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Electronic Structure and the Chemical Bond in Non-stoichiometric Refractory Compounds of Transition Metals in Sub-groups IVa and Va

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Studies of the electronic structure and of the chemical bond in non-stoichiometric binary compounds based on the transition metals of sub-groups IVa and Va are systematically reviewed. The main phenomenological models are examined, and the results of calculations by band and by cluster models of the distribution of electron density are compared; changes in the chemical bond caused by the presence of point vacancies in the metalloid and in the metal sub-lattice are discussed. Calculated results are compared with the results of studies of non-stoichiometric compounds by X-ray emission and photoelectron spectroscopy methods, and with various physicochemical properties. The relative merits of the two approaches (using band and cluster models respectively) in studies of electronic processes associated with the formation of point vacancies in crystals are discussed. 159 references.

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I. INTRODUCTION

Compounds of the transiton metals (TM) of sub-groups IVa and Va of the Periodic Table with the lighter s and p elements (carbon, nitrogen, oxygen) form a large class of substances with a number of unique physicochemical properties. They combine properties typical of covalently bonded crystals (high melting point, superior hardness, resistence to corrosion and radiation) with specific properties of electrical and thermal conduction, magnetism, and superconductivity[1-10].

The most striking feature of the monocarbides, mononitrides, and monoxides of the TM is their extensive homogeneity region, which allows the concentration of defects (point vacancies) in both sub-lattices to be varied by large amounts

without disrupting the original structure (type B1). Even in stoichiometric compositions the number of vacancies can be 15–25 at.%, increasing rapidly as the composition departs from the equi-atomic ratio: some compounds (for example, vanadium carbide) cannot be prepared in a strictly stoichiometric state under normal conditions. Furthermore in some binary compounds (VO_x, TiO_x, VC_x, etc.) the defects are partially ordered, with formation of defect clusters, and this can lead to the appearance of individual phases like V_6C_5, V_8C_7, $VO_{1.3}$, etc.[1-10]

Deviations from stoichiometry produce large changes in all the physicochemical properties of the compounds. Therefore the wide interest in the electronic structure of non-stoichiometric phases and in the electronic processes which accompany the formation of point vacancies in the crystal is not surprising.

A correct description of the electronic structure of non-stoichiometric phases (as opposed to that of an ideal crystal) should account for changes in the following properties: 1) the density of electronic states, 2) the position of the Fermi level, 3) the chemical bond near a defect. It should also correctly identify: 1) the nature of the vacancy states, their position in the overall energy spectrum, and the extent to which they are localised, and 2) the charge on the vacancies.

In this paper we shall attempt a systematic review of existing models of the electronic structure of MX_x binary compounds containing defects (where M is the metal and X is the non-metal), whether phenomenological or based on quantitative quantum-chemical calculations. We shall examine the relative merits of the different methods and approximations which have been used to describe the energy spectrum of electrons in the chemical bond of compounds with or without defects, and we shall compare them with data on MX_x compounds obtained by X-ray emission and photoelectron spectroscopy methods.

II. BAND AND CLUSTER MODELS USED IN THE CALCULATIONS OF THE ELECTRONIC STRUCTURE OF SOLIDS

Two alternative approaches to the calculation of the electronic structure of condensed phases are used at present: the band model and the cluster model. Both are based on the solution of the one-electron Schroedinger equation

$$\left\{-\frac{1}{2}\nabla^2 + V_{\text{coul}}(\mathbf{r}) + V_{\text{exch}}(\mathbf{r})\right\}\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r}) \qquad (1)$$

(where ∇^2 is the kinetic energy operator, $V_{\text{coul}}(\mathbf{r})$ is the coulombic potential energy of the electron, and $V_{\text{exch}}(\mathbf{r})$ is the exchange–correlation pontential), but they rely on radically different approximations.

In the energy band methods[11] special attention is paid to the properties of the energy spectrum arising from the presence of translational symmetry: the solid is treated as an infinitely large regular crystal. The wave function ψ_j is expressed as a combination of delocalised periodic functions of the Bloch type, and the electronic spectrum calculated in this way has continuous energy bands corresponding to the ground state of the ideal (defect-free) crystal, This approach is therefore useful for compounds which form bands (of any width), and it gives accurate values of the width and energy of the band. The characteristics which the band methods describe most correctly are those associated with delocalised electronic states (i.e. the kinetic properties).

The most serious weakness of this approach is that any deviation from the ideal crystal model (such as surfaces, impurities, defects, excited states, etc., which are found in the vast majority of real solids) will perturb the translational periodicity of the system and cause difficulties in the calculation of the energy bands in the disordered system.

Conversely, the molecular orbital cluster methods[12-14] describe the electronic structure as a set of discrete levels of energy ε_j, obtained by solving Eqn.(1) for a relatively small group of atoms (the cluster) chosen within the crystal. These methods retain the atomic orbital concept and rely on fairly simple computation schemes which are however applicable to compounds with crystal structures and compositions of any degree of complexity. Therefore the cluster methods are used mainly in calculations of electronic states and chemical bond effects in disordered solids containing defects, impurities, dislocations, etc. Cluster methods are most successful when applied to narrow-band crystals, and the most accurate results are obtained in calculations of characteristics associated with localised states.

One of the main shortcomings of the cluster approach is the difficulty of calculating kinetic parameters, and of describing wide-band systems.

Several independent methods are now available for band calculations (combined plane wave (CPW), orthogonalised plane wave (OPW), Green function, pseudo-potential methods, etc.) and for cluster calculations [semi-empirical or *ab initio* SCF MO LCAO methods, X_α-scattered wave (X_α-SW) methods, X_α-discrete variation (X_α-DV) methods, X_α-LCAO methods, etc.]. Since approximations have to be used even in non-empirical methods, and their validity may be doubtful, experimental tests of the results may be necessary. The most direct tests rely on X-ray emission and photoelectron spectroscopy. We shall therefore discuss the results of specific calculations in conjunction with relevant spectroscopic data in order to assess the validity of different models of the electronic structure of high-melting phases.

Before proceeding to our discussion of the electron energy spectrum (EES) of non-stoichiometric compounds we shall briefly examine the most important results relating to "complete" (i.e. ideal) binary phases, since these phases will be used later as reference systems when considering changes in electronic structure brought about by structural vacancies.

III. ELECTRONIC STRUCTURE AND THE CHEMICAL BOND IN STOICHIOMETRIC BINARY COMPOUNDS OF THE TRANSITION METALS

The earliest views on the electronic structure of high-melting compounds were formulated as two phenomenological models, each supported by a number of experimental facts[3,5,7-9]. According to the first of these models[15,16] interstitial phases can be treated as solid solutions of the metalloid in a matrix of the metal, where the main effects of chemical bonding arise from the collectivisation of the *d* electrons from the metal. The other model accounts for the hardness, refractoriness, and brittleness of these compounds by postulating a predominant contribution from covalent interactions between the metal and the metalloid[17-20].

The real structure of the EES of binary phases and the individual features of the electronic structure of particular compounds were successfully established by quantitative quantum-chemical calculations. Almost all the existing band and cluster methods have been applied to the calculation of the band structure of ideal binary compounds. The most important of these calculations are summarised in Table 1, which lists the methods applied to different materials and all the reported X-ray emission and photoelectron spectroscopy studies of these compounds.

Table 1. Bibliography of quantum-chemical calculations and X-ray emission (XE) and photoelectron spectroscopy (XPS) work on binary stoichiometric high-melting phases.

Compound	Band calculations				Cluster calculations		XE spectra	XPS spectra
	strong bond	CPW	Green function	empirical pseudo-potential	semi-empirical	$X\alpha$		
TiC	[21, 23, 26, 27, 53, 54]	[24, 34—37, 45—48]	—	[28, 29]	[67, 68, 70]	[57, 58, 60, 64, 65]	[77, 80—82, 84]	[34, 89]
TiN	[21, 53, 54]	[24, 35—37, 46]	—	—	[67, 70]	[60, 64]	[77, 78, 81, 82, 101, 158]	[92, 94, 95]
TiO	[21]	[24, 33, 35—37, 46]	—	—	[70]	[60, 64]	[77, 81—84]	[99]
VC	[26, 27, 53]	[34—40]	—	—	[67—69]	[59, 60, 64]	[80, 84, 85]	[34, 90]
VN	—	[35—39]	—	—	[67—69]	[59, 60, 64]	[78, 80, 85]	[96]
VO	—	[33, 35—37]	—	—	[69]	[60, 64]	[80, 85]	[100]
ZrC	[26, 27]	[34]	—	[29]	[62]	[58, 62]	[78, 79, 84]	[34]
ZrN	—	—	—	—	[62]	[62]	[78, 79]	—
«ZrO»	—	—	—	—	[62]	[62]	—	—
NbC	[26, 27]	[34, 42—44]	—	[30]	[71]	[61]	[79, 84, 86—88, 98]	[34, 89, 97]
NbN	[32]	[41, 43]	—	[30, 31]	[71]	[61]	[79, 86—88, 158]	[97]
NbO						[61, 66]	[66, 87, 88]	[66]
HfC	[26, 27]	[34, 49, 50, 52]	[55]	—	—	[63]	[84]	[34]
HfN	—	—	[56]	—	—	[63]	—	—
TaC	[26, 27]	[34, 49, 50, 52]	[55]	—	—	[63]	[84]	[34]
TaN	—	[51]	[56]	—	—	[63]	—	—

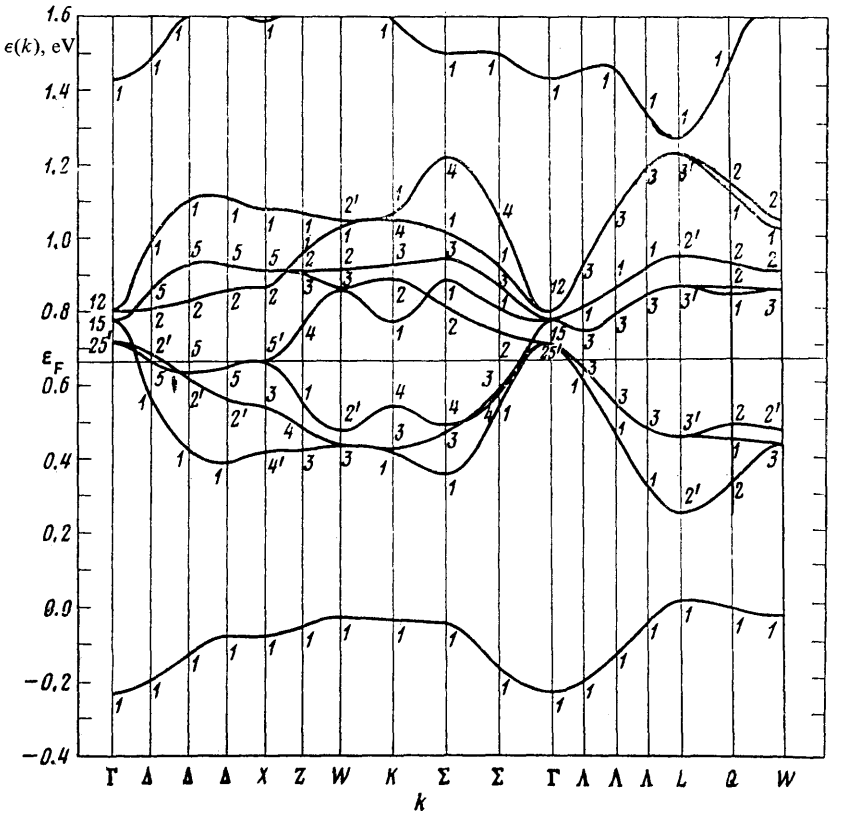


Figure 1. Band structure of titanium carbide (CPW calculation[36]).

The first calculation by Bilz[21] for TiC, TiN, and TiO by the strong bond method showed that the valence band of MX contains two sub-bands in which both M–X and M–M bonding can occur. However, the approximations used in that work[21] (such as the evaluation of two-centre integrals from data for the pure metals) led to some "averaging out" of the resulting band structure: this property was later put to use in the "quasi-rigid" band model, in which the general shape of the bands of the carbides, nitrides, and oxides of the *d* metals is assumed to be constant and only differences in the occupancy

of the energy bands (due to differences in the concentration of valence electrons between the different compounds) are considered.

Costa and Conte[22] confined their calculation for TiC to the *d* functions of the metal, which are split into t_{2g} and e_g components in the crystal field. They found that the M–M bond was stronger than in the pure metal, but their neglect of the Ti–C and C–C interactions makes this conclusion doubtful. This was pointed out by Lye and Logothetis[23], who evaluated the exchange integrals from spectroscopic data. In their band structure for TiC the e_g state of Ti was lower in energy than in the pure metal, giving a broad band of Ti–C interactions. This configuration of the bands should lead to high bond energies and to a melting point higher than that of titanium.

Conversely, in CPW calculations[24] for TiC, TiN, and TiO a transfer of charge in the opposite direction is obtained. The valence band is formed from the $2p(X)$ and the $3d$(Ti) states, and the Fermi level of TiC is found in a region of low density of electronic states $N(\varepsilon)$. As the atomic number z of the metalloid increases, the additional electrons populate the t_{2g} states in the metal, thus raising the level of ε_F. These results[24] were confirmed by an independent report[25] that charge (less than 1 electron) is transferred in the Ti → C direction.

Most of the calculations on binary MX phases were published during the 1970's and 1980's. Some special features of the EES of the IVa and Va carbides were established[26,27], but the $(n+1)p$ states of the metal were excluded from the basis without justification. Other workers[28–31] calculated the EES of TiC, ZrC, NbC, and NbN by an empirical pseudopotential method. The CPW method was used[32,33] to construct the band structure of Ti and V oxides, and also NbN. Ichara[34] calculated the EES for the monocarbides of the TM in sub-groups IVa and Va and obtained a density of states distribution in excellent agreement with the X-ray photoelectron spectra of the carbides.

The most accurate calculations in terms of band models for a wide range of MX binary compounds (M = Sc, Ti, V, Nb; X = C, N, O) by a self-consistent CPW method with an X_α exchange potential were reported by Neckel and coworkers[35–45].

The $\varepsilon(k)$ dispersion curves (Fig.1) calculated for titanium carbide by the SCF CPW method[36] show a valence band structure characteristic of this type of compound: a low-energy sub-band composed mainly of $2s$ (C) states and separated from the $3d$(Ti) and $2p$(C) mixed states by a gap of ~3 eV, followed by a sub-band of $3d$, $4s$ states of the metal and by a free $3d$, $4s$ band. The Fermi level lies in the overlap region of the p,d and d,s bands, which accounts for the metallic properties of these compounds.

The changes in the relative contributions from different states to the valence band in the carbide, nitride, and oxide series are shown in Fig.2 by the energy distribution of the partial densities of states $g_i(\varepsilon)$ for the MX compounds (M = Ti; X = C, N, O)[36]:

$$g(\varepsilon) = g_s^X(\varepsilon) + g_p^X(\varepsilon) + g_d^M(\varepsilon) .$$

Several problems in the methodology of applying local (cluster) models to the electronic properties of refractory compounds are discussed in Refs.58 and 59. It is stressed that the main features of the EES spectrum and the changes in the valence band in the carbide, nitride, and oxide series are accurately reflected by cluster calculations. Furthermore, the results from band and from cluster methods for the same level of approximation (CPW and X_α-SW) and using the same input parameters are not only qualitatively similar but they lead to quantitatively similar distributions of electrons in space and energy[59]. This confirms the validity of descriptions of the EES of high-melting compounds based on local models. The distribution of total charge density in MX crystals leads to the same conclusion: it can be inferred from X_α-DV calculations fro the $CTi_6C_{12}Ti_8$ cluster in titanium carbide[132] and from calculations for NbC and NbN by the pseudo-potential method[30].

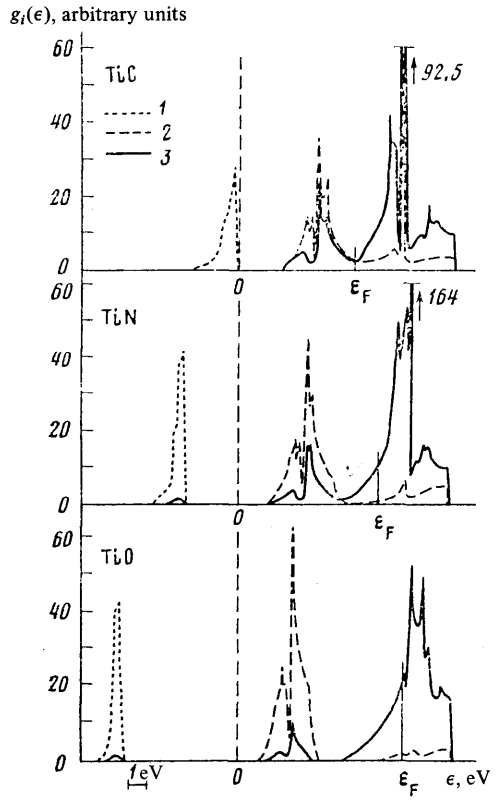


Figure 2. Partial densities of valency states[36] for TiX (X = C, N, O): *1*) and *2*) $2s$ and $2p$ states of X; *3*) $3d$ states of Ti.

The main features of the structure of the valence band and of the changes in this band for the series of binary compounds revealed by band[26–56] and by cluster calculations[57–71] can be summarised as follows.

1. The low-energy 2s(X) band, which includes small contributions from the *s*, *p*, and *d* states of the metal, is broadened and shifted towards higher energies in the transition from oxides to carbides and from sub-group IVa to sub-group Va metals. For the carbides and nitrides of Hf and Ta (whose oxides with a B1 structure are unstable) the $4f$ states are found to be core states and practically unaffected by chemical bonding[55,56,63].

2. The band mainly responsible for valence bonding is formed by the strong mixing of the $2p$(X) and d(M) functions. It rapidly widens on going from oxides to carbides, and less rapidly on replacing the IVa by a Va sub-group metal. The overall covalency is higher in the Va than in the IVa metal compounds, and increases with the atomic weight of the metal within each sub-group.

3. The high-energy partially filled conduction band is mainly of the nd(M) type with a small contribution from $2p$(X), $(n+1)p$(M) and $(n+1)s$(M) functions, and it widens very rapidly on going from the oxide to the carbide. This is accompanied by a downards shift of ε_F and by a decrease in the density of states at the Fermi level $N(\varepsilon_F)$.

The redistribution of the individual atomic states during the formation of interstitial phases causes partial charge transfer between metal and non-metal atoms and contributes an ionic component to the chemical bond.

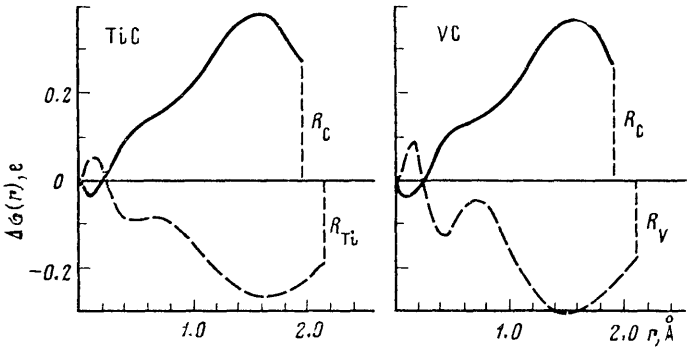


Figure 3. Difference between the crystal charge density (CPW) and the sum of the atomic charge densities in TiC and VC[36].

Strongly opposed views on the direction and magnitude of the charge transfer in MX compounds are held by different workers. Some[22,23] find that charge is transferred in the X → M direction. Others conclude from X-ray results[72,73] that the ionisation of the atoms in MX is very high (for example, almost +4 for Ti in TiC), and therefore they believe that the electrostatic energy is equivalent to ~90% of the cohesive energy of the crystal. However, the assertion[72,73] that the excess charges are strongly localised on the atoms is incompatible with most of the reported cluster and band calculations, with high-precision measurements by X-ray emission and photoelectron spectroscopy of the shifts in the internal levels for a wide range of carbides, nitrides, and oxides[36,37,53,54,57-70], and with the discussion in Section IV of this Review. Fig.3 shows the difference between the radial charge densities obtained in CPW calculations[36] for TiC and VC (σ_{cryst}) and as a superposition of the atomic densities (σ_{at}):

$$\Delta\sigma(r) = \sigma_{cryst}(r) - \sigma_{at}(r) .$$

In this case the excess of charge in the atomic spheres (i.e. the effective charge localisation on the atoms), given by

$$q^{eff} = Q_{cryst} - Q_{at} = \int_0^R \Delta\sigma(r)\,dr$$

is not large (~1e). There can be little doubt, at present, that charge transfer takes place in the M → X direction. The quantity q^{eff} increases slightly in the carbide, nitride, oxide sequence (see Table 2), thus increasing the coulombic contribution to the bond, but it remains much lower than the values postulated in the ionic model (+2, +3, and +4 for the metal in MO, MN, and Mc respectively).

By examining the atomic and the orbital composition of each type of state in the different energy ranges of the spectrum[35-37,57,59,63,64,69-71] it has been possible to identify the individual interatomic interactions and their relative contributions to the combined covalent-metallic-ionic bond found in high-melting phases. The crystal field causes splitting of the d(M) states, which become doubly (eg) or triply degenerate (t_{2g}). The t_{2g} states lying near ε_F are responsible for the M-M bond, and they are largely delocalised though they retain some thickening of the electron density in the M-M direction, characteristic of bonding interactions[62,63]. However, the system is diffuse and the M-M interaction is weak. The main chemical bonding effects are due to the strong interaction of the nd(M) and $2p$(X) functions, which forms interatomic bonds of σ and π type giving a three-dimensional network of orbitals with $eg(d_{x^2-y^2}, z^2)$ and $t_{2g}(d_{xy}, yz, xz)$ symmetry. As a result, the high-melting compounds are largely covalent, with a small ionic component in the bond.

Table 2. Orbital occupancies and charges (q^{eff}) on the metal atoms in the carbides, nitrides, and oxides of Ti, V, Zr, and Nb,[69-71]

Compound	$3d_\sigma$	$3d_\pi$	$3d$	q^{eff}	Compound	$4d_\sigma$	$4d_\pi$	$4d$	q^{eff}
TiC	0.85	0.44	2.97	0.50	ZrC	0.70	0.49	2.77	0.23
TiN	0.53	0.62	2.93	0.64	ZrN	0.42	0.71	2.89	0.42
TiO	0.31	0.79	3.02	0.78	«ZrO»	0.26	0.80	2.91	0.59
VC	0.97	0.70	4.05	0.39	NbC	0.78	0.79	3.95	0.24
VN	0.61	0.90	3.91	0.54	NbN	0.51	0.95	3.88	0.40
VO	0.35	1.05	3.96	0.67	NbO	0.34	1.14	4.10	0.54

The proportion of σ bonding is highest in titanium carbide, though the population of the π orbitals is double that of the σ orbitals. A marked redistribution of the occupancies of the t_{2g} and eg orbitals occurs in the carbide-nitride-oxide series, accompanied by a weakening of the σ bond (see Table 2). This results in destabilisation of the oxide lattice, making these compounds less refractory and less hard than the carbides[60,67,69-71].

These properties of the EES and of the charge distributions have been used to interpret X-ray emission[34,39,44,58-71] and photoelectron spectra[34,40,58-64,66,71] and appearance potential spectra[40], and also in studies of magnetic susceptibility[76], superconducting transition temperature[43], electronic specific heat[121,122], Hall coefficient[120], and Compton scatter profiles[74] for outlining the Fermi surface[34,75].

We should stress that all these calculations were for ideal, stoichiometric compounds, and in many cases (TiO, VO, VC, "ZrO") they were only model calculations.

IV. X-RAY EMISSION AND PHOTOELECTRON SPECTRA OF MX COMPOUNDS

Before attempting to describe the special features of the electronic spectrum of non-stoichiometric compounds we shall discuss the relationship between existing calculations for stoichiometric MX compounds and experimental data.

The experimental methods offering the most direct information on the distribution of electronic states over the whole depth of the valence band and on the energetics of the core levels are the spectroscopic X-ray photoelectron (XPS) and

X-ray emission spectroscopy (XE) methods. Spectral studies of most of the high-melting compounds discussed in this review have been reported (see Table 1). However, the extensive literature which has accumulated on this topic is literally "choked" with erroneous results: Zhurakovskii's recent monograph[126] is no exception. We shall not attempt to account fully for the inconsistencies in the experimental data, though the following general comments on the experimental problems of XE and XPS measurements on transition metal compounds may be helpful. On the one hand, errors in the calibration of the apparatus must lead to errors in the comparison of spectra from different series of components, and on the other hand errors can arise from differences in the surface layers of the samples electrically excited in the X-ray spectrometer.

Table 3. Bibliography of quantum-chemical calculations and X-ray emission and photoelectron spectroscopy work on non-stoichiometric compounds of the *d* metals.

MX_x	Band calculations		Cluster calculations		XE spectra	XPS spectra
	VC-CPW	CP	X_α	semi-empirical		
TiC_x	—	[124, 128]	[132]	[117, 129, 130, 136]	[129, 136, 137, 158]	[130, 138, 139, 147]
TiN_x	—	[125]	—	[129]	[142, 158]	[106]
TiO_x	[120]	[128]	—	[129, 131]	[85, 129, 131, 142, 143]	[99, 149]
VC_x	[34, 121, 122]	[127]	—	[129]	[85, 145]	[34, 147, 150]
VN_x	—	—	[134]	[129]	[144, 145]	[106]
VO_x	—	—	—	[129]	[85]	—
NbC_x	—	[127]	[133, 134]	[129, 135]	[87, 88, 146]	[98, 147, 148]
NbN_x	—	—	—	[129]	[145, 146]	[148, 159]
ZrC_x	[34]	—	—	[129]	—	[34]
HfC_x	—	[127]	—	[117]	—	—
TaC_x	[34]	—	—	—	—	[34]

The experimental results quoted in Tables 1–3 are those which we consider most relevant and useful to the present discussion. Interested readers wishing to examine the topic in more detail are referred to Zhurakovskii's monograph[126], which gives a full discussion of this type of work in the Soviet Union and abroad.

Measurements of the X-ray photoelectron spectra yield information on the density distribution of occupied electronic states over a wide range of energies[102] to the precision of the difference in photo-ionisation cross-section of the electronic sub-shells. The XPS spectra of the following compounds have been studied: TiC,[34,89,91–93] TiN,[92,94,95] VC,[34,90] ZrC,[34] NbC,[34,89,97] NbN,[97] NbO,[96] and HfC and TaC.[34] A series of XPS spectra for the valence band of *d* metal carbides has been obtained[34], and their parameters have been compared with CPW band calculations (Fig.4). Since the elements of the matrix which describes the transition probabilities in this energy region were assumed to be constant, the integral energy distribution of photoelectron intensity was compared directly with the calculated state densities. The relative intensity of peak II was found to increase in the TiC, ZrC, HfC series (Fig.4), and this was ascribed to the increase in the scattering cross-section of *d* electrons in the sequence 3*d*(Ti), 4*d*(Zr), 5*d*(Hf), since these electrons provide the main contribution to this part of the spectrum. Calculations based on the ionisation cross-sections of the sub-cells (after Scofield[103]) gave good agreement with experiment.

In the carbides of sub-group Va metals in the high-energy region we find a clear "outcrop" associated with the appearance of an additional *d* electron, and the relative intensity of peaks I and II increases with the atomic number of the metal (as in the carbides of sub-group IVa transition metals). Some of the difference between the theoretical and the experimental XPS spectrum of VC is due to the fact that stoichiometry was assumed in the calculation.

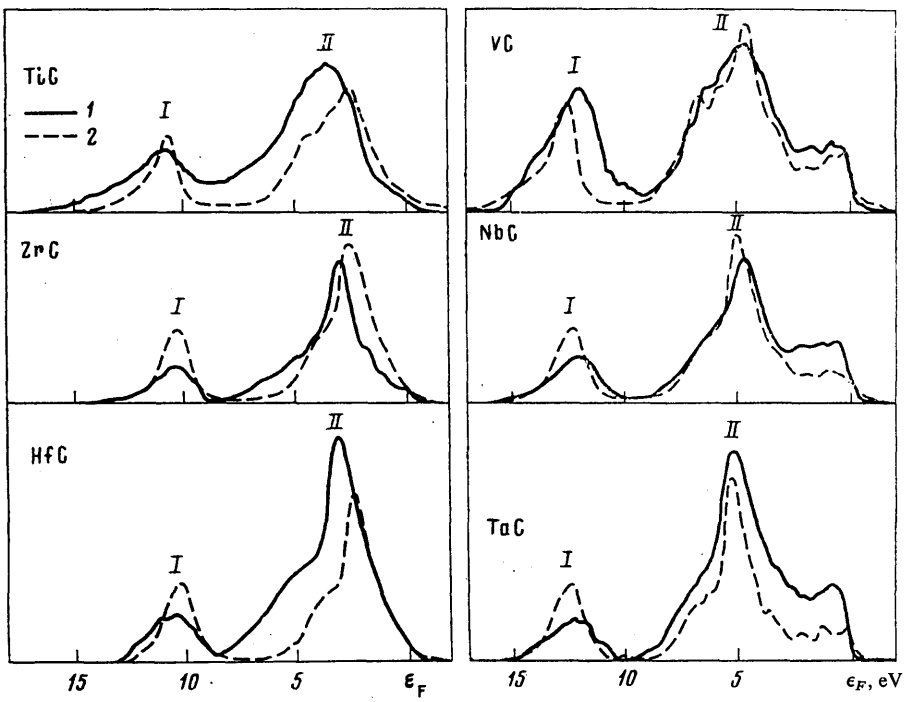


Figure 4. Experimental (*1*) and theoretical (*2*) XPS spectra of the carbides of transition metals in sub-groups IVa and Va.[34]

The relative advantages of band and cluster models for describing the XPS spectra have been discussed[58] in the case of TiC and VC. In the cluster approximation the spectrum was constructed by using the Gelius scheme[104], in which the intensities of the individual peaks (I_j) are defined in terms of the atomic photo-ionisation cross-sections σ_i:

$$I_j \sim \sum_i C_{ij}^2 \sigma_i ,$$

where C_{ij} are the coefficients of the MO in the LCAO expansion of the wave function. It was shown that the shape of the spectra for this class of compounds can be reproduced as accurately by the cluster approach as by band calculations if the bands are reasonably well localised.

As well as giving information on the structure of the valence band the XPS method can be used to measure the shifts in the core electron energy levels produced by the formation of mixed states in condensed phases, and it is an effective analytical technique for determining both the character of the chemical bond and the extent of charge transfer between the atoms[102].

Table 4 shows the changes in the energy ΔE of the inner levels of the carbides of the transition metals and the charges on the atoms (q^{eff}) calculated from data by Ramqvist[105] and Ichara[34]. We note that in all the carbides the shifts of the carbon levels are negative, and those of the metal levels are positive (relative to the energies of the corresponding levels in the neutral atoms). Thus a partial negative charge develops on the metalloid, and a partial positive charge on the metal. The discrepancy between the q^{eff} values obtained from data in Refs.34 and 105 is probably due to differences in surface preparation techniques in the two laboratories: in less carefully lapped surfaces[105] we expect a tendency for ΔE to increase.

Measurements[106] of the shifts of the 1s(N) and 2p(M) levels in the ScN, CrN, TiN, and VN series showed that in the nitrides also a small positive charge is localised on the metal atom, increasing from ScN to VN.

Table 4. Changes in the energies of core levels (ΔE, eV [105]) and in the ionic charges in TM carbides (q^{eff}). [34]

Carbide	$-\Delta E_C$	ΔE_M^*	q_M^{eff} (Ref.105)	$-q_C$	q_M	$\langle \lvert q_{C,M} \rvert \rangle^{**}$
TiC	3.3	1.3	0.40	0.25	0.13	0.19
ZrC	3.7	—	0.45	0.27	0.08	0.17
HfC	4.0	—	0.48	0.26	0.04	0.15
VC	2.6	1.8	0.32	0.15	0.17	0.16
NbC	2.9	1.2	0.35	0.17	0.24	0.20
TaC	2.9	1.6	0.35	0.16	0.27	0.22

*The ΔE_M values for $2p_{3/2}$(Ti), $2p_{3/2}$(V), $3d_{3/2}$(Nb), and $4f_{7/2}$(Ta) are given.

** Mean of the absolute values of q_C and q_M.

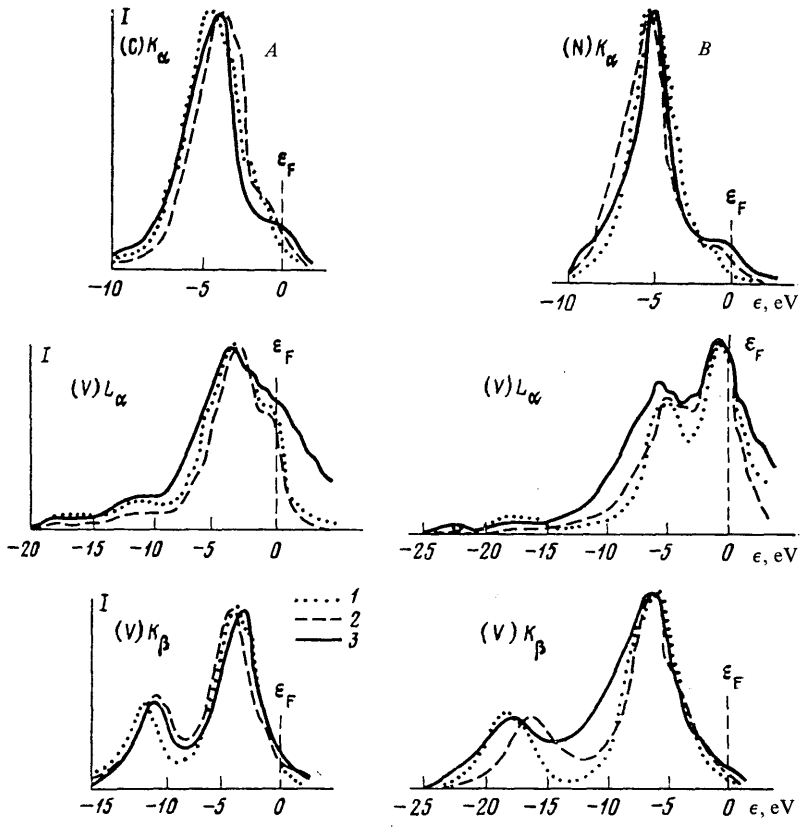


Figure 5. X-Ray emission spectra of VC (*A*) and VN (*B*): *1*) X_α-SW calculations, *2*) CPW calculations, *3*) experiment[59].

Direct calculations of the energy levels of the core electrons have been made by non-empirical X_α-SW and X_α-DV methods in a full basis for TiC, VO, and TiO.[107,108]. Allowance for relaxation effects (rearrangement of the electron shells under the influence of holes on the inner and valency levels) was made in Slater's transition state scheme[109]. Comparison of these results with the MO diagrams given by "unrelaxed" calculations shows that the valency states are almost unaffected, and that the uncorrected values can be used to calculate the energies of emission transitions. Relaxation effects become predominant for the inner levels, and by allowing for these effects we can calculate the absolute energies of the core levels in good agreement with XPS data.

More detailed information on the electronic energy spectra of high-melting compounds, including the configuration of the partial states of the individual components, can be obtained by the X-ray emission spectroscopy method[110]. Although the X-ray emission *K*, *L*, and *M* spectra of high-melting compounds have been observed by many workers (see Ref.10) their correct interpretation had to await the development of band calculations for TiC, TiN, and TiO,[24] and the identification of the long-wave satellites in the spectra of carbon, nitrogen, and oxygen compounds[81,111]. Even more exact interpretation of the XE spectra was made possible by cluster calculations[66,69,70].

In Fig.5 we show as an example the (C)$K\alpha$, (N)$K\alpha$, (V)L_{III}, and (V)$K\beta_5\beta''$ spectra of VC and VN [39] corresponding to the emitting transition $2p \rightarrow 1s$ (for C and N) and $3d, 4s \rightarrow 2p$ and $4p \rightarrow 1s$ (for V). By presenting these results on a unified energy scale with allowance for the different binding energies of the core electrons we find that a strong $2p$(X)–d(M) interaction occurs in all the compounds. The change from VC to VN affects most strongly the (V)L_{III} band: a high-energy element of structure is split off and produces a strong band, indicating an increased electron concentration in the nitride, with occupancy of the higher orbitals. In the (V)$K\beta_5\beta''$ spectrum of VN the $K\beta_5$ and $K\beta''$ sub-bands are significantly shifted towards longer waves, due to the decrease in the energy of the $2p$(N) and $2s$(N) states [as compared to the energy of the $2p$(C) and $2s$(C) states].

Correlations between the results of calculations by band methods and XE spectroscopy data are usually made in terms of the partial density of states $g(\varepsilon)$. The radial probabilities of emitting transitions have also been included in some calculations[39,44,112] of the intensities of XE spectra. The XE spectra calculated in this way for VC and VN by the X_α SW and CPW methods are shown in Fig.5. We note that (as in the XPS spectra) the main features of the XE spectra are satisfactorily described by small cluster calculations (both the position in energy of the maxima and their relative intensities), in full agreement with the results of CPW calculations[59].

The theoretical formulations[59–64,69–71] of the XE spectra of the carbides, nitrides, and oxides of Ti, V, Zr, Nb, Hf, and Ta allow a full interpretation of experimental data as well as the prediction of as yet unreported lines.

Thus the extensive applications of results from theoretical calculations and from spectroscopic investigations has yielded meaningful information on the EES and on the chemical interactions of high-melting compounds. As we shall show below, this approach has been successfully applied in studies of the rearrangement in space and energy of the electronic states caused by the appearance of structure defects.

V. ELECTRONIC STRUCTURE OF THE NON-STOICHIOMETRIC CARBIDES, NITRIDES, AND OXIDES OF THE *d* METALS

The marked effect of lattice vacancies on all the physicochemical properties of refractory compounds is well known[3–10]. Attempts to relate the observed dependences (of the property–defect density type) to changes in the electronic spectra led to the development of a number of qualitative models of the band structure in non-stoichiometric compounds, and stimulated some numerical calculations.

1. Phenomenological Models

The first attempt to allow for the effect of a variable concentration of vacancies on the EES of MX_x compounds relied on the rigid band model. It was assumed that the perturbation introduced by a vacancy into the crystal is generalised and does not affect the shape of the $N(\varepsilon)$ curve: only the occupancies are affected, depending on the concentration of valence electrons. By applying this postulate to calculations for stoichiometric TiC it was found[23] that an increase in the concentration of non-metal vacancies ($N_\square$) in the TiC_x compounds shifts the Fermi level towards the low-energy side of the spectrum, passing through a value (at the composition $TiC_{0.5}$) corrresponding to a maximum density of states in the bonding p–d band. We note that this conclusion is in sharp contrast with more recent XE [129,136,137,158] and XPS results [130,138,139], all of which imply a shift of ε_F in the opposite direction.

By using the same model Denker[113] explained the high equilibrium concentrations of vacancies in TiO_x in terms of the general decrease in the concentration of valence electrons (as compared to the stoichiometric composition), leading to a decrease in ε_F and in the total energy of the system and therefore to stabilisation of the structure. However, the neglect of the individual features of the band structure in particular compounds leads to the (generally incorrect) conclusion that any compound must be stabilised by the addition of vacancies.

Conversely, in the valence electron model[114] the defect is treated as a local perturbation of the electronic states in the crystal. When a non-metal atom is removed from an octahedral hole in the metallic matrix some of the previously screened M–M bonds become unscreened and can pass through the centre of the vacancy, and the d electrons set free by the breaking of the M–X bonds are accommodated in the high-energy local levels associated with the vacancy. As $N_\square$ increases, the local levels merge into a band: the result for the monocarbides of the IVa transition metals is a linear increase in ε_F, whereas for the monocarbides of metals in the Va sub-group a more complex dependence is obtained. Many changes in the kinetic and magnetic properties of monocarbides in their homogeneity region have been explained successfully by using this model[115].

Ichara's model[34], which is closely related to this theory[114], treats the EES of defect carbides as a superposition of the densities of states for the stoichiometric compound and for a hypothetic metal (with a face-centred cubic lattice) which forms clusters in the carbide structure by the conversion of carbon sites into carbon vacancies. The presence of strong M–M bonds in this case should lead to a stable value of ε_F.

Whereas the charge on the vacancy is not specified in the above models, Goodenough[116] proposed a model in which the vacancy carries a high charge (–2 for TiO_x) to compensate for the decrease in the Madelung energy in defect crystals, thus causing energy stabilisation of a substantial concentration of vacancies at equilibrium.

In the configurational electron localisation model[9] the main parameter used to define the electronic properties of the system is the statistical weight of an atom with stable configurations (SWASC), which is a measure of the deviation of the electronic configurations of the atoms in a stated compound

from the most stable configurations (i.e. free, half-filled, and completely filled). For the non-metal atoms in these compounds the stability of the bond is determined by the quasi-stable sp^3 configuration, whereas for the transition metals the maximum bond stabilisation corresponds to the d^5 configuration. The changes in the relative contributions of the various atomic states to the M–M and M–X bonds resulting from deviations from the stoichiometric composition are determined, according to this model, by the SWASC sp^3 and d^5. For example, for the compositions $TiC_{1.0}$ and $TiC_{0.67}$ semi-empirical estimates of these parameters give[117] 40.13 and 39.50% (SWASC sp^3) and 36 and 52% (SWASC d^5) respectively, indicating a weakening of the contribution from the p states to the strongest M–X bonds and a slight increase in strength of the M–M interactions in the defect carbides. These conclusions are qualitatively consistent with the development of metallic properties (increase in magnetic susceptibility, in low-temperature electronic specific heat, and in electrical conductivity) and with the decrease in micro-hardness and in T_f in carbides with a carbon deficit.

These phenomenological models of the electronic structure of non-stoichiometric phases offer a qualitative description of some of the experimentally observed variations in the physicochemical properties of MX compounds in their homogeneity region, but they cannot of course give any quantitative measure of the changes in the EES in space and energy: the parameters used in these models (such as the SWASC and the concentration of valence electrons) lend themselves only to the roughest qualitative estimates. Therefore the further development and quantification of our understanding of the nature of the chemical bond, of the interatomic interactions, and of the EES in these materials had to await the publication of correct quantumchemical calculations for individual compounds.

2. Calculations Using Band Models

Several calculations in which band methods are applied to non-stoichiometric compounds have been published (see Table 3). The first numerical calculation[119] by the strong bond method for TiC_x ($x = 1.0$, 0.8, 0.6) with explicit allowance for the presence of vacancies gave a Fermi level ε_F increasing with the concentration of defects in the non-metal sub-lattice. The next group of calculations for TiO_x,[120] VC_x, ZrC_x, and HfC_x,[34,121,122] relied on the virtual crystal approximation (*VC*-CPW), proposed by Schoen[123]. In this method allowance for the presence of vacancies was made by introducing functions of the concentration of vacancies into the expressions for the potential and for the matrix elements. The result was that the insertion of vacancies (whether in the metal or in the non-metal sub-lattice) does not produce new valency states which could be interpreted as vacancy levels[114] in any of the compounds examined. In a calculation[120] of the energy of formation of vacancies in TiO_x the difference between the bottom of the conduction band (which is fixed for all compositions) and ε_F was used as an average value of the energy for different compositions. This makes an oxide containing ~15% of vacancies in each sub-lattice the most stable composition[120]. It was also found[34] that as the concentration of X decreases, the energy of bands of the $2s$(X) and $2p$(X) type increases, but that of the d(M) type is relatively unaffected; the level ε_F decreases.

We should stress that these results were not confirmed by XPS measurements[34]: no significant shifts of the main spectral peaks were found, and an increase in the density of high-energy d states was noted. This inconsistency is due mainly to the use of ideal crystal potentials in the *VC*-CPW calculations for non-stoichiometric compounds[34,120–122], which is legitimate only for very low concentrations of vacancies.

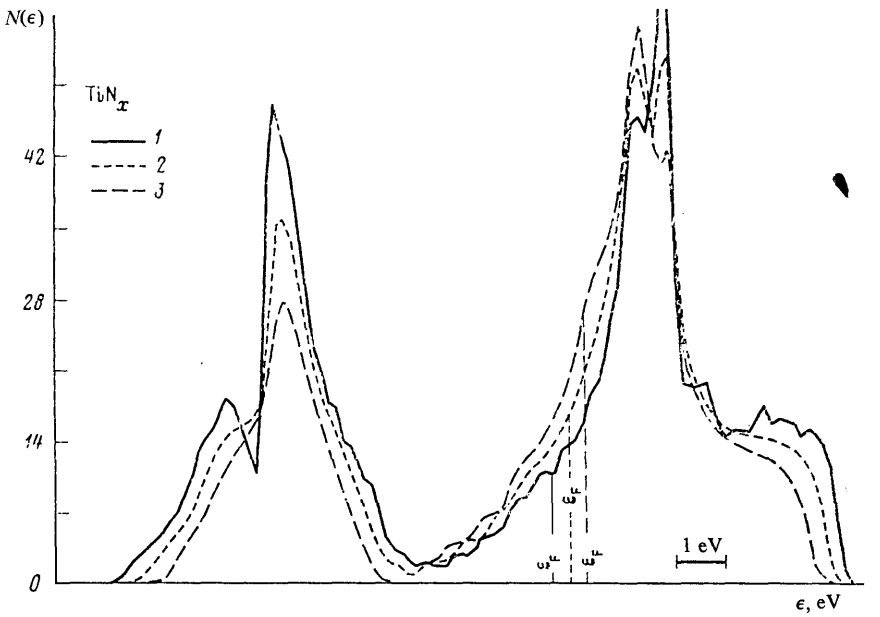


Figure 6. Full density of states in TiN_x; CP calculation[125] for $x = 0.0$ (*1*), 0.2 (*2*), and 0.4 (*3*).

This condition is not met in our case.

Calculations on TiC_x [124] and TiN_x [125] by the coherent potential (CP) method appear to be more reliable. In this work[124,125] the 2*s* states of C and N were excluded from the basis and assigned to the core states. An increase in $N_\square$ caused an increase in ε_F and a slight distortion of the energy dependence of the density of states (Fig.6). This is because an increase in $N_\square$ in TiC_x lowers the total number of carbon atoms in the *p* state, since $Np = 6-6_x$, whereas the number of expelled *p* electrons is $Npe = 2-2_x$. Under these conditions the Fermi level rises, and reaches the region of high density of states of the t_{2g} type. As a result $N(\varepsilon_F)$ also rises, as it does in the rigid band model, but for an entirely different reason, since in the rigid band model ε_F decreases, and the main contribution to $N(\varepsilon_F)$ comes from the e_g states.

Later calculations by the LCAO-CP method for NbC_x, TaC_x, and HfC_x ($0.7 \leq x \leq 1$) showed[127] that the spectra of sub-stoichiometric compounds do not contain any new structures identifiable as defect (vacancy) levels: the main effect is a small change in electron density $N(\varepsilon)$ as compared with the stoichiometric compounds, and the position in energy of the main $N(\varepsilon)$ spectral peaks stays almost constant, in contrast to earlier calculations[34,120-122]. In all the carbides ε_F moves upwards, the effect being most marked in HfC_x: $\Delta\varepsilon_F$ is 2.53 eV for $HfC_{0.7}$ as compared to 0.87 eV for $TaC_{0.7}$ and 0.72 eV for $NbC_{0.7}$. This is explained[127] in terms of the charge distributions in the carbides. In stoichiometric compositions a charge transfer of ~1*e* takes place in the M → C direction. Hence the removal of one C atom frees ~5 states, but only 4 electrons leave the crystal, so that 1 electron is transferred back to the metal and occupies its *d* band.

The parameters of the electronic structure of non-stoichiometric MX compounds calculated in this way[128] were used to calculate the energy of formation of defects in TiC and TiO. The formation of vacancies is due to the following common factors: 1) a change in the average energy of the bands, 2) the width of the band, 3) the creation of new levels of the defect type, 4) the position of the Fermi energy. A hypothetical binary compound AB was considered, with a band structure consisting of two bands (separated by an energy gap) corresponding to the states of the A and B components. It was shown[128] that the formation of vacancies in the sublattice of the atoms with lower electronic state energies can produce new (defect) levels with energies below ε_F, so that the total energy of the system is lowered by the transition of electrons to these new levels. This stabilising effect of the defect levels becomes more marked when ε_F rises as a result of an increase in $N_\square$. Under thse conditions the total

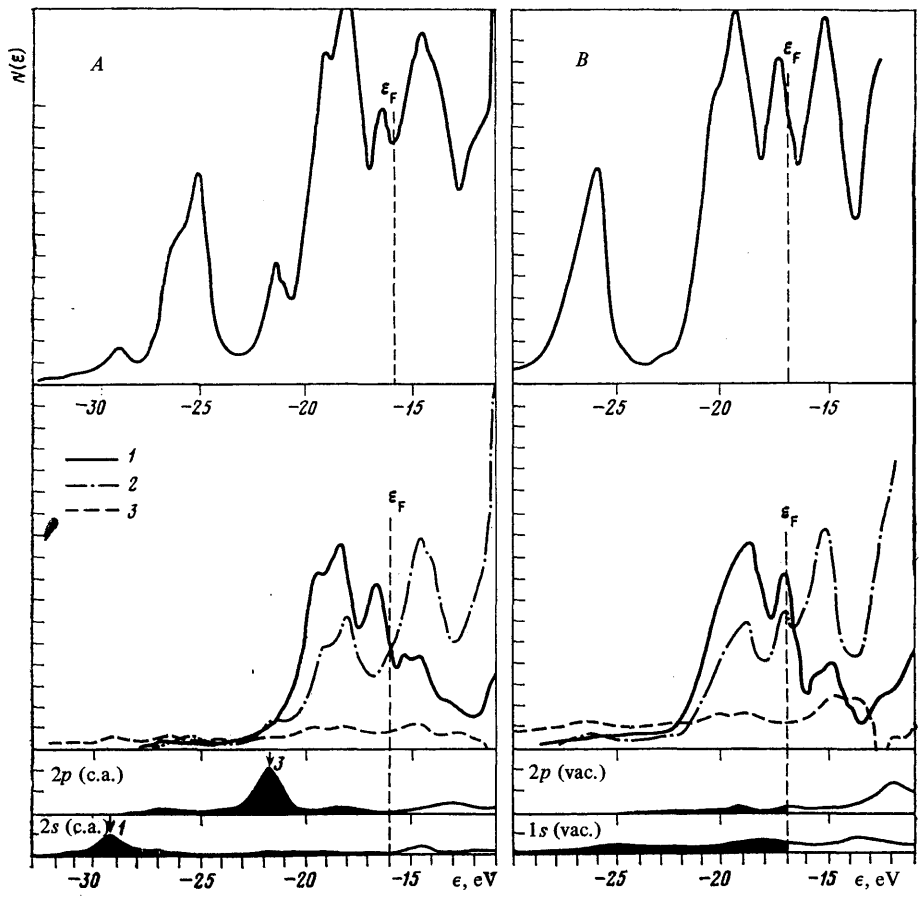


Figure 7. Full and partial densities of states in the stoichiometric cluster $CTi_6C_{12}Ti_8$ (*A*) and the defect cluster $\square Ti_6C_{12}Ti_8$ (*B*) used to model titanium carbide (X_α-DV method of calculation[132]): *1*) 2*p*(C), *2*) 3*d*(Ti), *3*) 4*s* + 4*p*(Ti). The lower outlines show the distribution of *s* and *p* states of the carbon central atom (c.a.) and of the vacancy (vac.).

energy of the system may go through a minimum at a certain concentration of vacancies, corresponding to the equilibrium concentration of defects. A calculation for TiC_x and TiO_x (by the Korringa–Kohn–Rostoker method in the averaged T matrix approximation) gave 0.0 ± 1.4 eV and 14 ± 1.4 eV respectively for the energies of formation of vacancies in TiC and TiO. Vacancy states lying below the Fermi level were found in the oxide but not in the carbide.

From the band calculations for MX_x compounds listed above[34,120–122,124,125,127,128] we may conclude that the general changes in band energetics and structure and in the position of the Fermi level are adequately described by this approach. However, problems concerning the rearrangement of the chemical bond in defect compounds and the nature of the vacancy states are largely unresolved. The solution of this type of problem, which basically arises from local changes in the electronic states close to a vacancy, was obtained by adopting cluster models.

3. Calculations by the Cluster Model

Several systematic calculations of the EES of carbides, nitrides, and lower oxides of the 3*d* and 4*d* metals (containing non-metal defects) by a semi-empirical SCF MO LCAO method in the cluster approximation have been reported[71, 129–131,136]. The vacancy was modelled by removing an X atom from the $[MX_6]$ fragment considered in the calculation (uncharged vacancy). As $N_\square$ was increased, the bands of $2s$(X) and $2p$(X) states became systematically narrower. The appearance of a vacancy is reflected most clearly by changes in the state of metal atoms in the immediate surroundings, since some of the *d* electrons genetically bound to these atoms are promoted to higher-energy levels, causing a sharp increase in the Fermi energy for compounds of metals in subgroup IVa. In compounds of the Va transition metals the shift of the Fermi level is much smaller.

The most important changes in the density of states take place near ε_F, because of the interaction[130,131] between nd and $(n+1)p$ orbitals of M in defect compounds. The occupancies also change, due to the increase in the charge of the cluster in the variable valency model. This model[129,136] assumes that the condition of overall electrical neutrality of the crystal can be applied to compounds of non-stoichiometric composition: $\sum_i x_i I_i = 0$, where x_i is degree of filling of the i-th sub-lattice, and I_i is the valency (state of charge) of its atoms. However, since (in TiC_x, for example) the carbon atoms keep the same surroundings, the valency of Ti should be lower in the non-stoichiometric than in the stoichiometric carbide in order to preserve the charge balance, and as a result the cluster containing vacancies acquires a partial negative charge. In this analysis the valency of the C atom is assumed constant, in keeping with the observed stability[139] of the $1s$(C) energy level in TiC_x.

This model was tested by comparing cluster calculations for sub-stoichiometric titanium carbides with the X-ray emission spectra[136]. Two variants of the calculation were described: for constant and for variable valency of the titanium respectively. In the latter case we observe the filling of the next higher metal d orbitals in the non-stoichiometric carbide, corresponding to the short-wave "outcrops" on the (Ti)L_α and (Ti)$K_{\beta 5 \beta''}$ bands of the emission spectrum of the $TiC_{0.65}$ sample. If constant valency of the Ti is assumed this effect is not found. The electronic energy spectra of NbC_x [133,134] and VN_x [134] compounds with non-metal defects have been studied by the X_α-SW method. The metalloid vacancy was modelled by an empty ("muffintin") sphere. The addition of a vacancy was found to raise the Fermi level by a small amount (~0.19 eV for NbC_x [133]). The changes in partial state densities arise from a slight redistribution of the states for the atoms adjacent to the vacancy and do not affect the more remote atoms, indicating a high level of localisation of the perturbations in the electronic distribution caused by individual vacancies. The rearrangement of the *d* states of the metal atoms nearest to the vacancies results in the appearance of a small charge in the sphere of the vacancy (0.7–0.8e), in contrast to the suggestion[116] that defects are highly charged. A new energy level, lying ~1.5 eV below ε_F, appears in the spectrum of occupied states.

The electronic nature of the vacancy in TiC_x has also been studied[132] by the non-empirical X_α-DV method. The calculation was carried out for a cluster of 27 atoms, using the pseudopotential from 96 external atoms as the boundary condition. Purely vacancy states were included in the basis in the form of 1s and 2p functions centred on the defect. These "vacancy" functions make a very small contribution to the filled band in the general spectrum of states (see Fig.7); since they are localised in the conduction band their perturbation is confined mainly to the spectrum of antibonding states. The change in structure of the states near the Fermi level following the introduction of a carbon vacancy has been ascribed[129–134] to the redistribution of the *d* states of the nearest metal atoms. Therefore the vacancy functions are localised (in space) within the first co-ordination sphere, and in energy well above ε_F (by 8–10 eV), and the presence of carbon vacancies does not produce any new occupied localised states.

As regards the charge on the vacancy, the additional electrons from the "broken" bonds are not captures by the vacancy (as shown by comparing the total charge density diagrams[132] for the integral and the defective cluster), and they fall into the 3*d* band of the metal instead. Similar conclusions are reached in calculations for clusters modelling vacancies in the metal sub-lattice[132]. Thus, since there is no marked localisation of the electrons on vacancies, the hypothesis of a continuously varying metal valency[129,130,136] in response to changes in the population of the 3*d* states caused by the formation of defects is confirmed.

We conclude that strict, non-empirical X_α-DV calculations have demonstrated the value of modelling the electronic structure of non-stoichiometric transition metal phases by extracting the appropriate atom from the fragment used in the calculation. They have also confirmed some earlier conclusions (see above) for other MX_x compounds which had been reached by semi-empirical MO LCAO methods[71,129–131,136].

VI. CALCULATION OF THE ELECTRONIC STRUCTURE OF NON-STOICHIOMETRIC COMPOUNDS FROM X-RAY EMISSION AND PHOTOELECTRON SPECTRA

For a long time the main problem in the study of non-stoichiometric MX_x compounds by XPS methods was the synthesis of sufficiently large single crystals (especially for studies of the valence bands). Therefore the early XPS measurements on non-stoichiometric compounds were limited to the effects produced by changes in the binding energy of the core levels [140,147]. XPS measurements of the valence bands became possible after the recent advances in the preparation of single crystals [which are so far limited to a few compounds, however (see Table 3)]. It was recently shown that almost metallic surfaces can be obtained by using hot-pressed samples of non-stoichiometric compounds[34,150], and that valence band studies by XPS are possible on these surfaces.

Let us examine the results of studies of MX_x compounds by XPS methods. Varying the composition of ZrC_x and TaC_x ($0.6 \leq x \leq 1.0$) did not produce substantial changes in the shape of the spectra[34]. Only some slight changes in the energy and width of peak II were noted (see Fig.8), together with a slight increase in the intensity of the "outcrop" on the short wavelength side of this peak, suggesting an increase in the occupancy of the t_{2g} band with decrease in the carbon content. We have already pointed out that this observation is inconsistent with the conclusions from VC-CPW calculations[34]. Conversely, by using the more strict CP method, changes in shape of the XPS peaks of NbC_x, HfC_x, and TaC_x consistent with experiment could be calculated[127]: in all these compounds an increase in $N_\square$ was found to produce a slight shift of the bands and a substantial increase in the sub-band close to ε_F (Fig.9).

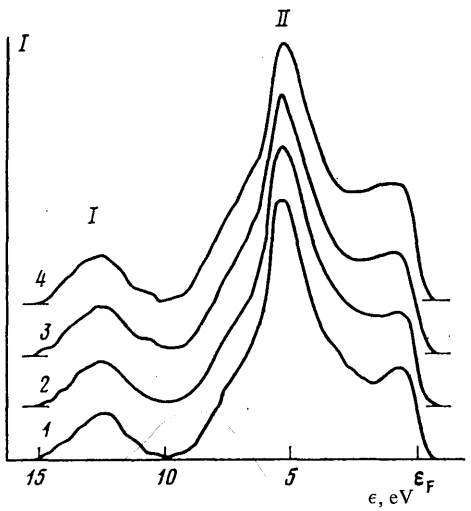


Figure 8. XPS peaks for the valence band of non-stoichiometric TaC_x [34] with the following x values: *1*) 1.0, *2*) 0.95, *3*) 0.9, *4*) 0.8.

A comparison[98] of the line shapes for $NbC_{0.98}$ and $NbC_{0.85}$ revealed a distinct new peak in the latter, located ~1.9 eV below ε_F, which was ascribed to the development of some p-type charge density localised in the sphere of the C vacancies[133].

The influence of variations in the number of defects on the XPS curve of TiC_x was studied by Johansson and coworkers[138,139]. They found that the half-width of the main peak, which reflects the range of p–d bonding, increases with $N_\square$. This effect was explained by MO (cluster) calculations[130] as an increased contribution from 3*d* electrons to the high-energy part of the filled band. Though this conclusion was confirmed by a special study[136] of the (Ti)L_α band in the X-ray emission spectra of carbon-deficient samples of TiC_x, the shape and the broadening of the reported XPS bands[138] need to be redetermined because the samples used in those measurements were contaminated with W which could have distorted the spectra because of its high 5*d*(W) electron photo-ionisation cross-section.

Table 5. Binding energy (ΔE) and chemical shifts (δ) of the core levels $3d_{5/2}$(Zr) and $4f_{7/2}$(Ta) in ZrC_x and TaC_x.[34]

ZrC_x			TaC_x		
1.0	179.3	0.4	1.0*	23.7	1.9
0.9	179.3	0.4	0.95	23.6	1.8
0.8	179.1	0.2	0.9	23.6	1.8
0.6	178.9	0.0	0.8	23.3	1.5
			0.7	23.3	1.5
			0.6	22.9	1.1

*For the 1s(C) level in TaC_x we have $\Delta E = 283.0$ eV and $\delta = -2.2$ eV; for the other levels 283.1 and −2.1 respectively. In the case of ZrC_x we have $\Delta E = 281.7$ eV and $\delta = -3.6$ eV for the 1s(C) state at all the values of x used in the work.

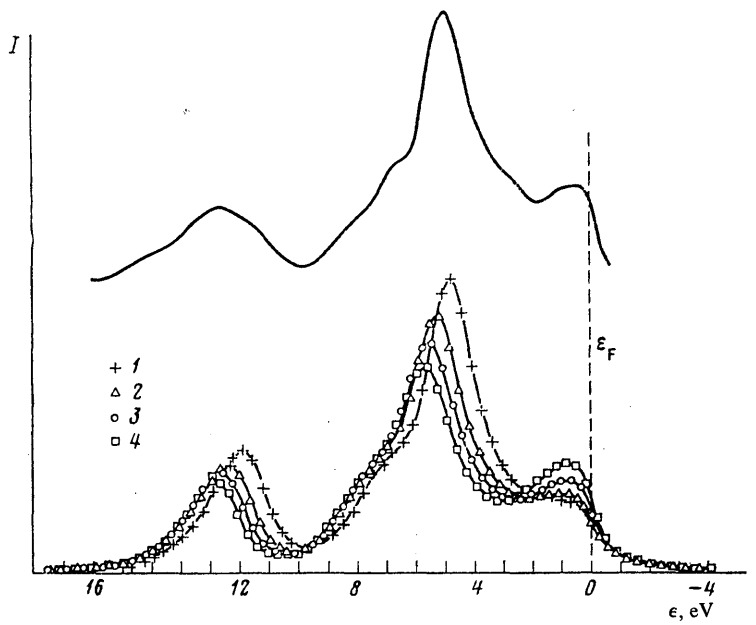


Figure 9. XPS spectra of TaC_x calculated[127] for x values of: *1*) 1.0, *2*) 0.9, *3*) 0.8, *4*) 0.7.

The photoelectron spectra of TiO_x [$x = 0.93$ or 1.15 (Ref.149), and $0.84 \leqslant x \leqslant 1.22$ (Ref.99)] showed a decrease in the intensity of the high-energy peak, which reflects mainly the 3d(Ti) states, with increasing oxygen content.

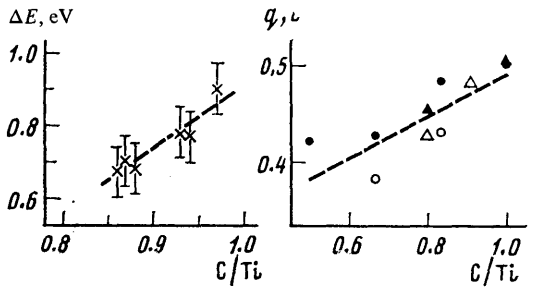


Figure 10. Shifts of ΔE for the $2p_{3/2}$(Ti) levels[139] and q^{eff} values for titanium[130] in TiC_x.

Interesting changes in the charge on the atoms in non-stoichiometric compounds were noted in measurements of the energy shifts of the inner levels of the X-ray photoelectron spectra of NbC_x,[148] NbN_x,[148] TiC_x,[138,139,147], and TaC_x and ZrC_x.[34] Shifts of the inner levels in low-carbon samples of TiC_x were also reported independently[140,147]. A systematic investigation of this effect[138,139] through the shift of the Ti $2p_{3/2}$ level showed a tendency for the shift to decrease as $N_\square$ increases (Fig.10), suggesting a change in the electronic configurations of the outer shells of Ti. Cluster calculations by the MO LCAO method[130] confirmed this. As Fig.10 shows, the effective charge q_{Ti} for clusters containing different numbers of vacancies decreases[130] as x decreases, denoting changes in the binding energy $E[2p_{3/2}(Ti)]$. Similar results have been reported[34] for ZrC_x and TaC_x (see Table 5). We note the fairly monotonic changes in the shifts $\Delta E[3d_{5/2}(Zr)]$ and $\Delta E[4f_{7/2}(Ta)]$, while the energy of the ls(C) levels remains practically constant: this can be ascribed to the constancy of the surroundings of the carbon atom in defect carbides, i.e. to the constant state of charge of the surroundings.

Attempts to examine the rearrangement of individual states in TiC_x as a function of N (by varying the energy of the exciting radiation) were inconclusive[139]. The use of X-ray emission spectroscopy methods seems more promising in this respect.

Most of the papers describing XE spectroscopic studies of the EES relate to non-stoichiometric oxides and carbides (see Table 3). For TiO_x ($x = 0.912$, 1.026, 1.19) the "centre of gravity" of the (O)$K\alpha$ band is shifted towards lower energies, and that of the (Ti)L_α band towards higher energies, by an increase in x, indicating[142] a decrease in charge density in the Ti and O spheres near ε_F and an increase in charge density in the deeper-lying states. Interesting rearrangements of the 4p(Ti) states have been observed[131] in a study of the (Ti)$K\beta_5\beta''$ spectra in TiO_x. In the region of non-stoichiometric compositions a high-energy structure element (K_{β_1}) was found, and its intensity was shown to increase with $N_\square$. The effect was interpreted[131] as a consequence of the 3d–4p mixing of the atomic orbitals of titanium on one lattice site, resulting from the lowering of the symmetry of the surroundings of the emitting atom produced by the formation of vacancies.

Direct confirmation of this conclusion was obtained in experiments with samples which had been exposed to high temperatures and pressures[131], in which the filling of vacancies (while retaining the overall composition $TiO_{0.88}$) caused a marked decrease in the intensity of the K_{β_1} sub-brand (see Fig.11). These results led to the recommendation[131] of X-ray emission as a method of calculating vacancy concentrations.

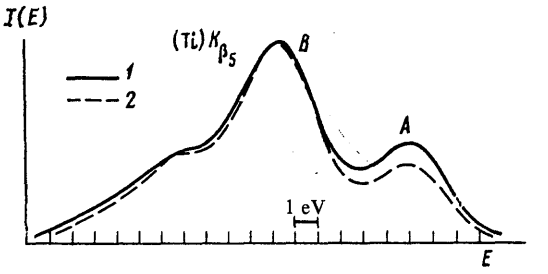


Figure 11. (Ti)K_{β_5} bands in the compound $TiO_{0.88}$: *1*) at normal pressure, *2*) at high pressure (90 kbar).[131]

The density of 3d(Ti) states near ε_F in titanium carbides is found to increase with $N_\square$ also from the behavour of the (Ti)L_α band[136,137], and direct confirmation of this increase has been obtained in cluster[129,136] and in band calculations[124]. A similar conclusion is reached from the shape of the (Nb)L spectra of NbC_x.[145] As regards the distribution of the 4p(Ti) states, identical Ti$K_{\beta_5}\beta''$ bands were observed for all the TiC_x compositions[126]. However, a more detailed study of $TiC_{1.0}$ and $TiC_{0.65}$ revealed[136] a clear $K^1\beta_5$ "outcrop" in the (Ti)K_{β_5} band of the non-stoichiometric compound which was absent in $TiC_{1.0}$ and can be interpreted as direct evidence of the appearance of 3d–4p interactions.

Far fewer studies of XE in non-stoichiometric nitrides have been reported. Nevertheless, existing X-ray emission L_α and $K_{\beta_5}\beta''$ spectra for compounds of composition TiN_x[142,158] and VN_x,[144,145] and calculations of the shape of the spectra by cluster (MO)[129] and band (CP) methods[125], suggest that the change in the valence band produced by an increase in the number of non-metal vacancies is the same for all the high-melting compounds of the transition metals: the density of d(M) states near the Fermi level increases, and the contribution from p(M) states (and also, in part, from the 2p(X) electrons) also increases in this region. This conclusion is confirmed by the shape of the (X)K_α spectra of TiC_x, VC_x,[85,129,137], TiN_x, VN_x,[126,142,145] and TiO_x,[142,143] all of which develop a distinct "outcrop" on the short-wave side when $N_\square$ increases.

VII. THE CHEMICAL BOND IN NON-STOICHIOMETRIC MX_x COMPOUNDS

We shall now examine the changes in the chemical bond in non-stoichiometric compounds. As was pointed out above (Section III), in this class of compounds the bond is of a combined covalent–metallic–ionic type, and the existing descriptions differ in the relative contribution to the overall bond energy from the different types of interaction which they postulate.

Table 6. Populations (α) of the orbitals and of the interatomic bonds, and charges on the metal atoms, for some non-stoichiometric high-melting transition metal compounds[71,129].

Compound	$[MX_6]$ $(MX_{1.0})$					$[MX_6\square]$ $(MX_{0.856})$					$[MX_4\square_2]$ $(MX_{0.66})$				
	$(n+1)s$	$(n+1)p$	nd	q (M)	α (M – X)	$(n+1)s$	$(n+1)p$	nd	q (M)	α (M – X)	$(n+1)s$	$(n+1)p$	nd	q (M)	α (M – X)
ZrC_x	0.327	0.669	2.773	+0.235	0.619	0.360	0.675	2.792	+0.172	0.514; 0.616(2); 0.689(2)	0.405	0.602	2.894	+0.139	0.563 (2); 0.701 (2)
NbC_x	0.315	0.780	3.747	+0.158	0.558	0.327	0.662	3.884	+0.127	0.503; 0.662(2); 0.729(2)	0.359	0.585	3.966	+0.092	0.867(2); 0.649(2)
TiN_x	0.224	0.202	2.931	+0.642	0.330	0.221	0.195	2.982	+0.602	0.328; 0.411(2); 0.431(2)	0.212	0.176	3.050	+0.562	0.421(2); 0.447(2)
NbN_x	0.277	0.433	3.882	+0.408	0.411	0.283	0.329	4.012	+0.376	0.316; 0.383(2); 0.445(2)	0.349	0.367	3.871	+0.413	0.521(2); 0.599(2)
VO_x	0.154	0.219	3.968	+0.660	0.208	0.318	0.163	4.075	+0.630	0.197; 0.233(2); 0.256(2)	0.123	0.140	4.153	+0.585	0.239(2); 0.294(2)

Band calculations[119–122,124,125,127,128] suggest a number of conclusions on the change in relative contributions brought about by an increase in the number of defects. Thus an increase in the width and in the population of the metal d band[124,125,127,128] can be treated as a strengthening of the M–M interactions, whereas a narrowing of the $2p$(X) band is equivalent to a weakening of the interaction of the $2p$(X) and d(M) functions (the covalent component of the M–X bond).

A simple "energy diagram" of this type of redistribution can be produced[124] by noting that the breaking of M–C bonds produces an upward shift in energy of the d states of ~2.7 eV (in TiC_x), due to the $e_g \rightarrow t_{2g}$ ($d_\gamma \rightarrow d_\varepsilon$) transition. This increase in the occupancy ratio $N^M(t_{2g})/(N^M(e_g)$ (i.e. the strengthening of the M–M bond) caused by an increase in $N_\square$ has been ascribed[127] to charge transfer effects, arising from the reversion to the d_γ(M) band of the additional electron on the carbon atom when the latter is removed from the carbide lattice.

By far the most successful approaches in studies of the chemical bond are the cluster (MO) calculations, which offer a clear description of the origin and structure of the interactions between particles and allow the contributions from the different types of bond to be assessed quantitatively. The parameters of the electronic structure obtained from cluster MO calculations for a series of Ti, V, Zr, and Nb carbides, nitrides, and oxides[129] are listed in Table 6. We note that in both the stoichiometric and the non-stoichiometric compounds the main contribution to the chemical bond comes from the interaction between the nd functions of the metals and the $2p$ states of the ligands. As $N_\square$ increases, the occupancies of the individual M–X bonds also increase, but the total number of electrons involved in bond formation between the metal and the nearest ligands (expressed per metal atom) decreases from 2.45 for $TiC_{1.0}$ to 1.61 for $TiC_{0.5}$. Furthermore the addition of defects makes the electron density of individual bonds strongly anisotropic.

An increase in defect density rapidly lowers the charge (q^{eff}) localised on the atoms, thus making the role of the ionic component of the chemical bond even less important[117,129,130,132,136].

The changes in bond type brought about by a nearby vacancy are made clear by comparing the wave function diagrams for the σ and π types of interaction in stoichiometric and in non-stoichiometric titanium carbide[132]: this shows that the formation of a vacancy does not produce new bonds passing through the centre of the vacancy. The interactions between the states of the nearest metal atoms and those of the vacancy are quite complex, and they can be interpreted as a form of vacancy–metal π bonding. However, as the diagrams for the M–M interactions show[132], these bonds are the same as in the ideal carbide, and strong unscreened M–M bonds directed through the centre of the vacancy[114] are not formed.

Similar conclusions follow from cluster calculations modelling vacancies of metal atoms[132]: no electrons are localised on the vacancy, and no bonding states are created near the vacancy. Obviously, this explains the reported instability of metal vacancies in titanium carbide.

The changes in chemical bonding discussed above for the case of TiC_x apply also to other defect compounds of the MX_x type[129–131,135] (see Table 6).

In the carbide–nitride–oxide series the population of orbitals of the t_{2g} type increases (i.e. the M–M interaction increases), but the M–X bonds remain predominant over the whole of the homogeneity region (though their anisotropy increases). The total number of electrons localised on the M–X bonds decreases.

In the compounds of 4d metals (Zr, Nb), as in the stoichiometric compounds, the d(M)–$2p$(X) bond becomes stronger.

In the carbides of the sub-group Va transition metals various parameters (micro-hardness, thermal expansion coefficient, etc.) were found to have an extremum near the composition $MX_{0.8}$.[9,10,115].

These effects are probably related to the observed ordering of the vacancies[151–154] in MX_x. Evidently, more accurate descriptions can be expected from future calculations with clusters large enough to allow for ordering of the vacancies in the crystal structure.

VIII. THE ELECTRONIC STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF NON-STOICHIOMETRIC COMPOUNDS

Many studies of the physicochemical properties of high-melting compounds containing defects have been reported[3–10,115]. The results are usually interpreted in terms of simple qualitative models, and attempts to relate the observed changes to the parameters of the electronic structure, or indeed to calculate these parameters, are uncommon[127,129–136]. The only exception is the series of calculations (mentioned above) on XPS and XE spectra. This is due partly to the difficulty and complexity of strict quantum-chemical calculations of the electronic spectrum of defect phases, and partly to the difficulty of preparing samples with different vacancy concentrations while excluding microstructure effects (grains, domains, etc.) and chemical impurities, so that the observed differences in properties can be reliably ascribed to the different defect concentrations[3–10].

Nevertheless various correlations (of the electronic structure–property type) have been proposed[127,129–136,155,156]. To discuss these results we must examine first of all the method

used to calculate the EES of the compound. Depending on the specific features of the chemical bond and of the electronic structure, all the physicochemical properties which describe a high-melting phase can be classified into two groups[9]. The first includes the "lattice" properties such as micro-hardness (H_μ), T_f, atomisation energy, thermal expansion coefficient, etc. In the second group we classify all the magnetic and electrical properties determined by the distribution and concentration of high-energy delocalised *d* electrons. In this case calculations based on cluster (local) models are the most effective for describing the first group of properties, whereas approaches based on the band model are preferable for processes determined by the behaviour of almost fully collectivised electrons in a periodic crystal field.

Unfortunately, only a few qualitative comparisons have been possible so far, because of the very limited range of band calculations now available[127]: known anomalies in the phonon spectra of NbC_x and TaC_x can be explained by the redistribution of density of t_{2g} sub-bands, and the changes in $N(\varepsilon)$ can be shown to be qualitatively consistent with changes in T_S, ρ, the Hall coefficient, and the electronic specific heat.

More precise correlations have been possible by using the results of cluster calculations[129-136]. Changes in the "lattice" properties (decrease in T_f, H_μ, and atomisation energy accompanied by an increase in the amplitude of thermal vibrations $\sqrt{u^2}$ and in thermal expansion coefficient[157]) caused by an increase in $N_\square$ (Fig.12) are ascribed to the general weakening of the covalent M-X interaction resulting from the decrease in the total number of electrons localised on neighbouring M-X bonds and from the large increase in the anisotropy of individual bonds (see Table 6). The observed increase in magnetic susceptibility, and decrease in ρ, are consistent with the increase in the number of *d*-type electrons close to ε_F. In some calculations[129,131,132] the defects were assumed to be fully disordered. Long-range order[152-154] (with a type of ordering dependent of composition) should cause departures from monotonic dependences, as has in fact been observed for some of the parameters of the carbides of sub-group Va metals (see Fig.12).

The main weakness of the parameter (the overlap population) used by several workers[129-136] to explain the physicochemical properties of MX_x compounds is that it cannot be measured by direct experiment. An energy scheme developed[67] for calculating chemical bond stabilities in stoichiometric TiC, TiN, VC, and VN has confirmed earlier conclusions based on bond populations on the changes in bond energetics in this series of compounds. We can therefore expect these conclusions to be extended to energy effects in the bonds of non-stoichiometric compounds.

An interesting new application of EES calculations in the cluster model is in the interpretation of the NMR spectra of MX_x.[156] The observed parameters of the NMR spectra have been correlated with changes in overlap populations of different types (σ and π). Direct quantum-chemical calculations of the electric field gradient in VC_x, VN_x, and VO_x showed that at the nuclei this parameter is determined by valency contribution from the 3*d*(V) electrons. The calculated quadrupole interaction constants were in reasonably good agreement with experiment ($\nu_Q = 0.48$ and 0.164 MHz respectively for VO_x).

A calculation[134] by a non-empirical X_α-SW method gave a temperature (T_S) for the transition to the superconducting state in NbC_x and VN_x in qualitative agreement with the experimental value. These results justify the hope of substantial new progress in the application of cluster methods

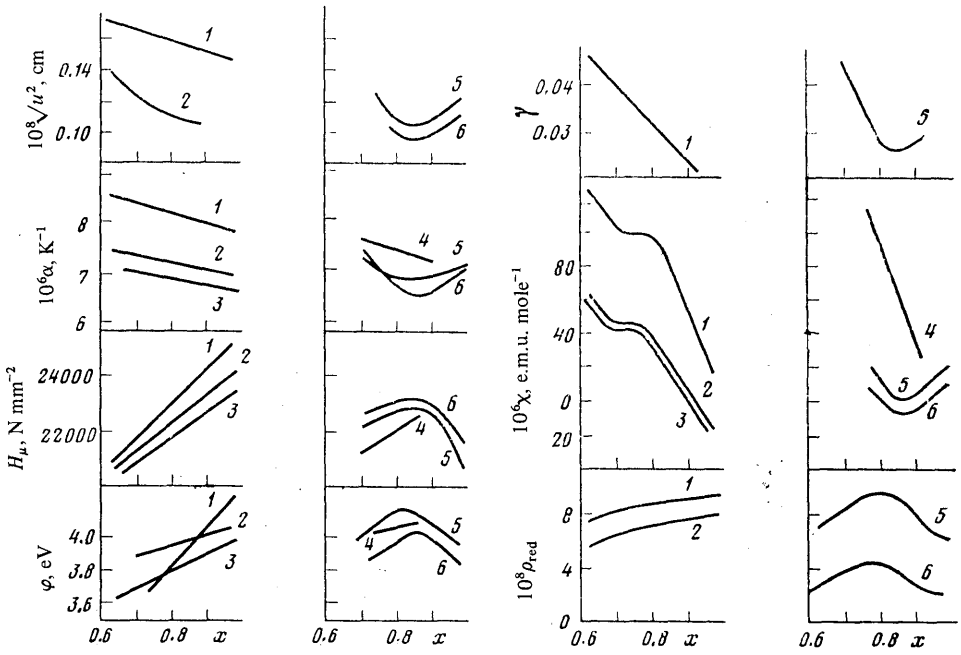


Figure 12. Changes in the amplitude of the thermal vibrations of the atoms ($\sqrt{u^2}$), thermal expansion coefficient (α), micro-hardness (H_μ), work function (ϕ), recombination coefficient of hydrogen atoms (γ), magnetic susceptibility (χ), and reduced electrical resistivity (ρ_{red}) in the homogeneity region of the carbides of: *1*) Ti, *2*) Zr, *3*) Hf, *4*) V, *5*) Nb, *6*) Ta.[9]

to the calculation of the physicochemical characteristics of defect phases.

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Thus the basic models and methods of calculation developed so far are adequate for meaningful studies of the EES of defect phases over a wide range of vacancy concentrations. The main features of the rearrangements in the electronic structure and of inter-particle interactions in MX_x compounds have been established. Further developments in our understanding of the EES of defect phases should include defect ordering and double defect structures. Another important future goal is the assessment of the energy of rearrangements in the chemical bond caused by the creation of vacancies, which could be immediately translated into a description of the mechanism of structural phase changes in MX_x. By developing a new formalism, and by adding to the existing fund of calculations of independently measurable physicochemical properties in the homogeneity region, new impetus could be given to the development of theoretical models of defect states offering a prescribed set of properties.

REFERENCES

1. G.V.Samsonov and I.M.Vinitskii, "Tugoplavkie Soedineniya" (Refractory Compounds), Izd.Metallurgiya, Moscow, 1976.
2. G.V.Samsonov (Editor), "Fiziko-khimicheskie Svoistva Oksidov" (Physicochemical Properties of the Oxides), Izd.Metallurgiya, Moscow, 1978.
3. E.K.Storms, "The Refractory Carbides" (Refractory Materials, Vol.2) Academic Press, New York, 1967, (Translated into Russian), Atomizdat, Moscow, 1970.
4. R.A.Andrievskii and Ya.S.Umanskii, "Fazy Vnedreniya" (Interstitial Phases), Izd.Nauka, Moscow, 1977.
5. L.E.Toth, "The Carbides and Nitrides of the Transition Metals" Academic Press, New York, 1971 (Translated into Russian), Izd.Mir, Moscow, 1974.
6. H.J.Goldsmid, "Interstitial Alloys" (Translated into Russian), Vols.1 and 2, Izd.Mir, Moscow, 1971.
7. G.V.Samsonov, G.Sh.Upadkaya, and V.S.Neshpor, "Fizicheskoe Materialovedenie Karbidov" (Physical Materials Science and Carbides), Izd.Naukova Dumka, Kiev, 1974.
8. G.V.Samsonov, "Nitridy" (Nitrides), Izd.Naukova Dumka, Kiev, 1965.
9. G.V.Samsonov, I.F.Pryadko, and L.F.Pryadko, "Elektronnaya Lokalizatsiya v Tverdom Tele" (Electron Localisation in Solids), Izd.Nauka, Moscow, 1976.
10. W.S.Williams, in "Progress in Solid State Chemistry", Vol.6 (H.Reiss and J.McCaldin, Editors), Pergamon, New York, 1971.
11. J.Callaway, "Theory of Energy Band Structures" (Translated into Russian) [This probably refers to Chapter 4 of "Quantum Theory of the Solid State" by this author, Academic Press, New York, 1974, Ed of Translation], Izd.Mir, Moscow, 1969.
12. R.Messmer and G.Watkins, Phys.Rev.Letters, 1970, **25**, 656.
13. R.P.Messmer, Symposium "Semi-empirical Methods of Calculating Electronic Structures" (Translated into Russian), (J.M.Segal, Editor), Vol.2, Izd.Nauka, Moscow, 1980, p.272.
14. V.A.Gubanov, V.P.Zhukov, and A.O.Litinskii, "Poluempiricheskie Metody Molekulyarnykh Orbital'ei v Kvantovoi Khimii" (Semi-empirical Molecular Orbital Methods in Quantum Chemistry), Izd.Nauka, Moscow, 1978.
15. K.Dempsey, Phil.Mag., 1963, **B86**, 285.
16. R.Kiessling, Met.Rev., 1957, **2**, 77.
17. J.D.Bernal, Ergebn.Tech.Röntgenkunde, 1954, **3**, 148.
18. W.Hume-Rothery, Adv.Phys., 1954, **3**, 225.
19. R.Rundle, Acta Cryst., 1948, **1**, 180.
20. H.Krebs, Z.anorg.Chem., 1955, **278**, 89.
21. H.Bilz, Z.Physik, 1958, **153**, 33.
22. P.Costa and R.Conte, Nuclear Met.Symp., 1964, **10**, 19.
23. R.Lye and E.Logothetis, Phys.Rev., 1966, **B145**, 622.
24. V.Ern and A.Switendick, Phys.Rev., 1965, **A137**, 1927.
25. J.Conclin and D.Silversmith, Internat.J.Quantum Chem.Symp., 1968, **2**, 243.
26. V.I.Potorocha, V.A.Tskhai, and P.V.Geld, Phys. Stat.Solidi, 1971, **48**, 119.
27. V.I.Potorocha, V.A.Tskhai, and P.V.Gel'd, Dokl. Akad.Nauk SSSR, 1972, **203**, 1118.
28. J.F.Alward, C.Y.Fong, M.El-Batanouny, and F.Wooten, Solid State Comm., 1975, **17**, 1063.
29. J.F.Alward, C.Y.Fong, M.El-Batanouny, and F.Wooten, Phys.Rev., 1975, **B12**, 1105.
30. D.J.Chadi and M.L.Cohen, Phys.Rev., 1974, **B10**, 496.
31. C.Y.Fong and M.L.Cohen, Phys.Rev., 1972, **B6**, 3633.
32. L.F.Mattheis, Phys.Rev., 1972, **B5**, 315.
33. L.F.Mattheis, Phys.Rev., 1972, **B5**, 290, 306.
34. H.Ichara, Researches of Electrotechnical Laboratory, 1977, p.775.
35. A.Neckel, K.Schwarz, R.Eibler, P.Rastl, and P.Weinberger, Microchim.Acta, 1975, **6**, 257.
36. A.Neckel, K.Schwarz, P.Weinberger, R.Eibler, and P.Rastl, Z.Elektrochem., 1975, **79**, 1053.
37. A.Neckel, K.Schwarz, P.Rastl, P.Weinberger, and R.Eibler, J.Phys.Chem., 1976, **9**, 579.
38. K.Schwarz, K.Rechter, and A.Neckel, J.Phys. Chem: Solid State Phys., 1975, **8**, 1663.
39. K.Schwarz and A.Neckel, Z.Elektrochem., 1975, **79**, 1071.
40. K.Schwarz, A.Neckel, and A.Bradshaw, Chem. Phys.Letters, 1976, **41**, 311.
41. K.Schwarz, Monatsh., 1971, **102**, 1400.
42. K.Schwarz, J.Phys.Chem: Solid State Phys., 1975, **8**, 809.
43. K.Schwarz, J.Phys.Chem.: Solid State Phys., 1977, **10**, 195.
44. K.Schwarz and E.Wimmer, J.Phys.F: Metal Phys., 1980, **10**, 1001.
45. P.Weinberger, Theor.Chim.Acta, 1977, **44**, 315.
46. J.Conclin, F.W.Averill, and T.M.Hattox, J.Phys. (Suppl.), 1972, **33**, 213.
47. H.Bross, G.Bohn, G.Meister, W.Shubö, and H.Ströhr, Phys.Rev., 1970, **B2**, 3038.
48. H.R.Trebin and H.Bross, J.Phys.Chem: Solid State Phys., 1975, **8**, 1181.
49. B.Klein and D.A.Papaconstantopulos, Phys.Rev. Letters, 1974, **32**, 1193.
50. B.Klein, L.I.Boyer, and D.A.Papaconstantopulos, Solid State Comm., 1976, **20**, 937.
51. E.S.Alekseev, R.G.Arkhipov, and S.V.Popova, Phys.Stat.Solidi, 1978, **b90**, **k133**.

52. M.Gupta and A.Freeman, Phys.Rev., 1976, **B14**, 5205.
53. L.P.Mokhracheva, V.A.Tskhai, and P.V.Gel'd, Phys.Stat.Solidi, 1978, **b87**, 49.
54. L.P.Mokhracheva, V.A.Tskhai, and P.V.Gel'd, Dokl.Akad.Nauk SSSR, 1977, **235**, 885.
55. P.Weinberger, R.Podloucy, C.P.Malett, and A.Neckel, J.Phys.Chem.: Solid State Phys., 1979, **12**, 801.
56. P.Weinberger, C.P.Malett, R.Podloucky, and A.Neckel, J.Phys.Chem: Solid State Phys., 1980, **10**, 173.
57. V.A.Gubabov and J.W.D.Connolly, Chem.Phys. Letters, 1976, **44**, 139.
58. V.A.Gubanov, A.L.Ivanovskii, G.P.Shveikin, and J.Weber, Solid State Comm., 1979, **29**, 743.
59. V.A.Gubanov, A.L.Ivanovskii, G.P.Shveikin, and J.Weber, Dokl.Akad.Nauk SSSR, 1979, **246**, 913.
60. V.A.Gubanov, Thesis, Novosibirsk, 1978.
61. M.Gupta, V.A.Gubanov, and D.E.Ellis, J.Phys. Chem.Solids, 1977, **38**, 499.
62. A.L.Ivanovskii, V.A.Gubanov, V.P.Zhukov, G.P.Shveikin, and J.Weber, J.Phys.Chem.Solids, 1980, **41**, 1333.
63. V.P.Zhukov, A.L.Ivanovskii, V.A.Gubanov, G.P.Shveikin, and J.Weber, Zhur.Neorg.Khim., 1980(2), **25**, 318 [Russ.J.Inorg.Chem., 1980(2)].
64. P.Weinberger, Theor.Chim.Acta, 1976, **42**, 165.
65. T.Hori, H.Adachi, and S.Imoto, Trans.Jap.Inst. Met., 1977, **18**, 31.
66. M.Erbudak, V.A.Gubanov, and E.Z.Kurmaev, J.Phys.Chem.Solids, 1978, **39**, 1157.
67. V.P.Zhukov, V.A.Gubanov, A.L.Ivanovskii, and G.P.Shveikin, Zhur.Neorg.Khim., 1980(3), 25, 639, [Russ.J.Inorg.Chem., 1980(3)].
68. K.L.Yip, A.B.Kunz, and W.S.Williams, Phys.Stat. Solidi, 1976, **b75**, 533.
69. V.A.Gubanov, B.G.Kasimov, and E.Z.Kurmaev, J.Phys.Chem.Solids, 1975, **36**, 861.
70. V.A.Gubanov, E.Z.Kurmaev, and G.P.Shveikin, J.Phys.Chem.Solids, 1977, **38**, 201.
71. A.L.Ivanovskii, Thesis, Sverdlovski, 1980.
72. M.P.Arbuzov and B.V.Khaenko, Poroshkovaya Metallurgiya, 1966, **4**, 74.
73. M.P.Arbuzov and B.V.Khaenko, Ukrain.Fiz.Zhur., 1971, **16**, 1421.
74. A.Seth, T.Paakari, S.Manninen, and A.N.Christensen, J.Phys.Chem.: Solid State Phys., 1977, **10**, 3127.
75. G.V.Vol'f and V.P.Shirokovskii, Fiz.Metallov i Metalloved., 1980, **49**, 67.
76. R.Eibler and A.Neckel, Monatsh., 1975, **106**, 577.
77. I.A.Brytov, V.S.Neshpor, and Yu.N.Romashchenko, Izv.Sibirsk.Otd.Akad.Nauk SSSR, Ser.Khim., 1975(4), 143.
78. A.S.Shulakov, T.M.Zimkina, V.A.Fomichev, and E.Z.Kurmaev, Fiz.Tverdogo Tela, 1973, **15**, 2092.
79. V.V.Nemoshkalenko, V.P.Krivitskii, A.P.Nesenyuk, A.S.Nikolaev, and A.Shpak, J.Phys.Chem.Solids, 1975, **36**, 227.
80. I.A.Brytov, E.Z.Kurmaev, and S.A.Nemnonov, Fiz.Metallov i Metalloved., 1968, **26**, 366.
81. S.A.Nemnonov and K.M.Kolobova, Fiz.Metallov i Metalloved., 1966, **22**, 680.
82. E.C.Kurmaev, G.P.Shveikin, and S.A.Nemnonov, Phys.Stat.Solidi, 1973, **b60**, k65.
83. M.A.Blokhin and A.I.Shuvaev, Izv.Akad.Nauk SSSR, Ser.Fiz., 1962, **26**, 429.
84. J.E.Holliday, in "Soft X-ray Band Spectra" (D.J.Fabian, Editor), Academic Press, London-New York, 1968, 101.
85. E.Z.Kurmaev, S.A.Nemnonov, A.Z.Men'shikov, and G.P.Shveikin, Izv.Akad.Nauk SSSR, Ser.Fiz., 1967, **31**, 996.
86. E.Källe and M.Pessa, J.Phys.F: Metal Phys., 1975, **8**, 1985.
87. S.A.Nemnonov, E.Z.Kurmaev, V.I.Minin, and G.P.Shveikin, Fiz.Metallov i Metalloved., 1969, **28**, 371.
88. V.E.Dolgikh, E.Z.Kurmaev, V.M.Cherkashenko, and G.P.Shveikin, Fiz.Metallov i Metalloved., 1975, **40**, 664.
89. J.H.Weaver and F.A.Schmidt, Phys.Letters, 1980, **A77**, 73.
90. A.M.Bradshaw and U.Krause, Z.Elektrochem., 1975, **79**, 1095.
91. L.I.Johansson, A.L.Hagström, B.E.Jacobson, and S.B.E.Hagström, J.Electron Spectr.Rel.Phen., 1977, **10**, 295.
92. L.I.Johansson, P.M.Stefan, M.L.Shek, and A.N.Christensen, Phys.Rev., 1980, **B22**, 1032.
93. J.H.Weaver, A.M.Bradshaw, J.F.van der Veen, F.J.Himpsel, D.E.Eastman, and C.Politis, Phys. Rev., 1980, **B22**, 4921.
94. L.I.Johansson, P.M.Stefan, M.L.Shek, and A.N.Christensen, Solid State Comm., 1980, **36**, 965.
95. L.I.Johansson, A.Callenas, P.M.Stefan, A.N.Christensen, and K.Schwarz, Phys.Rev., 1980, **B24**, 1883.
96. M.Romand and M.Roublin, J.Paris XVIII Colloquium Spectr.Intern.Commun., 50, 1975, A138,11.
97. H.Ichara and K.Watanabe, Solid State Comm., 1981, **38**, 1211.
98. H.Höchst, P.Steiner, S.Hüfner, and C.Politis, Z.Physik, 1980, **37**, 27.
99. K.Ichikava, O.Terasaki, and T.Sagava, J.Phys. Soc.Japan, 1974, **36**, 706.
100. H.F.Franzen, M.X.Umana, J.R.McCreary, and R.J.Thorn, J.Solid State Chem., 1976, **18**, 363.
101. V.I.Chirkov, S.M.Blokhin, and E.S.Vainshtein, Fiz.Tverdogo Tela, 1967, **9**, 1116.
102. K.Siegbahn, C.Nordling, A.Falman, R.Nordberg, K.Hamrin, J.Hedman, C.Johansson, T.Bergmark, S.Carlsson, I.Lindgren, and B.Lindberg, "Electron Spectroscopy" North Holland, Amsterdam, 1969, (Translated into Russian), Izd.Mir, Moscow, 1971.
103. J.H.Scofield, J.Electron Spectr.Rel.Phenom., 1976, **8**, 129.
104. U.Gelius in "Electron Spectroscopy" (D.A.Shirley Editor), North-Holland, Amsterdam, 1972, p.311.
105. L.Ramqvist, Jernkont.Ann., 1969, **153**, 159.
106. Yu.M.Shul'ga, V.N.Troitskii, M.I.Aivazov, and Yu.G.Borod'ko, Zhur.Neorg.Khim., 1976(10), **21**, 2621 [Russ.J.Inorg.Chem., 1976(10)].
107. V.A.Gubanov, J.Electron.Spectr.Rel.Phenom., 1976, **9**, 85.
108. V.A.Gubanov, D.E.Ellis, and A.K.Chirkov, Zhur. Strukturnoi Khim., 1976, **17**, 956.
109. J.C.Slater, "Self-consistent Field Methods for Molecules and Solids" International series in pure and applied Physics, Vol.4, McGraw Hill, New York, 1974, (Translated into Russian), Izd.Mir.Moscow, 1978.
110. A.Meisel, G.Leonhardt, and R.Szargan, "Rentgenovskie Spektry i Khimicheskaya Svyaz'" (X-Ray Spectra and Chemical Bonding, Izd.Naukova Dumka, Kiev, 1981; (Chem.Abs., 95, B 229, 134f).

111. S.A.Nemnonov and E.Z.Kurmaev, Fiz.Metallov i Metalloved., 1969, **27**, 816.
112. G.Karlsson and R.Manne, Phys.Scripta, 1971, **4**, 119.
113. S.P.Denker, J.Less-common Metals, 1968, **14**, 1.
114. P.V.Gel'd, Editor's concluding remarks in the Russian translation of Ref.5.
115. A.Boruchovich, Phys.Stat.Solidi, 1978, **b46**, 11.
116. J.B.Goodenough, Phys.Rev., 1972, **B5**, 2764.
117. G.V.Samsonov, Yu.N.Goryachev, L.N.Okhremchuk, I.A.Podchernyaeva, and V.S.Fomenko, Izv.Vys. Ucheb.Zaved., Ser.Fiz., 1977(1), 42.
118. G.P.Shveikin, V.A.Gubanov, and E.Z.Kurmaev, Materials Res.Bull., 1979, **13**, 1433.
119. H.Weiss, III Conf.Proszkow, Zakopane, 1971, 89.
120. J.M.Schoen and S.P.Denker, Phys.Rev., 1969, **184**, 864.
121. J.Zbasnik and L.E.Toth, Phys.Rev., 1973, **B8**, 492.
122 A.Neckel, P.Rastl, K.Schwarz, and R.Eibler-Mechtler, Z.Naturforsch., A, 1974, **29**, 107.
123. J.M.Schoen, Phys.Rev., 1969, **184**, 858.
124. J.Klima, J.Phys.Chem.: Solid State Phys., 1979, **12**, 3691.
125. J.Klima, Czech.J.Phys., 1980, **B30**, 905.
126. E.A.Zhurakovskii, "Elektronnaya Struktura Tugoplavkikh Soedinenii" (Electronic Structure in High-melting Compounds), Izd.Naukova Dumka, Kiev, 1976.
127. B.M.Klein, D.A.Papaconstantopulos, and L.L.Boyer, Phys.Rev., 1980, **B22**, 1964.
128. L.M.Huisman, A.E.Carlsson, C.D.Gelatt, and H.Ehrenreich, Phys.Rev., 1980, **B22**, 991.
129. A.L.Ivanovskii, V.A.Gubanov, G.P.Shveikin, and E.Kurnaev, J.Less-common Metals, 1981, **78**, 1.
130. A.L.Ivanovskii, V.A.Gubanov, E.Z.Kurmaev, A.L.Hagström, S.E.Karlsson, and L.I.Johansson, J.Electron Spectr.Rel.Phenom., 1979, **16**. 415.
131. G.P.Shveikin, A.L.Ivanovskii, V.A.Gubanov, E.Z.Kurmaev, V.A.Trofimova, Yu.G.Zainulin, S.I.Alyamovskii, and S.V.Popova, Dokl.Akad.Nauk SSSR, 1979, **246**, 400.
132. V.A.Gubanov, E.Z.Kurmaev, and D.E.Ellis, J. Phys.Chem.: Solid State Phys., 1981, **14**, 5567.
133. K.Schwarz and N.Rösch, J.Phys.Chem.: Solid State Phys., 1976, **9**, L433.
134. G.Reis and H.Winter, J.Phys.F: Metal Phys., 1980, **10**, 1.
135. G.V.Samsonov, Yu.M.Goryachev, I.A.Podchernyaeva, and L.M.Okhremchuk, Ukrain.Fiz.Zhur., 1977, **22**, 265.
136. E.Z.Kurmaev, M.P.Butsman, V.A.Trofimova, V.A.Gubanov, A.L.Ivanovskii, Yu.G.Zainulin, and G.P.Shveikin, Zhur.Strukturnoi Khim., 1981, **22**, 172.
137. V.S.Neshpor, I.I.Lyakhovskaya, and V.P.Nikitin, Vestnik Leningrad.Univ., Ser.Fiz.-khim., 1972, 55.
138. A.L.Hagström, L.I.Johansson, B.E.Jacobsson, and S.M.B.Hagström, Solid State Comm., 1976, **19**, 647.
139. L.I.Johansson, Thesis, Lincöping (Sweden), 1976.
140. L.Ramqvist, B.Ehlsting, E.Källe, E.Noreland, and R.Manne, J.Phys.Chem.Solids, 1971, **32**, 149.
141. E.A.Zhurakovskii, L.V.Nikitin, and N.D.Lyubaya, Izv.Akad.Nauk SSSR, Neorg.Materialy, 1972, **8**, 702.
142. I.A.Brytov, M.A.Rumsh, and A.S.Parobets, Fiz. Tverdogo Tela, 1968, **10**, 795.
143. E.E.Vainshtein and V.I.Chirkov, Dokl.Akad.Nauk SSSR, 1964, **381**, 388.
144. V.P.Dzeganovskii, Thesis, Kiev, 1971.
145. M.M.Kindrat, Thesis, Kiev, 1982.
146. V.G.Lifshits, Thesis, Donetsk, 1973.
147. L.Ramqvist, H.Hamrin, G.Johansson, U.Gelius, and K.Nordling, J.Phys.Chem.Solids, 1970, **31**, 2669.
148. Y.Kumashiro, K.Sakuma, Y.Kimura, H.Ichara, and S.Misava, J.Less-common Metals, 1980, **75**, 187.
149. V.E.Heurich, H.J.Ziegler, and T.B.Reed, Phys. Rev., 1978, **B17**, 4121.
150. V.M.Cherkashenko, A.V.Ezhov, M.P.Butsman, E.Z.Kurmaev, B.V.Mitrofanov, A.L.Ivanovskii, and V.A.Gubanov, Fiz.Metallov i Metalloved. (in press).
151. D.Watanabe and J.R.Castles, Acta Cryst., 1967, **23**, 307.
152. B.Andersson, J.Gijonnes, and A.R.Terauchi, J.Less-common Metals, 1978, **61**, 273.
153. J.B.Terauchi, A.Cohen, and T.B.Reed, Acta Cryst., 1978, **A34**, 556.
154. M.Morinaga and A.Cohen, Acta Cryst., 1979, **A35**, 745, 975.
155. J.Calais, Adv.Phys., 1977, **26**, 847.
156. A.L.Ivanovskii, A.V.Dmitriev, V.A.Gubanov, Yu.G.Zainulin, and R.N.Pletnev, Izv.Akad.Nauk SSSR, Ser.Fiz., 1981, **45**, 1747.
157. V.G.Samsonov, Izv.Akad.Nauk SSSR, Neorg. Materially, 1973, **9**, 2144.
158. V.V.Nemoshkalenko, M.M.Kindrat, V.P.Krivitskii, B.P.Mamko, V.M.Prokopendo, and A.N.Kharlamov, Metallofizika, 1981, **3**, 37.
159. W.K.Schubert, R.N.Shelton, and E.L.Wolf, Phys. Rev., 1981, **B24**, 6278.

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