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Electronic structure of the layered ternary carbides Ti_2SnC and Ti_2GeC

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Abstract. The electronic structure of the layered ternary carbides Ti_2SnC and Ti_2GeC has been investigated by means of *ab initio* linear combination of atomic orbital calculations. The calculated band structure shows that the electrical conductivity for both Ti_2SnC and Ti_2GeC is metallic and anisotropic with a high density of states at the Fermi level. The electrical conductivity of Ti_2SnC is, however, higher than that of Ti_2GeC . The major factors governing the electronic properties are pd hybridization from Ti 3d and C 2p states. Compared to the structure of TiC, the presence of Sn or Ge changes the Ti–C–Ti–C covalent bond chain into a Ti–C–Ti–Sn or Ti–C–Ti–Ge bond chain through its reaction with Ti, forming the layered structure.

1. Introduction

Inorganic compounds which possess layered crystal structure often exhibit a rich array of chemical and physical properties. Recently, we have become particularly intrigued by the family of layered ternary carbides referred to as H phase. The common formula of these layered ternary compounds is T_2MC , where T is a transition metal, M is a metatransition metal (a group IIIA or IVA element), and C is carbon [1]. These layered ternary compounds exhibit a unique combination of the properties such as high strength and modulus, damage tolerance at room temperature, high electrical conductivity, low density and hardness, and being readily machinable with conventional tools and the electrical discharge method. Ti_2SnC and Ti_2GeC are two interesting materials from this family [2, 3]. Previous work by Barsoum *et al* [4] demonstrated that polycrystalline Ti_2SnC has electrical conductivity of $14 \times 10^6 \Omega^{-1} \text{m}^{-1}$, which is the highest among those of the layered ternary carbides Ti_2SnC , Zr_2SnC , Hf_2SnC , and Nb_2SnC . The electrical conductivity of Ti_2SnC is higher than that of other layered ternaries like Ti_3SiC_2 [5], Ti_2AlC , and Ti_2AlN [6, 7]. Our early works [5, 8] demonstrated that the electrical conductivity of Ti_3SiC_2 is metallic and increases with decreasing temperature. Since the electrical conductivity of Ti_2SnC ($14 \times 10^6 \Omega^{-1} \text{m}^{-1}$) at room temperature [4] is much higher than that of Ti_3SiC_2 ($9.6 \times 10^6 \Omega^{-1} \text{m}^{-1}$) [8], we are particularly interested in understanding the anomalous electrical conductivity of Ti_2SnC . Ti_2GeC is a compound with crystal structure isomorphous with that of Ti_2SnC . Interest in Ti_2GeC emanates from the opportunity provided

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to tailor properties, since two distinct structurally related ternary phases Ti_2GeC and Ti_3GeC_2 are available in the Ti–Ge–C system [9]. Furthermore, the density of Ti_2GeC is lower than that of Ti_2SnC , which is attractive when it is used as a reinforcement for polymers and metals. Estimating the structural properties of Ti_2GeC is vital, because at present very few data on the properties of this layered compound are available.

The structure of Ti_2GeC and Ti_2SnC is usually described as layered with sheets of Ti_6C octahedra alternating with close-packed layers of Ge or Sn. This structural character combined with the anomalous conductivity and good mechanical properties encourages us to investigate the electronic structure of these compounds, which is the key to understanding the properties of solids. In this paper, we study the electronic structure and bonding properties of Ti_2SnC and Ti_2GeC by using a method based on density functional theory (DFT) within the local density approximation (LDA): the linear muffin-tin orbital (LMTO) method [13], which has been proven to be a powerful tool for the investigation of the electronic properties of solids. Our calculation will give a better picture of the electronic structure and bonding properties of these layered ternary carbides. For comparison, the electronic structure of TiC will also be discussed.

2. Crystal structure and calculation details

Before examining the electronic structure of Ti_2SnC and Ti_2GeC , it is useful 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, Ti_6C octahedra share edges.

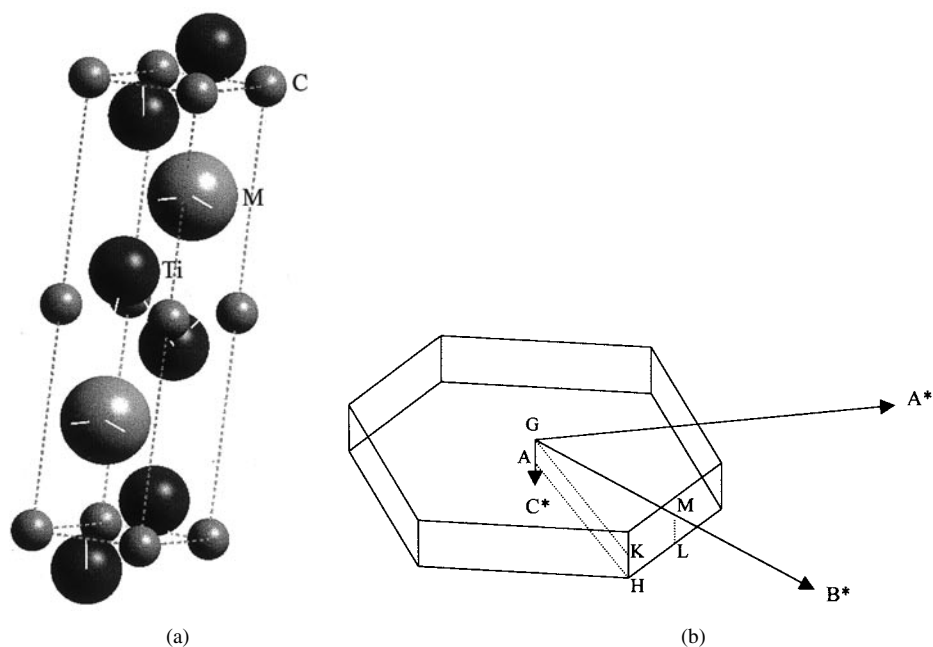


Figure 1. (a) The crystal structure of Ti_2MC ($M = \text{Sn, Ge}$), and (b) the Brillouin zone and high-symmetry points of the hexagonal structure.

Ti_2SnC has a crystal structure isotypic with that of Cr_2AlC (named H phase) and a hexagonal symmetry with the lattice parameters $a = 0.3186$ nm and $c = 1.363$ nm [2]. The space group is $P6_3/mmc$ and the atoms are located at the following positions: Ti at (4f) ($Z_{Ti} = 0.07852$), Sn at (2d) and C at (2a) Wyckoff positions. Ti_2GeC is isomorphous with Ti_2SnC , with the lattice parameters $a = 0.3079$ nm and $c = 1.293$ nm [3]. The crystal structure of Ti_2SnC and Ti_2GeC is shown in figure 1(a) and the corresponding Brillouin zone is depicted in figure 1(b).

Calculations of the electronic structure and density of states are based on density functional theory (DFT) in the local density approximation (LDA) [11, 12]. As a calculation scheme we employed the *ab initio* self-consistent atomic sphere approximation (ASA) [10] in its scalar-relativistic implementation. The approach taken to solve the crystal Schrödinger equation is based on the linear combination of atomic orbitals (LCAO) method. The basis set used is the LMTO one [13], in which each basis function, regardless of which atom it is centred on, is orthogonal to all core levels of the entire crystal. In this method, pseudo-atoms or empty spheres have to be inserted into the open crystal structure in order to ensure a continuous electric density in the open structures. The criterion is that the proportion of the volume taken up by sphere overlap is less than 15%. For Ti_2SnC and Ti_2GeC , the overlaps are 11.24% and 12.07%, respectively, and no empty sphere was inserted in either of the crystal structures in our calculations. The calculation introduces the Monkhorst–Pack scheme [14] to deal with a uniform mesh of k -points in reciprocal space. The atom radii are calculated using Vegard's law assuming that the size of the atoms in a complex unit cell is similar to the size of the atoms in an elemental solid. The basis set for the valence state used for the present calculation consisted of Ti 4s, 4p, and 3d orbitals, Sn 5s, 5p, and 5d orbitals, C 2s, 2p orbitals and Ge 4s, 4p, and 4d orbitals.

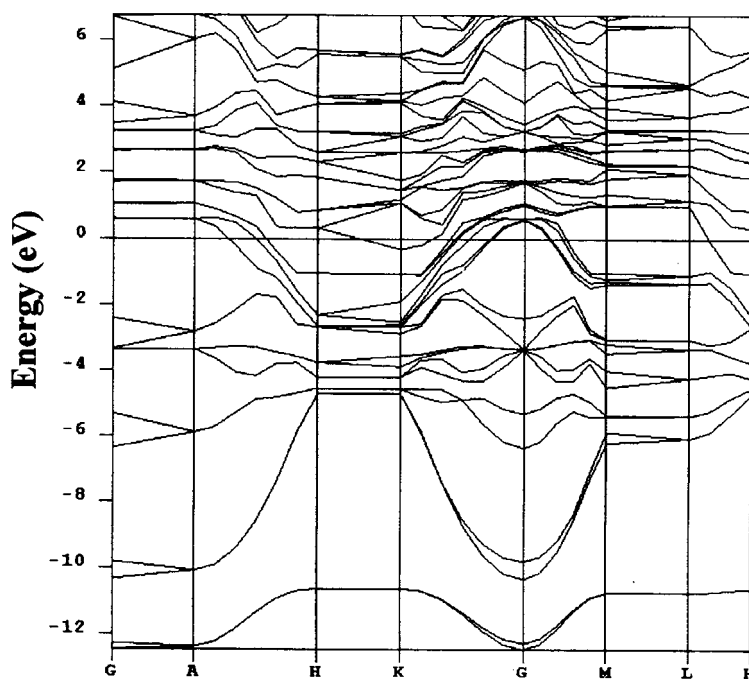
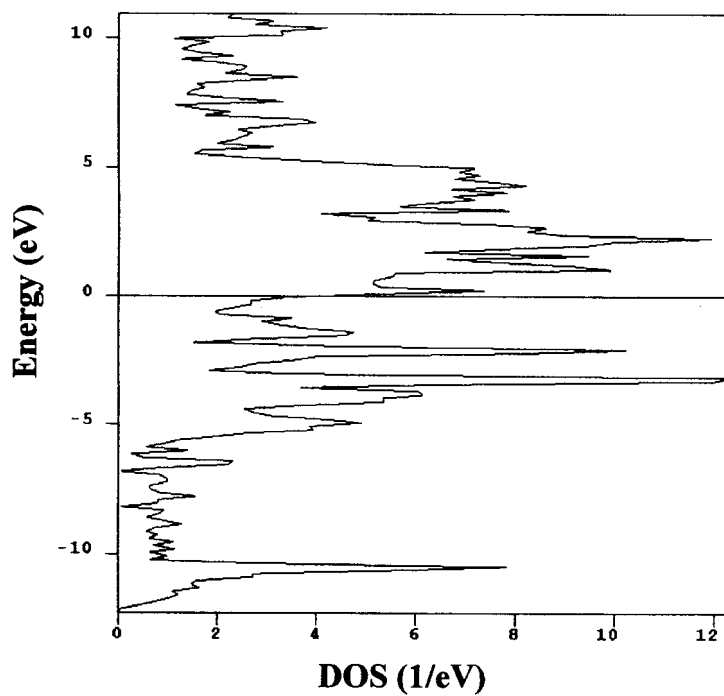
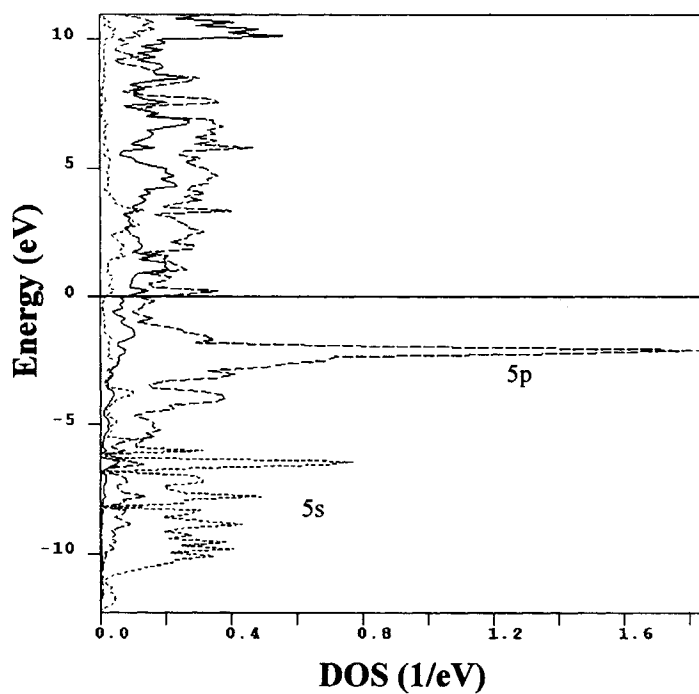


Figure 2. The calculated band structure of Ti_2SnC .

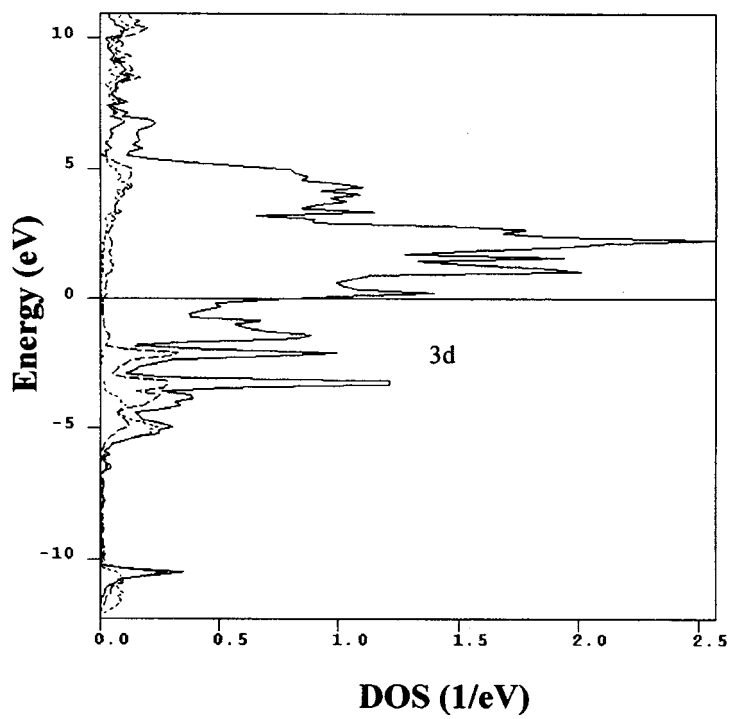


(a)

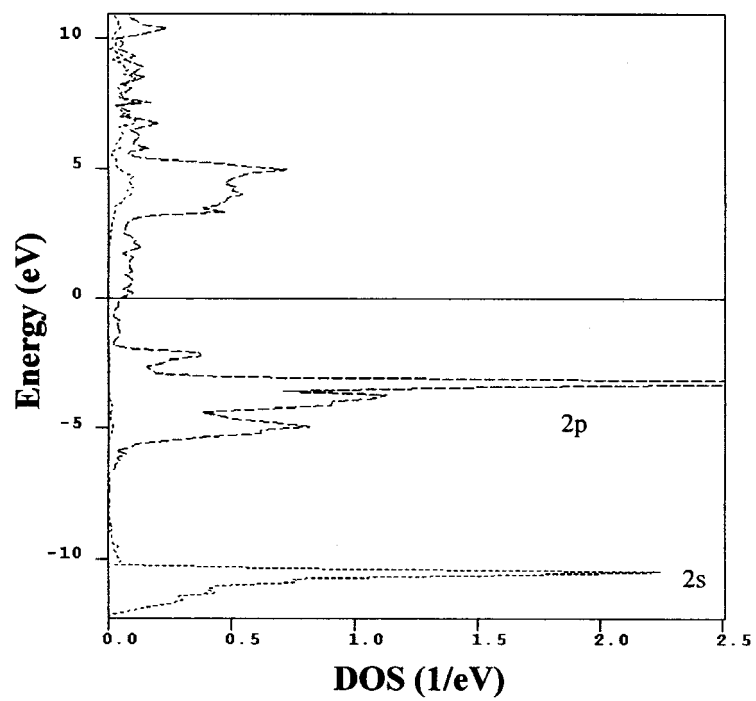


(b)

Figure 3. Ti_2SnC : (a) the calculated total DOS, and site-projected DOS of (b) Sn, (c) Ti, (d) C (dotted lines stand for s states, long-dashed lines for p states, solid lines for d states).



(c)



(d)

Figure 3. (Continued)

3. Results and discussion

3.1. Ti_2SnC

Figure 2 shows the calculated band structure of Ti_2SnC along selected high-symmetry lines within the first Brillouin zone of the hexagonal lattice. The corresponding total density of states (DOS) and the partial DOS of each element, broken up into site and angular momentum contributions, are shown in figure 3. Two characters are seen in figure 2. The first feature is that there is no gap at E_F : valence and conduction Ti 3d–Sn 5p–C 2p bands overlap significantly at the Fermi level. As a result, the conductivity of Ti_2SnC is strongly metallic, which agrees well with the reported electrical conductivity of polycrystalline Ti_2SnC [4]. The second feature of the band structure is the strongly anisotropic character with less c -axis energy dispersion. This can be seen from the reduced dispersion along the short H–K and M–L directions. The anisotropy of the band structure near and below E_F indicates that the conductivity is also anisotropic for single-crystal Ti_2SnC . Four groups of bands can be identified. The bottom valence band contains mainly 2s contributions from C atoms and a small contribution from Ti 3d states. For the energy window from -10 to -6 eV, the valence band contains mainly 5s contributions from Sn. In the energy range from -6 to -3 eV, the valence bands derive from strongly hybridized Ti 3d and C 2p states. The support for the pd hybridization comes from the striking similarity of the partial DOS of C 2p and Ti 3d in this energy range. From -3 eV to E_F , Ti 3d and Sn 5p states predominate.

Details on the bonding properties can be seen from the total and partial densities of states shown in figure 3. It is interesting to note from figure 3(b) that the width of the Sn 5s state is much larger than that of the C 2s state and there are quite a few peaks in the Sn 5s state. The characteristics of the Sn 5s state indicate that there is sp hybridization in Sn, i.e. the close-packed layer of Sn atoms is bonded through sp hybridization. For the energy range from -6 to -3 eV, there is high degree of hybridization of Ti 3d with C 2p states, which is indicative of a covalent interaction. The pd hybridization or p–d bonding stabilizes the structure. Thus, in Ti_2SnC , Ti 3d–C 2p hybridization is the driving bonding force, from which we can conclude that the heat of formation and melting point for Ti_2SnC may be high. For the energy window

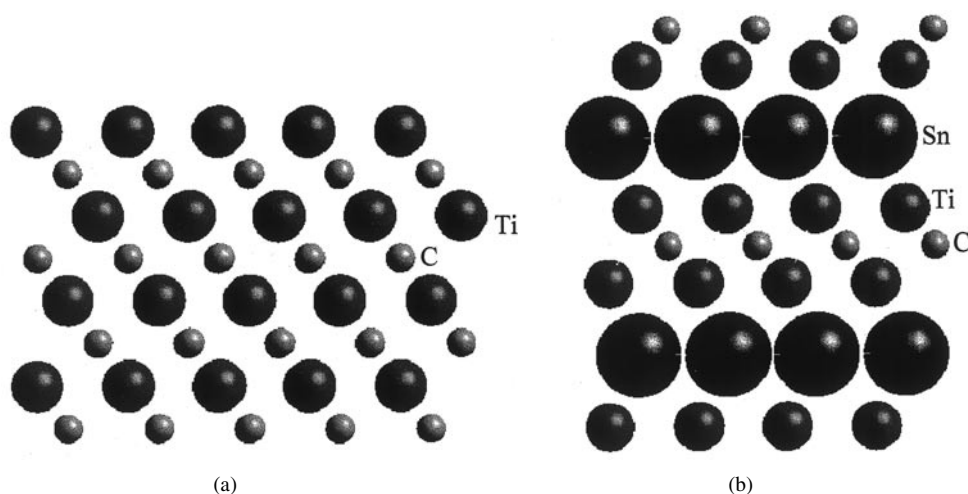


Figure 4. Projection of atoms on (a) the $(1\bar{1}0)$ plane of TiC and (b) the $(11\bar{2}0)$ plane of Ti_2SnC .

from -3 to -2 eV, the Sn 5p state interacts with the Ti 3d state. The presence of Sn changed the covalent bond chain Ti–C–Ti–C into Ti–C–Ti–Sn through its 5p states bonding to Ti. Therefore, the layered structure is formed due to the presence of Sn. At around the Fermi level, the DOS mainly originates from *nearly free-electron* states from Ti 3d states with less contribution from Sn 5p and C 2p states. Above the Fermi level, antibonding Ti 3d states dominate with less contribution from Sn 5p and C 2p states. From the above analysis, it can be concluded that all the 3d electrons of Ti and 5p electrons of Sn and 2p electrons of C have strong effects on the bonding in Ti_2SnC . The pd hybridization stabilizes the structure, whereas Sn changes the covalent Ti–C–Ti–C bond chain into Ti–C–Ti–Sn through its reaction with Ti.

At this point a comparison with the crystal and electronic structure of TiC is in order. The total DOS of TiC [15, 16] showing a minimum at the Fermi level is related to the refractory nature and its stability. The partial DOS of each element that is broken up into site and angular momentum contributions reveals that in the valence band and from 4 eV to higher energies, C 2p and Ti 3d states have strongly similar shapes, which is indicative of a covalent interaction between them. Previous work by Mater *et al* [15] demonstrated that in TiC, Ti 3d–C 2p bonding is the driving bonding force. Two types of Ti 3d–C 2p bonding were found with increasing energy, i.e. pd_σ predominates over pd_π in the valence band, whence the directional character of the bonding in TiC. In Ti_2SnC , the Ti–C–Ti–C bond chain is changed by the presence of Sn, which acts through its 5p states in its bonding to Ti. There is an increase in the amount of d character in the valence band, which can be seen from the larger occupation of Ti 3d in Ti_2SnC compared to the Ti d-band occupation in TiC.

To further illustrate the relationship between Ti_2SnC and TiC, the projections of atoms on the $(1\bar{1}0)$ plane of TiC and $(11\bar{2}0)$ plane of Ti_2SnC are shown in figure 4. Comparing the crystal structures and projections of atoms shown in figure 4, it is interesting to see that the dimensionality decreases from TiC to Ti_2SnC . In TiC, Ti and C atoms form a strong Ti–C–Ti–C

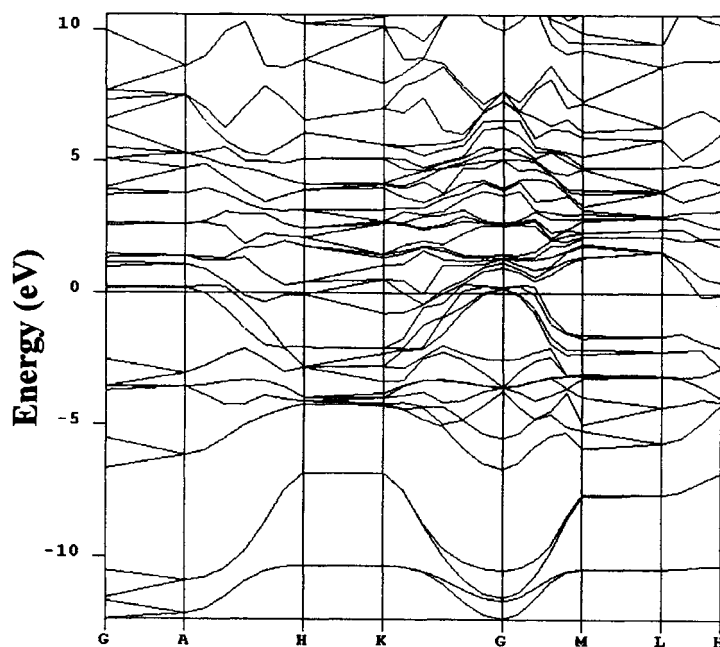
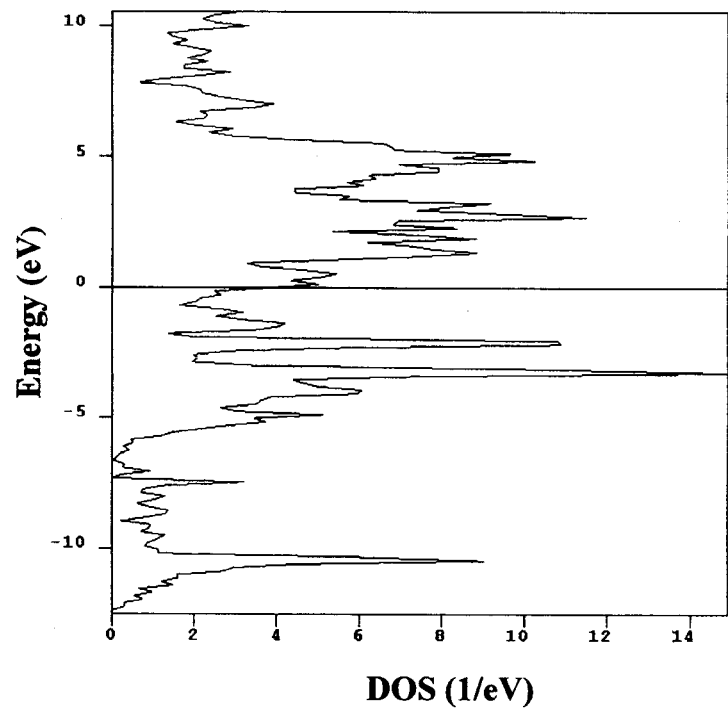
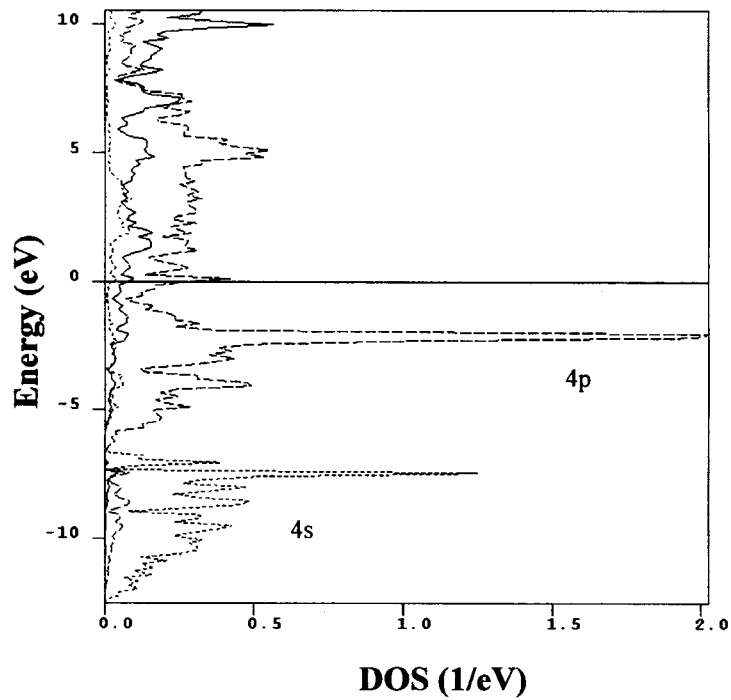


Figure 5. The calculated band structure of Ti_2GeC .

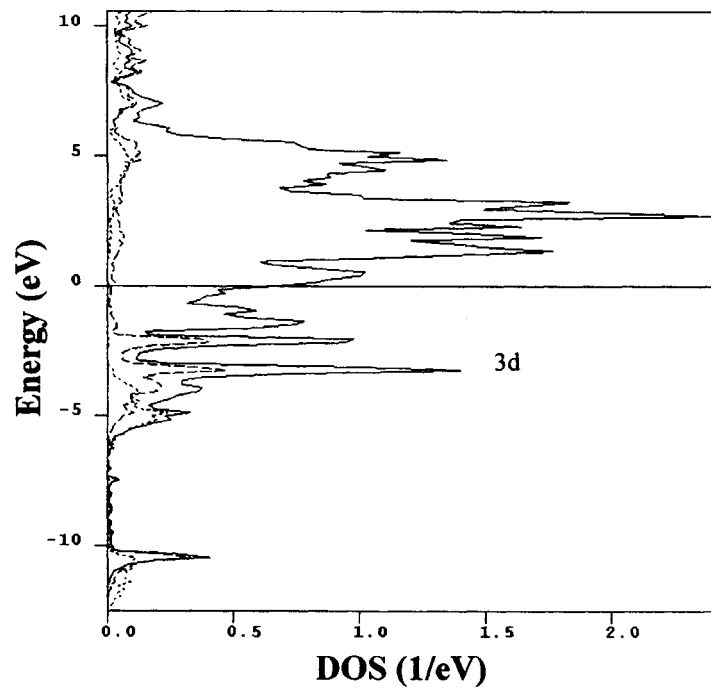


(a)

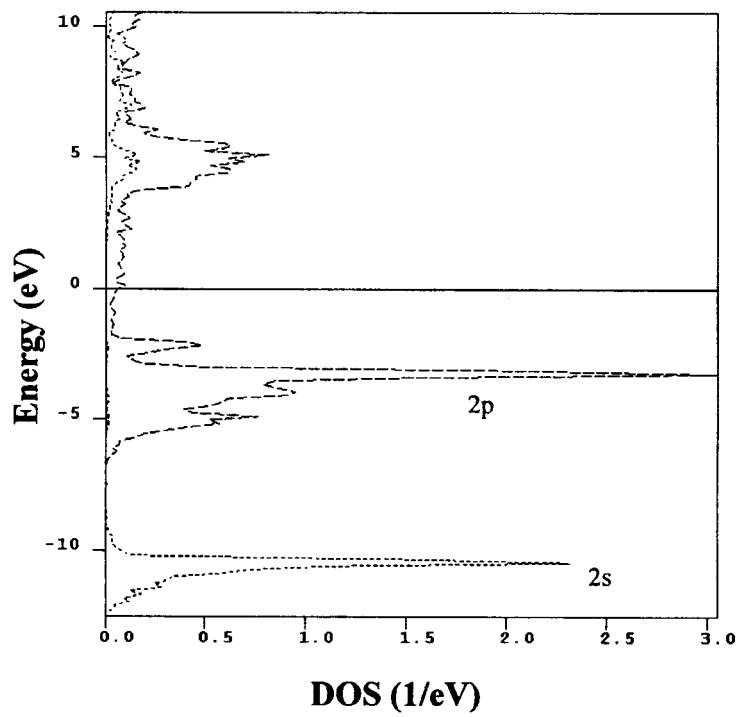


(b)

Figure 6. Ti_2GeC : (a) the calculated total DOS, and site-projected DOS of (b) Ge, (c) Ti, (d) C (dotted lines stand for s states, long-dashed lines for p states, solid lines for d states).



(c)



(d)

Figure 6. (Continued)

covalent bond chain, whereas in Ti_2SnC the adjacent Ti–C–Ti bond chains are linked by one Sn atom, forming a layered structure. Thus the structure of Ti_2SnC can be considered as a layer of Sn atoms periodically intercalated in between every pair of layers of Ti_6C octahedra. The intercalation of Sn in between each pair of layers of Ti_6C octahedra reduces the dimensionality of TiC, forming a layered structure.

3.2. Ti_2GeC

Figure 5 shows the calculated band structure of Ti_2GeC and figure 6 gives the total and partial DOS of each element—broken up into site and angular momentum contributions. Comparing the calculated band structure and total density of states of Ti_2GeC with those for Ti_2SnC , we find that the conductivity of Ti_2GeC is metallic because there is no gap at the Fermi level. The electrical conductivity for single-crystal Ti_2GeC is also anisotropic because of the anisotropic features of the band structure in figure 5. On the basis of a careful analysis of the total DOS for the two compounds (figure 3(a) and figure 6(a)), it is concluded that the electrical conductivity of Ti_2GeC is lower than that of Ti_2SnC because the DOS at the Fermi level for Ti_2GeC is lower than that for Ti_2SnC . Three groups of bands can be identified in figure 5. The bottom valence bands contain mainly 4s and 2s contributions from Ge and C atoms, and a small contribution from Ti 3d states. For the energy window from -6 to -3 eV, the valence band derives from hybridized p–d bonding states. Around the Fermi level, delocalized Ti 3d states dominate.

The total and partial DOS in figure 6 show that due to the more delocalized Ti 3d states and their hybridization with Ge 4p and C 2p states, the width of the valence band, about 13 eV, is large. For the energy range from -13 to -6 eV, Ge 4s interacts with C 2s and the Ge–C bonding predominates. It is interesting to note that the width of the Ge 4s state is larger than that of the C 2s state and there are more peaks in the Ge 4s state, which indicates the sp hybridization in Ge and sp–d hybridization between Ge sp and Ti 3d. Thus within the Ge layer, Ge atoms are bonded through sp hybridization, whereas the bonding of Ge with Ti is through its sp–d hybridization. For the energy window from -6 to -0.5 eV, Ge 4p and C 2p states hybridize with the Ti 3d state and p–d bonding dominates. The p–d bonding of Ti–C stabilizes the structure of Ti_2GeC while the presence of Ge changes the Ti–C–Ti–C covalent bond chain into a Ti–C–Ti–Ge bond chain through its reaction with Ti. Therefore, the layered structure of ternary Ti_2GeC is formed due to the presence of Ge. The structure of Ti_2GeC can be described as two-dimensional close-packed layers of Ge atoms intercalated between every pair of layers of Ti_6C octahedra. At around the Fermi level, the DOS mainly originates from *nearly free-electron* states from Ti 3d states with less contribution from Ge 4p states. Above the Fermi level, antibonding Ti 3d states dominate with less contribution from Ge 4p and C 2p states. We can see from the above analysis that all the 3d electrons of Ti, Ge 4s, 4p and C 2s and 2p states have strong effects on the bonding in Ti_2GeC . The Ti 3d–C 2p hybridization is the driving force in the structure and the presence of Ge changes the Ti–C–Ti–C covalent bond chain into a Ti–C–Ti–Ge bond chain, forming a layered structure. Ge atoms are bonded within the layer through sp hybridization.

4. Conclusions

We have investigated the electronic structure and bonding properties of the layered ternary carbides Ti_2SnC and Ti_2GeC by means of *ab initio* linear combination of atomic orbital calculations. The results show that the electrical conductivity is for both Ti_2SnC and Ti_2GeC metallic and anisotropic. The electrical conductivity of Ti_2SnC , however, is higher than that of Ti_2GeC . The major factors governing the electronic properties are pd hybridization from Ti 3d

and C 2p states. Comparing to TiC , the presence of Sn or Ge changes the Ti–C–Ti–C covalent bond chain into a Ti–C–Ti–Sn or Ti–C–Ti–Ge bond chain through its reaction with Ti, forming the layered structure. Within Sn or Ge layers, the atoms are bonded through sp hybridization. Thus the structure of Ti_2SnC and Ti_2GeC can be considered as two-dimensional close-packed layers of Sn or Ge intercalated between layers of Ti_6C octahedra.

Acknowledgments

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References

- [1] Jeitschko W, Nowotny H and Benesovsky F 1964 *J. Less-Common Met.* **7** 133
- [2] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 672
- [3] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 1201
- [4] Barsoum M W, Yaroschuk G and Tyagi S 1997 *Scr. Mater.* **37** 1583
- [5] Zhou Y C, Sun Z M, Sun J H, Zhang Y and Zhou J 2000 *Z. Metallk.* **91** 329
- [6] Barsoum M W, Brodtkin D and El-Raghy T 1997 *Scr. Mater.* **36** 535
- [7] Zhou Y C and Sun Z M 2000 *Phys. Rev. B* **61** 12 570
- [8] Sun Z M and Zhou Y C 1999 *Phys. Rev. B* **60** 1441
- [9] Kephart J S and Carim A H 1998 *J. Electrochem. Soc.* **145** 3253
- [10] Harrison W A 1980 *Electronic Structure and Properties of Solids* (New York: Dover)
- [11] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
- [12] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [13] Andersen O K 1975 *Phys. Rev. B* **12** 3060
- [14] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [15] Mater S F, Petitcorps Y L and Etourneau J 1997 *J. Mater. Chem.* **7** 99
- [16] Zhou Y C and Sun Z M 2000 *J. Phys.: Condens. Matter* **12** L457