Electronic Structure of Ti_3SiC_2

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Self-consistent calculations of the band structure, total and local densities of states and energy spectrum parameters of the ordered ternary phase Ti_3SiC_2 have been carried out using the full-potential LMTO method.

The ternary titanium carbosilicide Ti_3SiC_2 possesses a unique set of properties (high melting point, resistance to aggressive environments and to high-temperature oxidation along with high plasticity) and therefore has recently attracted much attention, in particular, as a promising material for producing novel construction ceramics.[1–6]

This paper presents the results of calculations of the band structure and electronic energy spectrum parameters of titanium carbosilicide performed by self-consistent full-potential LMTO method, the formalism of which is described in ref. 7.

The crystal structure of Ti_3SiC_2 has been studied in sufficient detail.[8–10] According to ref. 8, Ti_3SiC_2 has a hexagonal structure (space group D_{6h}^4-$P6_3/mmc$) with unit cell (containing 6Ti, 2Si and 4C atoms) parameters $a = 3.066$ and $c = 17.646$ A. A fragment of Ti_3SiC_2 structure is depicted in Fig. 1. It is clear that metal atoms occupy two structurally non-equivalent positions, one of which (Ti_1, 4 atoms in the unit cell) does have Si atoms as near neighbours while the other (Ti_2, 2 atoms in the unit cell) does not have Si atoms as nearest neighbours. The following interatomic distances[8] (in Å) have been used in the calculations:

Ti_1	Ti_1	(3.068)	Ti_2	Ti_2	(3.068)
	Ti_2	(2.971)		Ti_1	(2.971)
	Si	(2.696)		C	(2.135)
	C	(2.135)		C	(2.135)
C	Ti_1	(2.135)	Si	Si	(3.068)
	Ti_2	(2.135)		Ti_1	(2.696)

The computations have been performed in full basis, the radii of muffin-tin (MT) spheres being 1.92 (Ti_1, Ti_2), 2.89 (Si) and 2.14 (C) Å.

Fig. 2 gives the energy band structure of hexagonal titanium carbosilicide. The valence band dispersion curves may be divided into two basic groups: the low-energy group is composed mainly of metalloid states of s-symmetry and the next group of bands contains predominantly (Si,C)p and Ti s,d states. Attention is drawn to the fact that there is no direct overlap of C and Si s bands (the four lower and the two next bands, Fig. 2) and that the energy dispersion of the Si-like bands is much greater. This may be the result of participation of silicon atoms in different bond types (Si–Ti and Si–Si) whereas carbon atoms are located in a regular octahedral coordination (CTi_6) and take part only in Ti–C interactions. The energy gap between s- and p-d-like bands is very small: the indirect gap is 0.12 eV and the direct gap (in M and L points) is 0.91 and 1.04 eV, respectively.

It follows from the total and local densities of states (TDOS, LDOS) given in Fig. 3 that, as distinct from binary titanium carbide,[11] in the energy spectrum of the carbosilicide the Fermi level coincides with the peak of the titanium density of d-states [$N(E_F) = 4.76$ states eV^{-1}]. This circumstance should determine the metal-like properties of the Ti_3SiC_2 phase. The contributions to $N(E_F)$ from the states of the structurally nonequivalent titanium atoms in which the decisive role is played by Ti_1 states [$N(E_F : Ti_1)/N(E_F : Ti_2) \sim 3.76$] turn out to be considerably different as well.

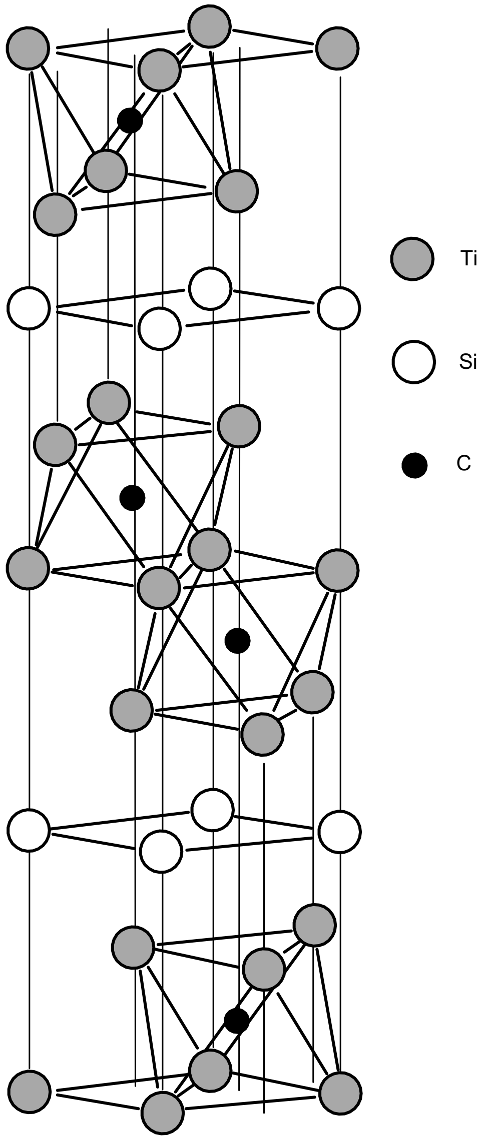

Fig. 1 Fragment of the crystal structure of Ti_3SiC_2.

The shape and energy distribution of the Ti_1 and Ti_2 LDOS also exhibit dissimilarity, Fig. 3. While for Ti_1 atoms surrounded both by Si and C atoms the LDOS contains two maxima coinciding in energy with C,Si-LDOS peaks, the valence states of Ti_2 atoms containing in the first coordination sphere only carbon atoms are shifted downwards on the energy scale (relative to the Ti_1 LDOS) and the LDOS shape of the Ti_2 centres has much in common with that of the C2p centres.

The charges in the MT spheres (9.386 – Ti_1; 9.359 – Ti_2; 4.304 – Si; 4.384e – C) enable us to estimate the effective atomic charges (+0.614 – Ti_1; +0.641 – Ti_2; −0.304 – Si; −0.384e – C). The values obtained are indicative of the partial charge transport (in the direction $Ti_{1,2} \rightarrow$ Si,C) which provides for the ionic component of the general system of chemical bonding to the carbosilicide.

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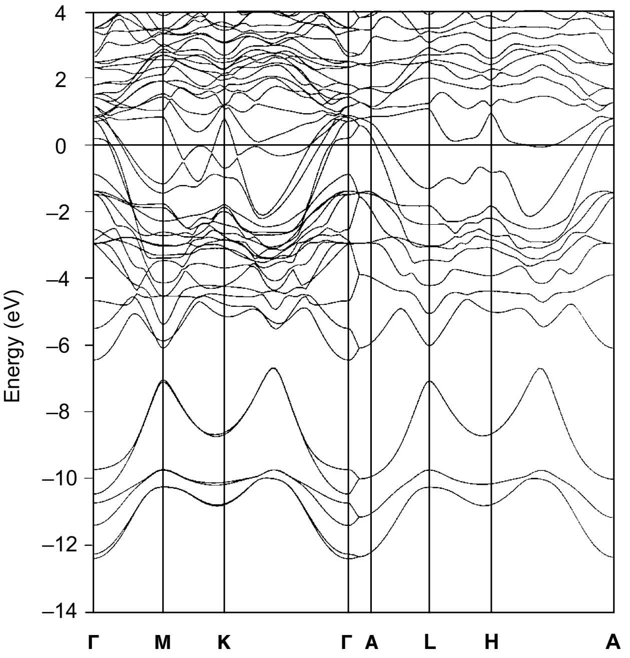

Fig. 2 Band structure of Ti_3SiC_2.

On the whole it is possible to assert that a complicated combined ionic–covalent–metallic type of chemical bonding is realized in Ti_3SiC_2 which is due to the following factors: charge polarization between metal and metalloid atoms, hybridization of valence states ($Ti_1$3d-Si3p, $Ti_1$3d-C2p, $Ti_2$3d-C2p, Si3p-Si3p) and collectivization of near-Fermi titanium d-states (mainly of Ti_1 atoms). A more detailed consideration of the chemical bonding in Ti_3SiC_2, its anisotropy and influence on the carbosilicide properties will be proposed in ref. 12.

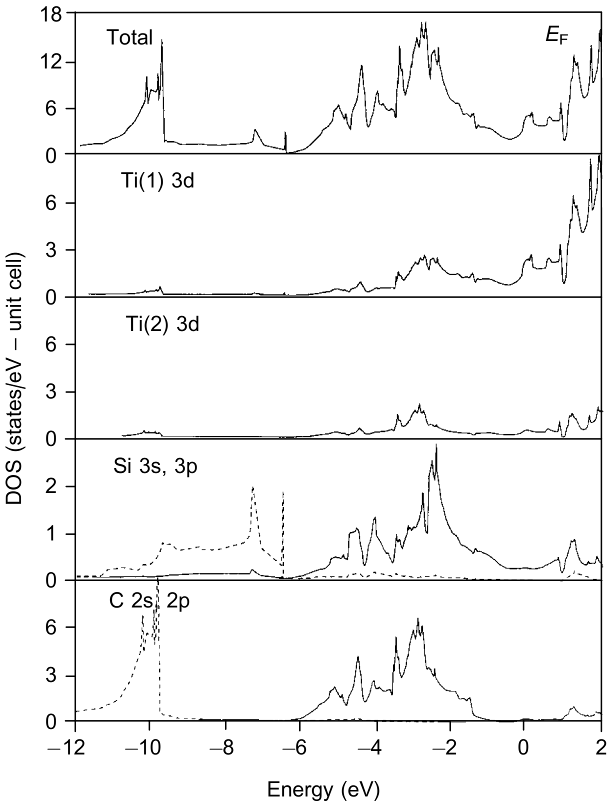

Fig. 3 Total and local densities of states of Ti_3SiC_2. Given are s (dashed line) and p (solid line) DOS of nonmetals and d states of titanium. For designations Ti_1 and Ti_2, see the text.

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