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LETTER TO THE EDITOR

Electronic structure and bonding properties in layered ternary carbide Ti_3SiC_2

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Abstract. *Ab initio* calculations based on the density-functional pseudopotential approach have been used to study the electronic structure and chemical bonding in layered machinable Ti_3SiC_2 ceramic. The calculations reveal that all three types of bonding—metallic, covalent and ionic—contribute to the bonding in Ti_3SiC_2 . The high electric conductivity is attributed to the metallic bonding parallel to the basal plane and the high modulus and high melting point are attributed to the strong Ti–C–Ti–C–Ti covalent bond chains in the structure.

Searching for new materials with a combination of the ductility, conductivity and machinability of metals and the high strength and modulus and excellent high-temperature-oxidation resistance of ceramics has been the purpose of many studies. Recently, a layered ternary carbide Ti_3SiC_2 demonstrated a unique combination of the properties of both metals and ceramics [1–11]. The salient properties of this compound include low density, high melting point, excellent high-temperature-oxidation resistance, significant ductility and high strength at high temperatures, good electrical conductivity, self-lubricated [12] and readily machinable by conventional tools [1]. Such unexpected properties embodied in a ceramic material are attractive to materials scientists and physicists. We are therefore intrigued by the relation between the electronic structure and the properties of this unusual material. To disclose the electronic structure and the bonding nature in Ti_3SiC_2 , an *ab initio* study was performed in this work.

Before examining the electronic structure of Ti_3SiC_2 , it is relevant to consider the crystal structure of TiC. It crystallizes in the NaCl-type structure (space group $Fm\bar{3}m$) with four formulae per unit cell. Ti and C are at the origin and $(1/2, 1/2, 1/2)$ positions, respectively. Ti and C are octahedrally coordinated with each other; consequently, the Ti_6C octahedra share edges.

Ti_3SiC_2 has a hexagonal crystal structure with a space group of $P6_3/mmc$ (as shown in figure 1(a)) [4]. The lattice parameters are $a = 3.068 \text{ \AA}$ and $c = 17.669 \text{ \AA}$ with two formulae per unit cell. The atomic positions of Ti correspond to $2a$ and $4f$ ($Z_{\text{Ti}} = 0.135$), Si to $2b$, and C to $4f$ ($Z_{\text{C}} = 0.567$). The structure of Ti_3SiC_2 can be described as two edge-shared Ti_6C octahedron layers linked together by a two-dimensional closed packed Si layer. For the convenience of discussion, we define the two apical Ti atoms in Ti_3SiC_2 as the Ti (1) atom and Ti (2) atom, respectively. The corresponding Brillouin zone is depicted in figure 1 (b).

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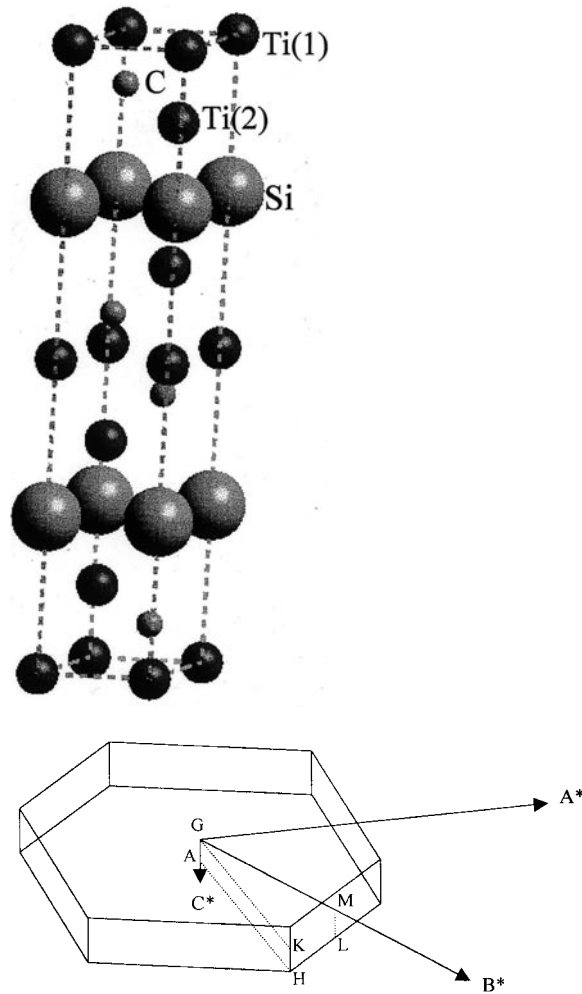


Figure 1. The hexagonal crystal structure of Ti_3SiC_2 (a), and the Brillouin zone and high-symmetry points for Ti_3SiC_2 (b).

The calculations are performed using the pseudopotential method with a plane-wave basis set and the conjugate gradients algorithm, employing the density-functional theory (DFT) [13–16]. The exchange-correlation potential used in these calculations is the functional of Ceperley and Alder as parametrized by Perdew and Zunger [17, 18]. The first-principles pseudopotentials in the Kleinman-Bylander representation were generated using the optimization scheme of Lin *et al* [19, 20].

Figure 2 shows the calculated band structure along the high-symmetry line of the hexagonal lattice. This exhibits metallic behaviour with bands crossing the Fermi level along the K–G and G–M directions, which results in a peak in the DOS at the Fermi level. The above results indicate that the electrical conductivity of Ti_3SiC_2 would be strongly metallic, which agrees with the experimental result [1]. The band structure near and below E_f is strongly anisotropic with little c -axis dispersion, indicating that the conductivity is also anisotropic for single crystal Ti_3SiC_2 .

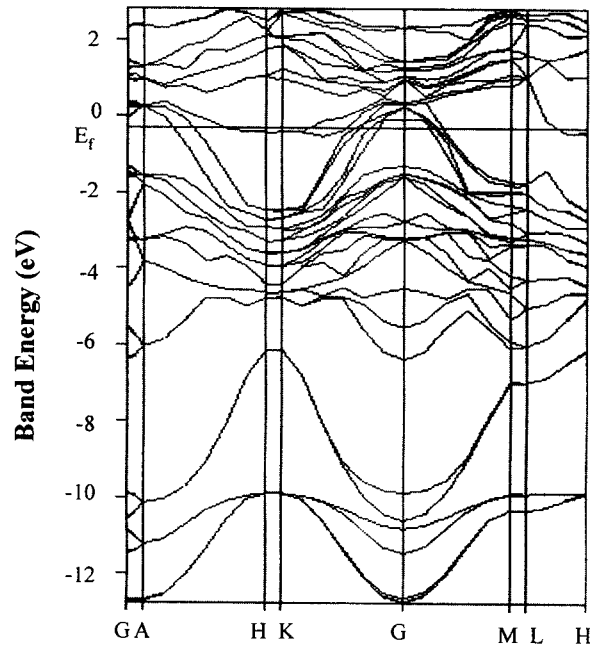


Figure 2. The calculated band structure of Ti_3SiC_2 .

The charge density distribution on different planes of Ti_3SiC_2 confirms the metallic and anisotropic character of electrical conductivity for Ti_3SiC_2 . Figures 3 (a) and (b) represent distributions of charge density on the Ti(1) and Ti(2) layers of Ti_3SiC_2 , which are parallel to the basal plane, while figure 3 (c) gives the distribution of charge density on the (110) plane of Ti_3SiC_2 . We note that there are free charge density distributions in the interstitial of atoms in the Ti(1) and Ti(2) layers. The free charge density distribution in the Ti(2) layer is higher, whereas that in the (110) plane is less and inhomogeneous along the c -axis. The electrical conductivity is thus anisotropic.

The chemical bonding in Ti_3SiC_2 is also anisotropic, as shown in figure 3. In the atomic layers that are parallel to the basal plane, the atoms are bonded together by metallic bonding. There is a difference in the distribution of charge density on the Ti(1) and Ti(2) layers, which implies that Ti(1) and Ti(2) play a different role in the chemical bonding. There is a greater proportion of metallic bonds in the Ti(2) layer, which contributes to the electrical conductivity. To understand the difference between Ti(1) and Ti(2), it is relevant to examine the distribution of charge density on the Ti layer in TiC. Comparing the distribution of charge density on Ti(1) and Ti(2) in Ti_3SiC_2 and that of the Ti layer parallel to the (111) plane of TiC, we find that the distribution of the charge density on Ti(1) is the same as that on the Ti layer in TiC. In contrast, the distribution of charge density on Ti(2) is quite different. The Ti(2) layer has more contribution to the conductivity of Ti_3SiC_2 .

The distribution of charge density on the (110) plane of Ti_3SiC_2 (figure 3 (c)) and on the $(1\bar{1}0)$ plane of TiC (figure 4) gives detailed information on the chemical bonding in the two structures. In figure 3(c), a character of chain structure in Ti_3SiC_2 is explicit. The unit chain is along the Ti(2)–C–Ti(1)–C–Ti(2) bond line, which is directional. Every two Ti(2)–C–Ti(1)–C–Ti(2) bond chains are linked together by a Si atom forming a zigzag chain couple. The

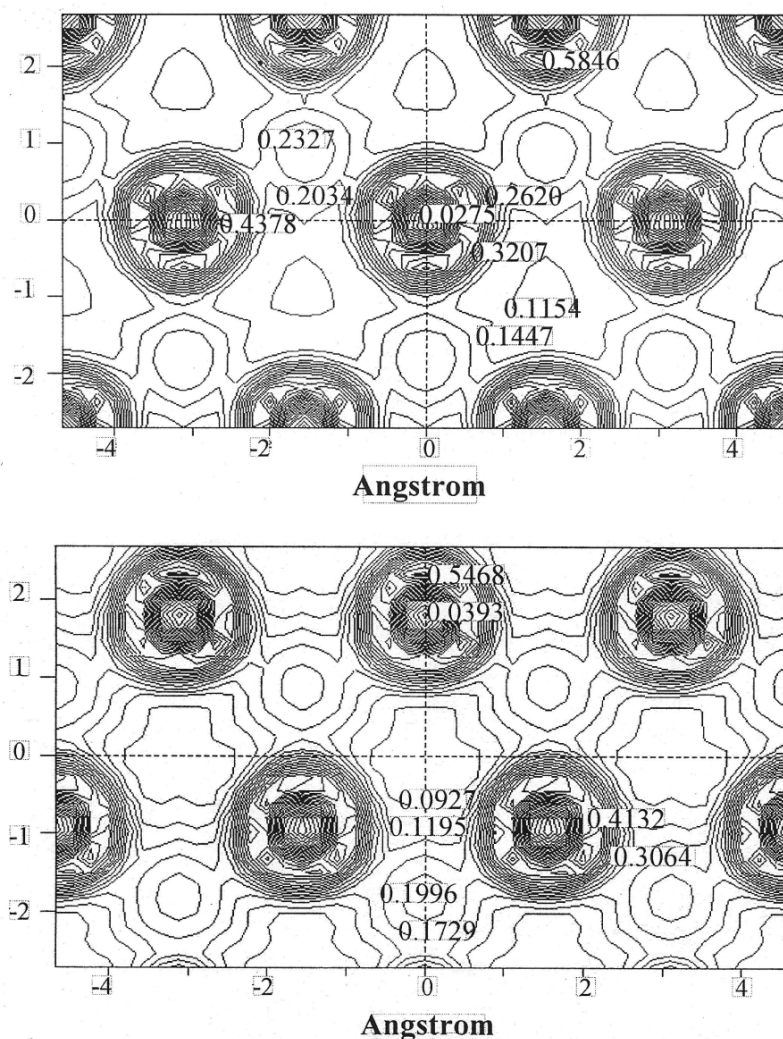


Figure 3. Distribution of charge density on Ti (1) (a) and Ti (2) (b) atomic layers that are parallel to the basal plane, and on the (110) plane (c) of Ti_3SiC_2 .

length of the chain couple in the c -direction is equal to the cell dimension c (17.669). The Ti(2)–C–Ti(1)–C–Ti(2)–Si chain couple periodically repeats three dimensionally, configuring the chain structure for Ti_3SiC_2 . The chains are bonded together by metallic bonding. In the Ti(2)–C–Ti(1)–C–Ti(2)–Si bond chain, the interatomic distance between Ti(1, 2) and C is 2.13 Å, and that between Ti(2) and Si is 2.67 Å, indicating that the chemical bonding between Ti–C and Ti–Si is covalent in nature. However, the bonding between Ti and C is stronger than that between Ti and Si. In addition, the polar character of the directional bonding implies that ionic bonding also contributes to the Ti–C and Ti–Si bonding. We thus conclude at this point that all three types of bonding—metallic, ionic, and covalent—contribute in Ti_3SiC_2 . In figure 4, Ti and C atoms also form a Ti–C–Ti bond chain. The interatomic distance between Ti and C in TiC is 2.16 Å, which is similar to that between Ti(1) and C in Ti_3SiC_2 . So the bonding environment of Ti(1) in Ti_3SiC_2 is similar to that of Ti in TiC. The difference between

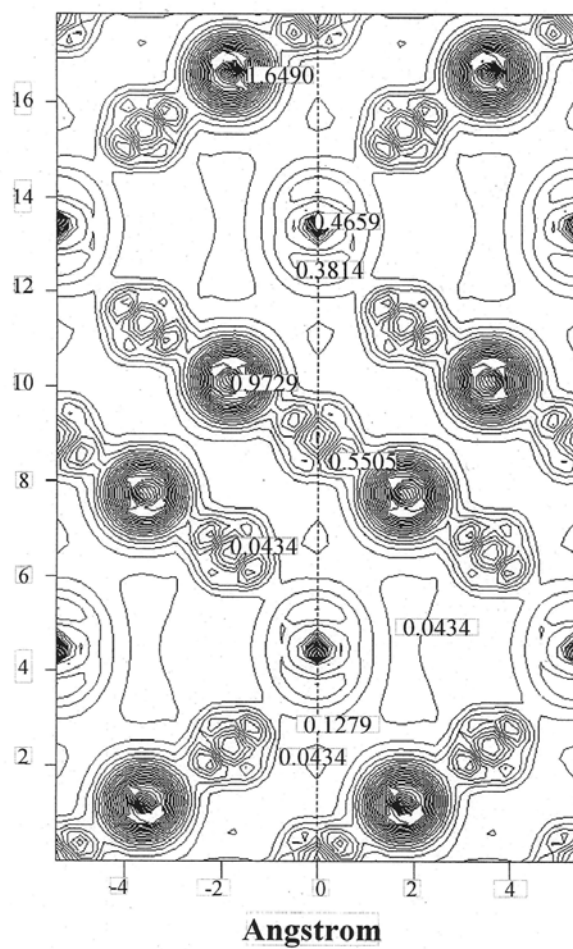


Figure 3. (Continued.)

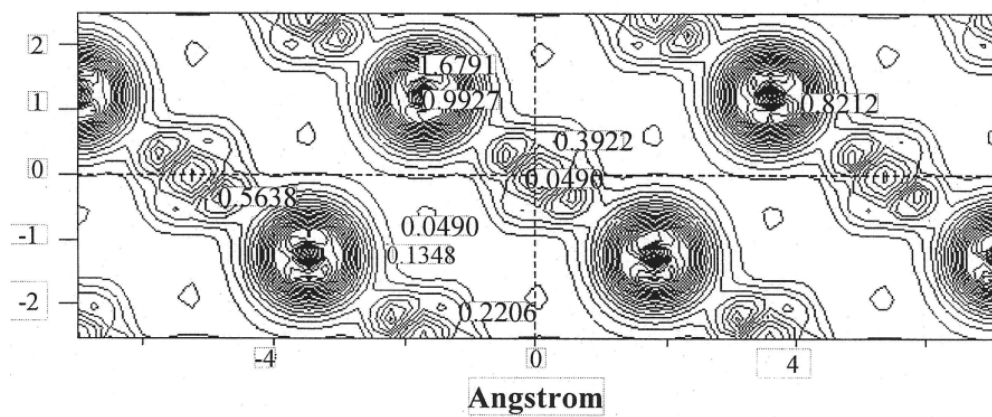


Figure 4. Distribution of charge density on (110) plane of TiC.

Ti (1) and Ti (2) is thus attributed to the presence of a Si atom which changes the bond chain of Ti–C–Ti in TiC to Ti(2)–C–Ti(1)–C–Ti(2)–Si in Ti₃SiC₂. In other words, it is relevant to consider the structure of Ti₃SiC₂ as a two-dimensional closed packed Si layer periodically inserted in between every two edge-shared Ti₆C octahedra (or two adjacent bond chains of Ti(2)–C–Ti(1)–C–Ti(2) linked by one Si atom).

Chain crystal structure is common in organic crystals. For inorganic solids, chain crystal structures are observed in group VI elemental crystals such as Se and Te. In these chain structures, atoms form a long spiral chain linked by covalent bonds, and the parallel chains are linked together by Van der Waals bonds. In Ti₃SiC₂, however, two adjacent covalent bond chains of Ti–C–Ti–C–Ti–Si form a chain couple with the length equal to the cell dimension in the *c*-direction, and the chains are bonded together by inhomogeneous metallic bonds. It is this specific bonding nature that determines the unusual properties of Ti₃SiC₂; i.e. a unique combination of the merits of both metals and ceramics. The high melting point and modulus are attributed to the strong bonding in the Ti–C–Ti–C–Ti unit. The high electrical conductivity is attributed to the metallic bonding parallel to the basal plane.

In conclusion, the chemical bonding in Ti₃SiC₂ is anisotropic and metallic–covalent–ionic in nature, with significant contributions from metallic and covalent bonds. Two adjacent Ti–C–Ti–C–Ti unit chains share one Si atom forming a chain couple with a length equal to the cell dimension in the *c*-direction. The long parallel Ti₃SiC₂ chains are bonded by inhomogeneous metallic bonds. In the atomic layers, especially the Ti layers that are parallel to the basal plane, strong metallic bonds contribute to the bonding in the chain structure. Owing to this special chain crystal structure and the metallic–covalent–ionic bonding nature, unusual properties are expected. This work is useful in predicting and designing new materials using the concept of ‘crystal engineering’. Tolerating metallic, covalent and/or ionic bonding within one crystal will give a new material that combines the properties of both metals and ceramics.

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