

On the heat capacity of Ti_3GeC_2

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Abstract

In this paper, we report experimental data of the heat capacities, c_p , of bulk polycrystalline samples of Ti_3GeC_2 in the 3–260 K temperature range. The results obtained are compared with those on Ti_3SiC_2 . The c_p results are analyzed using the Debye and Einstein models and are compared to the heat capacities values calculated from first principles. At temperatures up to 10 K the main contributors to c_p are electrons with $\gamma = 6.5$ (mJ/mol K²) and phonons with a Debye temperature θ_D of 556 K. In that temperature range only four atoms of the six in a formula unit—most likely one Ge and three Ti atoms—contribute to c_p . In the 10–120 K temperature range excellent fits were obtained using a θ_D of 513 K and an optical mode with an Einstein temperature θ_E of 139 K. For $T > 120$ K, five additional optical modes with $\theta_E = 870$ K are required to properly fit the experimental results. The ab initio calculations throughout the temperature range (4–1500 K) show reasonably good agreement with the experimental data obtained particularly at low temperatures.

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1. Introduction

The ternary carbides with the general formula $\text{M}_{n+1}\text{AX}_n$, where $n = 1–3$, M is an early transition metal, A is an A-group element (mostly IIIA and IVA), and X is C and/or N [1–4] form a large family of the layered hexagonal (space group $D6h\ 4-P6_3/mmc$) compounds with two formula units per unit cell. By now it is fairly well established that these phases constitute a new class of solid best described as polycrystalline nanolaminates as a consequence of their layered structure and their propensity to kink and delaminate during deformation [2].

The $\text{M}_{n+1}\text{AX}_n$ phases combine an unusual, and sometimes unique, set of properties [2–12]. Like their corresponding binary carbides and nitrides, they are elastically stiff [5,6], have relatively low thermal expansion coefficients, good thermal and electrical conductivities, and are resistant to chemical attack [2]. They are relatively soft (1–5 GPa) and most readily

machinable, thermal shock, and damage tolerant [2,4]. Moreover, some are fatigue [11], creep [12], and oxidation resistant [13]. At higher temperatures, they undergo a brittle to ductile transition [2]. At room temperature, they can be compressed to stresses up to 1 GPa and fully recover upon removal of the load, while dissipating 25% of mechanical energy [7]. The most studied of these phases is Ti_3SiC_2 compound [2].

Of special interest to this work is Ti_3GeC_2 and Ti_3SiC_2 . The unit cell of both compounds consists of Ti_3X_2 layers interleaved with layers comprised of hexagonal nets of pure Si or Ge [14]. Because the Si to Si and Ge to Ge distances along a (≈ 3.07 Å) in the ternaries are considerably longer than their covalent bonding in pure Si (2.35 Å) and Ge (2.44 Å) consequently, these atoms act as rattlers that tend to vibrate along the a -direction [2]. The bonding in these compounds is comparable to TiC, viz. a combination of ionic, covalent, and metallic characters [2,15]. However, the density of states (DOS) of 5 (eV unit cell)⁻¹ at the Fermi level for Ti_3SiC_2 [15] is considerably larger than in TiC. Ti_3SiC_2 is roughly twice as electrically and thermally conductive as Ti [16,17]. While currently the low temperature properties of Ti_3SiC_2 are

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reasonably well characterized [18–22], the same information for Ti_3GeC_2 does not exist. Recently, a number of papers have been published on the properties of Ti_3GeC_2 and its solid solutions with Ti_3SiC_2 [23,24]. In ref. 24 the room temperature elastic, and low (4–300 K) temperature transport properties of $\text{Ti}_3\text{Si}_x\text{Ge}_{1-x}\text{C}_2$ were measured and found to be quite insensitive to x . Young's modulus of Ti_3GeC_2 is 340 GPa and its thermal expansion coefficient in the 25–1200 °C temperature range is $7.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. In another paper [23] it was shown that the mechanical properties are also quite insensitive to x .

The purpose of this paper is to report on and analyze the heat capacities, c_p , for Ti_3GeC_2 over the 3–260 K temperature range. These results are compared with those of the isostructural Ti_3SiC_2 , as well as ab initio calculations of c_v .

2. Experiment

The synthesis procedure is described in detail in ref. [23]. In short, appropriate stoichiometric mixtures of Ti, C and Ge powders were hot pressed at 1600 °C for 6 h using an applied pressure of ~ 45 MPa. The samples were then annealed at 1600 °C for 48 h in an argon atmosphere to render the samples single phase. The polished samples were micro structurally characterized using an optical microscope (PMG3, Olympus, Tokyo, Japan) and a field emission scanning electron microscope, FESEM (XL-30, FEI-Philips, Hillsboro, OR) equipped with an energy dispersive spectroscopy, EDS (Edax Inc., Mahwah, NJ). The predominantly single phase samples contained ~ 3 vol.% TiO_2 . All samples were $>99\%$ dense.

The c_p measurements were carried out between 3 and 260 K, using two different adiabatic calorimeters. In the first, which operates in the 2–70 K temperature range, a small bulk sample (≈ 1 g) is thermally anchored by Apiezon N grease to a sapphire plate, which, in turn, is suspended by threads inside the adiabatic shield. Also mounted on the plate are a resistance thermometer Cernox 1030-3C and a nichrome ($R = 150 \text{ } \Omega$) heater. The calorimeter is fully automated. In the second device, which operates in the 2–280 K temperature range, a larger bulk piece (≈ 2.5 g) is thermally connected to a copper block. To maintain the adiabatic regime in the calorimeter, a vacuum chamber and two adiabatic shields controlled by ITC 503 temperature controllers were used.

Table 1
Thermodynamic functions of Ti_3GeC_2

T (K)	c_p ($\text{J mol}^{-1} \text{ K}^{-1}$)	S_T^0 ($\text{J mol}^{-1} \text{ K}^{-1}$)	$H_T^0 - H_0^0$ (J mol^{-1})	$-(G_T^0 - H_0^0)/T$ ($\text{J mol}^{-1} \text{ K}^{-1}$)
4	0.03	0.018	0.06	0.004
10	0.116	0.072	0.45	0.027
20	0.895	0.322	4.5	0.098
40	7.353	2.657	79.23	0.676
80	29.822	14.193	796.7	4.234
120	55.075	31.09	2497.88	10.274
160	77.59	50.131	5167.15	17.837
200	95.016	69.39	8632.23	26.228
240	110.051	88.064	12738.44	34.988
260	116.511	97.137	15006.3	39.421

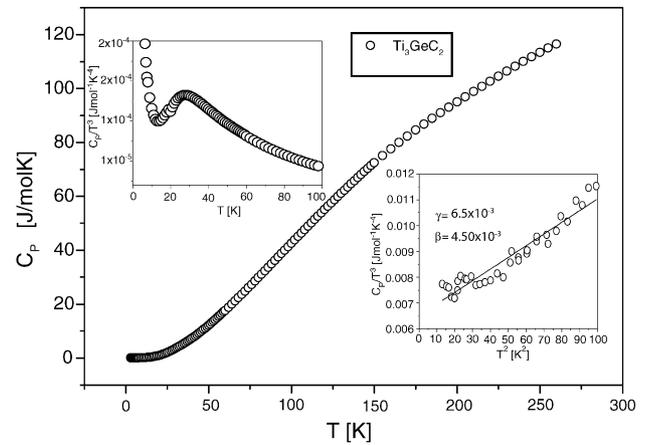


Fig. 1. Low temperature c_p of Ti_3GeC_2 . Lower inset details a plot of c_p/T vs. T^2 in the 3–10 K temperature range, whereas the upper inset shows the c_p data as a $c_p T^{-3}$ vs. T . For details see the text.

In both cases, a computer was used to control the set-up and acquire the data. The c_p of each sample was obtained by subtracting the addenda contributions.

3. Results and discussion

The temperature dependence of c_p for Ti_3GeC_2 is depicted in Fig. 1.

Table 1 list the c_p values for Ti_3GeC_2 together with its relevant thermodynamic functions.

For metallic-like, three-dimensional materials at the lowest temperatures, c_p can be approximated by the well-known relationship

$$c_p = \gamma T + \beta T^3 \quad (1)$$

where γ and β are the coefficients of electronic and lattice heat capacities, respectively.

A plot of c_p/T versus T^2 in the 3.3–10 K temperature range for Ti_3GeC_2 yields a straight line (lower inset in Fig. 1) with a slope $\beta = 4.5 \pm 0.1 \times 10^{-5} \text{ mJ/mol K}^4$ and intercept $\gamma = 6.5 \pm 0.1 \text{ mJ/mol K}^2$. The DOS at the Fermi level is thus calculated to be $5.52 \text{ (eV unit cell)}^{-1}$, which is not too different from the value of $5 \text{ (eV unit cell)}^{-1}$ obtained for Ti_3SiC_2

[19,20,22]. It is also in reasonable agreement with the value of $4.3 \text{ (eV unit cell)}^{-1}$ obtained from recent ab initio calculations [24]. In contradistinction with Ti_3SiC_2 no evidence was found here for an anomaly in c_p at the lowest temperatures [22].

At low temperatures, β in Eq. (1) is related to the Debye temperature θ_D by

$$\beta = \left(\frac{12}{45}\right) NR\pi^4(\theta_D)^{-3} \quad (2)$$

where N is the number of modes per formula unit, and R is the molar gas constant. For simple solids with atoms that are not too different in mass, $N=3r$, where r is the number of atoms per formula unit and the calculation of θ_D from Eq. (2) is straightforward. However, in cases when atoms with different masses are involved, not all of which may be participating fully in the acoustic vibrations—the latter an implicit assumption in Debye's theory—it is not obvious what the r values should be. Following the arguments described in detail in ref. [22], here we again conclude that only 12 modes, or four atoms—most likely three Ti and one Ge—effectively contribute to the Debye lattice part of c_p in the lowest temperature regime.

Assuming $N=12$ in Eq. (2) results in $\theta_D=556 \text{ K}$. Note that θ_D , as a rule, only describes the temperature dependence of c_p for $T < \theta_D/10$. To better understand the various terms that contribute (apart from Debye) to c_p at slightly higher temperatures, it is useful to plot the c_p data as a $c_p T^{-3}$ versus T (upper inset in Fig. 1). When plotted thusly, a maximum at $T_{\text{max}}=28 \text{ K}$ for Ti_3GeC_2 is evident. Such maximum is indicative of the presence of low ($20\text{--}150 \text{ cm}^{-1}$) frequency Einstein-like modes that accompany the Debye-like terms and contribute to the low temperature specific heat of many substances [25].

Assuming such modes are operative here, their contribution to the heat capacity is described by the Einstein function,

$$c_{v(E)} = N_1 R \left(\frac{1}{2x_E}\right)^2 \text{csch}^2\left(\frac{1}{2x_E}\right), \quad \left(x_E \equiv \frac{\theta_E}{T}\right) \quad (3)$$

where θ_E is the Einstein temperature. In the low temperature regime, c_p is thus the sum of the well-known Debye function:

$$c_p = \gamma T + \frac{NRT^3}{\theta_D^3} \int_0^{\frac{x^4 e^x}{(e^x - 1)^2}} dx, \quad \left(x \equiv \frac{\theta_D}{T}\right) \quad (4)$$

and Eq. (3). Keeping $\gamma = 6.5 \text{ (mJ/mol K}^2)$, $N=12$ in Eq. (4) and $N_1=1$ in Eq. (3), a least squares fit in the 30–80 K temperature range, yields $\theta_D=513 \text{ K}$, $\theta_E=139 \text{ K}$ (95 cm^{-1}). These parameters thus describe the specific heat of Ti_3GeC_2 in the 3–120 K temperature range (dashed line in Fig. 2).

The mode with an energy of $\theta_E^{\text{Ge}} = 139 \text{ K}$ (95 cm^{-1}) may be associated with a shear mode analogous to that of Ti_3SiC_2 at $\theta_E^{\text{Si}} = 219 \text{ K}$ (152 cm^{-1}) [22]. While $\theta_E^{\text{Si}} = 152 \text{ cm}^{-1}$ is very close to the frequency of $\omega = 159 \text{ cm}^{-1}$ found in the Raman spectra of Ti_3SiC_2 [26], the value of $\theta_E^{\text{Ge}} = 95 \text{ cm}^{-1}$ estimated in our heat capacity measurements is lower than the

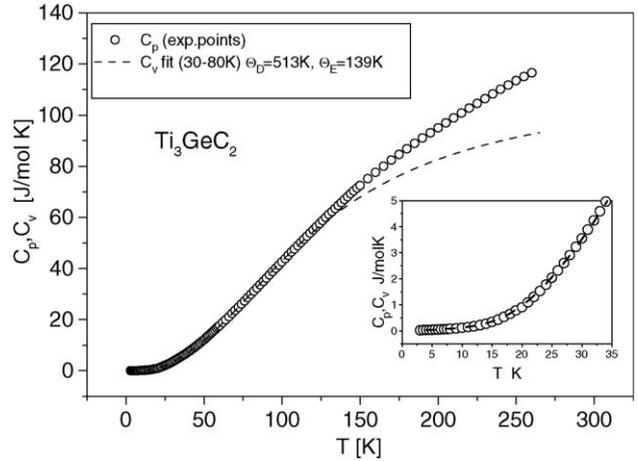


Fig. 2. Comparison of experimental c_p and calculated c_v results for Ti_3GeC_2 in the 3–260 K temperature range. Inset details the lowest temperatures.

peak at $\omega = 144 \text{ cm}^{-1}$ as measured in the Raman scattering from Ti_3GeC_2 [24]; this peak is attributed to the vibration of the Ge atoms along the a -direction.

To fit the experimental data at $T > 120 \text{ K}$, more optical modes in the phonon density of states must be taken into account. As noted previously for Ti_3SiC_2 [22] some optical vibration modes associated mainly with the Ti–C–Ti bonds in the Ti_6C octahedra become active only at higher temperatures. This conclusion is bolstered by recent Raman spectra studies [26] and ab initio calculations made for this compound [27]. In our previous paper [22] we modelled the contribution of the C atoms to c_p in Ti_3SiC_2 for $120 \leq T \leq 260 \text{ K}$ taking $\theta_E^{\text{C}} = 942 \text{ K}$ for the carbon modes as deduced from the Raman spectra analysis [26] and assuming $N^{\text{C}} = 6$ (see Fig. 9 in ref. [22]). To be sure that our assumption ($N^{\text{C}} = 6$) is valid also in the highest temperature range we repeated this calculation, but over a wider temperature range $120 \leq T \leq 1500 \text{ K}$ to enable comparison with experimental high temperature ($T > 500 \text{ K}$) c_p results for Ti_3SiC_2 taken from ref. [17]. All previously calculated low temperature parameters (see ref. [22]) were fixed here and the only variable was the number of carbon atom modes, N^{C} . As seen in Fig. 3, much better agreement between the calculated c_v and measured c_p is obtained for $N^{\text{C}} = 5$ rather than for $N^{\text{C}} = 6$, suggesting that one of the C atom modes is participating at lower temperatures. Note that at $T > 500 \text{ K}$ the agreement between the experimental and calculated results is pretty good; the difference ($c_v - c_p$) for $N^{\text{C}} = 5$, does not exceed 2% (Fig. 3). We neglected the possible difference $c_p - c_v$ caused by thermal expansion at high temperatures, which is at 1500 K smaller than 1.5 J/mol K . The fact that the ab initio calculations (see below) actually bridge the two sets of experimental results lends them even more credence.

Unfortunately, similar high temperature c_p data for Ti_3GeC_2 do not exist. Nevertheless, we calculated c_v of Ti_3GeC_2 up to 1500 K, assuming, per analogy to Ti_3SiC_2 , that at high temperatures only five of six carbon modes con-

Table 2
Summary of parameters deduced in this and previous work

	γ (mJ/mol K ²)	β (mJ/mol K ⁴)	θ_D (K)		θ_E (K)	
			$T < 10$ K, $N = 12$	$T > 20$ K, $N = 12$	Shear modes $N_1 = 1$	Carbon modes $N = 5$
Ti ₃ SiC ₂ ^a	6.41	0.041	575	552	218	942
Ti ₃ GeC ₂	6.50	0.045	556	513	139	870

^a Ref. [22].

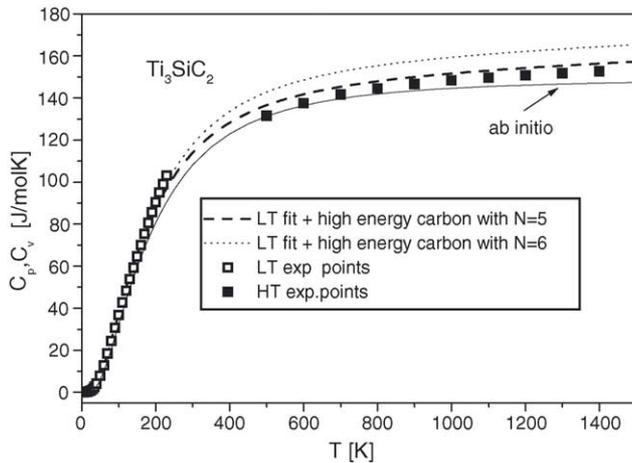


Fig. 3. Fitting of c_p results of Ti₃SiC₂ in the 4–1500 K temperature range with different number of C-atom modes contributing at high temperatures. Also included are ab initio calculations of the heat capacity c_v versus T for Ti₃SiC₂ compound. Experimental data taken from refs. [22,17] for $T > 500$ K.

tribute to c_p . The results shown in Fig. 4 by a dashed line in which the average high-temperature vibration energy of the C atoms was represented by a θ_E^C of 870 K. The results of our ab initio calculations (see below) are shown as full lines in Fig. 4; as in the case of Ti₃SiC₂ (Fig. 3) they appear to slightly underestimate c_p at higher temperatures. Again by analogy to Fig. 3, it is likely that the actual high temperature c_p values for Ti₃GeC₂ will probably fall in between the two lines shown in Fig. 4. These comments notwithstanding, c_p

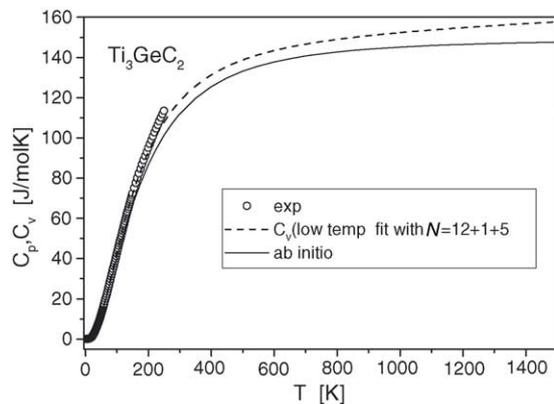


Fig. 4. Temperature dependence of c_p of Ti₃GeC₂ calculated in the 4–1500 K temperature range on the basis of thermodynamic parameters found at low temperatures. Included are the results of the c_p ab initio calculations (full line) for Ti₃GeC₂.

for Ti₃GeC₂ at ambient and higher temperatures should be measured.

The results of the ab initio calculations of c_v for Ti₃SiC₂ and Ti₃GeC₂ at temperatures from $2 < T < 1500$ K were carried out using the so-called first principles direct methods [28]. The calculated heat capacity were obtained directly from calculations of phonon dispersions and density of states in Ti₃GeC₂ [27] using the Vienna ab initio Simulation Package (VASP) [29] and PHONON [28]. Canonical positions of the Ti atoms were used, and a supercell of 108 atoms was constructed; supercell coordinates were “relaxed” prior to calculating structures with displaced atoms. Translational and rotational invariance conditions were enforced for the derivation of the force constants, and no approximation to LO/TO splitting was made. The agreement of these calculations with experimental data and with those calculate analytically at high temperatures is reasonably well.

All parameters measured or calculated in this study are summarized in Table 2.

4. Conclusions

Based on this work we surmise that the total phonon densities of states in Ti₃GeC₂ and Ti₃SiC₂ are comparable, as is expected from symmetry considerations and the fact that these compounds only differ in their A group element. In particular, we note differences in the energies of low temperature, shear-like modes. Furthermore, an improvement in the fit of c_p at $T > 500$ K is obtained if $N^C = 5$ compared with $N^C = 6$. It suggests that, apart from the Si in Ti₃SiC₂ and Ge atoms in Ti₃GeC₂, at least one of the vibrational modes involving the C atoms is a low-temperature mode. Therefore, only five modes appear to participate in c_p at higher temperatures.

Finally, the first principles calculations of the c_v show excellent agreement with experiment, particularly in the low temperature region. Further investigation is underway.

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