First-principles calculation of the lattice compressibility, elastic anisotropy and thermodynamic stability of V_2GeC*

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We investigate the elastic and the thermodynamic properties of nanolaminate V_2GeC by using the *ab initio* pseudopotential total energy method. The axial compressibility shows that the *c* axis is always stiffer than the *a* axis. The elastic constant calculations demonstrate that the structural stability is within 0–800 GPa. The calculations of Young's and shear moduli reveal the softening behaviour at about 300 GPa. The Possion ratio makes a higher ionic or a weaker covalent contribution to intra-atomic bonding and the degree of ionicity increases with pressure. The relationship between brittleness and ductility shows that V_2GeC is brittle in ambient conditions and the brittleness decreases and ductility increases with pressure. Moveover, we find that V_2GeC is largely isotropic in compression and in shear, and the degree of isotropy decreases with pressure. The Grüneisen parameter, the Debye temperature and the thermal expansion coefficient are also successfully obtained for the first time.

Keywords: V_2GeC, first principles, elasticity, thermodynamic properties

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1. Introduction

The $M_{n+1}AX_n$ phases, where M is an early transition metal, A is an A-group element (mostly IIIA or IVA elements), X is either C or N, and n varies from 1 to 3, have attracted more and more attention in recent years due to the fundamental properties usually associated with metals and ceramics.[1] Generally, the $M_{n+1}AX_n$ phases are machinable, exhibiting good damage tolerance, have excellent thermal shock resistance and good corrosion resistance. In addition, they are usually good thermal and electrical conductors. Their excellent electronic properties are comparable or even superior to those of the constituent transition metals. The unique combination of metallic and ceramic properties, including high strength and stiffness at high temperatures, resistance to oxidation and thermal shock, as well as high Young's modulus, low hardness and ultra-low solid friction coefficient, is promising for high-temperature and high-pressure applications.[1]

Under pressure, elements become denser as the atoms and molecules get closer together and the occupied volume decreases: non-metals turn into metals and even superconductors.[2] Under high pressure, the light alkali elements Li[3] and Na[4] experience unusual metal-to-semiconductor transition. Moreover, the transparent dense sodium[4] is particularly striking as it challenges traditional theory. As is well known, the structural parameter of a M atom ($M_{n+1}AX_n$) shifts with pressure and thus presents a different variation mechanism from that of the other hexagonal lattice with a similar structure. The shift of the M atom along the *c* axis might also contribute to the stiffness of the *c* axis.

Despite the numerous theoretical and experimen-

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tal studies devoted to M_2AX phases,[5] only a few have been fully studied. It is worthwhile to know the effects of high temperature and high pressure on physical properties. Experimentally, Manoun *et al.*[6] recently measured the compression behaviour of V_2GeC under 50 GPa. Theoretically, there were only two studies devoted to the electronic and the elastic properties of V_2GeC using *ab initio*.[7,8] In order to fully take advantage of the properties of V_2GeC for technological applications, a more detailed theoretical investigation of the structural, electronic and elastic properties under high temperature and high pressure is necessary. First-principles calculations offer one of the most powerful tools for carrying out theoretical studies of these properties.[3,9−18] Therefore, we here give a more detailed elastic and thermodynamic prediction under high temperature and high pressure for the first time.

2. Computational method

In the electronic structure calculations, we use the Vanderbilt-type[19] ultrasoft pseudopotential density functional theory with a generalized gradient approximation (GGA)[20,21] for the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functionals. Considering the computational cost, a plane-wave basis set with an energy cut-off of 310.0 eV is adopted, and the 10×10×2 Monkhorst–Pack mesh is used for the Brillouin-zone k-point sampling.[22] Pseudo atomic calculations are performed for V $3s^2$ $3p^6$ $3d^3$ $4s^2$, Ge $4s^2$ $4p^2$ and C $2s^2$ $2p^2$, where the self-consistent convergence of the total energy is set to be 5.0×10^{-7} eV per atom. All the electronic calculations are performed using the Cambridge Serial Total Energy Package (CASTEP).[23,24]

3. Results and discussion

3.1. Lattice parameter

V_2GeC crystallizes into the $P6_3/mmc$ (194) space group and there are 8 atoms in one unit cell, the V atoms are located at (1/3, 2/3, z), the Ge atoms (1/3, 2/3, 3/4) and the C atoms (0, 0, 0). Thus, the stable geometry can be uniquely determined by the lattice constants a ($b = a$) and c, as well as the structural parameter z. The optimized stable geometry has lattice parameters $a = b = 2.9985$ Å and $c = 12.2582$ Å, which are consistent with the experimental data and theoretical values. The optimized structural parameter z of V atom is also in agreement with the experimental data and theoretical results, as shown in Table 1. The excellent agreement further validate the selected theoretical methods, thereby ensuring the correctness of the present first-principles computations.

Table 1. The values of lattice parameter, elastic properties C_{ij}, bulk modulus B, shear modulus G, Young's modulus E, Possion's ratio σ and density ρ.

	Present	Exp.	Ref. [25]	Ref. [8]	Ref. [7]
a/Å	2.9985	3.038±0.005[6] 3.0[1,26] 3.001[27]	2.999	3.0028	2.9834
c/Å	12.2582	12.112±0.009[6] 12.25[1,26] 12.2601[27]	12.255	12.2252	12.0169
z	0.0876	0.0899[27]		0.0889	0.0899
B_0/GPa	183(163)	165±2[6] 201.9[27] 202.2[27]			185
B'	4.37(4.12)	4[6] 4.02[27] 4[27]			4.59
C_{11}/GPa	302			279.8	282
C_{33}/GPa	308			258.4	259
C_{44}/GPa	145			162.5	160
C_{12}/GPa	99			120.3	121
C_{13}/GPa	132			140.2	144
B/GPa	181			179.8	182.3
G/GPa	112			100.5	99.5
E/GPa	278			254.1	252.6
σ	0.244			0.265	0.269
ρ/g·cm^{-3}	6.49	6.88[1,26]			6.67

Note: the values of bulk modulus B_0 and its first-order derivative B' are fitted to the third-order Birch–Murnaghan equation of state[28] in the pressure ranges of 0–60 GPa (183, 4.37) and 0–1000 GPa (163, 4.12), respectively.

By fitting the pressure (P)–volume (V) data to the third-order Birch–Murnaghan equation of state,[28] we obtain the bulk modulus and its pressure derivative at 0 K (see Table 1). Note that the fitted results depend on the selected pressure–volume range, for example, our fitted bulk modulus and its first-order deviate are 183 and 4.37 within 0–60 GPa, whereas the values change to 163 and 4.12 within 0–1000 GPa with all correlation coefficients being larger than 0.999. The fitted results together with the structural parameter variations with pressure are plotted in Fig. 1. From Fig. 1, we see that our calculated volume compressibility agrees with the experimental data.[6] For better understanding the volume variations with pressure, we extend the compression range to 1000 GPa and obtain the least square fit as follows:

$$\begin{aligned} V/V_0 &= 0.99842 - 0.00496P + 4.45974 \times 10^{-5}P^2 \\ &\quad - 2.94568 \times 10^{-7}P^3 + 1.22427 \times 10^{-9}P^4, \\ R^2 &= 0.99996, \\ z &= 0.08766 + 1.70272 \times 10^{-4}P \\ &\quad - 1.90923 \times 10^{-6}P^2 + 1.36149 \times 10^{-8}P^3 \\ &\quad - 5.82638 \times 10^{-11}P^4, \\ R^2 &= 0.9996, \end{aligned}$$

where V_0 is the lattice volume at zero temperature and pressure, and R is the correlation coefficient.

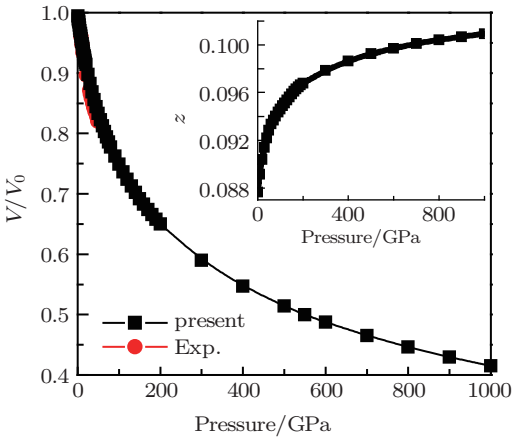


Fig. 1. (colour online) Equation of state of V_2GeC and the variation of structural parameter z of the V atom (the insert small figure) with pressure, with the experimental data cited from Ref. [6].

Over the last few years, much effort has been made to try to understand the axial compressibility to reveal the interatomic bonding along the a and c axes. For the most part, the relative shrinkage along the c-direction with pressure is greater than that along the a-direction. Our detailed calculations over a wide pressure range show that c axis is always stiffer than a axis, which is shown in Fig. 2. For a better understanding of the axial variations with pressure we extend the compression range to 1000 GPa and obtain the least square fit as follows:

$$\begin{aligned} a/a_0 &= 0.99947 - 0.00177P + 1.27385 \times 10^{-5}P^2 \\ &\quad - 8.20008 \times 10^{-8}P^3 + 3.45505 \times 10^{-10}P^4, \\ R^2 &= 0.9996, \\ c/c_0 &= 0.99951 - 0.00141P + 1.29785 \times 10^{-5}P^2 \\ &\quad - 7.04042 \times 10^{-8}P^3 + 2.169221 \times 10^{-10}P^4, \\ R^2 &= 0.9996, \end{aligned}$$

where a_0 and c_0 are the lattice parameters at zero temperature and pressure.

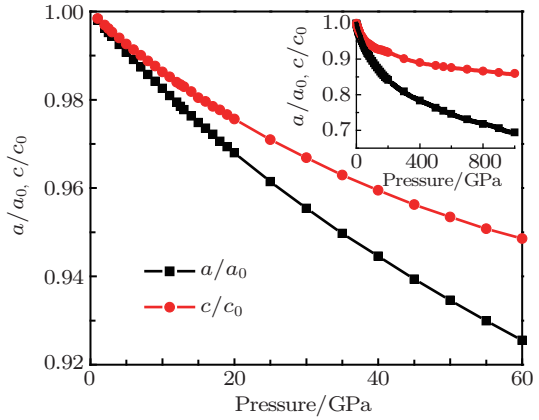


Fig. 2. (colour online) Axial compressibilities of V_2GeC varying with pressure. Insert shows the axial compresibilities of V_2GeC in the pressure range of 1000 GPa.

3.2. Elastic properties

For deep understanding of the stiffness of the c axis we need to study its elastic properties extensively. Elastic constants determine the response of the crystal to applied forces and play an important role in describing the mechanical properties of solid material. The elastic properties of a solid are closely related to many fundamental solid-state properties, such as the equation of state, specific heat thermal expansion, Debye temperature, and the Grüneisen parameter. From the elastic constants, one can obtain important information about the binding characteristics, the anisotropic feature, and the structural stability. Our calculated elastic constants are listed in Table 1 and Fig. 3, from which we can see that the five independent elastic constants agree well with other theoretical results. To reveal the high-pressure response of the elastic constants, we investigate the elastic constants under the

pressure of 800 GPa and the relevant results are shown in Fig. 3. According to the well-known elastic stability criteria,[29] i.e.,

$$C_{12} > 0, \quad C_{33} > 0, \quad (C_{11} - C_{12})/2 > 0, \quad C_{44} > 0,$$
$$(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0, \tag{1}$$

it is found that V_2GeC is mechanically stable up to 800 GPa. From the detailed analysis we find that the stability decreases, because the value of C_{11}–C_{12} gradually approaches zero at about 550 GPa. Moreover, the five elastic constants present almost linear dependence on applied pressure. However, C_{33} varies rapidly but C_{44} changes slowly with pressure compared with C_{11}, C_{12} and C_{13}.

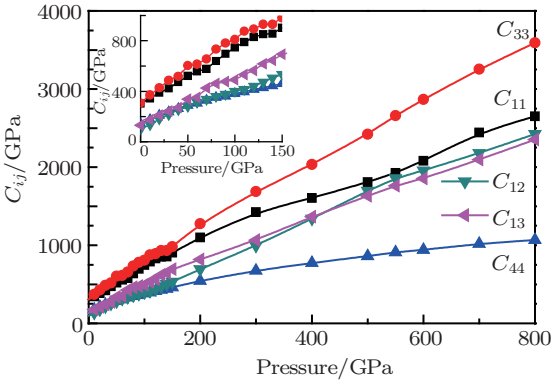


Fig. 3. (colour online) The elastic constants of V_2GeC varying with pressure. The insert shows the elastic constants of V_2GeC in the pressure range of 150 GPa.

The mechanical anisotropy of V_2GeC can be evaluated from the bulk moduli along the a and c axes (B_a and B_c), respectively[30]

$$B_a = a\frac{\mathrm{d}p}{\mathrm{d}a} = \frac{\Lambda}{2+\alpha}, \tag{2}$$

$$B_c = c\frac{\mathrm{d}p}{\mathrm{d}c} = \frac{B_a}{\alpha}, \tag{3}$$

$$\Lambda = 2(C_{11} + C_{12}) + 4C_{13}\alpha + C_{33}\alpha^2, \tag{4}$$

$$\alpha = \frac{C_{11} + C_{12} - 2C_{13}}{C_{33} - C_{13}}. \tag{5}$$

The calculated B_a and B_c values against pressure are presented in Fig. 4, which clearly show that B_c is always larger than B_a, and B_a increases linearly over a large pressure range, whereas B_c increases linearly only at low pressure and has some evident peaks at different pressures. Moreover, the discrepancy increases with pressure, the larger B_c at high pressure is consistent with the stiffness of c axis.

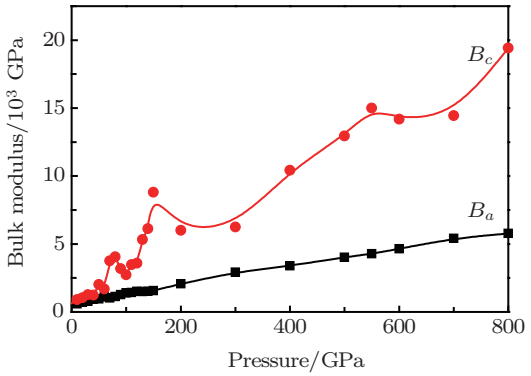


Fig. 4. (colour online) Anisotropic axial bulk moduli of V_2GeC varying with pressure.

To evaluate the elastic anisotropy of V_2GeC, we calculate its anisotropies in compression and shear,[31] respectively, as

$$A_{\mathrm{comp}} = \frac{B_{\mathrm{V}} - B_{\mathrm{R}}}{B_{\mathrm{V}} + B_{\mathrm{R}}}, \tag{6}$$

$$A_{\mathrm{shear}} = \frac{G_{\mathrm{V}} - G_{\mathrm{R}}}{G_{\mathrm{V}} + G_{\mathrm{R}}}, \tag{7}$$

where B and G are the bulk modulus and the shear modulus, respectively, and the subscripts V and R denote the Voigt approximation and the Reuss approximation respectively. The value 1 means that the crystal shows the maximal anisotropy and the value 0 represents isotropic properties. The calculated values of A_{comp} and A_{shear} for V_2GeC are 0.275% and 2.679%, respectively. Obviously, V_2GeC is greatly isotropic in compression and in shear, but the degree of isotropy decreases with pressure, particularly for the shear property, as shown in Fig. 5.

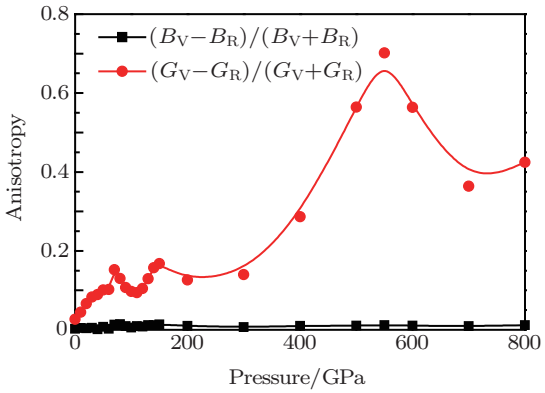


Fig. 5. (colour online) Elastic anisotropy of V_2GeC versus pressure.

According to the obtained elastic constants, we further study the Young's modulus, bulk modulus, Läme coefficient and shear modulus, and the relevant

results are shown in Fig. 6. It is found that the bulk modulus and Läme coefficient increase linearly with pressure, whereas the Young and shear moduli present the same tendency with pressure. Moreover, they display a certain softening behaviour under certain pressures, particularly at 300 GPa. Generally, these phenomena imply the possibility of the structural instability, and we attribute this softening behaviour to the elastic variation. Importantly, we find that the shear moduli obtained using different methods (Voigt, Reuss and Hill estimations) present significant differences under high pressure, differing from the case of the bulk modulus. Despite the different responses to the external pressure, they show a similar variation tendency, implying little difference in describing the stress–strain relationship.

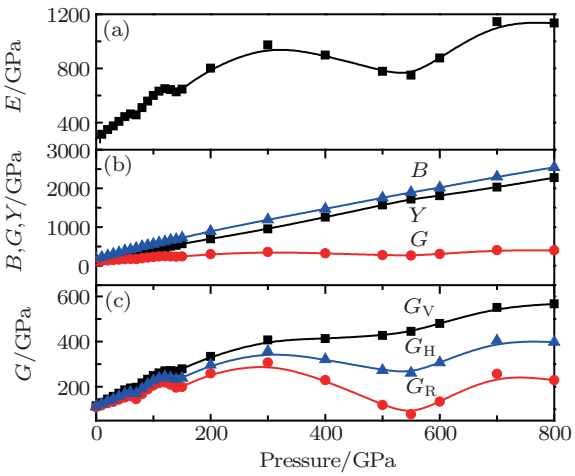


Fig. 6. (colour online) Young's moduli (a), bulk moduli, Läme coefficients (Y) (b) and shear moduli (c) varying with pressure.

For covalent and ionic materials, the typical relations between bulk modulus and shear modulus are $G \approx 1.1B$ and $G \approx 0.6B$, respectively. For our case the calculated values of G/B are in a range from 0.6165 at 0 GPa to 0.1565 at 800 GPa as shown in Fig. 7, indicating that the ionic bonding is more suitable for V_2GeC in ambient conditions and the degree of ionicity rises with pressure. To evaluate material ductility or brittleness, Pugh *et al.*[28] introduced the B/G ratio,[32] stating that the material is brittle if the ratio is less than the critical value (1.75) or the material is ductile if the ratio G/B is below 0.57. It is evident from Fig. 7 that our calculated samples are brittle ($B/G = 1.62$) at zero pressure, whereas they will turn ductile under lower pressure and the degree of ductility rises under high pressure. Moreover, the present B/C_{44} is 1.2528, within the typical members of MAX phases 1.2–1.7, and the value of B/C_{44} will be increased to 2.3817 at 800 GPa.

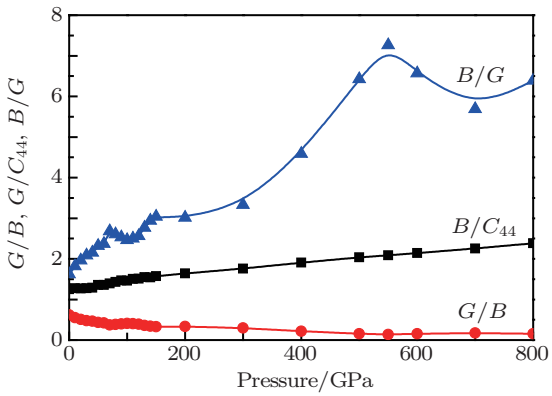


Fig. 7. (colour online) Brittleness and ductileness of V_2GeC versus pressure.

3.3. Thermodynamic properties

The thermodynamic properties of V_2GeC can be obtained by the quasi-harmonic Debye model, in which the phonon effects are considered, and the calculated details can be seen elsewhere.[33] The Debye temperature is a fundamental parameter of a material, related to many physical properties such as specific heat, elastic constants, and melting point.[34] The Debye temperatures under various temperatures and pressures are presented in Fig. 8. Our calculated Debye temperature at $T = 0$ K is 671 K, which is slightly larger than the theoretical result 565 K.[7] Considering the better agreement of the present lattice parameters with the experimental data, we thus rationally conclude that our results are more accurate. From Fig. 8, we can obtain the following results. (i) When the temperature keeps constant (0, 300, 600, 1100 K), the Debye temperature almost increases linearly with pressure. Moreover, the Debye temperature at 1100 K is slightly lower than that at 0 K, and the discrepancy seems to be ignorable. (ii) When the pressure keeps constant (0, 30, 60, 180 GPa), the Debye temperature almost decreases linearly with temperature. Moreover, the Debye temperature increases with pressure and the increment is weakened in the same pressure range. Again, it is found that the Debye temperature decreases very slowly with temperature under high pressure. The present investigations demonstrate that the Debye temperature shows a strong pressure dependence but a weak temperature dependence.

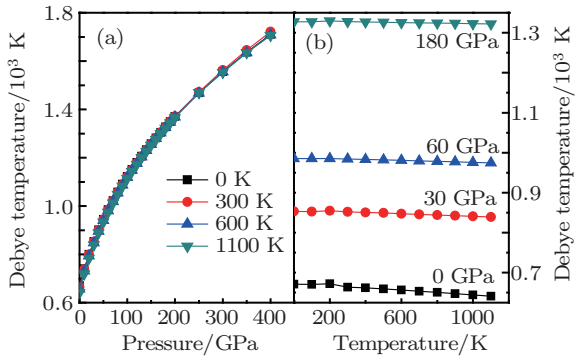


Fig. 8. (colour online) Debye temperatures of V_2GeC versus (a) pressure and (b) temperature separately.

From the analysis of the Grüneisen parameter γ shown in Fig. 9, we can obtain the following results. (i) When the temperature keeps constant, the Grüneisen parameter almost decreases linearly with pressure, and the discrepancy between different temperatures under the same pressure is very small, particularly under high pressure, which is consistent with the case of the Debye temperature. (ii) When the pressure keeps constant, the Grüneisen parameter almost increases linearly with temperature, and the Grüneisen parameter exhibits a weak temperature dependence under high pressure.

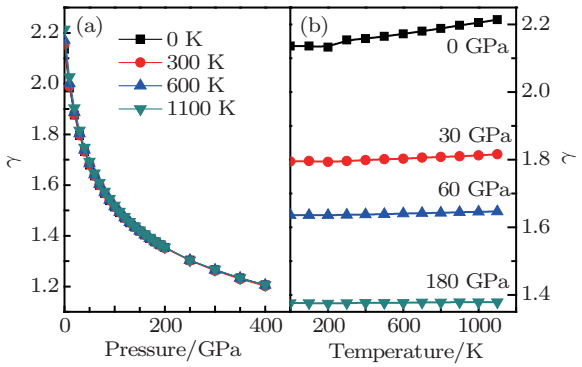


Fig. 9. (colour online) Grüneisen parameter of V_2GeC versus (a) pressure and (b) temperature separately.

From the investigations of the thermal expansion coefficient α shown in Fig. 10, we can obtain the following results. (i) When the temperature keeps constant (0, 300, 600, 1100 K), the thermal expansion coefficient decreases rapidly and the pressure dependence decreases. Moreover, the discrepancy between the results obtained at 600 K and 1100 K is small and the high temperature response is rapidly reduced. (ii) When the pressure keeps constant, the thermal expansion coefficient α increases rapidly at low temperature and the increasing trend becomes gentler. The effect of pressure on thermal expansion coefficient is larger at low temperature than that at high temperature. Further analysis of Fig. 10 indicates that the thermal expansion coefficient is subjected to a rapid change under low temperature (below 600 K) and pressure (below 30 GPa), and the lower the temperature/pressure, the faster the variation of thermal expansion coefficient. It can be found that the thermal expansion coefficient converges to a constant value under high temperature and pressure. Figure 10 shows its temperature and pressure dependences.

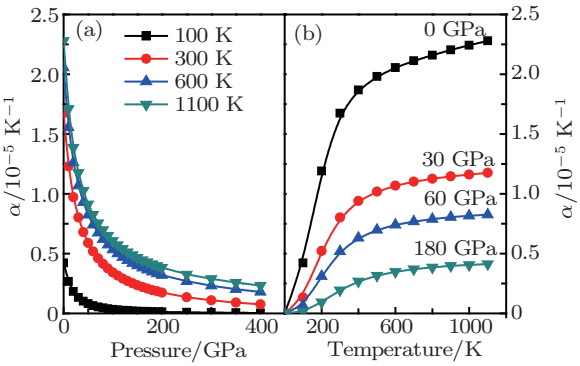


Fig. 10. (colour online) Thermal expansion coefficients of V_2GeC versus (a) pressure and (b) temperature separately.

Poisson's ratio is generally used to quantify the stability of the crystal against shear and provides more information about the characteristics of the bonding forces than elastic constant. Usually it ranges from -1 to 0.5, and the value of Poisson's ratio for covalent material is small ($\sigma = 0.1$), whereas for ionic material a typical value of σ is 0.25.[35] In our cases the values of σ for V_2GeC vary from about 0.2443, which is consistent with the theoretical value 0.265[8] or 0.269,[7] to 0.4256 within 0–800 GPa, which is shown in Fig. 11. Thus, a higher ionic or weaker covalent contribution to intra-atomic bonding for V_2GeC should be assumed.

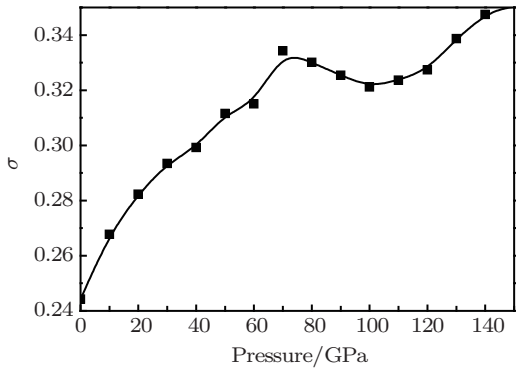


Fig. 11. Possion's ratio of V_2GeC as a function of pressure.

4. Conclusion

The V_2GeC is comprehensively investigated for the first time in this paper. From the investigations we obtain the following conclusions.

1) Our calculations show that the c axis is always stiffer than a axis over a wide pressure range of 0–1000 GPa, which is confirmed by the axial bulk modulus.

2) Study on elastic constants demonstrates that the V_2GeC is stable under pressure up to 800 GPa and no phase transition is observed.

3) Study of elastic modulus indicates that the bulk modulus and Läme coefficient increase linearly with pressure, where the Young and shear moduli display certain softening behaviours at about 300 GPa, implying a structural change.

4) Study of Possion's ratio shows that a higher ionic or weaker covalent contribution to intra-atomic bonding for V_2GeC should be assumed and the ionic nature increases with pressure increasing. Moreover, the B/G, G/B and B/C_{44} also reveal that V_2GeC is brittle in ambient conditions, whereas the brittleness decreases and ductility increases with pressure.

5) The analyses of Debye temperature, Grüneisen parameter, and thermal expansion coefficient indicate that the former two have a strong pressure dependence but a weak temperature dependence; the latter shows a strong pressure and temperature response.

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