Effect of metal and carbon vacancies on the electronic structure of hexagonal WC and cubic TaC

Alexander L. Ivanovskii* and Nadezhda I. Medvedeva

Institute of Solid State Chemistry, Urals Branch of the Russian Academy of Sciences, 620219 Ekaterinburg, Russian Federation. Fax: +7 3432 74 4445; e-mail: ivanovskii@ihim.uran.ru

10.1070/MC2001v011n01ABEH001375

The electronic states and energy characteristics of carbon and metal vacancies in hexagonal β-WC and cubic TaC were examined by the full-potential LMTO method.

Group IV–VI transition metal carbides are well-known non-stoichiometric compounds. For example, the concentration of carbon vacancies in Group IV and V transition metal cubic (B1 type) carbides can be as high as 30–55 at%. As a rule, the metal sublattice of carbides remains complete.[1]

The electronic properties of carbon vacancies and their effect on the physico-chemical characteristics of cubic (B1 type) 3*d*- and 4*d*-metal monocarbides were studied previously.[2–6] At the same time, the electronic states of vacancies in VI Group metal non-cubic carbides are still not clearly understood. Hexagonal tungsten carbide (β-WC) is one of the most interesting compounds of this kind. It possesses extreme thermomechanical properties and exhibits a catalytic activity comparable to the activity of platinum.[1]

β-WC exhibits a narrow range of homogeneity, in which the carbon content varies within the limits 37–48 at%. Until recently, the metal lattice of WC was considered to be fully occupied. Recently,[7] the presence of both C- and W-vacancies in WC was found by the positron annihilation method.

We report here the results of studies concerning the electronic states of both of the types of lattice defects — carbon (V_C) and metal (V_W) vacancies — in hexagonal WC. By now, only the electronic structure of an 'ideal' (complete) β-WC crystal was examined.[6] For comparison, we also calculated the electronic states of V_C and V_{Ta} vacancies in cubic TaC, a typical B1 carbide, which is characterised by a wide range of homogeneity.[1]

The carbides MC (M = W and Ta) were simulated by 16-atomic M_8C_8 supercells in hexagonal (β-WC) and cubic (TaC) structures. The $M_8C_7V_C$ and $M_7V_MC_8$ supercells described defect carbides of the formal compositions $MC_{0.875}$ and $M_{0.875}C$, respectively.

The electronic structures of MC, $MC_{0.875}$ and $M_{0.875}C$ were calculated by the self-consistent full-potential linear muffin-tin orbitals method (FP-LMTO)[8,9] with the Hedin–Lundqist exchange potential in the electron density functional approximation.[10,11] Valence electrons (6*s*, 6*p* and 5*d* for Ta and W and 2*s* and 2*p* for C) were calculated in a scalar relativist version. Vacancies in both sublattices were modelled by empty spheres with zero charges and 1*s*, 2*s* orbitals in the basis. Muffin-tin orbitals were calculated using a 3*k* basic set with the kinetic energies of *s*-, *p*- and *d*- functions $-k^2 = 0.01$, 0.1 and 2.3 Ry. Integration over the Brillouin zone was performed by the linear method of tetrahedra. Structural data for WC and TaC are consistent with published data.[1,7]

Figure 1 demonstrates the densities of states (DOS) for β-WC. The valence band (VB) of the carbide is represented by two fundamental bands (A, B) separated by a forbidden gap. Lower band A is formed by contributions from C 2*s* states, and mixed-type band B is formed by overlapping W 5*d*–C 2*p* states. The Fermi level (E_F) is located at a local DOS minimum between the bands of bonding and antibonding W–C states. Note that this case corresponds to the highest cohesive properties because all bonding states are occupied and all antibonding states are vacant.

Figures 2 and 3 show the densities of states of defect $WC_{0.875}$ and $W_{0.875}C$. The introduction of C-vacancies (V_C) results in the appearance of a new DOS peak (D′) and in a change in the

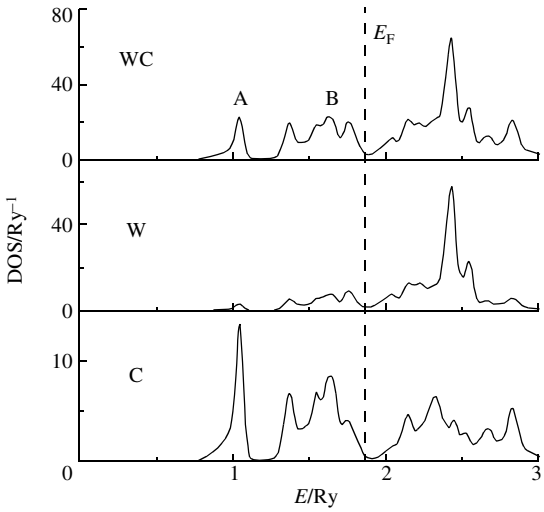

Figure 1 Total (top) and local densities of states for β-WC.

DOS distribution in the region of the Fermi level (Figure 2). These changes are associated with the formation of 'vacancy' states (VS). Figure 2 demonstrates that VS form two relatively large peaks D and D′ in the spectrum of $WC_{0.875}$. They originated from the partial removal of the *d*-states for W atoms surrounding a vacancy (solid line) into bonding and antibonding states. As a result, a portion of W *d*-states 'returned' into the nonbonding state. 'Vacancy' DOS peaks D and D′ reflect a decrease and an increase in the energy of bonding (peak D) or antibonding (peak D′) W *d*-states, respectively, as compared to those in complete WC (Figure 1).

The effect of W-vacancies (V_W) on the spectrum of WC depends on a change in the electronic states of carbon atoms nearest to the vacancy. The transition of a portion of C 2*p*-states into the region of nonbonding states is clearly defined in the DOS of carbon atoms nearest to a vacancy (solid line in Figure 3). As a result, the emptying of a part of bonding states takes place in the presence of both C- and W-vacancies, the Fermi level is shifted to the lower energy range and the DOS on the Fermi level [$N(E_F)$] increases (Table 1). The shift of the Fermi level is more pronounced for $W_{0.875}C$ and the larger part of bonding states is empty. This results in lower cohesive properties as compared with $WC_{0.875}$.

The calculations for B1-TaC $TaC_{0.875}$ and $Ta_{0.875}C$ showed that the general mechanism of changes in the electronic spectrum of the cubic carbide is similar to that described above (see also ref. 6). Differences in the VS energy between TaC and WC depend on differences between the coordination polyhedra in the structures of these carbides (regular octahedra in TaC and trigonal prisms in WC).

We evaluated the effects of lattice vacancies on the energy characteristics of carbides in terms of the FP-LMTO method. For this purpose, we calculated[11] the cohesive energies (E_{coh}) as a total energy difference between carbide and free atoms and then estimated the energy of vacancy formation (E_v) as a difference between the cohesive energies of stoichiometry and

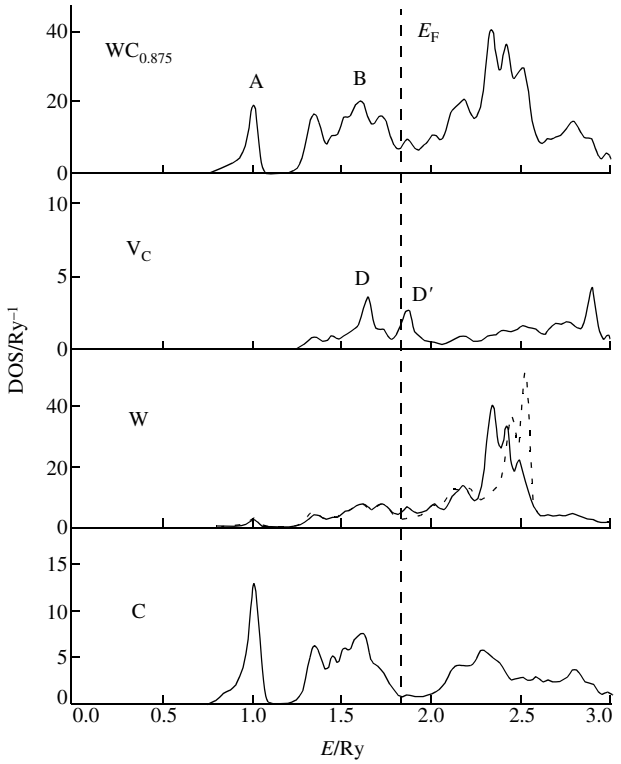

Figure 2 Total (top) and local densities of states (LDOS) for $WC_{0.875}$. The LDOS of W atoms nearest to the V_C-vacancy are shown by a solid line; the mean values of all nonequivalent C atoms in the $W_8V_CC_7$ supercell are shown for carbon.

defect carbides. The results indicate that in both of the carbides the presence of both carbon and metal vacancies impairs the cohesive properties of carbides and $E_v(M) > E_v(C)$. This fact is in agreement with our conclusion on worse cohesive properties of the carbide with metal vacancies, which was obtained from the DOS comparison. The above inequality is consistent with

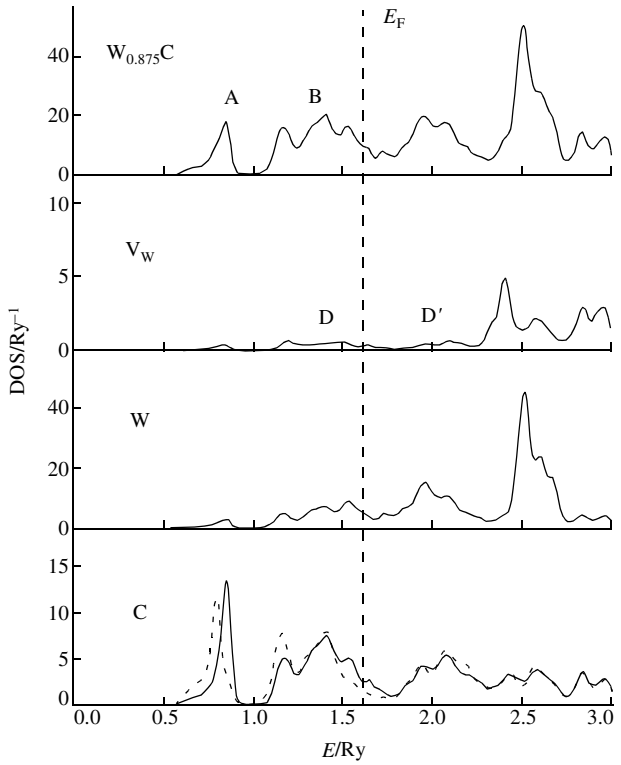

Figure 3 Total (top) and local densities of states for $W_{0.875}C$. The LDOS of C atoms nearest to the V_W-vacancy are shown by a solid line; the mean values of all nonequvalent W atoms in the $W_7V_WC_8$ supercell are shown for tungsten.

Table 1 Cohesive energies E_{coh}, vacancy formation energies E_v, Fermi energies E_F and densities of states at the Fermi level $N(E_F)$ for complete WC and TaC and carbides containing structure vacancies.

Carbide	E_{coh}/Ry	E_v/Ry	E_F/Ry	$N(E_F)$/Ry^{-1}
WC	1.76	—	1.86	3.16
$WC_{0.875}$	1.63	0.13	1.84	8.26
$W_{0.875}C$	1.56	0.20	1.62	9.37
TaC	1.64	—	1.80	8.90
$TaC_{0.875}$	1.58	0.09	1.75	9.27
$Ta_{0.875}C$	1.52	0.15	1.53	6.88

experimental data,[1] according to which vacancies in the carbon sublattice are primarily formed in carbides, whereas the formation of M-vacancies requires special conditions (for example, annealing after electron irradiation[7]). In turn, the energy of formation of C-vacancies in B1-TaC is considerably lower than that in hexagonal WC. This result can explain differences between the equilibrium defect contents of these carbides. As was found experimentally, TaC exhibits a much wider range of homogeneity (as compared with β-WC).

In summary, note that the electronic structures of nonstoichiometric WC_x and W_yC carbides were almost not examined experimentally. Preliminary data on charge-density distributions in β-WC were obtained by positron annihilation.[7] The life time of positron trapped by a C-vacancy ($\tau_C \sim 136$ ps) was found[7] to be much shorter than that for a W-vacancy ($\tau_W \sim 175$ ps). The longer value of τ_W was explained[7] by a lower electron density near metal vacancies surrounded by carbon atoms, whereas tungsten atoms with a higher electron density form the environments of C-vacancies to result in $\tau_C < \tau_W$.

We calculated the electron-density distribution in the spheres of W- and C-vacancies. We found that $Q(V_W) = 0.51e < Q(V_C) = 0.67e$, which is consistent with the relation $\tau_C < \tau_W$. Taking into account that in β-WC positrons primarily annihilate with electrons remote from positively charged nuclei,[11] we also compared so-called 'intrasphere' electron densities (Q_{is}). The corresponding values were $Q_{is}(WC_{0.875}) = 2.98e > Q_{is}(W_{0.875}C) = 2.77e$, which are also consistent with the differences between τ_C and τ_W in β-WC. Of course, to estimate the values of τ quantitatively, a special problem should be solved with the introduction of positron wave functions into the basis.

References

1 L. E. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971.
2 W. E. Pickett, B. M. Klein and R. Zeller, *Phys. Rev.*, 1986, **B34**, 2517.
3 P. Marksteiner, P. Weinberger, A. Neckel, R. Zeller and P. H. Dederichs, *Phys. Rev.*, 1986, **B33**, 812.
4 A. L. Ivanovskii, V. I. Anisimov, D. L. Novikov, A. I. Lichtenstein and V. A. Gubanov, *J. Phys. Chem. Solids*, 1988, **49**, 465.
5 D. L. Novikov, A. L. Ivanovskii and V. A. Gubanov, *Phys. Status Solidi B*, 1987, **139**, 257.
6 V. A. Gubanov, A. L. Ivanovskii and V. P. Zhukov, *Electronic Structure of Refractory Carbides and Nitrides*, University Press, Cambridge, 1994.
7 A. A. Rempel, R. Wurschum and H.-E. Schaefer, *Phys. Rev.*, 2000, **B61**, 5945.
8 M. Methfessel, C. Rodriquez and O. K. Andersen, *Phys. Rev.*, 1989, **B40**, 2009.
9 M. Methfessel and M. Scheffler, *Physica B*, 1991, **172**, 175.
10 M. Methfessel, *Phys. Rev.*, 1988, **B38**, 1537.
11 N. I. Medvedeva, D. L. Novikov, A. L. Ivanovskii, M. V. Kuznetzov and A. J. Freeman, *Phys. Rev.*, 1998, **B58**, 16042.
12 A. A. Rempel, *Usp. Fiz. Nauk*, 1996, **166**, 33 (*Phys. Usp.*, 1996, **39**, 31).

Received: 14th September 2000; Com. 00/1702