

*Ab initio* geometry optimization and ground state properties of layered ternary carbides

$\text{Ti}_3\text{MC}_2$  (M = Al, Si and Ge)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 10001

(<http://iopscience.iop.org/0953-8984/13/44/313>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 15:06

Please note that [terms and conditions apply](#).

# *Ab initio* geometry optimization and ground state properties of layered ternary carbides $Ti_3MC_2$ (M = Al, Si and Ge)

Yanchun Zhou<sup>1</sup>, Zhimei Sun, Xiaohui Wang and Shengqi Chen

High-Performance Ceramic Division, Shenyang National Laboratory for Material Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China

E-mail: yczhou@imr.ac.cn

Received 5 July 2001

Published 19 October 2001

Online at [stacks.iop.org/JPhysCM/13/10001](http://stacks.iop.org/JPhysCM/13/10001)

## Abstract

The crystal structures of all layered ternary carbides called '312' phases including  $Ti_3AlC_2$ ,  $Ti_3SiC_2$  and  $Ti_3GeC_2$  have been fully optimized by means of *ab initio* total-energy calculations. The equilibrium lattice parameters, the atomic positions in the unit cell and interatomic distances have been determined. The differences between the calculated and the measured lattice constants are generally less than 1%. It is also shown that  $c/a$  of the hexagonal lattices decreases from  $Ti_3AlC_2$  to  $Ti_3GeC_2$ . The calculated bulk moduli are 190 GPa for  $Ti_3AlC_2$ , 202 GPa for  $Ti_3SiC_2$  and 198 GPa for  $Ti_3GeC_2$ , respectively, which are comparable to that of TiC. The electronic structures reveal that the Ti(1,2) and C atoms form a strong Ti(2)–C–Ti(1)–C–Ti(2) covalent bond chain, while the bonding between Ti(2) and M (M = Al, Si, Ge) is relatively weak. The strong Ti(2)–C–Ti(1)–C–Ti(2) covalent bond chain corresponds to the high strength and modulus, while the metallic bond corresponds to the metallic conductivity of these ternaries.

## 1. Introduction

Inorganic compounds with a layered crystal structure often exhibit a rich array of chemical and physical properties. Recently, we have become particularly intrigued by the layered ternary carbides  $T_3MC_2$ , where T is a transition metal, M is a IIIA or IVA element and C is carbon. Up to now three carbides, i.e.  $Ti_3SiC_2$  [1],  $Ti_3GeC_2$  [2] and  $Ti_3AlC_2$  [3] have been found to belong to this family. These layered ternaries have a unique combination of the properties of both metals and ceramics. The salient properties of these materials include low density, high

<sup>1</sup> Author to whom correspondence should be addressed.

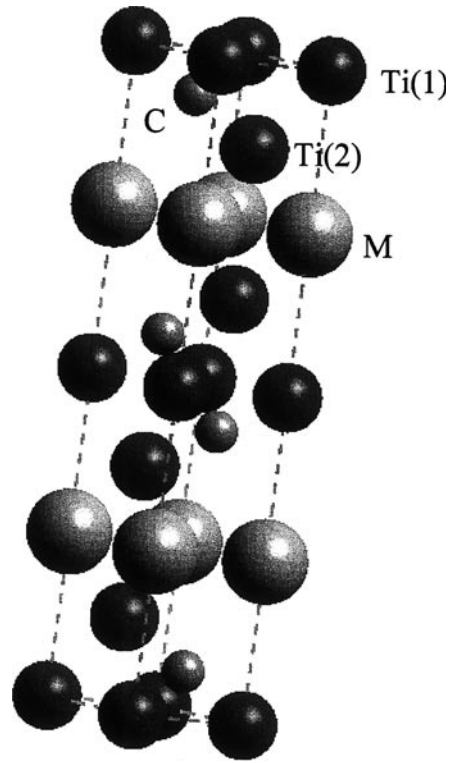
strength and modulus, damage tolerance at room temperature, being readily machinable by conventional high-speed tools, resistance to thermal shock and high temperature oxidation. The macroscopic properties of these ternary carbides are believed to strongly relate to the electronic and structural properties and we are intrigued by the relations established between them.

Quantum mechanical modelling of solids through calculations of first principles has proven to be a powerful tool to obtain microscopic information, which is helpful in understanding the macroscopic properties of the solids. Thus, investigation of the electronic structure and bonding properties is essential for understanding the various properties of the layered carbides. The electronic structure and bonding properties of  $\text{Ti}_3\text{SiC}_2$  [4, 5] and  $\text{Ti}_3\text{GeC}_2$  [6] were investigated using the full-potential linear-muffin-tin-orbital (FLMTO) method [4] and a linear combination of atomic orbitals (LCAO) approach [5, 6]. However, very little information on the electronic structure and chemical bonding properties of  $\text{Ti}_3\text{AlC}_2$  is available. Furthermore, although the lattice parameters of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  have been determined experimentally [1–3], no calculations of first principles have been reported for determining the equilibrium configuration of these ternaries with respect to the coordinates of the atoms in the unit cell. In this work, we calculate the equilibrium atomic structure with respect to the inner coordinates of the atoms in the unit cell as well as the lattice parameters of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  by total energy minimization. We also analyse the chemical bonding and bond orders for the ground state of the three ternaries. Although a complete understanding of these layered carbides would require incorporating the effects of a high concentration of defects, the present calculation for the ideal structure should provide a useful starting point for further analysis. In section 2, a brief description of the crystal structure of these carbides and the calculation method are given, and section 3 contains the results and discussion. The final section gives concluding remarks.

## 2. Crystal structure and calculation method

Our previous work demonstrated that the crystal structure of the layered ternary carbides was strongly related to that of TiC [8], which can be described as a layer of two-dimensional closed-packed M (Al, Si or Ge) atoms periodically intercalated in the (1 1 1) twin boundaries of TiC. These layered carbides have a hexagonal symmetry with the space group of  $P6_3/mmc$ . The atoms are located at the following positions: Ti at  $2a$  and  $4f$ , M (Al, Si or Ge) at  $2b$  and C at  $4f$  Wyckoff positions. The lattice parameters for the three ternaries are listed in table 1. Figure 1 shows the crystal structure of  $\text{Ti}_3\text{MC}_2$  ( $M = \text{Al, Si and Ge}$ ). For the convenience of discussion, we define the Ti atoms located at  $2a$  positions as Ti(1) atoms and those located at  $4f$  positions as Ti(2) atoms. The Ti(1) atoms are bonded only to C, while the Ti(2) atoms are bonded to both C and M.

For the ground-state electronic structure calculations within the density functional theory (DFT) [9–11] method we used the CASTEP code, which employs a plane-wave basis set for the valence electrons, the atomic cores being incorporated by first-principles separable pseudopotentials. The CASTEP code was well described in [11] and is not repeated here. One of the main features of the CASTEP code is that the internal coordinates can be automatically relaxed so that the structure with the minimum total energy is obtained. The norm-conserving pseudopotentials for Ti, M ( $M = \text{Al, Si and Ge}$ ) and C were generated using the optimized version of Kerker's scheme [12] and transformed into the separable form of Kleinman–Bylander pseudopotentials [13]. A gradient-corrected form of the exchange-



**Figure 1.** Crystal structure of layered ternary carbides  $\text{Ti}_3\text{MC}_2$  ( $M = \text{Al, Si, Ge}$ ).

**Table 1.** Comparison of the calculated and experimental (in brackets) lattice parameters and internal coordinates for  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$ .

Compound	Lattice parameters			Internal coordinates			
	$a$ (Å)	$c$ (Å)	$c/a$	Ti(1)	T(2)	M	C
$\text{Ti}_3\text{AlC}_2$	3.0720 (3.0753) <sup>1</sup>	18.732 (18.578)	6.098 (6.041)	0, 0, 0	$1/3, 2/3, z$ $z = 0.1290$ (0.1280)	$0, 0, 1/4$ $M = \text{Al}$	$1/3, 2/3, z$ $z = 0.5701$ (0.5640)
$\text{Ti}_3\text{SiC}_2$	3.0705 (3.068) <sup>2</sup>	17.670 (17.669)	5.755 (5.759)	0, 0, 0	$1/3, 2/3, z$ $z = 0.1370$ (0.1350)	$0, 0, 1/4$ $M = \text{Si}$	$1/3, 2/3, z$ $z = 0.5741$ (0.5675)
$\text{Ti}_3\text{GeC}_2$	3.0823 (3.077) <sup>3</sup>	17.711 (17.76)	5.746 (5.770)	0, 0, 0	$1/3, 2/3, z$ $z = 0.1361$	$0, 0, 1/4$ $M = \text{Ge}$	$1/3, 2/3, z$ $z = 0.5737$

correlation functional (generalized gradient approximation (GGA-PW91)) was used. The calculations were made using a plane-wave cut-off  $E_{\text{cut}}$  of 670 eV. This cut-off yields well-converged properties of the fully relaxed structure. The Brillouin zone (BZ) sampling was performed using special  $k$ -points generated by the Monkhorst–Pack scheme with parameters  $4 \times 4 \times 2$  [14].

### 3. Results and discussion

#### 3.1. Optimization of structure

Previous investigations on  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  were limited to equilibrium lattice constants and volumes without optimizing the internal parameters [5–7]. In this work, first calculations of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  were performed with full optimization of both the lattice parameters and the coordinates of atoms in the unit cell. The calculated lattice parameters  $a$  and  $c$  of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  are listed in table 1 together with the experimental values. The calculated lattice parameters are in satisfactory agreement with the experimental data. The differences in the lattice constants are  $-0.11\%$  for  $a$  and  $0.83\%$  for  $c$  of  $\text{Ti}_3\text{AlC}_2$ ,  $0.81\%$  for  $a$  and  $0.005\%$  for  $c$  of  $\text{Ti}_3\text{SiC}_2$  and  $0.17\%$  for  $a$  and  $-0.27\%$  for  $c$  of  $\text{Ti}_3\text{GeC}_2$ . The experimental internal parameters for atoms in  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{SiC}_2$  are also well reproduced. Since no experimental data for the internal parameters of atoms in  $\text{Ti}_3\text{GeC}_2$  are available, the calculated data from full relaxation are useful in understanding the structure of  $\text{Ti}_3\text{GeC}_2$ . It is also seen from table 1 that the  $c/a$  of the hexagonal lattices determined from both the experimental values and the calculated lattice parameters decreases in the order of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$ . This means that increasing the size of M atoms (from Al to Ge) resulted in the reduction of  $c/a$  or decrease in the distances between the  $\text{Ti}_6\text{C}$  layers in the  $c$  direction. We will discuss this in a later section.

Secondly, we examined the energy–volume curves of the three carbides near the equilibrium volume where we optimized the atomic positions for several volumes. In each calculation with a specific volume expansion or contraction, the  $c/a$  is fixed at an equilibrium value, while all internal parameters of the crystals are relaxed. Figure 2 shows the total energy (TE) as a function of cell volume for  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$ . The curves in figure 2 were obtained by fitting the data to a fourth-order polynomial. At the equilibrium volume, we calculated the bulk moduli of the stable structure of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  from the total energy–volume curves. The bulk modulus  $B_0$  of each crystal is obtained by fitting the data to the fourth-order polynomial expansion. The estimated bulk modulus is 190 GPa for  $\text{Ti}_3\text{AlC}_2$ , 202 GPa for  $\text{Ti}_3\text{SiC}_2$  and 198 GPa for  $\text{Ti}_3\text{GeC}_2$ , respectively. Until now there has been very limited information on the bulk moduli of these carbides. Onodera *et al* [15] deduced the bulk modulus of 206 GPa for  $\text{Ti}_3\text{SiC}_2$  from the volume versus pressure data, which is close to that of TiC. The estimated bulk modulus of  $\text{Ti}_3\text{SiC}_2$  in the present work is consistent with the value reported by Onodera *et al* [15].  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{GeC}_2$  are isostructural with  $\text{Ti}_3\text{SiC}_2$  and share many of its characteristics. The bulk moduli of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{GeC}_2$  estimated are useful for further reference.

We analysed the bond lengths of the equilibrium atomic configurations for the three ternaries, which are listed in table 2. The bond lengths determined experimentally are available only for  $\text{Ti}_3\text{SiC}_2$  [1, 16]. Comparing the calculated bond lengths with the experimental data for  $\text{Ti}_3\text{SiC}_2$  [16], we find good agreement between the theoretical and experimental data although small deviations existed in Ti(2)–Si. The early work of Jeitschko *et al* [1] gave an average Ti–C bond length of 2.135 Å for  $\text{Ti}_3\text{SiC}_2$ . However, our results show that the bond lengths of Ti(1)–C and Ti(2)–C are different in all of the three ternaries, i.e. the local atomic arrangement inside the unit cell exhibits two types of Ti–C bonds. The bond lengths of Ti(1)–C in  $\text{Ti}_3\text{MC}_2$  are longer than that of Ti(2)–C. This difference in the bond lengths of Ti(1)–C and Ti(2)–C was experimentally identified in  $\text{Ti}_3\text{SiC}_2$ , i.e. the Ti–C bonds adjacent to the Si layers were shorter than those in the centre of the unit cell [16]. Since the bonding environments of Ti(1) and Ti(2) atoms are different, the existence of the difference between the bond lengths of Ti(1)–C and Ti(2)–C in  $\text{Ti}_3\text{MC}_2$  should not be surprising. The interatomic distances of Ti–M

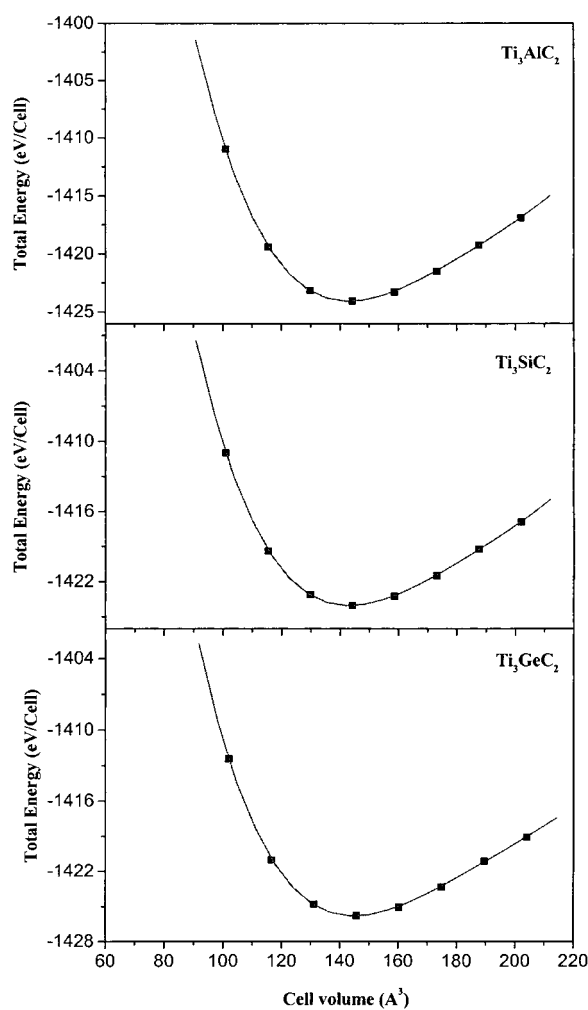


Figure 2. Total energy as a function of cell volume for  $Ti_3AlC_2$ ,  $Ti_3SiC_2$  and  $Ti_3GeC_2$ .

( $M = Al, Si$  and  $Ge$ ) are 2.878, 2.6697 and 2.6898 Å, respectively, in the three ternaries. Although the covalent radii of Al, Si and Ge atoms are larger than that of C, the bond lengths of Ti–Al, Ti–Si and Ti–Ge are longer than those of Ti(1, 2)–C. The longer interatomic distances between Ti and M ( $M = Al, Si$  and  $Ge$ ) indicate that the bonding between them is relatively weak. Breaking of the weak bond would be expected through basal plane slip and may correspond to the ultra-low basal plane friction coefficient and plasticity of the carbides [17].

### 3.2. Electronic structure and bonding properties

The mixed chemical bonding characters of the layered ternaries  $Ti_3AlC_2$ ,  $Ti_3SiC_2$  and  $Ti_3GeC_2$  can be seen from the calculated density of states (DOS) and partial density of states (PDOS) shown in figure 3. For  $Ti_3AlC_2$ , the DOS and PDOS in figure 3(a) show that the lowest valence bands of the total DOS are formed by the carbon 2s states with a small mixture of Ti 4s and 3d

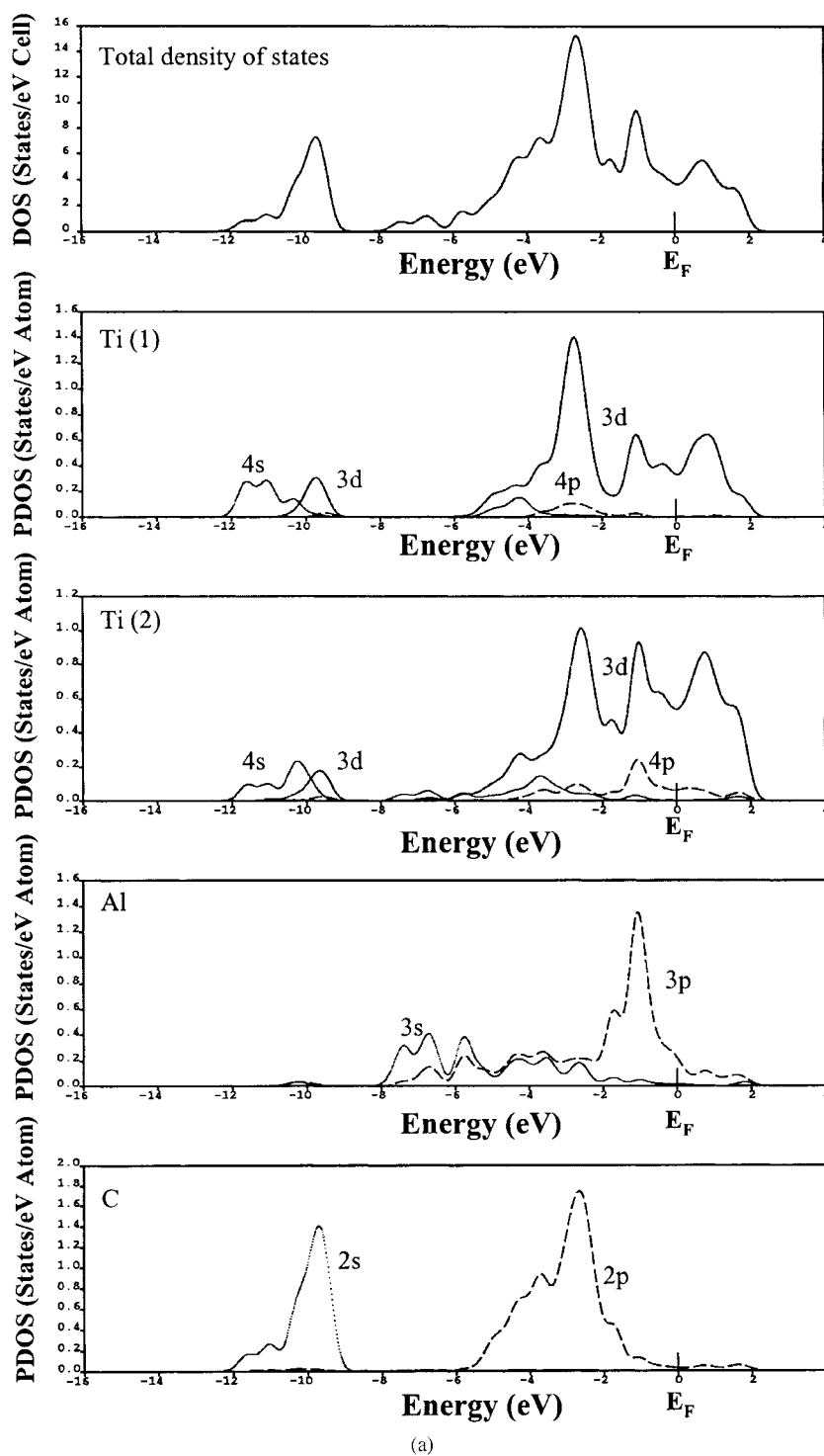
**Table 2.** Calculated and experimental bond lengths of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$ .

Compound	Ti(1)–C	Ti(2)–C	Ti–M (M = Al, Si, Ge)	Ti(1)–Ti(2)
$\text{Ti}_3\text{AlC}_2$	2.2068	2.0886	2.8783	2.9972
$\text{Ti}_3\text{SiC}_2$	2.2033 (2.135) <sup>2</sup> (2.1814) <sup>16</sup>	2.0931 (2.135) (2.085)	2.6697 (2.696) (2.693)	2.9720 (2.971)
$\text{Ti}_3\text{GeC}_2$	2.2078	2.0943	2.6898	2.9965

states. The higher valence bands from  $-8$  to  $-5$  eV are formed almost entirely by Al 3s states. The valence bands in the range  $-5$  to  $-2$  eV are formed by strongly hybridized Ti 3d and C 2p states. The top valence band is related to hybridized Ti(2) 3d and Al 3p states. At around the Fermi level, the DOS mainly originates from the states of Ti(2) 3d and Ti(1) 3d. The DOS at Fermi is 3.72 (states/eV cell) and coincides with a local minimum. The conduction bands are provided almost entirely by the Ti 3d states. The hybridized Ti(2) 3d–Al 3p and Ti(1, 2) 3d–C 2p states indicate the covalent interaction between Ti(1, 2)–C and Ti(2)–Al, whereas the zero gap and finite value at Fermi level reveal the metallic bonding in  $\text{Ti}_3\text{AlC}_2$ . For  $\text{Ti}_3\text{SiC}_2$ , the DOS and PDOS in figure 3(b) show that the lowest valence bands of the total DOS are formed by the carbon 2s states with a small mixture of Ti 4s, 3d and Si 3s states. The higher valence bands come from Si 3s bands. No gap can be seen in the entire range of the valence bands, which is different from that of  $\text{Ti}_3\text{AlC}_2$  shown in figure 3(a). From  $-6$  to  $-1$  eV, the valence bands are derived from hybridized Ti(1, 2) 3d–C 2p and Ti(2) 3d–Si 3p states. Ti(1) reacted with only C, while Ti(2) reacted with both C and Si; thus two adjacent peaks appear in the PDOS of Ti(2). At around the Fermi level, the DOS mainly originates from states of Ti(2) 3d and Ti(1) 3d. The DOS at Fermi level is 4.38 (states/eV cell) and corresponds to a local maximum indicating that  $\text{Ti}_3\text{SiC}_2$  is less stable than  $\text{Ti}_3\text{AlC}_2$ . The conduction bands are formed mainly by the Ti 3d states with less contribution from Si 3p states. As in  $\text{Ti}_3\text{AlC}_2$ , the hybridized Ti(2) 3d–Si 3p and Ti(1, 2) 3d–C 2p states correspond to the covalent interaction between Ti(1, 2)–C and Ti(2)–Si, whereas the zero gap and finite value at the Fermi level indicate metallic bonding in  $\text{Ti}_3\text{SiC}_2$ . The above conclusions are in agreement with previous calculations [4–7]. For  $\text{Ti}_3\text{GeC}_2$ , the TDOS and PDOS shown in figure 3(c) are similar to those of  $\text{Ti}_3\text{SiC}_2$ , only with a slightly higher DOS (4.65 states/eV cell) at the Fermi level. The details for DOS and PDOS of  $\text{Ti}_3\text{GeC}_2$  are not described here. From the analysis of the DOS of the three-layered compounds, it can be concluded that  $\text{Ti}_3\text{AlC}_2$  is more stable than  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  because the Fermi level in  $\text{Ti}_3\text{AlC}_2$  coincides with a local minimum in DOS.

#### 4. Conclusions

We have investigated the electronic structure and bonding properties of the layered ternary carbides  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$  by the *ab initio* total-energy pseudopotential method. The equilibrium lattice parameters, the atomic positions and the interatomic distances for the stable configuration have been determined. The differences between the experimental and calculated lattice parameters are less than 1%. The calculated bond lengths of  $\text{Ti}_3\text{SiC}_2$  agree well with the experimentally determined values, while the calculated bond lengths of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{GeC}_2$  are useful in understanding the structure of these ternaries since no experimental data are available. It has been demonstrated that there is strong covalent bonding between



**Figure 3.** Calculated total DOS, and sited projected PDOS of Ti(1), Ti(2), M and C atoms of  $Ti_3AlC_2$  (a),  $Ti_3SiC_2$  (b) and  $Ti_3GeC_2$  (c) atoms (the dotted line stands for an s state, the long dashed line for a p state, the solid line for a d state).



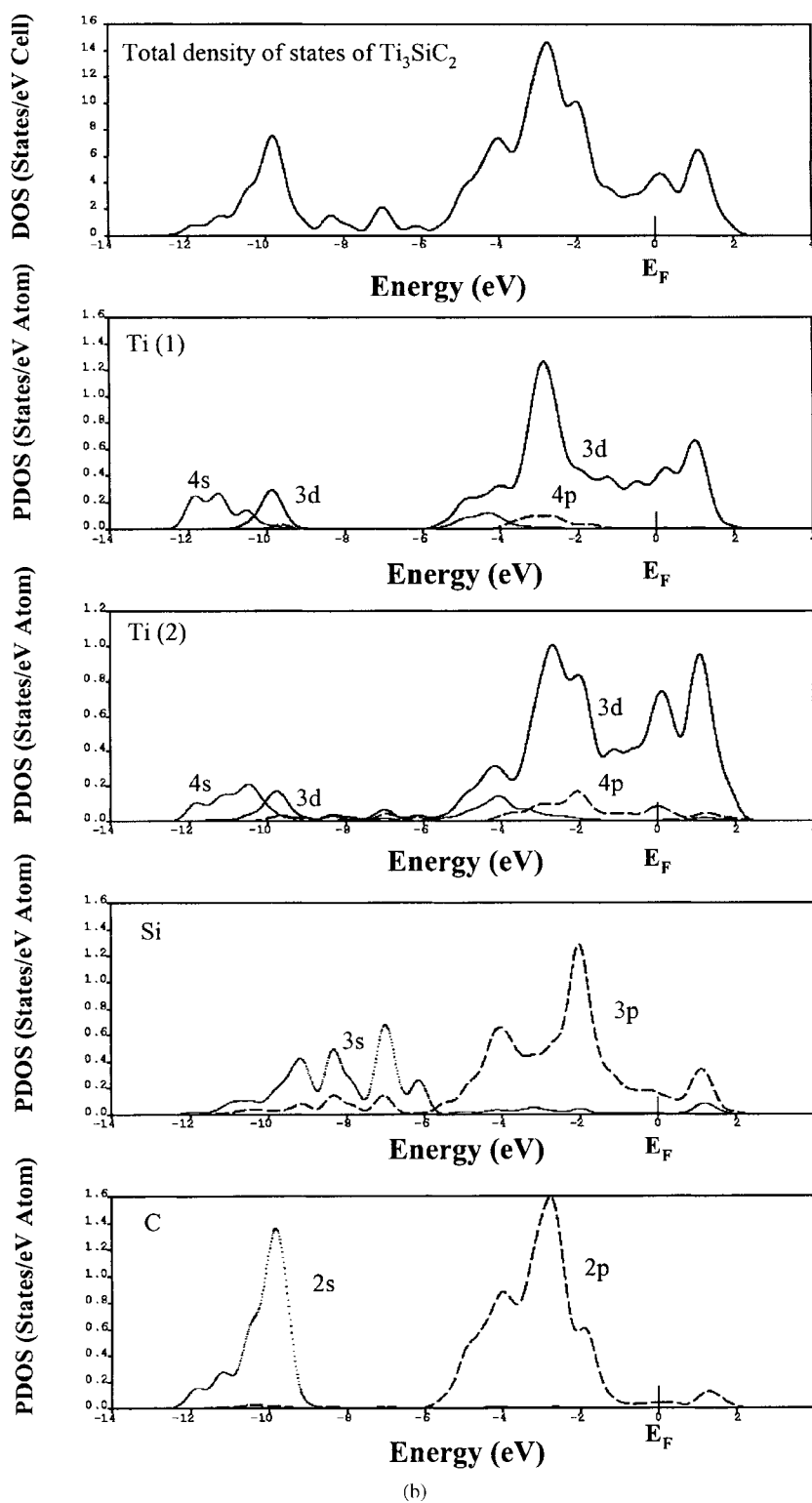


Figure 3. (Continued)

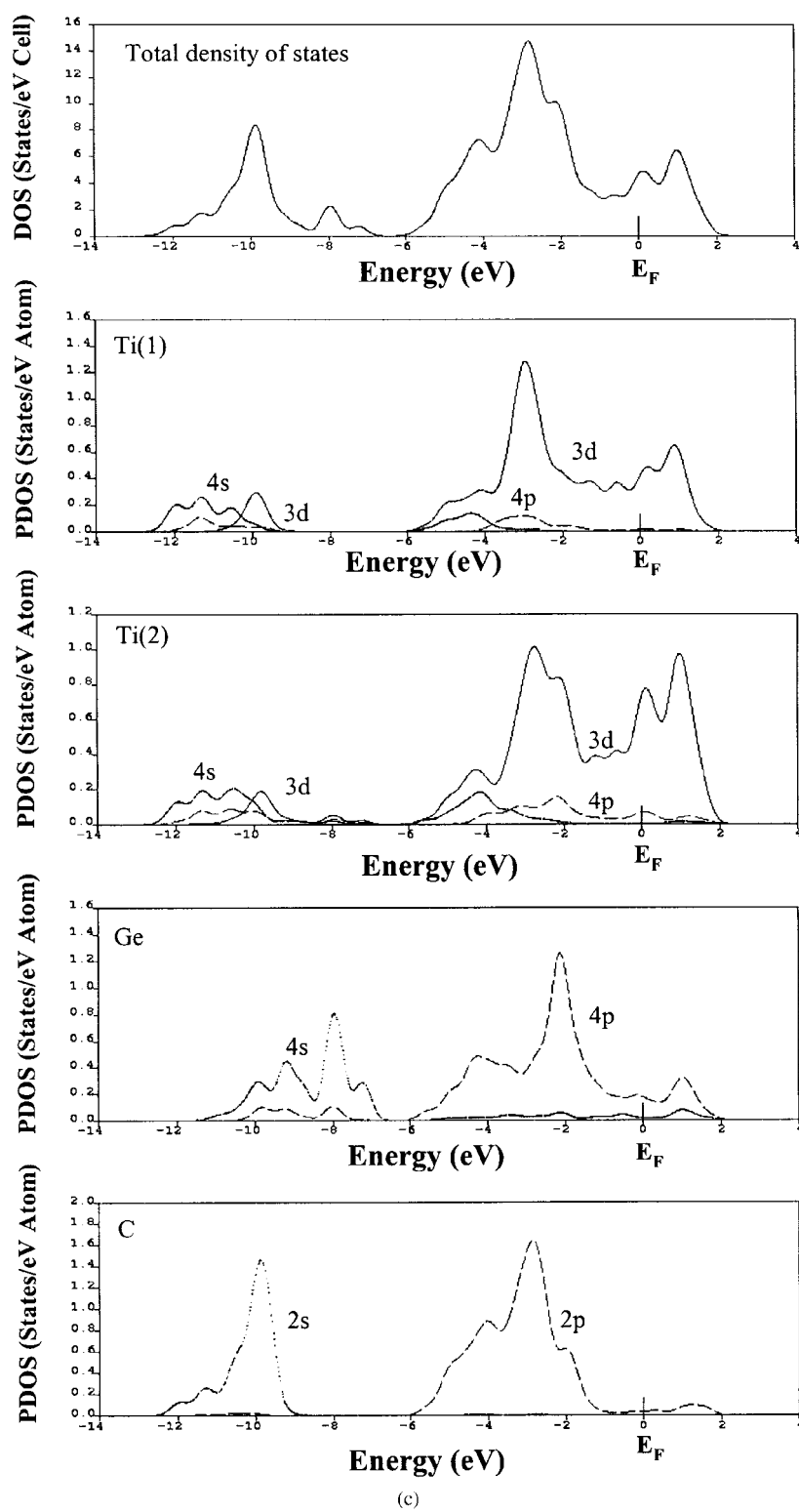


Figure 3. (Continued)

Ti(1, 2) and C and relatively weak bonding between Ti(2) and M (M = Al, Si Ge). The strong Ti(2)–C–Ti(1)–C–Ti(2) covalent bond chain corresponds to the high strength and modulus, while the metallic bond corresponds to the metallic conductivity of these ternaries.

### Acknowledgments

This work was supported by National Outstanding Young Scientist Foundation of China for YCZ under grant no 59925208, National Science of Foundation of China under grant no 50072034.

### References

- [1] Jeitschko W and Nowotny H 1967 *Monatsh Chem.* **98** 329
- [2] Wolfsgruber H, Nowotny H and Benesovsky F 1967 *Monatsh Chem.* **98** 2403
- [3] Pietzka M A and Schuster J C 1994 *J. Phase Equilib.* **15** 391
- [4] Medvedeva N, Novikov D, Ivanovsky A, Kuznetsov M and Freeman A 1998 *Phys. Rev. B* **58** 16042
- [5] Sun Z M and Zhou Y C 1999 *Phys. Rev. B* **60** 1441
- [6] Zhou Y C and Sun Z M 1999 *J. Appl. Phys.* **86** 1430
- [7] Zhou Y C 2000 *J. Phys.: Condens. Matter* **12** L457
- [8] Zhou Y C and Sun Z M 2000 *Mater. Res. Innovat.* **3** 286
- [9] Hohenberge P and Kohn W 1964 *Phys. Rev. B* **136** 864
- [10] Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133
- [11] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045
- [12] Lin J-S, Qteish A, Payne M C and Heine V 1993 *Phys. Rev. B* **47** 4174
- [13] Kleinman L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425
- [14] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [15] Onodera A, Hirano H, Yuasa T, Gao N F and Miyamoto Y 1999 *Appl. Phys. Lett.* **74** 3782
- [16] Barsoum M W, El-Raghy T, Rawn C J, Porter W D, Wang H, Payzant E A and Hubbard C R 1999 *J. Phys. Chem. Solids* **60** 429
- [17] Crossley A, Kisi E, Summers J W B and Myhra S 1999 *J. Phys. D: Appl. Phys.* **32** 632