Chemical Bonding in Refractory Transition Metal Compounds with 8, 9, and 10 Valence Electrons*

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The chemical bonding in the refractory transition metal compounds TiC, TiN, and VN is investigated by experimental and theoretical techniques. High-precision X-ray diffraction is used to determine the electron densities in these three compounds experimentally. The X-ray structure factors and the respective valence electron densities are used twice, once to understand the chemical bonding and once to relate the experimental charge densities to those obtained from band structure calculations. These calculations, which in general are in very good agreement with experimental data, utilize the linearized augmented plane wave (LAPW) method. Theory and experiment lead to a detailed analysis of the chemical bonding in these compounds with 8, 9, and 10 valence electrons. By decomposition of the theoretical charge density into contributions from different states (energy regions), it was possible to show the strong covalent nonmetal p–metal d interaction, which is otherwise apparent only in TiC, but not in TiN or VN. In the latter two compounds the additional electrons occupy mainly metal d states with t_{2g} symmetry, so that in the total valence charge densities the most important bonding feature is covered. In addition to covalent interactions all compounds have a metallic bonding contribution as well as a considerable charge transfer from the metal to the nonmetal site. This mixture in chemical bonding accounts for the unusual combination of properties such as ultrahardness, high melting points, and good conductivity. © 1987 Academic Press, Inc.

1. Introduction

Refractory metal compounds, especially carbides and nitrides, are of great interest both in technology and in theory. This is because they exhibit unusual combinations of physical and chemical properties such as ultrahardness and high melting points (typical of covalently bonded semiconductors) and good electrical and thermal conduc-

tivity (typical for metallic systems). Many of these compounds crystallize in the sodium chloride structure, which is common in ionic compounds, but often has defects on one or both of its sublattices. The number of valence electrons per formula unit lies between 8 and 10 and within these limits a variety of compounds with a more or less ideal NaCl structure exist. The unusual mixture of properties has challenged both theorists and experimentalists to study the chemical bonding in these

* Dedicated to Dr. H. Nowotny.

systems. The relation between crystal structure, chemical bonding, and hardness in refractory metal compounds has been discussed by Nowotny as early as 1953 (1, 2). Theoretical work as well as a detailed comparison with experimental data is given in recent reviews by Neckel (3) and Schwarz (4).

In the present work we focus on TiC, TiN, and VN as representative examples of compounds with 8, 9, and 10 valence electrons. These compounds, which exist in nearly stoichiometric composition, have been investigated previously both theoretically by band structure techniques (5–8) and experimentally by X-ray diffraction methods (9, 10). Here we make a comparison of these three compounds and discuss chemical bonding and X-ray structure factors determined both theoretically and experimentally.

2. Methods for the Investigation of the Chemical Bonding

One can use many different approaches to investigate chemical bonding, but here we focus on two main tools, a theoretical method using band structure calculations and an experimental method using high-precision X-ray diffraction. Both approaches allow information to be obtained about the spatial distribution of the valence electron density, which under favorable circumstances can be directly related to bonding features.

The theoretical results are based on energy band structure theory using the local density approximation. We utilize the linearized augmented plane wave (LAPW) method to solve Schroedinger's equation and treat the potential in the common muffin-tin approximation (6) (spherical averaged potential inside touching atomic spheres and constant potential outside) and in the more sophisticated full potential method (8), where the potential is not re-stricted in its shape. The resulting energy bands are the basis from which further insight is obtained by related quantities such as partial charges, total and partial densities of states, valence electron densities, and X-ray structure factors. A detailed description of the method and explicit definitions can be found elsewhere (5–7).

The experimental results are based on high-precision, high-resolution X-ray diffraction measurements performed at room temperature on well-characterized spherical single crystals of composition $TiC_{0.94}$, $TiN_{0.99}$, and $VN_{1.00}$. Experimental details are given elsewhere (9, 10).

3. Electronic Structure

The following description of the electronic structure in this class of compounds is based on theoretical results which are in very good agreement with experimental X-ray structure factors (see Sect. 4), but also with other experimental data (3).

As mentioned above an accurate band structure calculation provides the best basis for an explanation of the chemical bonding. In Fig. 1 the Γ–Δ–X sections of the band structure for TiC, TiN, and VN are
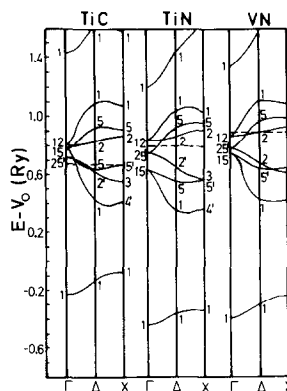

FIG. 1. Section of the energy bands of TiC, TiN, and VN along the Γ–Δ–X direction in the first Brillouin zone. Energies (in Ry) are with respect to the constant MT potential.

presented. The lowest lying band originates mainly from the nonmetal site and is denoted as the s-band. This band is significantly lower in energy in nitrides than in carbide, while there is almost no change in going from TiN to VN. The next three bands, denoted nonmetal p-band, overlap more (TiC) or less (TiN, VN), with the next five bands called metal $3d$ bands (or shortened; d-band). Again there is a much more pronounced change going from the carbide to nitrides than changing the metal atom. In particular the order of the Γ_{15} and $\Gamma_{25'}$ states is interchanged in the carbide with respect to nitrides. The main difference between TiN and VN is a higher Fermi energy in the latter due to one additional valence electron, but also a somewhat stronger overlap between the p- and d-bands.

The partial charges are listed in Table I according to their origin from different bands. In the p-band one immediately observes the strong admixture of metal d-states with nonmetal p-states. The metal–nonmetal interaction is strongest in TiC, decreases in TiN, but increases again in VN. In all cases the pd_σ bond (originating

from d-states with e_g symmetry) is found to be more pronounced than the pd_π bond. In terms of a covalent picture the p- and d-bands can be regarded as the bonding and antibonding states of the nonmetal p–metal d interaction (as reflected in the corresponding partial charges). For example the $p(d)$ partial charge in the p-band is highest (lowest) in TiN and lowest (highest) in TiC.

The d-band is unoccupied in TiC, but accommodates one or two electrons in TiN and VN, respectively. Apart from the higher occupancy in VN the small number of electrons with e_g symmetry is of interest. While in TiN almost all electrons in the d-band with this symmetry are shifted above E_F, in VN about 0.1 electron occupies states with e_g symmetry. Nevertheless, states with t_{2g} symmetry, which form metal–metal dd_σ bonds, dominate in both cases.

It is possible to derive such conclusions from local densities of states or partial charges (corresponding to integrated local densities of states), but the valence electron densities provide a more direct representation of the chemical bond in terms of spatial distribution and overlap between different wavefunctions as was illustrated before (6).

Figure 2a shows the theoretical valence electron densities of TiC, TiN, and VN in the ($1\bar{1}0$) plane. Comparison with experimental valence densities (Fig. 2b) is discussed in Sec. 4. The following observations can be made:

(i) The densities around the nonmetal sites are essentially spherically symmetric, as expected for p-states in an octahedral crystal field. The densities increase proceeding from the carbide to the nitrides, while those around the metal site remain about constant in TiC and TiN, but increase toward VN.

(ii) The most pronounced feature is the change in the nonspherical component of the charge density around the metal site in

TABLE I

LAPW PARTIAL CHARGES OF THE
p- AND d-BANDS FOR
TiC, TiN, AND VN
(IN ELECTRONS PER UNIT CELL)

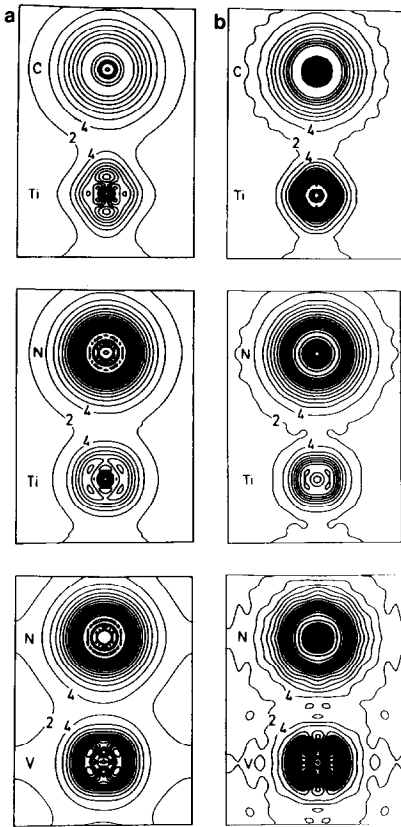|	Compound		
	TiC	TiN	VN
N_{val}: 8		9	10
d-band			
t_{2g}		0.58	1.24
e_g		0.01	0.11
X–p		0.14	0.24
Out		0.23	0.33
p-band			
t_{2g}	0.75	0.43	0.56
e_g	0.83	0.59	0.74
X–p	2.40	3.20	2.88
Out	1.66	1.45	1.49

FIG. 2. Valence charge density $\rho(r)$ of TiC, TiN, and VN in the $(1\bar{1}0)$ plane. Contours are at 0.2 electron/Å^3; labeled contours must be divided by 10 to obtain electrons per Å^3. The endpoints of the plots correspond to 0, 0, 0; 0.5, 0.5, 0; and 0, 0, 1 (taken in part from Refs. (7, 9, 10)). (a) Theoretical densities. (b) Experimental densities.

this series. In TiC the maxima near the Ti atom point toward the C sites and the excess of e_g-like charge implies a pd_σ bond, in agreement with the conclusions drawn from the partial charges. In TiN the density already shows a slight excess of t_{2g}-like charge, but from the valence density alone one cannot deduce a distinct binding mechanism. In VN the t_{2g} symmetry around the metal site dominates even more than in TiN, so that one would assume mainly strong metal–metal bonds, neglecting metal–nonmetal interactions.

The statements above could also have been made based on the experimental electron densities given in Fig. 2b. In both cases the total valence electron densities suggest a dominance of metal–metal bonds in TiN and VN, in contradiction to LAPW partial charges. This discrepancy can be easily resolved by theory when the total valence charge density is decomposed into contributions from different energy regions. In Fig. 3 the valence density of VN in the (100) plane is decomposed into the density of the sp bands (8 electrons) and of
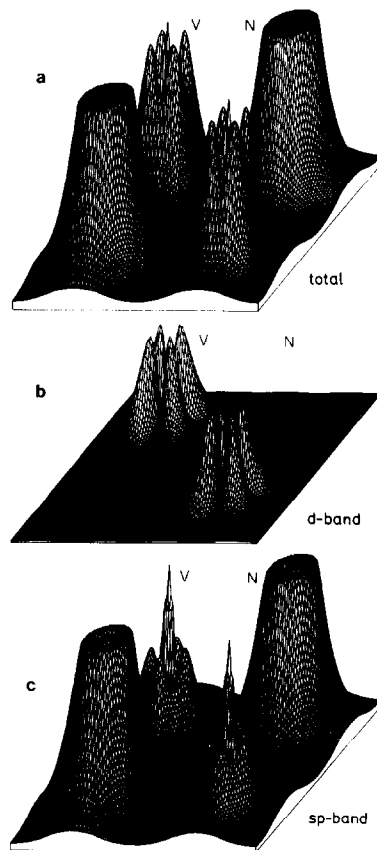

FIG. 3. Valence charge density $\rho(r)$ of VN in the (100) plane obtained by full potential LAPW calculations (cutoff at 3.0 e/Å^3). (a) Total valence bands (10 valence electrons). (b) Occupied part of the d band (2 valence electrons). (c) s- and p-band (8 valence electrons).

the d-band (2 electrons). The density of the sp band looks very much the same as the one of TiC (see Refs. (6, 7)) and again shows the strong metal–nonmetal σ-bond. In the d-band almost only V d-states with t_{2g} symmetry occur, but it is also evident that the overlap between the localized d-wavefunctions is not very strong. It is only the *sum* of both contributions (experimentally available) which hides the most important bonding contribution, namely, the pd_σ bond.

4. Comparison of Theoretical and Experimental X-Ray Structure Factors

In order to perform such a comparison, the basic conditions for theory and experiment should be identical. Band structure calculations describe the electronic structure of ideal (perfect) infinite crystals at 0 K (neglecting zero-point motion). On the other hand in an X-ray diffraction measurement a real (imperfect) finite crystal at higher temperature is used, and thermal motion, extinction, absorption, and non-stoichiometry dominate the results.

It was found that for $TiC_{0.94}$ the 6% vacancies have such drastic effects on the X-ray structure factors (9) that a direct comparison between the raw X-ray data and theory was not at all possible. The main reason was that a static displacement of the Ti atoms (around the C-vacancy sites) by about 0.1 Å must be taken into account.

Conventionally, experimental X-ray structure factors are refined against (spherical) atomic scattering factors with some corrections for thermal motion, absorption, and extinction. Such a model, however, does not account for nonspherical electron density distributions or for imperfections such as static atomic displacements caused by vacancies in the measured crystal.

In order to provide a more realistic description of the real solid, Dunand *et al.* (9) and Kubel *et al.* (10) developed an atomic model that incorporates all the effects mentioned above. Such a model consists of atomic orbital scattering factors, orbital occupancies p, κ parameters controlling expansion or contraction of the orbital scattering factors, harmonic and anharmonic thermal vibrations, a description of anisotropic inhomogeneous extinction, and non-stoichiometry effects. The latter are described by occupation parameters of the different sites and a mean displacement x_D of the metal atoms next to a vacancy in the [100] direction. For such a model two basic requirements exist: First, the model should be able to reproduce the experimental data sufficiently well, and second, all parameters of this model should have physical significance. If both are fulfilled, it should be possible to extrapolate the experimental data to that of an ideal crystal, as long as the imperfections do not alter the electronic structure of the individual atoms by too much; in addition it is required that the experimental data be accurate enough to avoid possible correlations between some parameters of the fit.

A nonlinear least-squares fit to the experimental and theoretical X-ray structure factors was performed (7–10) and the fitted parameters are given in Table II.

As a first step we want to discuss the relevant parameters and make a comparison between theoretical and experimental results:

(i) Only in TiC was a significant nonstoichiometry found in the experimental data, leading to a large static displacement (0.1 Å) of the metal atoms presumably away from the vacancy (9, 11).

(ii) The metal $4s$ population is larger in the fit to the theoretical structure factors than in the experimental one; however, the error bars are very large and thus it is not possible to draw a definite conclusion. A direct comparison with the LAPW partial charges (Table I) leads to the striking obser-

TABLE II

PARAMETERS OBTAINED BY NONLINEAR LEAST-SQUARES FIT OF THE STRUCTURE FACTORS OF TiC, TiN, AND VN

| | TiC | | TiN | | VN | | |
| | | | | | Theor. | | |
	Theor.	Exp.	Theor.	Exp.	MT	FP	Exp.
p_x	1.00	0.94	1.00	0.99	1.00	1.00	1.00
$x_D(\text{Å})$		0.097					
p_{4s}	1.20(13)	0.44(40)	1.20(10)	1.09(38)	1.42(6)	1.66(24)	1.47(17)
$p_{t_{2g}}$	0.72(3)	0.76(04)	1.00(4)	0.65(05)	1.70(3)	1.58(9)	1.79(05)
p_{e_g}	0.80(3)	0.75(04)	0.51(3)	0.35(04)	0.77(3)	0.88(10)	0.54(07)
p_{2s}	1.28(9)	3.07(37)	1.17(11)	1.81(65)	1.41(7)	1.26(25)	1.70(15)
p_{2p}	4.01(19)	3.11(63)	5.12(17)	5.12(66)	4.69(11)	4.6(4)	4.50(21)
κ_{4s}	1.01(5)	0.94(10)	1.00(5)	0.91(06)	1.08(4)	1.03(15)	0.92(14)
$\kappa_{t_{2g}}$	1.18(3)	1.77(08)	1.14(3)	1.40(08)	1.09(1)	1.12(4)	1.31(04)
κ_{e_g}	1.10(3)	1.47(07)	1.17(5)	1.42(12)	1.04(2)	0.96(8)	0.86(11)
κ_{2s}	0.99(3)	0.79(05)	0.90(3)	0.78(08)	0.95(1)	0.95(8)	0.84(03)
κ_{2p}	0.92(2)	1.23(07)	0.95(1)	0.96(06)	0.95(1)	0.94(3)	1.00
$Q(\text{Me})$	1.29(13)	2.05(38)	1.29(11)	1.91(37)	1.10(6)	0.87(24)	1.20(14)
$p-3d(\text{sph.})$	1.20	1.27(06)	1.28	0.88(11)	1.93	2.21	1.36(18)
$p-3d(\text{nonsph.})$	0.32	0.24(05)	0.23	0.12(09)	0.54	0.26	0.97(11)
$p-3d(\text{total})$	1.52	1.51(05)	1.51	1.00(07)	2.47	2.47	2.33(09)

Note. MT and FP denote the fit to the structure factors derived from the muffin-tin and the full potential calculation, respectively. Values for TiC and TiN are taken from Refs. (*7, 9*); theroetical values for VN were obtained by using the same model and the refinement program as for TiC and TiN; experimental values are taken from Ref. (*8*).

vation that the metal $4s$ partial charges are found to be much smaller in the LAPW formalism (about 0.1–0.3 e^-) than in the fits. This can be understood from the spatial distribution of the diffuse $4s$ wavefunction and the different concepts used in defining partial charges in LAPW (spatial partitioning, only the *l*-like charge inside a sphere is integrated) and orbital occupancies in the fit (*l*-decomposition similar to a Mullikan population analysis). The very diffuse $4s$ contributions are not found mainly in the LAPW $4s$ partial charge, but are included to a large extent in the term corresponding to the region outside the atomic spheres labeled "out" (interstitial region).

(iii) The nonmetal $2s$ and $2p$ populations also are not in very good agreement, but as the unphysical value of 3.07 for the C $2s$ population in TiC indicates, strong cor-

relations take place between parameter estimates involving diffuse orbitals, e.g., $Me-4s$ and $X-2s$, $X-2p$.

(iv) The total metal $3d$ population is generally in good agreement between theory and experiment, as is the number of nonspherical $3d$ electrons. In all cases the question whether d-electrons with t_{2g} or e_g symmetry dominate is answered consistently. One also notes that in TiN the total d-population is somewhat larger in theory than in experiment and that in VN a smaller nonsphericity is found by theory. These discrepancies, however, are small compared to the error bars of the experimental data.

(v) There is a clear charge transfer from the metal to the nonmetal atom for all compounds. A quantitative estimate of this charge transfer, however, is difficult due to

the uncertainties in the occupancies of the diffuse orbitals.

(vi) For VN we have performed two different theoretical calculations: one using the common muffin-tin approximation (the same as used for TiC and TiN) and the other with the full potential. The latter avoids the spherical averaging of the charge density and the potential inside the muffin-tin spheres and does not set these quantities to a constant in the interstitial region. A comparison between these two calculations shows that the X-ray structure factors agree to within 1% with each other (8). It is interesting to note, however, that the spherical averaging procedure of the muffin-tin calculation yields a charge density which deviates more from spherical symmetry than what is found in the full potential calculation. The latter is more sophisticated, yet deviates somewhat more from the experimental data than that of the muffin-tin calculation. Due to the experimental uncertainties this statement should not be taken too seriously. We expect similar differences between a muffin-tin and a full potential calculation for TiC and TiN as found for VN.

(vii) The most pronounced difference between theoretical and experimental parameters is found in some κ values which are introduced to allow orbital contraction or expansion. Experimental values are found to be as large as 1.77(8) or as small as 0.78(8). This corresponds to unphysically large contractions (expansions) of the radial wavefunctions between the free atom and the solid. As long as κ remains close to 1 ($\pm 10\%$) they seem to be reasonable, but larger deviations of κ from 1 again indicate some correlations in parameter estimates or shortcomings in either the atomic model used or in the experimental measurements. For a detailed discussion of the κ parameters see Ref. (7).

Despite the objections mentioned above we can use these parameters and calculate experimental valence electron densities for an ideal crystal which can be compared to theoretical data (Fig. 2). In general very good agreement between theoretical and extrapolated experimental densities is found, in particular the nonspherical electron density distribution around the metal sites and the densities around the nonmetal atoms agree well, while the magnitude of the $3d$ maxima are much higher in the experimental maps due to the large κ values (see Ref. (7)). Note that the densities obtained from X-ray diffraction data are more reliable in the bonding region than those near the nuclei.

5. Bonding Mechanism and Conclusions

The unusual combination of properties in these systems has challenged theorists to propose explanations in terms of chemical bonding for a long time. Different authors have drawn completely different conclusions about the actual bonding situation (7), starting from a crystallographic point of view (1, 2), using symmetry considerations or semiempirical band structure calculations. Some authors favor metal to metal bonding and neglect nonmetal atoms ("interstitial compounds"); others argue with covalently bonded XM_6 building blocks. In some theories a charge transfer from the metal to the nonmetal atom was found, while in others a charge transfer in the opposite direction was predicted.

Even with modern *ab initio* band structure methods the importance of the metal to metal or metal to nonmetal interaction is not determined unambiguously, as a recent controversy in the literature demonstrates (12, 13). For that purpose it is important to have experiments which can prove or disprove various theoretical approaches.

The following synopsis is based on the facts found in Sections 3 and 4 and therefore is in agreement with both theory and

experiment. We can summarize the bonding mechanism in refractory metal compounds as follows:

All compounds discussed here show metallic character as is evident from the finite density of states at the Fermi energy and the relative high electron density in regions far away from the individual atoms. In fact all compounds have metallic conductivity comparable to the free metals.

There is a considerable charge transfer from the metal to the nonmetal atom and this ionic character is in agreement with simple electronegativity arguments.

As a very important part of the bonding, the covalent contributions, in particular the nonmetal to metal pd bond, must be considered. This bonding feature is directly evident from the experimental electron densities in TiC, but theory is able also to detect these contributions in TiN or VN by partitioning the electron densities into certain energy ranges. Indirect evidence for the importance of the nonmetal to metal bonds also comes from the magnitude of the experimentally observed static atomic displacements in $TiC_{0.94}$. Approximately one-third of the metal atoms in this compound relax by about 0.1 Å in the [100] direction, presumably away from the empty nonmetal sites and thus reducing the Ti–C bond length from 2.17 to 2.07 Å. These distances are *shorter* than those found in most of the so-called complex carbides (*14*) which contain various [Ti_6C] octahedral networks.

From the covalent bonding contribution it is clear that the nonmetal atoms play a very important role and the name "interstitial compounds" is not justified at all. This is also evident in many chemical and physical properties, which depend critically on the composition of the compound.

Finally it should be noted that theory and experiment agree very well in these cases and that both tools are equally important in order to investigate the electronic structure and the chemical bonding. If such interpretations are based on either theory or experimental data only, it is easy to draw conclusions which are not valid, even when the observed facts are correct. This was demonstrated for VN whose total valence electron density suggests mainly a metal to metal dd_σ bonding, but does not reveal the important vanadium–nitrogen bond.

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