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Quantum-chemical simulation of the electronic structure and chemical bonding in the new 'superstoichiometric' titanium carbonitride Ti_2CN_4

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The electronic properties and the nature of interatomic interactions in the new 'superstoichiometric' metal-like titanium carbonitride Ti_2CN_4 with the spinel structure have been predicted using the *ab initio* DFT-DV calculaions of large clusters.

Two classes of compounds provide the basis for the quest of novel ceramic and composite materials. The first class includes compounds of *d* metals (M) with light *sp* elements. Among them are cubic (B1-type) carbides and nitrides [M(C,N)][1] which (i) have wide homogeneity regions [containing a variable number of vacancies in the non-metallic sublattice $M(C,N)_y$ $0.5<y<1.0$] and (ii) form mutual solid solutions. The properties of solid solutions (for example, carbonitrides MC_xN_y, $x + y \leq 1.0$) change non-monotonically with concentration.[1,2] It is important that atoms in these systems have an octahedral environment and the relative content of atomic components does not exceed $(C,N)/M \leq 1.0$. The exception being several 'superstoichiometric' nitrides ($MN_{y>1}$ obtained as films) where the ratio $N/M > 1.0$ is achieved due to the presence of vacancies in the M sublattice.[3]

The second class comprises refractory compounds of *sp* nonmetals [carbides, nitrides and oxides of B, Si and Al, multicomponent phases, for instance, silicon oxynitrides (Si_2N_2O), sialons ($Al_{x+y}Si_{6-x}O_xN_{8-x+y}$), *etc.*[4]] characterised by a tetrahedral atomic coordination.

Recently, the synthesis (at $P = 15$ GPa and $T \approx 2000$ K) of the new polymorphous modification of silicon nitride with the cubic structure (c-Si_3N_4) was reported.[5] According to estimates,[5] its cohesive properties are similar to those of the hardest modification of SiO_2 (stishovite). The new c-Si_3N_4 phase is of the spinel structural type and contains silicon atoms in octahedral $[Si^oN_6]$ and tetrahedral $[Si^tN_4]$ surroundings ($Si^o:Si^t = 2:1$).

Table 1 Overlap populations (OP, e) of the valence orbitals of neighbouring atoms in TiN, Ti_2CN_4 and C_3N_4 (×10^3, per pair of interacting centres) and effective atomic charges (Q_{ef}, e) in TiN, Ti_2CN_4 and C_3N_4 (the charges obtained according to the Mulliken scheme are given in brackets).

OP		TiN		Ti_2CN_4		C_3N_4	
		N 2*s*	N 2*p*	N 2*s*	N 2*p*	N 2*s*	N 2*p*
$Ti(C^o)$	3*d*	33	121	37	174	—	—
	4*s* (2*s*)	–25	77	–1	73	–7	130
	4*p* (2*p*)	87	68	53	48	79	229
C^t	2*s*	—	—	14	205	–15	202
	2*p*	—	—	173	349	127	348
Q_{ef} [Ti (C^o)]		1.43 (0.82)		1.49 (0.88)		0.57 (0.29)	
Q_{ef} (C^t)		—		0.55 (0.36)		0.54 (0.34)	
Q_{ef} (N)		–1.59 (–0.83)		–0.93 (–0.53)		–0.42 (–0.23)	

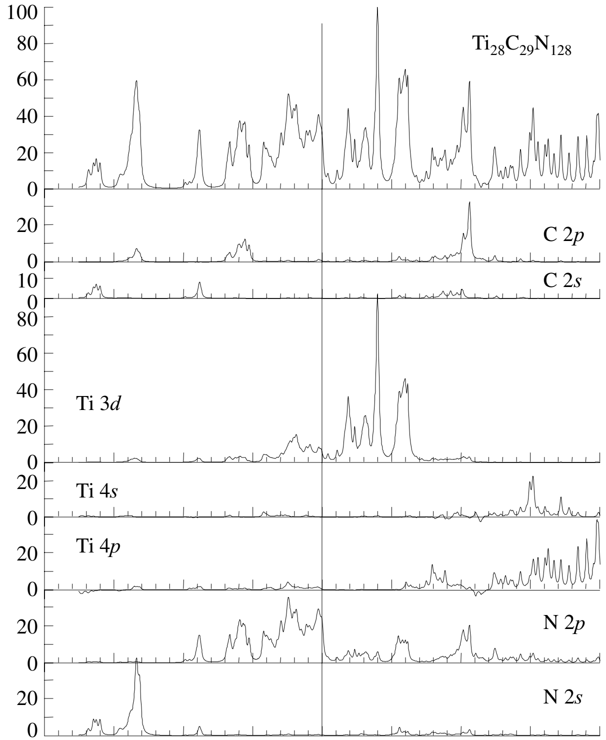

Figure 1 Total (top) and partial densities of states for the $Ti_{28}C_{29}N_{128}$ cluster.

By substituting C or Ti for silicon in c-Si_3N_4, the simulation of novel compounds, namely, the cubic carbon nitride ($C_2^oC^tN_4$)[6] and the 'superstoichiometric' titanium nitride ($Ti_2^oTi^tN_4$)[7] was made. These hypothetical phases include 2/3 (C^o) or 1/3 (Ti^t) cations in an octahedral or tetrahedral environment, which are not typical (in the corresponding binary phases C_3N_4 and TiN), *i.e.*, the proposed[6,7] compounds are difficult to synthesise.

According to our opinion, it is more realistic to obtain a new cubic phase with the spinel structure, *viz.*, the 'superstoichiometric' titanium carbonitride of the formal composition Ti_2CN_4, which will be isoelectronic and isostructural with c-Si_3N_4 and will contain C and Ti cations in inherent to them (in binary nitrides) octahedral $[Ti^oN_6]$ and tetrahedral $[C^tN_4]$ coordinations. It may be suggested that, assembled of the main 'structural fragments' TiN and C_3N_4, the 'superstoichiometric' carbonitride Ti_2CN_4 may possess an unusual combination of their most attractive properties: the plasticity of a metal-like titanium nitride[1,2] and the hardness of a high-covalence carbon nitride.[8]

We performed a quantum-chemical simulation of the electronic structure and interatomic bonds in Ti_2CN_4 and compared them with those of the known nitrides TiN and C_3N_4. The electronic structure was calculated in the density functional theory (DFT) approximation using the original code of the self-consistent discrete variational (DV)[8] cluster method with local exchange-correlation potential.[9] The basis set of numerical atomic orbitals (AO), which were the solutions of Hartree–Fock–Slater equations for isolated neutral atoms, included Ti 4*p* functions in addition to occupied AOs. The Diophantine integration grid with 4000 and 2000 sample points per each Ti and C(N) site, respectively, was used for the calculations of matrix elements. Ti_2CN_4 was simulated by the 185-atomic cluster $Ti_{28}C_{29}N_{128}$ (point group symmetry T_d). It is known[10] that the positions of atoms in the spinel structure (space group $Fd3m$–O_h^7) are determined by two parameters *a* and *x*. Assuming that the parameters of the coordination polyhedra $[Ti^oN_6]$ and $[C^tN_4]$ for Ti_2CN_4 are equal to those for TiN ($R_{Ti-N} = 2.122$ Å) and C_3N_4 ($R_{C-N} = 1.585$ Å), we derived the values $a = 8.098$ Å and $x = 0.363$. To compare the electronic structure of Ti_2CN_4 and C_3N_4 obtained using a similar

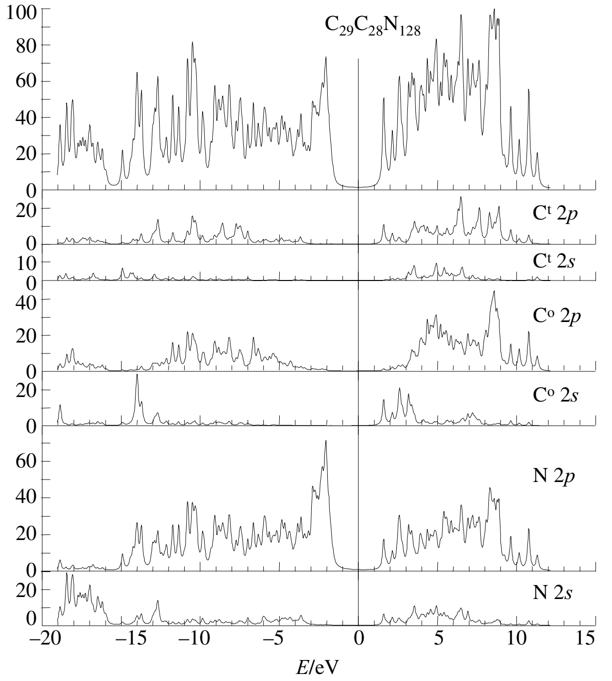

Figure 2 Total (top) and partial densities of states for the $C^o_{28}C^t_{29}N_{128}$ cluster.

approach, we also performed DFT-DV calculations of the cluster $C^o_{28}C^t_{29}N_{128}$ in the C_3N_4 structure with bond lengths of 1.585 and 1.676 Å for C^t–N and C^o–N, respectively.[6] Boundary conditions in the 'extended cluster' scheme[11,12] were used.

The model densities of states (MDOS) of the cluster $Ti_{28}C_{29}N_{128}$ are presented in Figure 1. The total band width of bonding states is about 10 eV. It is made up of the contributions from hybrid Ti 3*d*–N 2*p* (0–5 eV), N 2*p*–C 2*p* (5–7.5 eV) and N 2*p*–C 2*s* orbitals [7.5–10 eV below the Fermi level (E_F)] that form Ti–N and C–N bonds in $[Ti^oN_6]$ and $[C^tN_4]$ polyhedra. Ti_2CN_4 has no forbidden gap (FG) and will exhibit metal-like properties.

A comparison with DFT-DV results for the cluster $Ti_{79}N_{140}$ used to model TiN[13] shows that the most essential differences in the electronic structures of TiN and Ti_2CN_4 concern the mutual arrangement of the Ti 3*d* and N 2*p* states. In the nitride, the upper edge of the N 2*p* band (total width of 5 eV) is 4 eV below E_F located in the region of π-like antibonding Ti 3*d* states.[13]

The cubic C_3N_4 has a FG of more than 3 eV according to our calculations (1.14 eV according to ref. 7); its spectrum (Figure 2) contains a continuous N 2*s*,*p*–C 2*s*,*p* band of the total width of 17 eV. The differences in the MDOS of C^t centres in C_3N_4 and Ti_2CN_4 are attributed to the considerable broadening of C^t 2*s*,2*p* bands, their shift to lower binding energies and a decrease of C^t 2*s*,2*p*–N 2*s* hybridization in the nitride. The differences in the MDOS of C^t and C^o in C_3N_4 concern the different hybridization effects in $[C^tN_4]$ and $[C^oN_6]$ polyhedra. The orbital overlap populations (OP) of TiN, C_3N_4 and Ti_2CN_4 obtained by the same cluster DFT-DV method are listed in Table 1. It can be seen that on going from TiN to Ti_2CN_4 the OP of Ti 3*d*–N 2*p* AO, which provides the major contribution to the Ti–N bonding, increase appreciably, whereas the OP of Ti 4*p*–N 2*s* and Ti 4*p*–N 2*p* AO decrease slightly. In general, the Ti–N chemical bonding in the simulated carbonitride is not weaker than that in TiN. A comparison of the OP of C^t centres with the neighbours in Ti_2CN_4 and C_3N_4 shows that the C^t–N bonds in the carbonitride are stronger due to the C^t 2*p*–N 2*s* hybridization. The fact that the octahedral coordination is less advantageous for carbon is evident from a comparison of the OP of C^t–N and C^o–N in C_3N_4: all the contributions forming the C^o–N bonding are on the average 1.5 times smaller than those for C^t–N.

Let us compare effective atomic charges (Q_{ef}) in TiN, Ti_2CN_4 and C_3N_4 (Table 1), which were obtained by three-dimensional integration in the space between nuclei.[11] The values of Q_{ef} at Ti in TiN and Ti_2CN_4 appear to be similar, whereas the charges at nitrogen atoms in the carbonitride are only ≈ 60% of the corresponding values for TiN. The fundamental difference between Ti_2CN_4 and the known *B*1 carbonitrides MC_xN_y $(x + y \leq 1.0)$ incorporating carbon in the anionic state[2] is the cationic form of C^t, the effective charges of C^t in Ti_2CN_4 and C_3N_4 being very close. The charges at N in C_3N_4 are half as large as in Ti_2CN_4 and are lower than those in TiN by a factor of 4, *i.e.*, Ti_2CN_4 is intermediate in the degree of ionicity among the binary nitrides under consideration. In conclusion, note that due to the similarity of the simulated 'superstoichiometric' titanium nitride Ti_2CN_4 and the familiar interstitial phase TiN, Ti_2CN_4 may be expected to have properties[2] typical of those of titanium nitride, such as nonstoichiometry in the N sublattice (Ti_2CN_{4-y}-type compositions) or the formation of multicomponent solid solutions by replacing Ti atoms by other *d* metals (for example, $Ti_{2-x}Zr_xCN_4$ and $Ti_{2-x}Hf_xCN_4$). The synthesis of more complicated phases, where Si or Ge partially substitute for carbon, is possible.

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