perturbation method (Eq. (18)) is at least as good as in the case of substitutional alloys [9]. Note that the curves of figure 7 give a nice illustration of the interest of the generalized perturbation method which allows us to calculate energy differences directly. Indeed, from a numerical point of view, the exact curve actually requires the knowledge of about twenty times as many points in energy as for the pair interaction curve, in order to achieve the same kind of accuracy.

Another way to justify this pair interaction expansion is to compare the stability energies between various ordered structures calculated in § 4.1 (ΔE_{stab}^{n-m} , Eq. (10)) with those obtained as sums of pair interactions (Eq. (14)). This comparison is illustrated in figure 4 for $n = 1$ (CuPt) and $m = 2-4$ (CuAu, A_2B_2 and segregation). Here also the agreement is as satisfactory as for substitutional alloys [70].

Finally, let us point out that the agreement between the « exact » and « approximated » curves of figures 4 and 7 is not appreciably modified by truncating the summations in equations (14) and (18) to the second neighbour pair interaction instead of the fourth one. Therefore it is justified not only to use the pair interactions defined by equation (13) and shown in figure 5 to study ordering processes in carbides, but also to restrict these interactions to the first two ones. In other words, a (V_1, V_2) diagram is sufficient to analyse most of the ordered structures occurring in carbides. Considering the band fillings typical of the carbides of interest here ([0.31, 0.45], see table III) and the curves of figure 5, these structures must be found in the region $\{V_2 > 0, V_2 \gg V_1\}$ which is indeed the region where the observed structures are found in figure 1.

4.2.3 From carbides to nitrides : influence of parameters. — Having justified the effective pair interaction formalism in the particular case of carbides, it is natural to apply it to nitrides, whose parameters have been deduced from those of carbides, as explained in § 3.1.2. As previously discussed, this choice allows us to characterize and understand the way the pair interactions vary when going from carbides to nitrides. We recall that the two relevant parameters that have been identified are the values of the metalloid-metalloid coupling (which decreases from carbon to nitrogen) and of the atomic level ($|e_C^p - e_M^d|$ larger in nitrides than in carbides). In order to determine the influence of these parameters, we have chosen to completely neglect the N-N coupling and to overestimate $|e_N^p - e_M^d|$:

$$pp\sigma = pp\pi = 0$$

$$e_N^p - e_M^d = 2(e_C^p - e_M^d).$$

From the simple moment arguments developed in the previous section, it is easy to predict that cutting the N-N couplings should mainly affect V_1 . More

precisely, it should suppress its μ_2 -contribution (see Fig. 6a) so that only the μ_4 -contribution should be of importance, i.e. V_1 should have two zeros and then should become positive for some intermediate values (see Fig. 6b : full line). On the other hand, varying $|\varepsilon_X^p - \varepsilon_M^d|$ should modify the positions of the zeros. As a result, one can suspect that the zeros of V_2 and — now — V_1 move in such a way that $V_1 > 0$ and $V_1 \gtrsim 2 V_2$ for some filling range.

With these arguments in mind, we have performed a full calculation, the results of which are shown in figure 8. They are not completely satisfactory : actually,

Fig. 8. — From carbides to nitrides

a(α) : carbide ($X-X \neq 0$; $\varepsilon_X^p = -0.12$)

b(β) : $X-X = 0$, $\varepsilon_X^p = -0.12$

c(γ) : « nitride » ($X-X = 0$, $\varepsilon_X^p = -0.25$)

(a, b, c) correspond to Schwarz's ratio (-0.56) for $pd\pi/pd\sigma$ and (α, β, γ) to a different ratio ($pd\pi/pd\sigma = -0.3$).

even if one can now find a domain where $V_1 > 0$ and $V_1 \gtrsim 2 V_2$ (for band fillings $N_e \sim 0.52$ near those of nitrides : $0.42 < N_e < 0.58$) this domain is very narrow and the corresponding values of V_1 are really too small to be significant. In fact, instead of the $\delta\mu_4$ -behaviour of V_1 which was expected after cutting N-N bonds (see Fig. 6), V_1 is very small everywhere. In order to understand this result, we have to go a little further — numerically — in the analysis of the

various moment contributions to V_1 (Fig. 6b : dotted line). If we do this, we find that the contribution of the {4-5-6-5-4} path is proportional to $(pd\pi^4 + \frac{1}{4}pd\sigma^4)$ whereas that of {4-5-6-7-4} is proportional to $-(pd\sigma)^2(pd\pi)^2$. We have already mentioned that these contributions have opposite signs, but in addition, we find that their absolute values are equal when :

$$(pd\pi/pd\sigma) = -\frac{1}{\sqrt{2}} \simeq -0.7. \text{ This is nearly the value}$$

deduced from the interpolation scheme of Schwarz for carbides, namely $(pd\pi/pd\sigma) = -0.56$, which explains why V_1 vanishes when the bonding between metalloid atoms is suppressed.

Let us however recall that, due to the way the parameters of nitrides have been derived from those of carbides, keeping the metal-metal hopping parameters constant was only a simplifying assumption, so that using values which are so close to the critical values ($pd\pi \simeq -0.7 pd\sigma$) raises some problems. In the spirit of our process, we have to check the sensitivity of our results to the variations of these parameters, in order to separate the physical from the fortuitous effects. This is illustrated in figure 9 in which one can see the variations of V_1 and V_2 with the ratio $pd\pi/pd\sigma$. It is clear that V_1 has the expected $\delta\mu_4$ -behaviour as soon as $pd\pi/pd\sigma$ differs significantly from the value $(-1/\sqrt{2})$. To recover the physical effect induced by the weakening of the X-X coupling from carbides to nitrides without changing the other significant features of the curves, we slightly vary the metalloid-metal hopping integrals so that $pd\pi/pd\sigma = -0.3$. The corresponding curves are shown in figure 8. The general trends are now as expected : cutting N-N bonds affects mainly V_1 whereas the variation of ε_X^p leads to a small reduction of V_2 and to a narrowing of the domain in which it is positive. Moreover (and this could not be deduced from simple moment arguments) the zeros of V_1 and V_2 are not at the same position, which opens a large domain ($0.53 \leq N_e \leq 0.66$) in which V_1 is not too small and $V_1 > V_2 > 0$. This domain

Fig. 9. — Influence of the value of the ratio $pd\pi/pd\sigma$ on the shape of V_1 (-----) and, to a less extent, V_2 (——) when X-X bondings are suppressed : $pd\pi/pd\sigma = -0.56$ (α), -0.5 (β); -0.4 (γ), -0.3 (δ).

is reduced while V_2 slightly decreases when $|\varepsilon_X^p - \varepsilon_M^d|$ increases so that finally we find that $V_1 > V_2 > 0$ for $0.47 \leq N_e \leq 0.53$. Since nitrides exist in the range $0.42 \leq N_e \leq 0.58$, one can conclude that, at least semi-quantitatively, going from carbides to nitrides change pair interactions such as ($V_2 > 0$; $V_2 \gg V_1$) into pair interactions such as ($V_1 \gtrsim V_2$; $V_1 > 0$).

5. Conclusion : calculated (V_1 , V_2) diagram for carbides and nitrides.

To summarize, we have shown in this work that it is justified to treat the ordering of vacancies in substoichiometric transition metal carbides and nitrides in terms of pairwise interactions calculated from the electronic structure of the disordered state. Neglecting other multiatom interactions is at least as valid as for transition metal alloys. We have also verified that, contrary to what occurs in the latter case, the predominant interaction here is that between second neighbours, and that a (V_1 , V_2) diagram is relevant to classify ordered structures observed in carbides and nitrides.

In such a diagram, the calculated pairwise interactions are such that $V_2 > 0$, $V_2 \gg V_1$ for carbides and $V_1 \gtrsim V_2$, $V_1 > 0$ for nitrides. This is illustrated in figure 10 in which the hatched areas correspond to the range of values taken by V_1 and V_2 , calculated for three vacancy concentrations, $\alpha = 1/2$, $1/4$, $1/6$ (which is easy within the generalized perturbation method), for the band fillings characteristic of carbides and nitrides, respectively (see Table III). We have performed the calculations for two values of the ratio ($pd\pi/pd\sigma$) : -0.56 (Schwarz's parameters) which is well suited to the case of carbides (see Fig. 10a) and -0.3 which displays the physical change when going from carbides to nitrides (Fig. 10b). From the

comparison between both diagrams, it is clear that varying this ratio is of small importance in the case of carbides which are characterized by a large positive value of V_2 and a small value of V_1 , the sign of which is not unambiguously determined. As for nitrides, the main effect is a reduction of V_2 (which can even change sign) and an increase of V_1 which becomes positive (see Fig. 10b). The final result is in fair agreement with the experimental results displayed in figure 1. More precisely, the separated domains of existence in a V_1 , V_2 diagram, of ordered carbides and nitrides, deduced from our calculation, are indeed (roughly for nitrides) the regions where the corresponding observed structures are found (see inset of Fig. 10).

However, it is worth noticing that this is only an overall agreement and that some problems may occur when considering a specific system. In particular, this is the case if the band filling of this system corresponds to the sharp maximum of V_2 ($N_e \sim 0.3$, see Fig. 5) since an imprecise knowledge of N_e can lead to appreciable errors on the numerical value of V_2 . For example let us consider Ti_2C ($N_e = 0.38$) for which pair potentials can be derived [88] from the short range order parameters measured by neutron diffuse scattering experiments [28, 29]. This treatment leads to a very small value of V_1 ($V_1^{exp} \simeq 0^+$), negligible if compared with V_2 , which is in good agreement with our results (see Fig. 10). Unfortunately, the experimental value of V_2 is much smaller than the theoretical one ($V_2^{cal} \simeq 4 V_2^{exp}$). In other words the ordering transition temperature deduced from our calculation for Ti_2C is too high (an order of magnitude of T_c , for an Ising model with $V_1 = 0$, is given by : $kT_c \simeq 1,1 V_2$ and $T_c^{exp} \simeq 1000$ K for Ti_2C). The agreement would be improved by slightly varying the filling corresponding to Ti_2C in our calculation. Nevertheless it remains that in this case, $V_2 \gg V_1$

Fig. 10. — Calculated (V_1 , V_2) diagram for two values of the ratio $pd\pi/pd\sigma$ (-0.56 , -0.3). $////$ domain of existence for ordered carbides, $\\\\$ domain of existence for ordered nitrides. In the inset, we recall the corresponding ground state of the Ising model where hatched areas correspond to the observed ordered phases for carbides and nitrides.

so that V_1 is no longer relevant. It is then necessary to include further interactions V_3 and V_4 to predict an ordered structure different from CuPt for Ti_2C (which is confirmed by the observation of other phases such as Ti_8C_5 , see Table I). Note that the same analysis [88] of similar experiments on Nb_2C [28, 29] leads to $V_2^{\text{exp}} \gtrsim V_1^{\text{exp}} > 0$ and unambiguously sets NbC_x in region I of the diagram of figure 1, which is consistent with the observation of the phase Nb_6C_5 . Finally, even if our derivation of nitride parameters might be too crude to use the diagram of figure 10b to classify a given nitride system, it is encouraging to find Ti_2N and Mo_2N close to region II of figure 1. Note however that we have partly failed to make V_1 sufficiently positive, perhaps due to the existence of a positive elastic contribution to V_1 which of course is not included here.

We have shown that a proper calculation, based on a tight binding description of the electronic structure of carbides and nitrides, leads to effective pair

interactions which allow us to clearly separate the domains of existence of carbides and nitrides on a (V_1, V_2) diagram, in agreement with the experimental observations. Going beyond this semi-quantitative theory, in order to calculate precise pair interactions for a given compound, would require more sophisticated calculations. Such calculations should be, in our opinion, a necessary step towards a complete understanding of ordering processes in carbides and nitrides. Another complementary work, currently under progress, is the extension of the present calculation to the study of hexagonal carbides and nitrides.

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