

Nitrogen vacancy and chemical bonding in substoichiometric vanadium nitride

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Abstract. The effect of the nitrogen vacancy on the bonding in the VN_x crystal is investigated by means of the CNDO/2 cluster calculations. It is shown that the existence of the N vacancy leads to local lattice relaxation and rearrangement of the interatomic bonds in its neighbourhood. One of the most interesting results is the appearance of strong V–V bonds through the vacancy site. The presence of the vacancy leads to the lowering of the total energy of the cluster and stabilization of the defect phase.

1. Introduction

Refractory metal compounds such as carbides and nitrides of the IVB and VB transition-metal subgroups possess an interesting combination of physical properties (extreme hardness, high melting temperatures and good electrical and thermal conductivity) and have wide application in engineering [1].

These materials also display deviations from stoichiometry caused by vacancies on the non-metal sublattice. The rock salt phase, however, remains stable over a wide range of the non-metal concentrations. The desirable physical and chemical properties are very strongly affected by the presence of vacancies and this circumstance has challenged theorists to study the influence of vacancies on the electronic structure.

In recent years, significant results have been achieved in the description of the electronic structure of substoichiometric refractory metal carbides and nitrides (for a detailed review see [2]). One important problem is the correct description of the ordering of vacancies. The following examples will illustrate the main trends in the study of the electronic structure of substoichiometric compounds.

The band theory can be applied assuming the long-range order of vacancies (the supercell method). This method was used in the case of $\text{TiC}_{0.75}$ and $\text{TiN}_{0.75}$ [3, 4]. The early studies of substoichiometric compounds with a statistical distribution of vacancies were performed using the virtual-crystal approximation [5, 6] for ZrC_x and Zr_yC [7], the tight-binding coherent-potential approximation (CPA) for TiC_x and TiN_x [8, 9], for NbC_x , HfC_x and TaC_x [10] and the average **T**-matrix approximation for TiC_x and TiO_x [11].

In recent years the Green function (GF) method has been used successfully for the analysis of the electronic states in solids containing defects. The muffin-tin GF method for NbC_x [12], the Korringa–Kohn–Rostoker (KKR) GF and KKR CPA methods were used in the case of TiC_x , TiN_x , VC_x and VN_x [13] and the LMTO GF method was used for the study of the non-metal and metal vacancies in TiC_x , TiN_x , TiO_x , VN_x and VO_x [14].

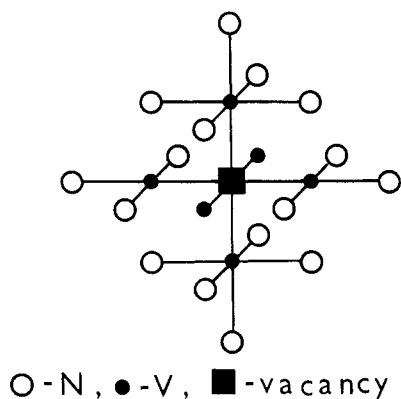


Figure 1. The cluster $\square V_6 N_{18}$ used in the calculations. In the non-defect cluster $NV_6 N_{18}$ the vacancy is replaced by the N atom.

The cluster approach is a useful method for investigating vacancy-induced changes of the electronic structure because the local charge redistribution in the vacancy neighbourhood obtained by this method provides more deep insight into the vacancy formation. The cluster approximation has been used for TiC_x , TiO_x [15], NbC_x [16] (the X_α discrete variational method) and for NbC_x , VN_x [17, 18] (the X_α multiple-scattering wave method).

In this paper we use the cluster approach to study the effect of the N vacancy on the electronic structure of VN_x clusters. This problem was first investigated by Ries and Winter [18] using the X_α multiple-scattering wave method. They found in their calculations an additional 'vacancy peak' in the density of states and the electronic structure was discussed in connection with the superconductivity. The KKR GF method and KKR CPA methods were used to study the electronic structure of the substoichiometric VN_x by Marksteiner *et al* [13] who revealed the vacancy states in the spectra of the compounds VN_x , VC_x , TiN_x and TiC_x .

Experimental studies of non-stoichiometric phases carried out by many workers showed the existence of static displacements of atoms adjacent to the vacancy (lattice relaxation). The magnitudes of the atomic displacements obtained by measurements of the Debye–Waller factor, diffuse scattering, ion channelling and EXAFS for substoichiometric carbides and nitrides are summarized in [19]. Owing to the importance of the lattice relaxation, we take this effect into account in our calculations.

2. Method of calculation

Stoichiometric and non-stoichiometric vanadium nitrides are represented by the clusters $NV_6 N_{18}$ and $\square V_6 N_{18}$ (figure 1). The electronic structure of the clusters has been determined by the complete neglect of differential overlap version 2 (CNDO/2) method [20]. The molecular wavefunctions $\Psi_i(\mathbf{r})$ are expressed in the LCAO basis as

$$\Psi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \Phi_{\mu}(\mathbf{r}) \quad (1)$$

where $\Phi_{\mu}(\mathbf{r})$ are atomic orbitals of s, p and d type. The matrix elements of the density matrix $P_{\mu\nu}$ are given by

$$P_{\mu\nu} = \sum_i g_i c_{\mu i} c_{\nu i} \quad (2)$$

where $g_i = 0, 1$ or 2 is the occupation number of the i th energy level. The atomic bond orders are defined as

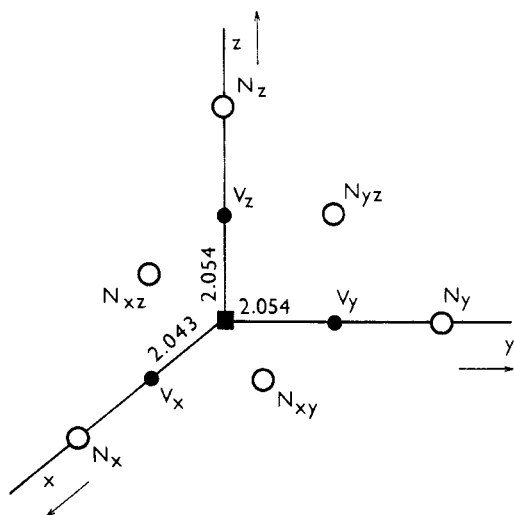


Figure 2. Atomic positions in the cluster $\square V_6 N_{18}$. The distances of V atoms from the centre of the cluster are expressed in ångströms. The positions of the N atoms are the same as in the non-defect cluster $NV_6 N_{18}$.

$$P_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}. \quad (3)$$

The number of the valence electrons at atom A equals

$$P_A = \sum_{\mu \in A} P_{\mu\mu} \quad (4)$$

where the summation runs over all the valence orbitals at atom A. The valence one-electron charge density equals

$$\rho(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \Phi_{\mu}(\mathbf{r}) \Phi_{\nu}(\mathbf{r}). \quad (5)$$

The first calculation on the defect-free cluster $NV_6 N_{18}$ was aimed at determining the equilibrium positions of atoms in the regular lattice. Then, introducing the lattice relaxation for six V atoms nearest to the central N vacancy, we carried out the calculations for the cluster $\square V_6 N_{18}$. Three parameter displacements of V atoms along the *x*, *y* and *z* axes were changed to minimize the total energy of the cluster. The positions of other atoms remained the same as in the $NV_6 N_{18}$ cluster.

3. Results

3.1. Static displacements and binding energy

The equilibrium interatomic V–N distance in the non-defect cluster $NV_6 N_{18}$ corresponding to the minimum of the total energy was calculated to be 2.038 Å.

The minimum of the total energy of the cluster $\square V_6 N_{18}$ was obtained for the shifted positions of V atoms as shown in figure 2. We can see from figure 2 that on introduction of the static displacements into the cluster $\square V_6 N_{18}$ the original high symmetry (O_h) of the cluster becomes lower (D_{4h}). The calculated N vacancy–V atom distances are 2.054 Å in the directions along the *y* and *z* axes and 2.043 Å along the *x* axis (D_{4h} symmetry). Comparing these results with the N–V distance in the non-defect cluster $NV_6 N_{18}$ (2.038 Å) we get the static displacements of V atoms in the neighbourhood of the N vacancy. The static displacement along the *y* and *z* axes is $S_{y(z)} = 0.016$ Å. For the *x* direction we get $S_x = 0.005$ Å. Both values are positive.

Table 1. The binding energy E_b per one electron and the total energy E_{total} of the cluster.

Cluster	E_b (eV)	E_{total} (eV)
NV_6N_{18}	1.8966	-6946.041
$\square\text{V}_6\text{N}_{18}$	2.1981	-6671.305

The reason for the lowering of the cluster symmetry is the same as in the Jahn–Teller theorem [21, 22]. For the O_h symmetry there is a number of doubly and triply degenerate occupied one-electron energy levels corresponding to two- and three-dimensional representations of the O_h group. The highest occupied, triply degenerate energy level (Fermi level) having t_{2g} symmetry is partially filled by four electrons. As a result, the ground state has orbital degeneracy. The transition to the symmetry D_{4h} , which has only one- and two-dimensional representations, removes this degeneracy. We note that the D_{4h} symmetry was obtained with accuracy of the positions of the V atoms better than 0.001 \AA . This is due to numerical errors.

The experimental values of the static displacements of metal atoms in substoichiometric carbides and nitrides obtained by various experimental methods lie between 0.04 and 0.12 \AA [19]. No experimental study of VN_x has been published. However, the comparison of our results with the experimental values is difficult. The experimental data give the average atomic displacements in a non-stoichiometric compound whereas, in our calculation, only one isolated vacancy is considered.

The atomic displacement field around a vacancy including second- and third-neighbour shells was investigated for $\text{TiN}_{0.82}$ using elastic diffuse neutron scattering [23]. From this work it follows that the atomic shifts for N atoms surrounding a N vacancy are about 30% of those for Ti atoms nearest to the vacancy. The estimation of the effect of our assumption (fixed N atoms close to N vacancy) is difficult. It may be expected, however, that because of the weaker bonding of metal and non-metal atoms the displacements of N atoms in VN_x are smaller than in TiN_x .

Comparison of the binding (cohesive) energy per one electron and the total energy of NV_6N_{18} and $\square\text{V}_6\text{N}_{18}$ clusters (table 1) shows the enhancement of the binding energy in the substoichiometric VN_x . This means that the vacancy has a stabilizing effect.

This is in good agreement with the experimental results [24, 25]. It has been shown in [24] that the microhardness of VN_x increases with increasing vacancy concentration in the range $x \in (0.72, 1)$. Other experimental evidence for hardening of the substoichiometric vanadium nitride is the dependence of the phonon dispersion and the density-of-states measurements for VN_x on the nitrogen content [25]. With increasing vacancy concentration a distinct shift of the phonon density-of-states curve to a higher energy has been observed [25].

3.2. Atomic charges

Partial and total atomic charges represented by the partial and total number of valence electrons for both clusters are summarized in tables 2 and 3. We see from table 2 that the charge transfer in the ideal cluster occurs from the metal to non-metal atoms. This charge transfer leads to electrostatic interactions and contributes to an ionic component of the binding. Comparing atomic charges for NV_6N_{18} and $\square\text{V}_6\text{N}_{18}$, we see that the greatest changes are exhibited for the V_x atoms adjacent to the vacancy in the direction

Table 2. The partial and total numbers P_A of the valence electrons for the NV₆N₁₈ cluster. The indices x, y, z denote the position of atoms in cluster (see figure 2).

	P_A			
	N_{central}	V_x	N_x	N_{xy}
s-p	5.204	1.830	4.998	5.087
d	—	2.964	—	—
Total	5.204	4.794	4.998	5.087

Table 3. The partial and total numbers P_A of the valence electrons for the cluster □V₆N₁₈. The values for the atoms in the x - z plane are not given here, because the differences between the corresponding values of the x - z and y - z planes are negligible (about 0.1%).

	P_A					
	V_x	V_y	N_x	N_y	N_{xy}	N_{yz}
s-p	1.995	1.936	5.117	5.195	5.023	5.032
d	2.680	2.897	—	—	—	—
Total	4.675	4.833	5.117	5.195	5.023	5.032

Table 4. Atomic bond orders P_{AB} .

	P_{AB}		
	sp-sp	sp-d	d-d
		NV ₆ N ₁₈	
$N_{\text{central}}-V_x$	0.233	0.290	—
$V_{+x}-V_{-x}$	0.00653	0.00169	0.00753
V_x-V_y	0.123	0.00954	0.0135
		□V ₆ N ₁₈	
$V_{+x}-V_{-x}$	0.0513	0.0139	0.396
$V_{+y}-V_{-y}$	0.0424	0.00934	0.00801
V_x-V_y	0.165	0.0185	0.0594
V_y-V_z	0.159	0.0169	0.0305

of the smaller static displacements (see figure 2). As follows from a comparison of the NV₆N₁₈ and □V₆N₁₈ cluster in tables 2 and 3, the changes in the atomic charge are more significant for N_x, N_y and N_z atoms than for N_{xy}, N_{yz} and N_{xz} atoms.

3.3. Bonding mechanism

To discuss the rearrangement of the interatomic interactions we present in table 4 the values of the atomic bond orders P_{AB} calculated from equation (3). The comparison of the atomic bond orders for the NV₆N₁₈ and □V₆N₁₈ clusters (see table 4) leads to the following conclusions.

- (i) In the stoichiometric vanadium nitride, the V-N bonds are dominating.

Table 5. Matrix elements of the density matrix $P_{\mu\nu}$.

	Matrix elements of $P_{\mu\nu}$	
	NV_6N_{18}	$\square V_6N_{18}$
$V_{+x}-V_{-x} (d_{yz}-d_{yz})$	-0.0363	0.6227
$V_x-V_y (d_{yz}-d_{xz})$	-0.0431	0.2183

(ii) The presence of the vacancy leads to a significant change in the character of the V–V interactions.

(iii) A large strengthening of the V–V bond via the vacancy along the x axis (direction of the smaller shift of V atoms) can be seen from the results on the $\square V_6N_{18}$ cluster; compare the $V_{+x}-V_{-x}$ (d–d) bonds for NV_6N_{18} and $\square V_6N_{18}$ in table 4.

(iv) d–d bonds of V_x-V_y and V_y-V_z , respectively, become more important in $\square V_6N_{18}$ than in NV_6N_{18} .

A similar bonding situation was found in the ordered $TiN_{0.75}$ crystal by Herzig *et al* [4] (the self-consistent APW band-structure method) who reported the increasing importance of Ti–Ti bonds via the vacancy.

Analysing the bonding mechanism in more detail, we restrict ourselves to discussion of $V_{+x}-V_{-x}$ (d–d) and V_x-V_y (d–d) bonds where the effect of the vacancy is most significant (tables 4 and 5).

Analysis of the density matrix $P_{\mu\nu}$ (equation (2)) showed that the very large change in V_x-V_{-x} (d–d) bond in the presence of the vacancy can be ascribed to the dramatic change in the $d_{yz}-d_{yz}$ interaction (see table 5). A slightly smaller strengthening of the V_x-V_y (d–d) bond in the $\square V_6N_{18}$ cluster is again the result of changes in the $P_{\mu\nu}$ -values. In this case, the largest change is exhibited by the $d_{yz}-d_{xz}$ bond.

3.4. Electron densities

In order to visualize the vacancy-induced changes in the charge distribution we calculated the contour maps of the valence one-electron density $\rho(\mathbf{r})$. Figure 3 shows the valence electron density of the NV_6N_{18} cluster in the x – y plane. Two main features of the charge density distribution may be seen from figure 3.

(i) The nitrogen valence charge density is spherically symmetric around the N nuclei and is much larger than the vanadium charge density.

(ii) The vanadium charge distribution is anisotropic with the local maximum along the V–V directions.

Our contour maps are in good agreement with the results obtained from the full-potential linearized augmented-plane-wave method calculations on VN presented in [26]. Comparison with the corresponding experimental maps of the valence electron density determined from x-ray diffraction experiments [27] confirms the spherically symmetric nitrogen charge density and the charge anisotropy around the vanadium sites. Similar contour maps of the valence charge density were calculated for TiN in [4].

The valence electron density of the defect cluster $\square V_6N_{18}$ is shown in figure 4 (x – y plane) and figure 5 (y – z plane). Comparing the charge density near the V atom in NV_6N_{18} and $\square V_6N_{18}$ (figures 3–5) we see an increase in the electron density near V atoms in the substoichiometric vanadium nitride cluster.

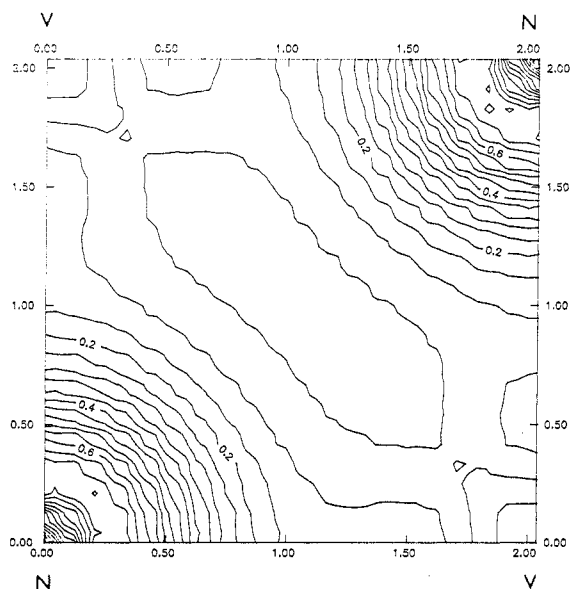


Figure 3. Valence electron density $\rho(r)$ in the x - y plane of the non-defect cluster in electrons per cubic ångström.

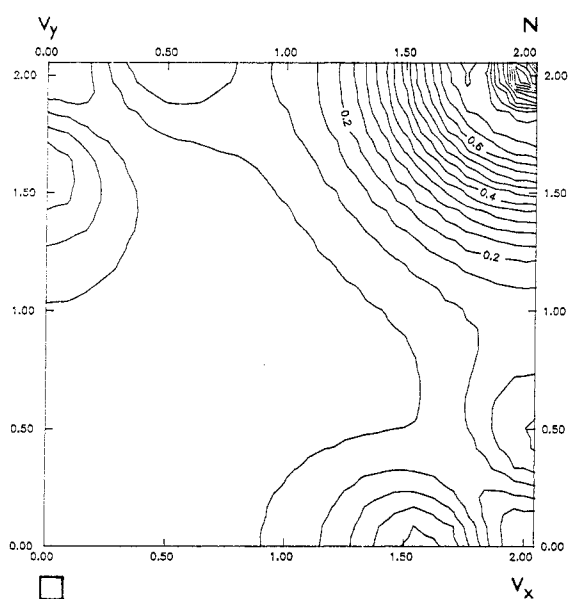


Figure 4. Valence electron density $\rho(r)$ in the x - y plane of the $\square V_6N_{18}$ cluster (position see figure 2) in electrons per cubic ångström.

It follows from figures 4 and 5 that the enhancement of the valence electron density is more pronounced around V atoms on the x axis than on the y or z axis. It corresponds to the existence of the strong d—d bonding of V_{+x} — V_{-x} atoms via the vacancy (see tables 3 and 4). The contour maps presented in figures 3–5 illustrate all the results concerning the atomic charges (tables 2 and 3) and the bonding mechanism (tables 4 and 5).

The presented calculations showed also the importance of the local lattice relaxation of the vacancy neighbourhood which increases the stability of the substoichiometric compound. When the static displacements of V atoms were taken into account, dramatic changes in the charge distribution and bonding character in the vicinity of the N vacancy were obtained.

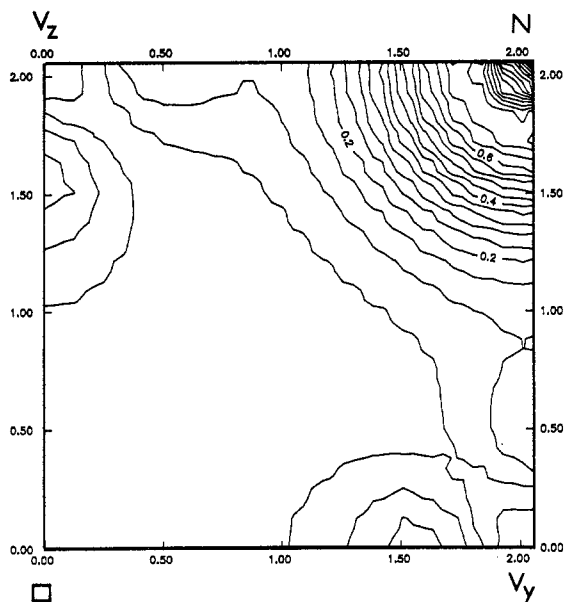


Figure 5. Valence electron density $\rho(r)$ in the y - z plane of the $\square V_6N_{18}$ cluster in electrons per cubic ångström.

The results of this work show that it is desirable to perform CNDO/2 calculations for larger clusters with two neighbouring vacancies where the local atomic arrangement and bonding situation for a higher vacancy concentration can be investigated. Except for this, such calculations may give information on the vacancy ordering in the substoichiometric vanadium nitride.

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