Processing and Application of Ceramics 11 [2] (2017) 82–86
https://doi.org/10.2298/PAC1702082Y

An ab initio prediction study of the electronic structure and elastic properties of V_3GeC_2

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Received 9 September 2016; Received in revised form 13 March 2017; Accepted 24 March 2017

Abstract

The electronic structure and elastic properties of the ternary layered carbide V_3GeC_2 were investigated by the first-principle plane-wave pseudopotential total energy calculation method based on density functional theory. It is found that the computed P6$_3$/mmc lattice constants and internal coordinates are a = 2.9636 Å, c = 17.2256 Å and z_{V_2} = 0.1325, z_C = 0.5712, respectively. The predictable cohesive energy of V_3GeC_2 reflects that it could be a stable $M_{n+1}AX_n$ phase like Ti_3GeC_2 and V_2GeC, while the band structure shows that the V_3GeC_2 has anisotropic electrical conductivity, with a high density of states at the Fermi energy. The V_3GeC_2 exhibits potential anisotropic elastic properties, as well as self-lubricating and ductile behaviour, related to the V–Ge bonds being relatively weaker than the V–C bonds.

Keywords: *V_3GeC_2, first-principle calculation, electronic structure, elastic properties*

I. Introduction

Recently, much attention has been devoted to the $M_{n+1}AX_n$ phases (M = early transition metal, A = IIIA or IVA element, X = C and/or N) due to their promising combination of the merits of both metals and ceramics [1–7]. Experimental and theoretical studies on the synthesis and properties of $M_{n+1}AX_n$ phases, both bulk materials and films, attracted great interest [8–10]. Subsequently, many new phases have recently been experimentally and theoretically studied, e.g. Ti_3GeC_2 [10], Ti_4SiC_3 [11], Ti_4GaC_3 [12–14], V_4AlC_3 [15], Ta_2AlC [16,17], Nb_4AlC_3 [18], Ta_4AlC_3 [18,19] and so on.

To our knowledge, the $M_{n+1}AX_n$ phases containing the transition metal vanadium were confirmed experimentally or theoretically as V_2GeC [4,8,20,21], V_2AlC [16,22–24] and V_4AlC_3 [15,24]. Kerdsongpanya *et al.* [25] proved the existence of $(Ti,V)_3GeC_2$ and $(Ti,V)_4GeC_3$ phases using experimental results on the nucleation and growth of $(Ti,V)_{n+1}GeC_n$ thin films. It was also reported that previously unknown V_3GeC_2 phase can be partially stabilized through alloying with Ti. However, experimental report and more detailed theoretical studies on V_3GeC_2 are lacking. Thus, in this work we present a prediction study on the crystal structure, electronic and elastic properties of V_3GeC_2 by using the first-principle calculations, as well as the V_2GeC phase for comparison. The obtained optimized lattice constants and internal coordinate are in good agreement with the trend of experimental and calculated values of related $M_{n+1}AX_n$ phases. It is also predicted that V_3GeC_2 could be a stable $M_{n+1}AX_n$ phase under a certain condition and exhibits a potential self-lubricating and ductile properties and anisotropic conductivity.

II. Computational details

The lattice parameters optimization and ground states electronic structure of V_3GeC_2 were calculated by using the standard CASTEP code [26], which is a plane-wave pseudopotential total energy calculation method based on density functional theory (DFT) [27]. The plane wave energy cut off and the Brillouin zone sampling were fixed at 450 eV and 10×10×2 special k-point meshes, respectively. Interactions of electrons

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with ion cores were presented by the Vanderbilit-type ultrasoft pseudopotential [28]. The electronic exchange-correlation energy was performed according to Perdew-Wang generalized-gradient approximation (GGA-PW91) [29]. Broyden-Fletcher-Goldfarb-Shanno (BFGS) [30] minimization scheme was used to minimize the total energy and internal forces. For the geometry optimization, the tolerances of the difference in total energy, the maximum ionic Hellmann-Feynman force, the maximum ionic displacement and the maximum stress were set to within 5×10^{-6} eV/atom, 0.01 eV/Å, 5×10^{-4} Å and 0.02 GPa, respectively. The elastic coefficients, as reported by Milamn *et al.* [31], were determined by applying a set of given homogeneous deformations with a finite value and calculating the resulting stress with respect to optimizing the internal atomic freedom, with a maximum strain value of 0.3%. Then the elastic stiffness was determined by a linear fit of the calculated stress as a function of strain. The criteria for convergences of optimization on atomic freedom was set as the difference in total energy, the maximum ionic Hellmann-Feynman force, and the maximum ionic displacement being within 1×10^{-6} eV/atom, 0.002 eV/Å, and 1×10^{-4} Å.

III. Results

3.1. Crystal structure

Crystal structures of V_3GeC_2 and V_2GeC with hexagonal *P6₃/mmc* space group are shown in Fig. 1. The calculated lattice constants, internal coordinates, density of states (DOS) at the Fermi energy, cohesive energy and density of states for V_3GeC_2 and V_2GeC are listed in Table 1. The values for the lattice constants and internal coordinates for V_3GeC_2 are a = 2.9636 Å, c = 17.2256 Å and z_{V_2} = 0.1325, z_C = 0.5712, respectively, which is only slightly smaller than the values for Ti_3GeC_2 [10]. In addition, it is consistent with the trend observed for $(TiV)_3GeC_2$ (experimental data) [25], Ti_3GeC_2 (calculated values) [10] and V_2GeC [20]. The lattice constants of the related comparable V_2GeC phase are a = 2.9939 Å, c = 12.2415 Å, where c/a value (4.0888, 4.1070 or 4.0465 [20]) is lower than that 5.8124 for V_3GeC_2 (Table 1). The total DOS (TDOS) at the Fermi level (E_f) for V_3GeC_2 is 9.094 states/eV/unit cell and for V_2GeC is 5.140 states/eV/unit cell, which suggests that V_3GeC_2 and V_2GeC would be conductive.

The cohesive energy was a measure of the strength of the forces that bind atoms together in the solid state, and was very descriptive in studying the phase equilibrium. Here, the cohesive energies $E_{coh}^{V_3GeC_2}$ and $E_{coh}^{V_2GeC}$ are defined as the total energy of the constituent atoms at infinite separation minus the total energies of the compounds V_3GeC_2 and V_2GeC respectively:

$$E_{coh}^{V_3GeC_2} = \frac{6E_{atom}^{V} + 2E_{atom}^{Ge} + 4E_{atom}^{C} - E_{total}^{V_3GeC_2}}{12} \tag{1}$$

$$E_{coh}^{V_2GeC} = \frac{4E_{atom}^{V} + 2E_{atom}^{Ge} + 2E_{atom}^{C} - E_{total}^{V_2GeC}}{8} \tag{2}$$

where $E_{total}^{V_3GeC_2}$ is the total energy of a V_3GeC_2 cell at equilibrium configuration, $E_{total}^{V_2GeC}$ is the total energy of a V_2GeC cell at equilibrium configuration and E_{atom}^{V}, E_{atom}^{Ge} and E_{atom}^{C} are the pseudo-atomic energies of the pure constituents, which are calculated in the same CASTEP code by using the plane-wave basis. Considering that the cell contains two formulae, six V, two

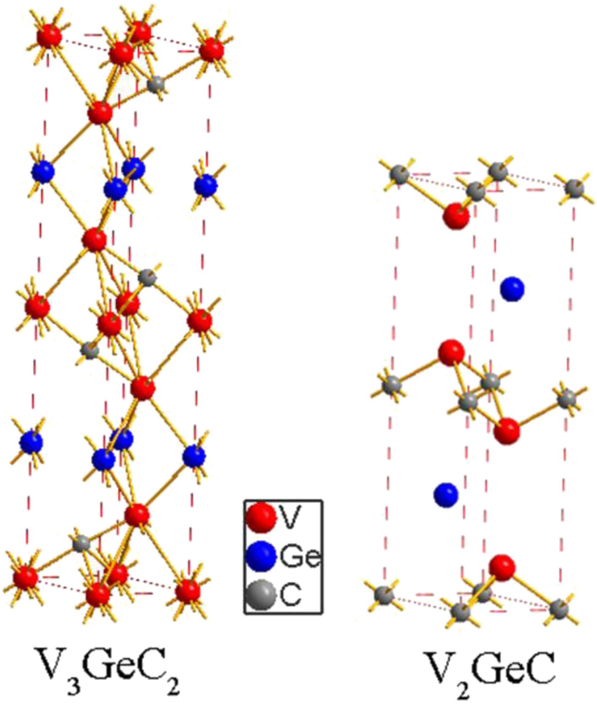

Figure 1. Crystal structures of V_3GeC_2 and V_2GeC

Table 1. The calculated lattice parameters a (Å), c (Å), internal coordinates z_M, z_{M_2} and z_c, density of states at the Fermi energy N_{E_f} (states/eV/unit cell), cohesive energy E_{coh} (eV/atm) and density ρ (g/cm³) of V_3GeC_2, V_2GeC [20] and Ti_3GeC_2 [10], including the experimental data of $(TiV)_3GeC_2$ [25] for comparison

	a	c	c/a	z_M	z_{M_2}	z_c	ρ	N_{E_f}	E_{coh}
V_3GeC_2	2.9636	17.2256	5.8124	-	0.1325	0.5712	6.324	9.094	9.24
$(TiV)_3GeC_2$, exp. [25]	-	17.4	-	-	-	-	-	-	-
Ti_3GeC_2, cal. [10]	3.0741	17.697	5.7568	-	0.1338	0.5723	-	4.323	8.778
V_2GeC	2.9939	12.2415	4.0888	0.0877	-	-	6.519	5.140	8.31
V_2GeC, exp. [20]	2.99	12.28	4.1070	-	-	-	-	-	-
V_2GeC, cal.	3.01	12.18	4.0465						

Ge and four C atoms were used in the V_3GeC_2 calculation and four V, two Ge and two C atoms were used in the V_2GeC calculation. The calculated cohesive energies of V_3GeC_2 and V_2GeC are 9.24 eV/atom and 8.31 eV/atom, respectively. In order to explore the stability of the V_3GeC_2 phase, stability calculations vs. relevant competing phases for the MAX phases are sometimes required, which was reported by Dahlqvist *et al.* [32,33]. Herein, compared with the E_{coh} of Ti_3GeC_2 [10] and V_2GeC, it is reflected that V_3GeC_2 could be a stable $M_{n+1}AX_n$ phase under a certain condition as shown by the cohesive energy results. This is also in agreement with the reported experimental data showing that V_3GeC_2 can be partially stabilized through alloying with Ti [25].

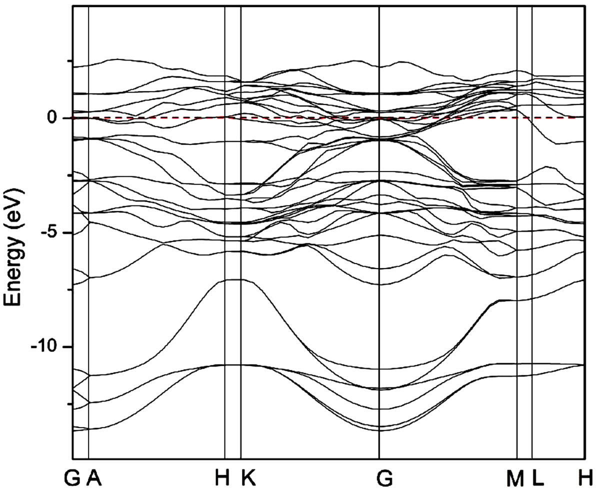

Figure 2. Band structure along the principal high-symmetry directions in the Brillouin zone of V_3GeC_2 (the Fermi energy E_f is set to be 0 eV, and is marked by a horizontal dashed line)

3.2. Electronic properties

The band structure of the V_3GeC_2 within the first Brillouin zone of the hexagonal lattice is shown in Fig. 2. The valence and conduction bands overlap considerably and there is no band gap at the Fermi level E_f, indicating that V_3GeC_2 exhibit metallic properties. There is strongly anisotropic character with lower *c*-axis energy dispersion, which can be seen from the reduced dispersion along the H-K and M-L directions, suggesting it to be an anisotropic conductivity. The total density of states (TDOS) and partial density of states (PDOS) of V_3GeC_2 are shown in Fig. 3a. It is observed that carbon does not contribute to the DOS at the Fermi level and therefore is not involved in the conduction properties. The states near and above Fermi energy are mainly attributed to V-d to V-d interactions and antibonding states. It can be observed that the lowest valence bands from -12.5 to -10.1 eV of the TDOS are formed by the C-s states with a small mixture of V-p,d hybridized

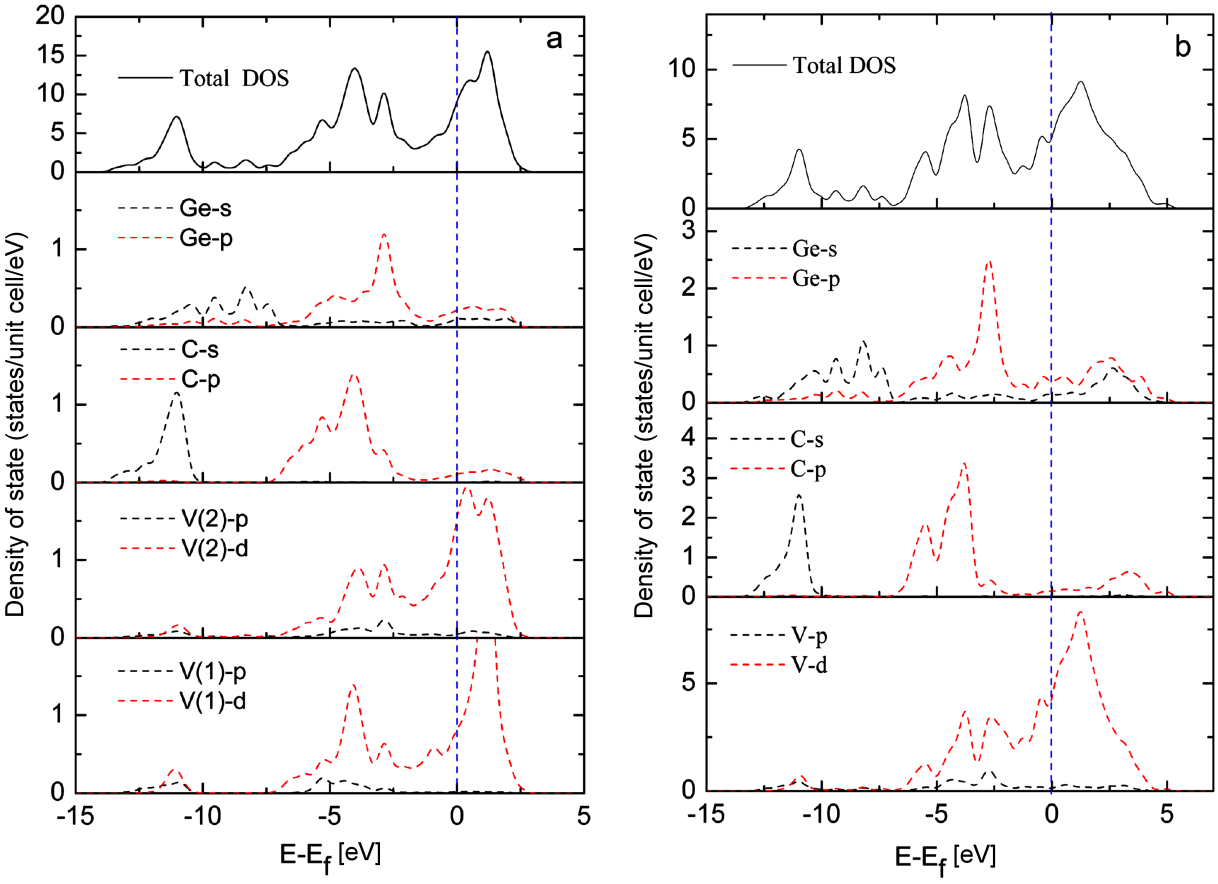

Figure 3. The total density of states (TDOS) and partial density of states (PDOS) for: a) V_3GeC_2 and b) V_2GeC

Table 2. The calculated second-order elastic constants c_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν and shear-modulus-to bulk-modulus ratios G/B

	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	c_{66}	B	G	E	ν	G/B
V_3GeC_2	344	140	137	345	130	103	207	113	266	0.28	0.55
V_2GeC	314	108	137	312	147	103	189	114	244	0.36	0.60
Ti_3GeC_2, cal. [10]	357	94	97	333	143	132	180	134	322	0.20	0.74
(TiV)-Ge-C film, exp. [25]	-	-	-	-	-	-	-	-	241±15	-	-
V_2GeC film, exp. [21]	-	-	-	-	-	-	-	-	189±13	-	-

states. The higher valence bands in the range from -9.9 to -7.0 eV are almost entirely formed from Ge-s,p states. The energy states from -7.0 to -3.2 eV are dominated by the strong covalent bonding of V-d and C-p states. There is the band related to weak hybridized V-d and Ge-p states at the top valence bands, which indicates the covalent interaction between V-d and Ge-p states. The total density of states (TDOS) and partial density of states (PDOS) of V_2GeC exhibit the same trend of electric behaviour and details could be found elsewhere. The carbon is also not involved in the conduction properties of V_2GeC. V-d to V-d interactions and antibonding states contribute to the states near and above Fermi energy. The C-s states with a small mixture of V-p,d hybridized states and weak hybridized V-d and Ge-p states could be found in the V_2GeC.

3.3. Elastic properties

The elastic properties of V_3GeC_2 as well as V_2GeC [21], Ti_3GeC_2 [10] and (TiV)-Ge-C [25] were predicted for comparison from the calculated second-order elastic constants c_{ij}, as listed in Table 2. The bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio ν and shear-modulus-to-bulk-modulus ratio G/B for V_3GeC_2 are calculated to be 207 GPa, 113 GPa, 266 GPa, 0.28 and 0.55, respectively. It is found that Ti_3GeC_2 has higher elastic moduli than V_3GeC_2, which indicates that the elastic moduli increase with the Ti–C slabs. The elastic modulus E of V_3GeC_2 is related with that experimental result of (TiV)-Ge-C film [25] while the small difference may be due to the elastic recovery of the smaller film indent after indentation. Anisotropy factor $A = c_{33}/c_{11}$ suggests that the V_3GeC_2 is an anisotropic material, related to the V–Ge bonds being relatively weaker than the V–C bonds. Typical Poisson's ratio ν is used to be 0.1 for covalent materials, 0.25 for ionic materials and 0.33 for metallic materials [34]. The calculated value of ν for V_3GeC_2 is 0.28 at 0 GPa, which indicates a higher metallic and ionic (or weaker covalent) character, whereas the calculated Poisson's ratio ν for V_2GeC is 0.36, which exhibits a higher metallic (or weaker ionic and covalent) character. Compared with the typical relations between bulk and shear moduli $G \approx 1.1B$ for covalent material and $G \approx 0.6B$ for ionic material [35], it is indicated that the ionic bonding is more suitable for V_3GeC_2 ($G = 0.55B$) at ambient conditions. According to the G/B ratio introduced by Pugh [36], the material is brittle if the ratio is less than the critical value (1.75) or ductile if the ratio G/B is below 0.57. It is found that our calculated V_3GeC_2 is ductile ($G/B = 0.55$) at zero pressure, which indicates that the M-site metal affects the ductility of $M_{n+1}AX_n$ phases (Ti_3GeC_2, $G/B = 0.74$).

IV. Conclusions

In this paper, we have studied the crystal structure, electronic properties and elastic properties of V_3GeC_2 using a plane-wave pseudopotential total energy calculation method. The calculated predicted results for the lattice constants are in good agreement with the trend of the experimental and calculated results. The bulk modulus, shear modulus, Young's modulus, Poisson's ratio and shear-modulus-to-bulk-modulus ratio are predicted to be 207 GPa, 113 GPa, 266 GPa, 0.28 and 0.55, respectively. The band structure shows that the V_3GeC_2 has anisotropic electrical conductivity with a high density of states at the Fermi energy. The weaker V–Ge bond in V_3GeC_2 results in the lower shear-modulus-to-bulk-modulus ratio, which indicates the self-lubricating, ductile and anisotropic elastic properties.

Acknowledgements: This work is supported by National Natural Science Foundation of China (Grant No. 11302068), China Postdoctoral Science Foundation (Grants Nos. 2014T70465 and 2013M531261) and the Fundamental Research Funds for the Central Universities (Grants Nos. 2013B04914 and 2015B21814).

References

1. M.W. Barsoum, "The $M_{N+1}AX_N$ phases: A new class of solid", *Prog. Solid State Chem.*, **28** [1-4] (2000) 201–281.
2. H.I. Yoo, M.W. Barsoum, T. El-Raghy, "Ti_3SiC_2 has negligible thermopower", *Nature*, **407** [6804] (2000) 581–582.
3. M.W. Barsoum, L. Farber, "Room-temperature deintercalation and self-extrusion of Ga from Cr_2GaN", *Science*, **284** [5416] (1999) 937–939.
4. P. Eklund, M. Beckers, U. Jansson, H. Hogberg, L. Hultman, "The $M_{n+1}AX_n$ phases: Materials science and thin-film processing", *Thin Solid Films*, **518** [8] (2010) 1851–1878.
5. G.B. Ying, X.D. He, M.W. Li, S.Y. Du, W.B. Han, F. He, "Effect of Cr_7C_3, on the mechanical, thermal, and electrical properties of Cr_2AlC", *J. Alloys Compds.*, **509** [31] (2011) 8022–8027.
6. G.B. Ying, X.D. He, M.W. Li, Y.B. Li, S.Y. Du, "Synthesis and mechanical properties of nano-layered composite", *J. Alloys Compds.*, **506** [2] (2010) 734–738.
7. G.B. Ying, X.D. He, M.W. Li, W.B. Han, F. He, S.Y. Du, "Synthesis and mechanical properties of high-purity

Cr_2AlC ceramic", *Mater. Sci. Eng: A*, **528** [6] (2010) 2635–2640.

8. A. Bouhemadou, "Calculated structural and elastic properties of M_2InC (M = Sc, Ti, V, Zr, Nb, Hf, Ta)", *Appl. Phys. A*, **96** [4] (2009) 959–967.
9. H.I. Faraoun, F.Z. Abderrahim, C. Esling, "First principle calculations of MAX ceramics Cr_2GeC, V_2GeC and their substitutional solid solutions", *Comput. Mater. Sci.*, **74** (2013) 40–49.
10. Y.L. Bai, X.D. He, Y. Sun, C.C. Zhu, M.W. Li, L.P. Shi, "Chemical bonding and elastic properties of Ti_3AC_2, phases (A = Si, Ge, and Sn): A first-principle study", *Solid State Sci.*, **12** [7] (2010) 1220–1225.
11. T.H. Scabarozi, J.D. Hettinger, S.E. Lofland, J. Lu, L. Hultman, J. Jensen, P. Eklund, "Epitaxial growth and electrical-transport properties of $Ti_7Si_2C_5$, thin films synthesized by reactive sputter-deposition", *Scripta Mater.*, **65** [9] (2011) 811–814.
12. Y.L. Bai, X.D. He, Y.B. Li, C.C. Zhu, M.W. Li, "An ab initio study of the electronic structure and elastic properties of the newly discovered ternary carbide Ti_4GaC_3", *Solid State Commun.*, **149** [47-48] (2009) 2156–2159.
13. J. Etzkorn, M. Ade, D. Kotzott, M. Kleczek, H. Hillebrecht, "Ti_2GaC, Ti_4GaC_3, and Cr_2GaC - Synthesis, crystal growth and structure analysis of Ga-containing MAX-phases $M_{n+1}GaC_n$, with M = Ti, Cr and n = 1, 3", *J. Solid State Chem.*, **182** [5] (2009) 995–1002.
14. X.D. He, Y.L. Bai, C.C. Zhu, M.W. Barsoum, "Polymorphism of newly discovered Ti_4GaC_3: A first-principles study", *Acta Mater.*, **59** [14] (2011) 5523–5533.
15. C.F. Hu, J. Zhang, J.M. Wang, F.Z. Li, J.Y. Wang, Y.C. Zhou, "Crystal structure of V_4AlC_3: A new layered ternary carbide", *J. Am. Ceram. Soc.*, **91** [2] (2008) 636–639.
16. Z.M. Sun, S. Li, R. Ahuja, J.M. Schneider, "Calculated elastic properties of M_2AlC (M = Ti, V, Cr, Nb and Ta)", *Solid State Commun.*, **129** [9] (2004) 589–592.
17. C.F. Hu, L.F. He, J. Zhang, Y.W. Bao, J.Y. Wang, M.S. Li, Y.C. Zhou, "Microstructure and properties of bulk TaAlC ceramic synthesized by an in situ reaction/hot pressing method", *J. Eur. Ceram. Soc.*, **28** [8] (2008) 1679–1685.
18. Y.L. Du, Z.M. Sun, H. Hashimoto, W.B. Tian, "Bonding properties and bulk modulus of M_4AlC_3 (M = V, Nb, and Ta) studied by first principles calculations", *Phys. Status Solidi B*, **246** [5] (2009) 1039–1043.
19. Y.L. Du, Z.M. Sun, H. Hashimoto, W.B. Tian, "First-principles study of polymorphism in Ta_4AlC_3", *Solid State Commun.*, **145** [9] (2008) 461–464.
20. M. Magnuson, O. Wilhelmsson, M. Mattesini, S. Li, R. Ahuja, O. Eriksson, U. Janson, "Anisotropy in the electronic structure of V_2GeC investigated by soft X-ray emission spectroscopy and first-principles theory", *Phys. Rev. B*, **78** [3] (2008) 035117.
21. O. Wilhelmsson, P. Eklund, H. Högberg, L. Hultman, U. Jansson, "Structural, electrical and mechanical characterization of magnetron-sputtered V-Ge-C thin films", *Acta Mater.*, **56** [11] (2008) 2563–2569.
22. C. Zhang, Z. Zhang, P. Wang, Y. Wang, J. Dong, N. Xing, "First-principles study of electronic structure of V_2AlC and V_2AlN", *Solid State Commun.*, **144** [7-8] (2007) 347–351.
23. J.M. Schneider, R. Mertens, D. Music, "Structure of V_2AlC studied by theory and experiment", *J. Appl. Phys.*, **99** [1] (2006) 092102.
24. J. Etzkorn, M. Ade, H. Hillebrecht, "V_2AlC, V_4AlC_{3-x} (x ≈ 0.31), and $V_{12}Al_3C_8$: Synthesis, crystal growth, structure, and superstructure", *Inorg. Chem.*, **46** [18] (2007) 7646–7653.
25. S. Kerdsongpanya, K. Buchholt, O. Tengstrand, J. Lu, J. Jensen, L. Hultman, P. Eklund, "Phase-stabilization and substrate effects on nucleation and growth of $(Ti,V)_{n+1}GeC_n$ thin films", *J. Appl. Phys.*, **110** [5] (2011) 053516.
26. M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, J.D. Joannopolous, "Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients", *Rev. Mod. Phys.*, **64** (1992) 1045–1097.
27. P. Hohenberg, W. Kohn, "Inhomogeneous electron gas", *Phys. Rev. B*, **136** (1964) 864–871.
28. D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism", *Phys. Rev. B*, **41** [11] (1990) 7892–7895.
29. J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation", *Phys. Rev. B*, **46** [11] (1992) 6671–6687.
30. B.G. Pfrommer, M. Côté, S.G. Louie, M.L. Cohen, "Relaxation of crystals with the Quasi-Newton method", *J. Comput. Phys.*, **131** [1] (1997) 233–240.
31. V. Milman, M.C. Warren, "Elasticity of hexagonal BeO", *J. Phys.: Condensed Matter*, **12** [2] (2001) 241–251.
32. M. Dahlqvist, B. Alling, J. Rosén, "Stability trends of MAX phases from first principles", *Phys. Rev. B*, **81** [22] (2010) 220102.
33. P. Eklund, M. Dahlqvist, O. Tengstrand, L. Hultman, J. Lu, N. Nedfors, J. Rosén, "Discovery of the ternary nanolaminated compound Nb_2GeC by a systematic theoretical-experimental approach", *Phys. Rev. Lett.*, **109** [3] (2012) 035502.
34. J. Haines, J.M. Leger, G. Bocquillon, "Synthesis and design of superhard materials", *Ann. Rev. Mater. Res.*, **31** [1] (2001) 1–23.
35. Z.J. Yang, J. Li, R.F. Linghu, X.S. Song, X.L. Cheng, Z.H. Zhu, X.D. Yang, "Equation of state and electronic properties of Cr_2GeC via first-principles", *Eur. Phys. J. B*, **86** [5] (2013) 1–7.
36. S.F. Pugh, "XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals", *Philo. Mag.*, **45** [367] (1954) 823–843.