JOURNAL OF
Materials
CHEMISTRY

The electronic structure and chemical bonding of Ti_3GeC_2

Zhimei Sun and Yanchun Zhou*

Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110015, P. R. China. E-mail: yczhou@imr.ac.ca

Received 24th August 1999, Accepted 17th November 1999

We have investigated the electronic structure and chemical bonding properties of Ti_3GeC_2 by performing *ab initio* pseudopotential total-energy calculations. Our results show that the crystal structure of Ti_3GeC_2 is a characteristic zigzag chain of Ti–C–Ti–C–Ti–Ge, running parallel to the *c*-axis. The chemical bonding in Ti_3GeC_2 is anisotropic and metallic–covalent–ionic in nature with significant contributions from metallic and covalent bonds, which result in the combination of metallic and ceramic properties in Ti_3GeC_2.

Ceramics generally have either covalent or ionic bond structures, or bonds intermediate between them, which result in high melting points, brittleness, high hardness and low electrical conductivity at low temperatures. However, a novel family of ceramics, *i.e.* the so-called "312" phases, demonstrate anomalous behavior deviating from that of classical ceramics.[1] Recent extensive studies on one of the "312" phases, Ti_3SiC_2, demonstrate that this family of ceramics exhibit the combined properties of both metals and ceramics,[1–8] which make them attractive for many diverse high temperature applications. The salient properties of these ceramics are high melting point, low density, high Young's modulus and good high-temperature-oxidation resistance, low hardness, high strength at high temperatures, good machinability with conventional tools, and excellent thermal and electrical conductivity. The measured room-temperature electrical conductivity of Ti_3SiC_2 is $9.6 \times 10^6\ \Omega^{-1}\ m^{-1}$, from our previous work,[9] and it increases with decreasing temperature, while Barsoum *et al.*[1,2] reported a value of $4.5 \times 10^6\ \Omega^{-1}\ m^{-1}$ for both less pure Ti_3GeC_2 and pure Ti_3SiC_2 materials. The unique properties of this family of ceramics have attracted the interest of material scientists and physicists seeking to understand them, thus in-depth theoretical studies are needed to reveal the nature of these ceramics.

The electronic structure and chemical bonding of Ti_3SiC_2 has been extensively investigated in previous work.[10,11] Ti_3GeC_2 is another "312" phase, which has similar properties to Ti_3SiC_2, but less data on the former is available. The electronic structure of Ti_3GeC_2 was investigated by means of *ab initio* linear combination of atomic orbitals (LCAO) methods in our previous work,[11] which gave a better picture of the electronic structure and bonding properties of Ti_3GeC_2. The detailed chemical bonding behavior in this compound is, nevertheless, unclear. During this work, we gained an insight into the structure of Ti_3GeC_2 by applying the pseudopotential total-energy method, discovering that Ti_3GeC_2 has a chain structure with a metallic–covalent–ionic bond nature.

Ti_3GeC_2 has a layered hexagonal structure, belonging to the space group $P6_3/mmc$ [Fig. 1(a)].[4] The lattice constants are $a = 3.077$ and $c = 17.76$ Å. The traditional description of the structure is two edge-shared TiC octahedral layers linked together by a two-dimensional close-packed Ge layer. For convenience of discussion, we define the two apical Ti atoms as Ti(1) and Ti(2). The corresponding Brillouin zone is depicted in Fig. 1(b).

Our study is based on the *ab initio* pseudopotential total-energy method,[12] for which we employed density-functional theory (DFT) in the local-density approximation (LDA).[13,14] We used Perdew and Zunger's parameterization[15] for the exchange-correlation energy and norm-conserving Kerker pseudopotentials[16] in the Kleinman–Bylander form.[17] The nonlocal potentials are treated in real space, using the method proposed by King-Smith, Payne and Lin.[18]

Fig. 2(a) and (b) show the calculated band structure of Ti_3GeC_2 and its corresponding total density of states (DOS), respectively. There is no band gap between the valence and conduction bands. These bands overlap significantly around the Fermi level (E_F). Another feature of Fig. 2(a) is the strongly anisotropic character of the band structure, in which there is much less energy dispersion along the short H–K and M–L directions. The DOS at the Fermi level in Fig. 2(b) is about 0.18 states (per unit cell), a little lower than that of Ti_3SiC_2 [0.19 states (per unit cell)], which may explain the slightly lower electrical conductivity of Ti_3GeC_2. As a result, Ti_3GeC_2 has metallic properties, and the electrical conductivity is anisotropic for single crystal Ti_3GeC_2, *i.e.* the electrical conductivity along the *c*-axis is much lower than that in the basal plane.

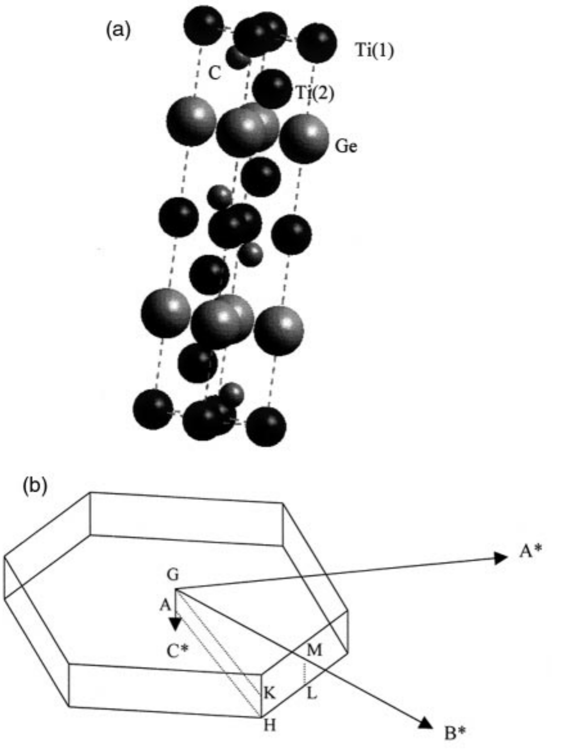

Fig. 1 (a) The crystal structure of Ti_3GeC_2, and (b) the corresponding Brillouin zone and high-symmetry points.

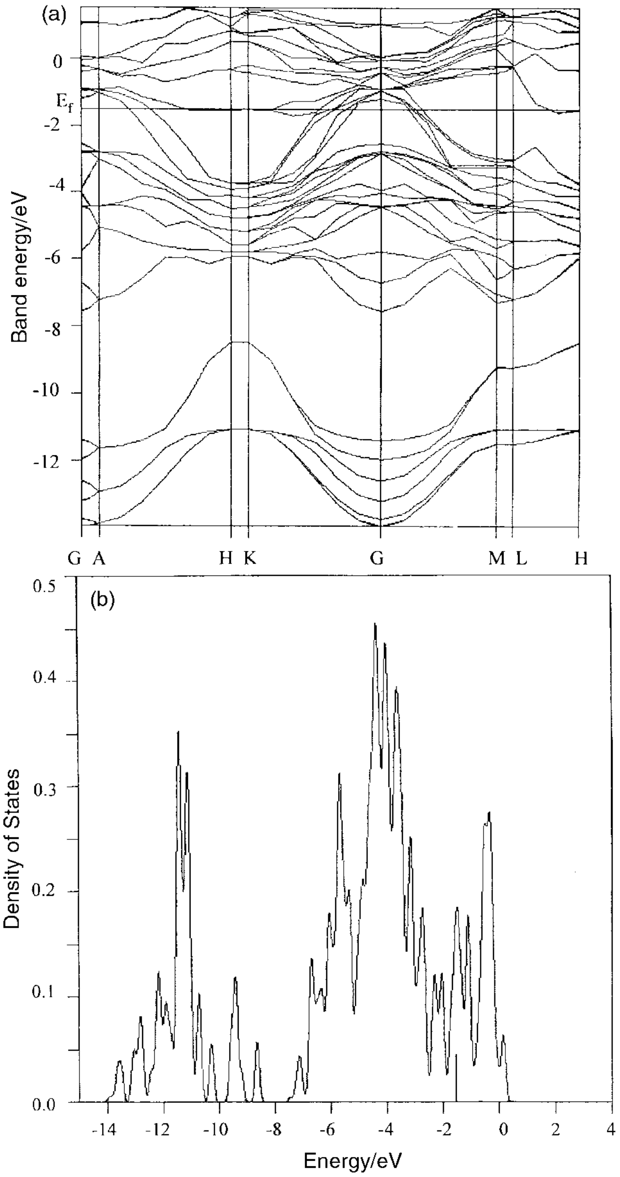

Fig. 2 (a) The calculated band structure of Ti_3GeC_2, and (b) the total density of states for Ti_3GeC_2.

The metallic properties of Ti_3GeC_2 and its anisotropic character can be seen in Fig. 3, which show the charge-density distributions in atomic layers of Ti, Ge and C that are parallel to the basal plane, and on the (110) plane. For convenience of discussion, a 2 × 2 × 1 cell was used in Fig. 3. The network of metallic bonds in the Ti(1) and Ti(2) planes are shown in Fig. 3(a) and (b), in which the Ti–Ti bonds of the Ti(1) and Ti(2) atoms differ considerably, implying that Ti(1) and Ti(2) play different roles in the electrical conductivity and chemical bonding in Ti_3GeC_2. The discrepancy is obvious in Fig. 3(e), in which there is directional bonding with polar character between the Ti(1) and C atoms, while the Ti(2) atoms have directional bonding with both C and Ge atoms. The interaction between the Ti(1,2) and C atoms is strong covalent bonding, while the Ti(2)–Ge interaction is much weaker. There are also free charge-density distributions in the interstices between the Ge and C planes, however, the Ge atoms form rigid covalent Ge–Ge bond networks inside the Ge monolayers [Fig. 3(c)]. Hexagonal layers of Ge and C atoms mediate the interaction between Ti planes. Therefore, the metallic properties of Ti_3GeC_2, such as electrical conductivity, are attributed to the delocalized charge-density distribution, and are anisotropic, *i.e.* Ti_3GeC_2 shows strong metallic properties in the basal planes, while weaker metallic properties are expected in the direction parallel to the *c*-axis. This strong anisotropy of chemical bonding is typical for many layered compounds and may cause the plasticity of the Ti_3GeC_2 ceramic.

The charge-density distribution on the (110) plane gives detailed information on the chemical bonding between different atoms [Fig. 3(e)]. Surprisingly, we have found a chain structure in Ti_3GeC_2. The unit chain is along the Ti–C–Ti–C–Ti bond line which is strongly directional. Each pair of Ti–C–Ti–C–Ti bond chains share one Ge atom, forming a zigzag linear chain couple with an angle of about 90° between the two chains. The length of the chain couple in the *c* direction is equal to the cell parameter *c* (17.76 Å). The Ti–C–Ti–C–Ti–Ge chain couple periodically repeats three-dimensionally, forming the chain structure of Ti_3GeC_2. In the Ti–C–Ti–C–Ti–Ge bond chain, the interatomic distance between the Ti(1,2) and C is 2.13 Å, indicating that the chemical bonding between Ti and C is covalent in nature, furthermore, the polar character of the directional bonding suggests ionic bonding between the Ti(1,2) and C atoms. The interatomic distance between the Ti(2) and Ge atoms is 2.73 Å, which indicates much weaker covalent bonding. There are free charge-density distributions in the long zigzag channels between neighbouring chains, indicating metallic bonding. The chains are separated by relatively large distances, which results in extreme anisotropy in the electronic, vibrational, and mechanical properties. Thus, we conclude at this point that Ti_3GeC_2 can be described as a "two-dimensional" chain-like structure with metallic, covalent and ionic bonding.

Chain-like crystal structures are common in organic crystals and in Group VI elemental crystals, such as Se and Te. However, these structures usually have a degree of covalent bonding character as well as Van der Waals bonds. The present study shows that the chain-like Ti_3GeC_2 compound is metallic–covalent–ionic in nature, that the atoms form zigzag Ti–C–Ti–C–Ti–Ge chains, through covalent and ionic bonding running parallel to the *c*-axis, and that these chains are linked together by inhomogeneous metallic and covalent bonding. Therefore, this unique chemical bonding may result in the interesting properties of Ti_3GeC_2, *i.e.* a unique combination of the properties of both metals and ceramics. The extremely high melting point and high Young's modulus are attributed to the strong covalent and ionic bonds, while the metallic properties, such as high electrical and thermal conductivity, are attributed to the strong metallic bonds. These theoretical predictions are in good agreement with the experimental results. Thus, the high melting point, relatively low density ($5.57\ \mathrm{g\ cm^{-3}}$),[1] good thermal and electrical conductivity, and high strength and plasticity at high temperatures suggest that Ti_3GeC_2 is another promising compound with diverse applications. Therefore, the synthesis and study of this material is of technological importance.

Our investigations show that the chemical bonding in Ti_3GeC_2 is anisotropic and metallic–covalent–ionic in nature with significant contributions from metallic and covalent bonds. Thus, a unique combination of metallic and ceramic properties are expected in Ti_3GeC_2. It was also found that Ti_3GeC_2 has a chain-like structure with zigzag Ti–C–Ti–C–Ti–Ge chains running parallel to the *c*-axis. The discovery of this chain-like crystal structure with metallic–covalent–ionic bonding has significant technological importance for the design and prediction of new materials. With metallic, covalent and/or ionic bonding within a single crystal, amazing materials with the properties of both metals and ceramics can be envisaged.

Acknowledgements

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

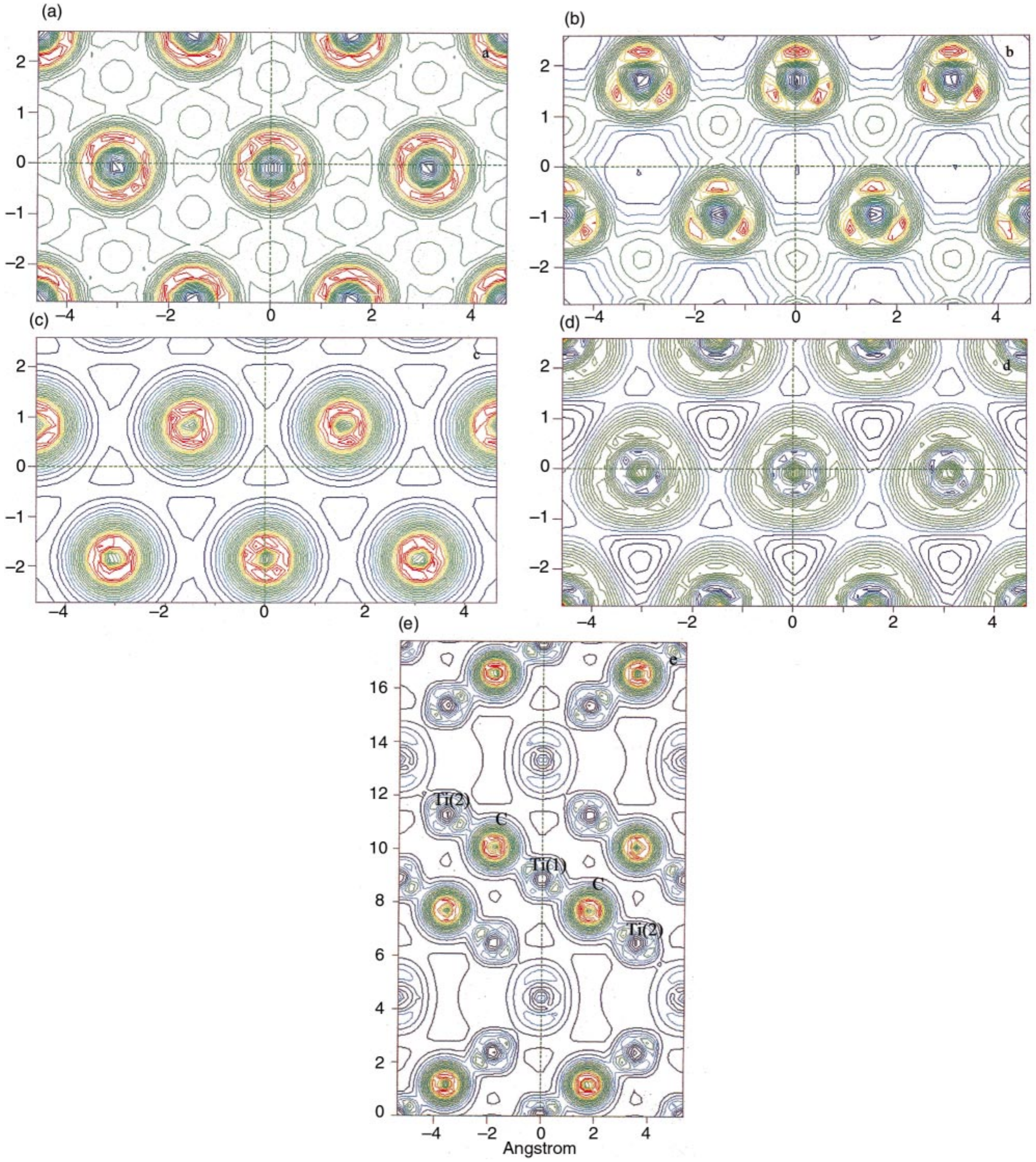

Fig. 3 Distribution of charge density on the Ti(1) (a), Ti(2) (b), Ge (c) and C (d) atomic layers that are parallel to the basal plane, and on the (110) plane (e).

a National Young Scientist Award, and by the Chinese Academy of Sciences.

References

1 M. W. Barsoum, D. Brodkin and T. El-Raghy, *Scr. Mater.*, 1997, **36**, 535.
2 M. W. Barsoum and T. El-Raghy, *J. Am. Ceram. Soc.*, 1996, **79**, 1953.
3 Y. C. Zhou, Z. M. Sun, S. Q. Chen and Y. Zhang, *Mater. Res. Innovat.*, 1998, **2**, 142.
4 W. Jeitschko, H. Nowotny and F. Benesovsky, *Monatsh. Chem.*, 1967, **98**, 2403.
5 T. Goto and T. Hirai, *Mater. Res. Bull.*, 1987, **22**, 1195.
6 J. Lis, Y. Miyamoto, R. Pampuch and K. Tanihata, *Mater. Lett.*, 1995, **22**, 163.
7 S. Arunajatesan and A. H. Carim, *Mater. Lett.*, 1994, **20**, 319.
8 M. W. Barsoum and T. El-Raghy, *Metall. Mater. Trans. A*, 1999, **30**, 363.
9 Z. M. Sun and Y. C. Zhou, *Phys. Rev. B*, 1999, **60**, 1441.
10 N. I. Medvedeva, D. L. Novikov, A. L. Ivanovsky, M. V. Kuznetsov and A. J. Freeman, *Phys. Rev. B*, 1998, **58**, 16042.
11 Y. C. Zhou and Z. M. Sun, *J. Appl. Phys.*, 1999, **86**, 1430.
12 P. Car and M. Parrinello, *Phys. Rev. Lett.*, 1985, **55**, 2471.
13 P. Hohenbery and W. Kohn, *Phys. Rev. B*, 1964, **136**, 864.
14 W. Kohn and L. J. Sham, *Phys. Rev. A*, 1965, **140**, 1133.
15 J. P. Perdew and A. Zunger, *Phys. Rev. B*, 1981, **23**, 5048.
16 G. P. Kerker, *J. Phys. C*, 1980, **13**, L189.
17 L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.*, 1982, **48**, 1425.
18 P. D. King-Smith, M. C. Payne and J-S. Lin, *Phys. Rev. B*, 1991, **44**, 13063.

Paper a906865a