Ab initio calculation of titanium silicon carbide

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(Received 29 December 1998)

The electronic structure and properties of the layered ceramic Ti_3SiC_2 have been examined by *ab initio* linear combination of atomic orbital calculations. With the calculated results we predict that the electronic conductivity of Ti_3SiC_2 is metallic and anisotropic. The major factors governing the electronic properties are hybridized Ti $3d$, Si $3p$, and C $2p$ states and the p-d bonding stabilizes the structure. [S0163-1829(99)12127-1]

Titanium silicon carbide (Ti_3SiC_2) is a promising ceramic material that has only been extensively studied in recent years.[1–9] It combines the merits of both metals and ceramics. Briefly, it has high melting point of 3200 °C, low density of 4.53 g/cm^3, high Young's modulus of 320 GPa, low Vickers hardness of 4 GPa, high strength, and behaving ductility at high temperature. Ti_3SiC_2 is also thermally and electrically conductive. As far as we know, the measured room temperature electrical conductivity was $4.5\times 10^6\ \Omega^{-1}\,\mathrm{m}^{-1}$ by Barsoum and El-Raghy[1] and $9.6\times 10^6\ \Omega^{-1}\,\mathrm{m}^{-1}$ by the present authors, which is unexpected for such a complex ceramic. Ti_3SiC_2 cannot only be used as a structure ceramic but also is attractive in such applications as commutating brushes for ac motors because of its high temperature stability and high electrical conductivity.

However, many of its properties are still not understood owing to the difficulty of synthesis. But up to now, to our knowledge, nothing is known about the electronic structure and chemical bonding properties. In this Brief Report we investigate these questions by means of the *ab initio* linear combination of atomic orbitals (LCAO),[10] which has been proven to be a powerful tool for calculating electronic structure and properties of solids. Our calculation will give a better picture of the electronic structure and the bonding properties in this system.

Ti_3SiC_2 crystallizes in hexagonal structure with space group of $P6_3/mmc$,[6] which is shown in Fig. 1. The unit cell of Ti_3SiC_2 consists of alternating layers of Si and two layers of an edge-shared TiC octahedron. The lattice constants are $a=3.068$ Å and $c=17.645$ Å with two formulas per unit cell.[2] The atomic positions of Ti correspond to the $2a$ ($Z_{\mathrm{Ti}}=0.135$), Si to $2b$, and C to the $4f$ ($Z_{\mathrm{C}}=0.567$).[9] For the convenience of discussion we define the Ti atoms at the corner of the unit cell as Ti(1) atoms and those inside the cell as Ti(2) atoms. The titanium silicon carbide (Ti_3SiC_2) investigated in this work contained 12 atoms per unit cell.

The calculations are based on density functional theory[11] (DFT) in the local-density approximation[12,13] (LDA) and the *ab initio* self-consistent atomic sphere approximation[10] (ASA) in its scalar-relativistic implementation. In this method, empty spheres are needed to reduce the volume overlap between atomic spheres. The criterion is that the volume overlap should not amount to 15% of the unit cell volume in our program. The overlap is 12.4% without any empty sphere for Ti_3SiC_2 and no empty sphere was inserted in the crystal structure in our calculation. The basis set is a very special type of linear combination of atomic orbitals[10] in which each basis function, regardless of which atom it is centered on, is orthogonal to all core levels of the entire crystal. The basis set for the valence state used for the present calculation consisted of Ti $4s$, $4p$, and $3d$ orbitals, Si $3s$, $3p$, and $3d$ orbitals and C $2s$,$2p$ orbitals. The calculation introduced the Monkhorst-Pack scheme to perform a uniform mesh of k points in reciprocal space. The atom radii are calculated using Vegard's law in which the size of the atoms in a complex unit cell is similar to the size of the atoms in an elemental solid.

Figure 2 shows the band structure of Ti_3SiC_2 along selected high-symmetry lines within the first Brillouin zone of the hexagonal lattice, which is given in Fig. 3. The corresponding total density of states (DOS) and the partial DOS of every element that is broken up into site and angular momentum contributions are shown in Figs. 4 and 5, respectively. The X axis gives the DOS per atom and unit energy ($\mathrm{atom}^{-1}\,\mathrm{eV}^{-1}$). As seen from Fig. 2, no gap appears at E_F: valence and conduction Ti $3d$–Si$3p$–C$2p$ bands overlap at the G point and there is another overlap between the valence and conduction bands from A to H point. There are five and three bands crossing E_F along K-G and G-M lines, respectively; two also cross along the long A-H direction. The conductivity of Ti_3SiC_2 turns out to be strongly metallic. From the picture of the band structure for Ti_3SiC_2, one will

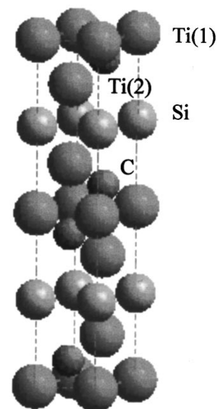

FIG. 1. The crystal structure of Ti_3SiC_2, Ti(1) is defined as Ti atoms at the corner of the lattice cell and Ti(2) is defined as Ti atoms within the lattice cell.

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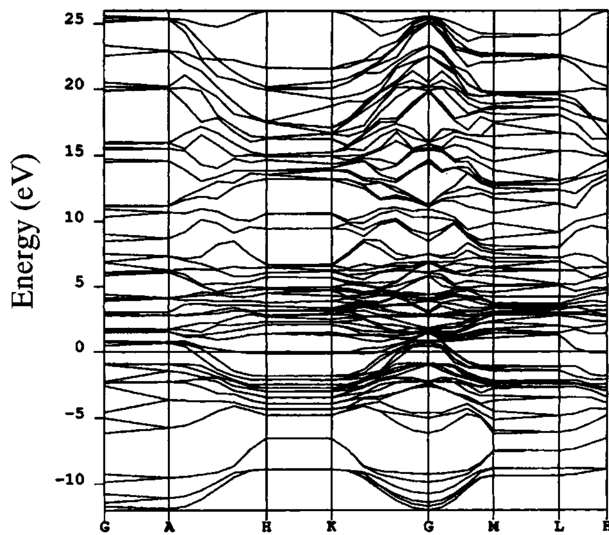

FIG. 2. Calculated band structure of Ti_3SiC_2.

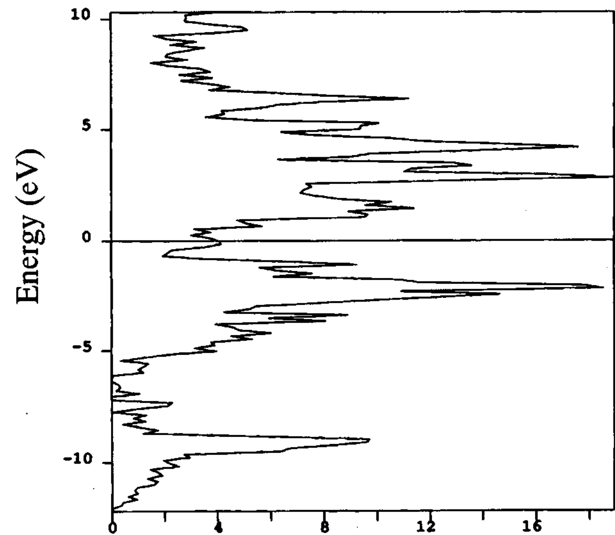

FIG. 4. Calculated total density of states for Ti_3SiC_2.

not be surprised to get high conductivity for Ti_3SiC_2 in our experiment. Two groups of bands are also clearly identified. The bottom valence band (VB), combining with Fig. 5, contains mainly $3s$ and $2s$ contributions from Si and C atoms, respectively. There is also a little contribution from Ti $3d$ states. At the energy range from -5 to -0.5 eV, the top valence bands derive from strongly hybridized Ti $3d$, Si $3p$, and C $2p$ states. Further support for the *pd* hybridization comes from the striking similarity of the partial density of states below the Fermi energy (E_F) and the strong in-plane dispersions of the energy bands. Finally, the band structure near and below E_F is strongly anisotropic with very little c-axis dispersion, which is evident from the fact that there is no dispersion along the short G-A, H-K, M-L, and L-H directions. It can be concluded from the above analysis that the conductivity is also anisotropic for single crystal Ti_3SiC_2.

The total and partial densities of states (Figs. 4 and 5) show that due to the more delocalized $3d$ states and their higher degree of hybridization with Si $3p$ and C $2p$ states, the width of the valence band, about 13 eV, is large. Carefully studying Figs. 5(a)–5(d), we see that from -5 to about -0.5 eV, Si $3p$ and C $2p$ states hybridize with Ti $3d$ states, and d-d, d-p, and p-p bonding dominate. And Si $3p$ states have a stronger hybridization with Ti(2) $3d$ states than that with Ti(1) $3d$ states, while C $2p$ hybridized with Ti(1) $3d$ states more strongly than that with Ti(2) $3d$ states. It is easy

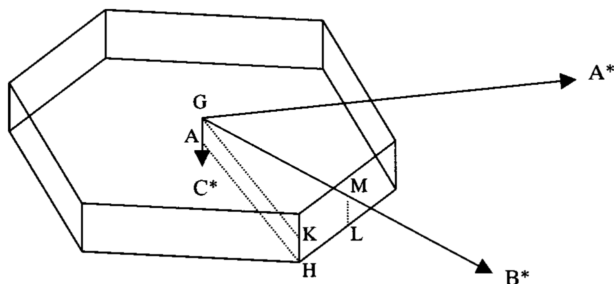

FIG. 3. Brillouin zone and high-symmetry points of the hexagonal structure.

to understand this hybridization character combining with the structure of Ti_3SiC_2 since Ti(2) atoms are the nearest to Si atoms while Ti(1) atoms are the nearest to C atoms. It can be inferred that there is stronger bonding between Ti(2) $3d$–Si $3p$, and the Ti(1) $3d$–C $2p$ bonding is also stronger. It can also be inferred that Ti(1) and Ti(2) atoms play a different role in the bonding of the compound and the valence of Ti(1) should be different from that of Ti(2) atoms. In addition, Si $3p$–C $2p$ and Ti(1) $3d$–Ti(2) $3d$ also have bonds in the same energy range and contribute to the stability of the structure. These *pd* hybridization or d-d, d-p, and p-p bonding stabilize the structure, for which we can conclude that the heat of formation and melting point for Ti_3SiC_2 may be very high. From this point of view, it is not

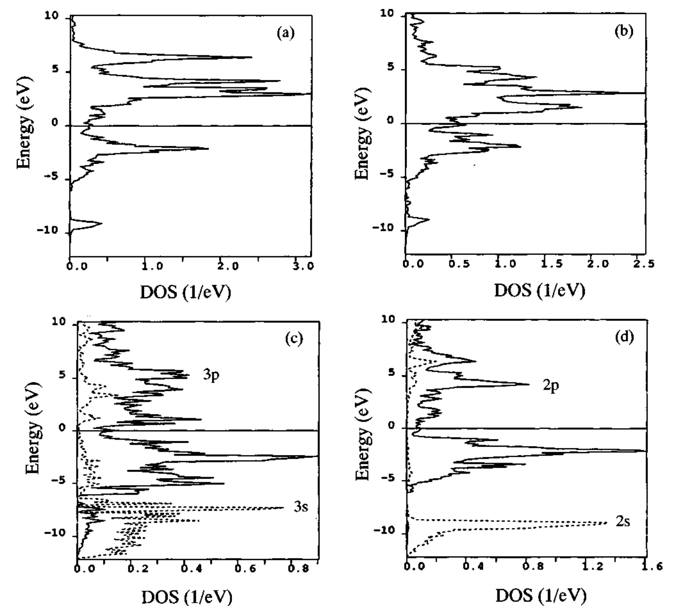

FIG. 5. Calculated partial density of states for Ti_3SiC_2. (a) Ti(1) $3d$, (b) Ti(2) $3d$, (c) Si $3s$ and $3p$ states (the dotted line stands for $3s$ states and the solid line stands for $3p$ states), (d) C $2s$ and $2p$ states (the dotted line stands for $2s$ states and the solid line stands for $2p$ states).

difficult to understand why Ti_3SiC_2 has a high melting temperature of 3200 °C and associates with a high synthesis temperature. It can be concluded from the above analysis that all the $3d$ electrons of Ti and $3p$ electrons of Si and C have strong effects on the bonding in the compound.

In summary, we have given theoretical insight into the electronic structure of Ti_3SiC_2 by means of *ab initio* LCAO calculations, although the details of the present results may not survive more rigorous treatments owing to the use of the ASA scheme. Some conclusions can still be made from the calculation result. The electrical property of Ti_3SiC_2 was dominated by Ti $3d$, Si $3p$, and C $2p$ states. The electronic conductivity is metallic and anisotropic. There is strong *pd* hybridization in the compound and the p-d bonding generally stabilizes the structure.

This work was supported by the National Sciences Foundation of China under Grant No. 59572013, Grant No. 59772021, and the Chinese Academy of Sciences.

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