

## LETTER TO THE EDITOR

## Interaction of Octahedral Bonds in Transition Metal Carbides and Nitrides

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Local-density total energy calculations within the parameter-free self-consistent augmented-spherical-wave method are performed on ordered nonstoichiometric rock-salt-type structures of  $VC_{0.75}$  and  $VN_{0.75}$ . Starting from the idea of two kinds of building units,  $M_6X$  and  $M_6\Box$  ( $M$ ,  $X$ , and  $\Box$  are the transition metal, a nonmetal, and the vacancy, respectively), we investigate interactions of octahedral bonds formed by the octahedral arrangement of transition metals  $M_6\Box$ . Using enlarged unit cells with the same composition we have found ordered structures with contacting corners of octahedra (corner-sharing structures) energetically favorable for both carbide and nitride as compared to the ordered structure of noncontacting octahedra. The interaction of the octahedral bonds in the corner-sharing structure of the carbide ( $E_{st} = -4.9$  mRy/V atom) does not seem strong enough to predominate in forming carbide superstructures since vacancies avoid *fcc* second-neighbor positions. On the other hand, significantly larger stabilization in nitride ( $E_{st} = -13.2$  mRy/V atom) agrees well with *fcc* second-neighbor positions of vacancies in nitride superstructures. © 1994 Academic Press, Inc.

Carbides and nitrides of transition metal elements (e.g., Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W) are considered to be typical interstitial compounds. They are nonstoichiometric with compositions ranging within certain limits. For all of them the nonstoichiometry is due to the vacancies in their rock salt structure, in which the metallic sublattice remains completely occupied. Depending on thermal treatment these vacancies may be found ordered or disordered. An experimental review of ordering phenomena was presented in (1-3). Landesman (4) proposed a classification in terms of stacking of octahedra made of carbons and vacancies, centered on a metal atom.

Using a formal analogy of the carbon-vacancy sublattice to a *fcc* binary alloy, two methods based on the generalized Ising Hamiltonian have been established. Both generalized perturbation (5) and cluster expansion (6) methods have successfully described the configuration-

dependent properties of nonstoichiometric transition metal carbides and nitrides (TMCN). Ozoliņš and Häglund have recently evaluated effective cluster interactions in  $VC_{1-x}$  compounds (7). In terms of pair interactions they accurately described the energetics of ordered structures. They found that it is energetically unfavorable to form disordered  $VC_{1-x}$  compounds. Nevertheless, their pair-interaction-based formalism did not enable them to reveal the mechanism of interactions leading to the stabilization of ordered structures.

In this work we adopt the idea of considering  $M_6\Box$  octahedra as building units in addition to the usual  $M_6X$  octahedra ( $M$ ,  $X$ , and  $\Box$  represent a metal atom, a nonmetal atom, and a vacancy, respectively). The reasons for doing so are as follows. Numerous theoretical works on TMCN rock salt structures with vacancies have shown the creation of octahedral bonds (OBs) inside  $M_6\Box$  and their stabilization effect. Both the supercell band structure approach (8-10) and the Green's function technique (11, 12) provide the same picture of chemical bonding in accordance with XPS spectra (13), where a pronounced peak appears corresponding to the vacancy-induced states of OBs. The mechanism of the creation of OBs is reported in detail in (14). TM *d* orbitals, being dominant components, are combined into two types of bonds. In  $\sigma$  bonds ( $\pi$  bonds) the electron density maximum is located in (out of) the center of a vacancy (*s*- and/or *p*-like symmetry). Both  $\sigma$  and  $\pi$  bonds show pronounced directional properties (14) allowing interconnections into 3D networks. In the present work we ask a simple question: can the interaction of OBs stabilize the structure, and what kind of interaction is most effective? The concept of  $M_6\Box$  building units makes such investigations possible in a simple and instructive way.

We perform local-density total energy calculations based on the parameter-free self-consistent augmented-spherical-wave method (15). The computational unit cells (Fig. 1) raise  $V_8X_6$  periodic structures shown in Fig. 2 ( $X$

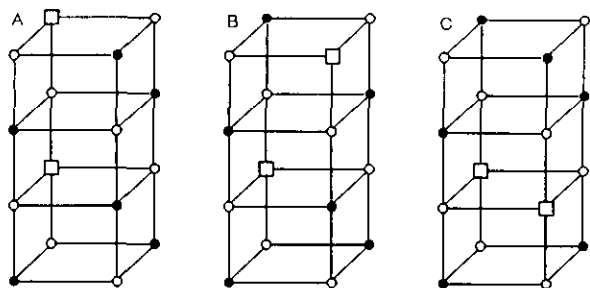


FIG. 1. Computational unit cells for nonstoichiometric ordered  $VX_{0.75}$  ( $X = C, N$ ). ●, nonmetal atoms; ○, vanadium atoms; □, vacancies.

stands for the nonmetal atom). Structure A, possessing  $Fm\bar{3}m$  symmetry, represents the three-dimensional system of corner-sharing octahedral bonds. In structure B every second two-dimensional layer of the corner-sharing octahedra is shifted, thus breaking the interconnection of the octahedra in the vertical direction. The nonmetal sublattice of structure C consists of alternately empty and full 001 planes of octahedral bonds. The total energies obtained using the same  $k$ -point mesh for  $VC_{0.75}$  and  $VN_{0.75}$  are summarized in Table 1 (the experimental lattice pa-

TABLE 1  
Total Energies for  $VC_{0.75}$   
and  $VN_{0.75}$  (mRy/V atom)

	$VC_{0.75}$	$VN_{0.75}$
A	-4.9	-13.2
B	—	—
C	+8.1	+11.7

rameters (11) are  $a_0(VC_{0.75}) = 7.84$  a.u.,  $a_0(VN_{0.75}) = 7.70$  a.u.). Taking structure B as the reference level we see that structure A is stabilized and structure C destabilized in both systems. This result is direct evidence for the interaction of octahedral bonds (nothing is changed except mutual arrangement of vacancies). The full 001 plane of the edge-sharing octahedra is energetically less favorable than the ordered structure of noncontacting octahedra in both carbide and nitride. Structure stabilization via corner sharing was recently predicted, based on symmetry analysis (14) as it favors interconnections of both  $\sigma$  and  $\pi$  octahedral bonds into three-dimensional networks (Fig. 3). The stabilization in nitride is more than twice as large as that in carbide. To explain this fact we recall conclu-

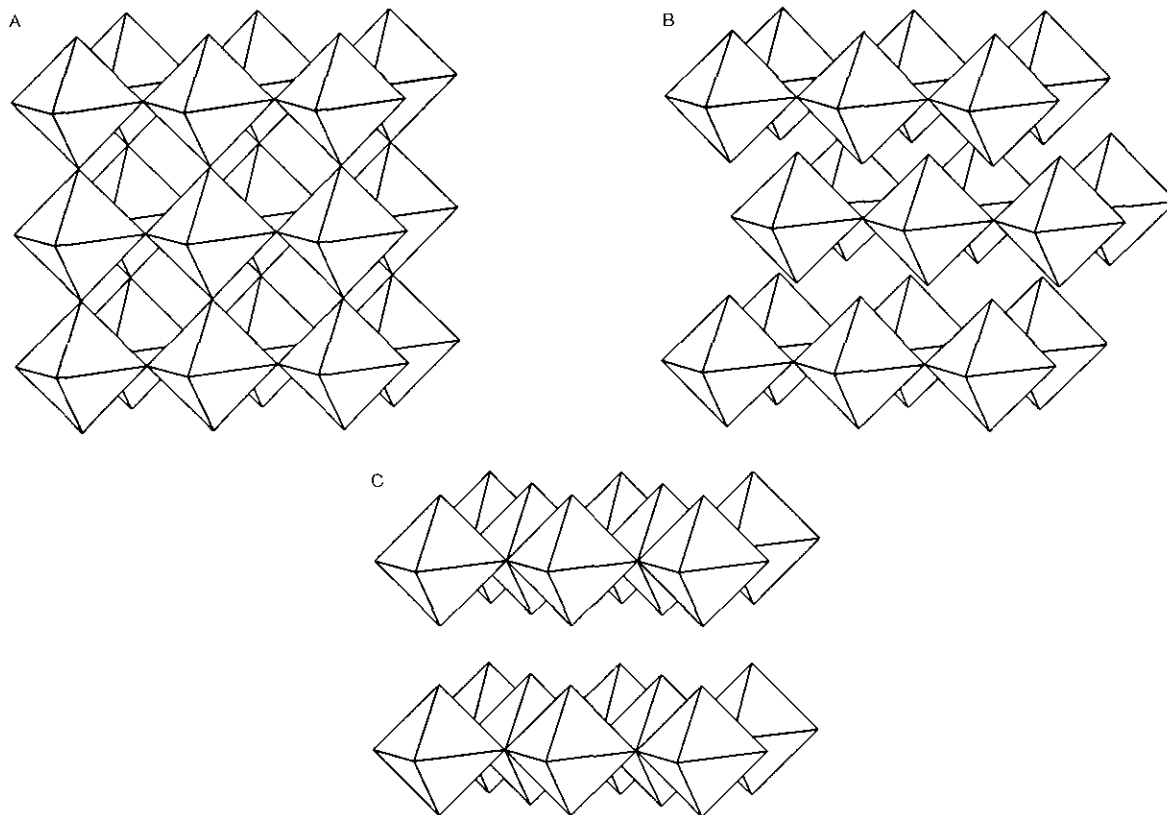


FIG. 2. Ordered periodic structures of  $V_3X_6$  (only the  $V_6$ □ octahedra are displayed for clarity). (A) Corner-sharing octahedra. (B) Sheets of corner-sharing octahedra noncontacting in the  $z$ -direction. (C) A structure with alternating empty and full-edge-sharing octahedra.

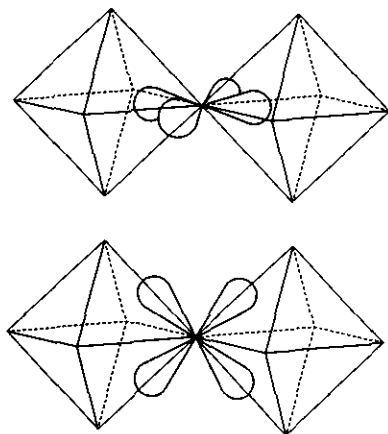


FIG. 3. Interconnection scheme of octahedral bonds via  $\sigma$   $d$  orbital (top) and  $\pi$   $d$  orbital (bottom).

sions of the work (16) in which the metal-to-metal interactions of the rock salt TMCN are studied. The chemical bonding here is controlled by two dominant components, the nonmetal  $p$  and the metal  $d$  orbitals (17). While in carbide the energy difference of the interacting atomic levels is small, it is significantly larger in nitride (0.4 and 2.0 eV, respectively), causing the smaller part of the  $d$  states to be included into the bonding  $p$ - $d$  interaction. In nitride, a part of the  $d$  orbitals is therefore left free to create the so-called "net  $d$ - $d$  states". These are located at the bottom of the  $d$  band, and even though they are less stabilized than states participating in the main bonding  $p$ - $d$  interaction, they contribute to the overall stability of the system via increased interaction of OBs as shown in Table 1.

According to Ozoliņš and Häglund (7) the ordered  $V_8C_7$  and  $V_6C_5$  have even lower enthalpies of formation than the stoichiometric VC. Our results on interacting OBs support their conclusions that these ordered substoichiometric compounds represent stable phases. Moreover, they allow us to understand why  $V_6C_5$  is more stable than  $V_8C_7$  (Fig. 5 in (7)). The unit cell for  $V_8C_7$  (7, 18) contains only noncontacting OBs. On the other hand, all three unit cells proposed for superstructures in  $V_6C_5$  (7, 19–21) yield the same pattern of corner sharing by OBs, thus stabilizing the system, which explains the fact that equal total energies are obtained for all three  $V_6C_5$  periodic structures.

All experimental data published on nitride superstructures (Ti, V, Nb, Mo) (3) lead to similar features: long-range ordering with vacancies in  $fcc$  second-neighbor positions. The interaction of OBs via corners seems strong enough to play an important role in structure buildup not only of superstructures, but of the stable phases as well. An example of TM nitride structure with corner-sharing OBs is tetragonal  $\epsilon$ - $Ti_2N$ , which possesses the antirutile structure (22). Discussing the stability of the  $\epsilon$ -phase compared to the superstructure of  $\delta'$ - $Ti_2N$ , Eibler stresses the

role of  $d$ - $d$   $\sigma$  bonding between  $Ti_2N$  units (23), which in fact represents one component of OB-to-OB interaction.

Nonstoichiometric carbides behave differently than nitrides. In their superstructures vacancies avoid  $fcc$  second-neighbor positions (3). Though such an arrangement is energetically favorable, the stabilization is much lower than that in nitrides (cf. Table 1, structure type A). Apparently some other mechanism of OB-to-OB interaction predominates, e.g., combined OB corner- and edge-sharing.

*Ab initio* total energy calculations on ordered unrelaxed structures  $VC_{0.75}$  and  $VN_{0.75}$  demonstrate unambiguously the stabilizing effect of the interaction of octahedral bonds via shared corners on structures, both carbides and nitrides. Much larger stabilization revealed for nitrides is in good agreement also with superstructures and structures of stable phases. Interactions of octahedral bonds occurring in shared octahedra stacked in the 111 plane, which is the case for superstructures in carbides (3), are the subject of our present study.

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#### REFERENCES

1. C. H. de Novion and V. Maurice, *J. Phys. Colloq.* **38**(C7), 211 (1977).
2. B. V. Khaenko, *Neorg. Mater.* **15**, 1535 (1979).
3. C. H. de Novion and J. P. Landesman, *Pure Appl. Chem.* **57**, 1391 (1985).
4. J. P. Landesman, Thesis. Université de Strasbourg, January 1985.
5. F. Ducastelle and F. Gautier, *J. Phys. F* **6**, 2039 (1976).
6. F. Ducastelle, "Order and Phase Stability in Alloys." North-Holland, Amsterdam, 1991.
7. V. Ozoliņš and J. Häglund, *Phys. Rev. B* **48**, 5069 (1993).
8. J. Redinger, R. Eibler, P. Herzig, A. Nickel, R. Podloucky, and E. Wimmer, *J. Phys. Chem. Solids* **46**, 383 (1985).
9. J. Redinger, R. Eibler, P. Herzig, A. Neckel, R. Podloucky, and E. Wimmer, *J. Phys. Chem. Solids* **47**, 387 (1986).
10. P. Herzig, J. Redinger, R. Eibler, and A. Neckel, *J. Solid State Chem.* **70**, 281 (1987).
11. P. Marksteiner, P. Weinberger, A. Neckel, R. Zeller, and P. H. Dederichs, *Phys. Rev. B* **33**, 812 (1986).
12. P. Marksteiner, P. Weinberger, A. Neckel, R. Zeller, and P. H. Dederichs, *Phys. Rev. B* **33**, 6709 (1986).
13. H. Höchst, R. D. Bringans, P. Steiner, and T. Wolf, *Phys. Rev. B* **25**, 7183 (1982).
14. Ľ. Benco, *J. Solid State Chem.* **110**, 58 (1994).
15. A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., *Phys. Rev. B* **19**, 6094 (1979).
16. Ľ. Benco, submitted for publication.
17. Ľ. Benco, submitted for publication.
18. C. Froidevaux and D. Rossier, *J. Phys. Chem. Solids* **28**, 1197 (1967).
19. J. D. Venables, D. Kahn, and R. G. Lye, *Philos. Mag.* **18**, 177 (1968).
20. J. Billingham, P. S. Bell, and M. H. Lewis, *Philos. Mag.* **25**, 661 (1972).
21. A. I. Gusev and A. A. Rempel, *Phys. Status Solidi A* **93**, 71 (1986).
22. B. Holmberg, *Acta Chem. Scand.* **16**, 1255 (1962).
23. R. Eibler, *J. Phys. Condens. Matter* **5**, 5261 (1993).