On the heat capacities of $\text{Ta}_2\text{AlC}$, $\text{Ti}_2\text{SC}$, and $\text{Cr}_2\text{GeC}$

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Herein we report on the heat capacities $c_p$ of bulk predominantly single-phase polycrystalline samples of $\text{Ti}_2\text{SC}$ and $\text{Cr}_2\text{GeC}$ in the 3–1500 K temperature range and $\text{Ta}_2\text{AlC}$ in the 3–260 K range. At temperatures up to 10 K the main contributors to $c_p$ for $\text{Ta}_2\text{AlC}$ and $\text{Cr}_2\text{GeC}$ are electronic, with electronic coefficients $\gamma$ of 7.13 and 26.12 mJ/mol K$^2$, respectively. The latter is exceptionally high and is a record for this family of layered ternary carbides and nitrides also known as the MAX phases. In $\text{Ti}_2\text{SC}$ another low-temperature contribution—in addition to a $\gamma$ of 3.8 mJ/mol K$^2$—is manifested by an upturn in $c_p/T$ observed at the lowest temperatures. This feature, appearing as a Schottky-like anomaly, has a local maximum near 4.5 K and an intensity of $\sim 1.9 \times 10^{-2}$ J/mol K. A defect concentration of $\sim 3 \times 10^{21}$/mol presumably on the $S$-sublattice, is proposed as the origin of a two-level energy system responsible for this anomaly. As in previous work on these compounds, the lattice contributions to $c_p$ in all compounds are analyzed using the Debye and Einstein model approximations. The main effect of increasing the atomic number of the transition metal is a reduction in Debye temperature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2956511]

I. INTRODUCTION

The ternary carbides $M_{a+1A}X_n$ (where $M$ is an early transition metal, $A$ is an A group element, and $X = C$ or $N$) (MAX) comprise a family of layered hexagonal (space group $P6_3/mmc$) compounds.1,2 By now it is fairly well established that these phases possess an unusual, and sometimes unique, set of properties.3–13 In general they have relatively low thermal expansion coefficients, and good thermal and electrical conductivities.3,9,13 They are relatively soft, readily machinable, thermal shock resistant, and damage tolerant. At higher temperatures, they undergo a brittle-to-plastic transition.3–6,11 Some such as $\text{Ti}_2\text{AlC}$ are exceptionally oxidation resistant and are candidate materials for high-temperature structural industrial applications.14

Generally, accurate knowledge of the constant-pressure heat capacity $c_p$ of a material, over its entire stability regime, is of vital scientific and technical importance. Without it a compound’s thermodynamic parameters cannot be calculated. Furthermore, low-temperature $c_p$ measurement is an established technique to experimentally determine the density of states (DOS) at the Fermi level. The latter in turn is crucial for comparison with DOS calculated from first-principles methods. By using such density-functional theoretical simulation methods, accurate theoretical predictions of values of bulk moduli and the DOS can be made.15–19

By now it is well established that the low-temperature $c_p$ of the MAX phases can be described by the well-known relationship

$$c_p = c_v = \gamma T + \beta T^3,$$

where $\gamma$ and $\beta$ are the coefficients of electronic and lattice contributions to the heat capacity, respectively, and $c_v$ is the heat capacity at constant volume and is assumed throughout this paper to be equal to $c_p$.

The coefficient $\beta$ is related to the Debye temperature $\Theta_D$ by

$$\Theta_D = \frac{12\pi^4R}{15\beta}N_D,$$

where $N_D = 3r$ is the number of Debye-like modes, $r$ is the number of atoms per f.u., and $R$ is the molar gas constant.

Strictly speaking, Eq. (2) is only valid for a pure element or $r$ atoms of equal mass. We have argued in several papers22–25 that $N_D = 3r$ is an oversimplification for the MAX phases. For example, we have also shown that $N_D$ for the $M_2AX$ phases is $< 12$. A similar situation is encountered in metal hydrides containing a variable number of light interstitial atoms without a concomitant change in the measured $\beta$; including them in $N_D$, a false variation of $\Theta_D$ would be obtained.26 Moreover, while $c_p$ for some of the MAX phases have already been measured,22–25,27 that for the vast majority of the more than 50+ compounds have not. A preliminary, short report on the $c_p$ of $\text{Ti}_2\text{SC}$ in the 3–300 K temperature range will be reported elsewhere.28 In that work we showed that if one assumes a simple Debye model, viz., $N_D = 3r$, $\Theta_D$ is 765 K. Herein we present a more comprehensive measurement of $c_p$, collected over a wider temperature range, along with a more nuanced interpretation of $c_p$.

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The purpose of this paper is thus to report on, and interpret, the temperature variations of \( c_p \) and Ti\(_2\)SC and Cr\(_2\)GeC in the 3–1500 K temperature range and Ta\(_2\)AlC in the narrower range of 3–260 K.

II. EXPERIMENTAL AND MODELING DETAILS

The sample fabrication details for Ti\(_2\)SC, Ta\(_2\)AlC, and Cr\(_2\)GeC can be found elsewhere.\(^\text{29-31}\) In brief, the Ta\(_2\)AlC samples were fabricated by hot isostatically pressing at 1100 °C for 0.3 h under ~70 MPa from Ta\(_2\)AlC powders (>92%, 3-ONE-2, Voorhees, NJ). X-ray diffraction phase-pure, ~325 mesh Ti\(_2\)SC powders (3-ONE-2, Voorhees, NJ) were hot pressed in a graphite-heated, vacuum atmosphere hot press (HP) (series 3600, Centorr Vacuum Industries, Somerville, MA). The powder was poured and wrapped in graphite foil, which, in turn, was placed in a graphite die and heated at 10 °C/min to 1500 °C for 5 h.\(^\text{29}\)

Phase-pure ~325 mesh Ti\(_2\)SC powders (3-ONE-2, Voorhees, NJ) were hot pressed in a graphite-heated, vacuum atmosphere HP. The powders were held for ~5 h at 1500 °C under a load that corresponded to a stress of ~45 MPa, which was applied at 500 °C and maintained throughout the entire process.\(^\text{30}\)

Stoichiometric powder mixtures of chromium (99% pure, ~325 mesh, Alfa Aesar, Ward Hill, MA), germanium (99% pure, ~325 mesh, Cerac, Milwaukee, WI), and carbon (99.0% pure, ~300 mesh, Alfa Aesar, Ward Hill, MA) were ball milled for 24 h and dried in a low vacuum atmosphere for 24 h at 180 °C. The mixed powders were poured and wrapped in graphite foil, placed in a graphite die and heated in the HP at 10 °C/min to 1350 °C and held at temperature for ~6 h. A load, corresponding to a stress of ~45 MPa, was applied at 500 °C and maintained throughout the heating process.\(^\text{31}\)

The low-temperature \( c_p \) measurements—the details of which can be found in Ref. 23 were carried out between 3 and 260 K, using two different adiabatic calorimeters. The \( c_p \) for each sample was obtained by subtracting the addenda contributions. The high-temperature \( c_p \) measurements were performed with a Setaram-Multi HTC high-temperature and high-sensitivity calorimeter. Compared to more conventional Differential Scanning Calorimetry (DSC) devices, this apparatus enables us to work under inert gas up to 1420 °C, with typical heating/cooling rates ranging from 1 up to 10 K/min. The samples used were cylindrical shaped specimens 5 mm diameter and 12 mm height (typical sample weight ~1 g). This facility makes it possible to measure the heat flow between the tested sample and an inert reference sample. Temperature and enthalpy measurements were calibrated using known melting points of several standard metals (In, Al, Au, etc.). The tests were carried out under purified He atmospheres, with a flow rate of ~0.6 l/h. For these conditions, the accuracy of the measurement is estimated to be around ±5%. The \( c_p \) measurements of the samples tested were derived by applying the “continuous method.”\(^\text{32}\) For all the measurements, the samples were first heated at 473 K for 1 h, followed by a heating at 3 K/min up to 1473 K at which time the furnace is cooled down to 293 K.

![Density-functional theoretical simulations of electronic structure and lattice dynamics were performed using the Vienna ab initio simulation package (VASP) as implemented within MEDEA.](http://jap.aip.org/jap/copyright.jsp)
TABLE I. Summary of the electronic and lattice coefficients measured herein for Ta2AlC, Ti2SC, and Cr2GeC. Also included, for comparison’s sake, are previous results for V2AlC, Ti2AlC, Cr2AlC, and Nb2AlC (Ref. 27).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma$ (J/mol K$^2$)</th>
<th>$N(E_F)$ (eV UC)$^{-1}$</th>
<th>$\beta$ (J/mol K$^2$)</th>
<th>$N_D$ (K)</th>
<th>$\Theta_D$ (K)</th>
<th>$N_E$ (K)</th>
<th>$\Theta_E$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta2AlC</td>
<td>7.13</td>
<td>6.0</td>
<td>22.5 $\times$ 10$^{-5}$</td>
<td>6</td>
<td>281</td>
<td>2</td>
<td>304</td>
</tr>
<tr>
<td>V2AlC$^{a}$</td>
<td>8.83</td>
<td>7.5</td>
<td>2.46 $\times$ 10$^{-5}$</td>
<td>9</td>
<td>625</td>
<td>2</td>
<td>259</td>
</tr>
<tr>
<td>Nb2AlC$^{b}$</td>
<td>6.0</td>
<td>5.06</td>
<td>4.90 $\times$ 10$^{-5}$</td>
<td>12</td>
<td>540</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Cr2GeC</td>
<td>26.12</td>
<td>22.0</td>
<td>7.46 $\times$ 10$^{-5}$</td>
<td>9</td>
<td>429</td>
<td>1</td>
<td>168</td>
</tr>
<tr>
<td>Cr2AlC$^{a}$</td>
<td>17.15</td>
<td>14.6</td>
<td>2.85 $\times$ 10$^{-5}$</td>
<td>9</td>
<td>594</td>
<td>2</td>
<td>260</td>
</tr>
<tr>
<td>Ti2SC</td>
<td>3.8</td>
<td>3.2</td>
<td>...</td>
<td>11</td>
<td>631</td>
<td>1</td>
<td>278</td>
</tr>
<tr>
<td>Ti2AlC$^{a}$</td>
<td>4.6</td>
<td>3.9</td>
<td>1.87 $\times$ 10$^{-5}$</td>
<td>9</td>
<td>672</td>
<td>3</td>
<td>270</td>
</tr>
</tbody>
</table>

$^{a}$Reference 24.
$^{b}$Reference 27.

large mass differential between Ta, on the one hand, and Al and C, on the other, it is likely that the modes possessing acousticlike dispersions mainly involve displacements of Ta atoms, and these modes, viz., $N_D=6$, are largely responsible for the lattice contribution to $c_p$ at the lowest temperatures. Like other MAX phases, the contributions of the other atoms to $c_p$ can be represented by Einstein-like modes. Said otherwise, $c_p$ can be approximated by the sum of three components,

$$c_p = \gamma T + N_D c_V(D) + N_E c_V(E),$$

(3)

where the first two terms on the right-hand side are defined in Eq. (1). The third term reflects the contribution to $c_p$ from Einstein-like vibration modes,

$$N_E c_V(E) = \frac{N_E R}{4(\theta_E T)^2} \csc h^{-2} \left(\frac{1}{2 \theta_E T} - 1\right),$$

(4)

where $\Theta_E$ is the Einstein temperature.

Assuming $\gamma=7.13$ J/mol K$^2$, $N_D=6$ in Eq. (3), and selecting different values of $N_E$, the best fit of the experimental $c_p$ data in the wide 15–270 K temperature range is obtained by selecting two low-energy Einstein-like modes ($N_E^{L}=2$) and four high-energy Einstein modes ($N_E^{H}=4$). Least squares fits of the data with $\Theta_D$ and low- and high-energy Einstein mode temperatures $\Theta_E^{L}$ and $\Theta_E^{H}$ yield $\Theta_D$ = 281 K, $\Theta_E^{L}$ = 304 K, and $\Theta_E^{H}$ = 665 K. The agreement between experimental (open squares in Fig. 1) and calculated data (full line in Fig. 1) for the most part is quite good.

In contradistinction, for V2AlC, the lattice contribution to $c_p$ is well described by nine Debye-like and three Einstein-like modes over the entire temperature range. This indirectly confirms the observation that the distribution of lattice vibrational energy between Debye-like and Einstein-like modes depends on the atomic mass ratios in a given compound and confirms that the dispersion characteristics of the low-energy optical phonon branches are acousticlike, as seen in the calculated phonon dispersions for Ta2AlC, Cr2GeC, and Ti2SC (shown in Fig. 5).

B. Cr2GeC

The $c_p$ measurements for Cr2GeC are shown in Fig. 2. A plot of $c_p/T$ vs $T^2$ (upper inset in Fig. 2) yields $\gamma = 26.12$ J/mol K$^2$ and $\beta = 7.46 \times 10^{-5}$ J/mol K$^3$. Analysis of the $c_p$ results for Cr2GeC was carried out in a manner similar to that for Ta2AlC. However, because atomic masses Cr and Ge are close to each other, it is reasonable to assume that their lattice vibrational energies have the same Debye-like characteristics and number of $N_D$ modes to be 9. Before carrying out the full-fitting procedure, the rough number of Einstein modes and their energies at low temperatures need to be estimated. To do so, we plot $(c_p - \gamma T)/T^2 - \beta$ vs $T$ (lower inset in Fig. 2). This curve is well described if one assumes $N_E=1$, with a $\Theta_E=168$ K. Taking $\gamma=26.12$ J/mol K$^2$, the fit of $c_p$ with Eq. (3) in the temperature range measured was attempted. The least squares procedure yields a $\Theta_D=429$ K and $\Theta_E=168$ K for $N_D=9$ and $N_E=1$, respectively. Unfortunately, good agreement between experimental and calculated curves was obtained only in the 4–170 K temperature range. Further ef-

FIG. 2. Temperature dependencies of experimental $c_p$ (open circles) and calculated $c_p$ (solid line) results for Cr2GeC sample in the 3–260 K temperature range. Top inset plots $c_p/T$ vs $T^2$ in the 3–20 K temperature range. Lower inset plots $[(c_p - \gamma T)/T^2 - \beta]$ vs $T$. Also plotted for the sake of comparison are the results for Ta2AlC from Ref. 24.
dependence for $T > 170$ K were unsuccessful, in spite of fact that there are two additional modes—presumably connected with the C atoms—that are not accounted for. The reason for the large increase of $c_p$ in the $170–260$ K temperature range is not understood. The same problem was encountered for Cr$_2$AlC$^{29}$ the agreement between the experimental and calculated values was acceptable only up to about 180 K.

At 22 (eV UC)$^{-1}$ the DOS at the Fermi level in Cr$_2$GeC is by far the highest measured to date for a MAX phase. Interestingly, with a DOS of 14.6 (eV UC)$^{-1}$, that of Cr$_2$AlC is the second highest. It thus appears that the Cr-containing 211 MAX phases have quite large DOS at the Fermi level.

C. Ti$_2$SC

Figure 3 plots $c_p$ vs $T$ in the 3–300 K temperature range; the upper inset plots $c_p/T$ vs $T^2$ for $T < 20$ K. The visible upturn of $c_p/T$ at the lowest temperatures precludes the direct use of Eq. (1), as done to date for all other MAX phases.$^{22–25}$ This upturn indicates that in addition to the electronic $\gamma$ term, additional low-energy thermal excitations exist. To extract the latter, Eq. (3) was used but only in the 10–40 K results. Least squares fitting resulted in a $\gamma$ = 3.8 mJ/K$^2$ mol and a $\Theta_D$ equal to 631 K, assuming $N_D$ = 11 and $\Theta_F = 278$ K ($N_L = 1$). These parameters describe $c_p$ from 14 up to 260 K (see full line in Fig. 3 and Table I).

Using the same results, the low temperature $c_p$ excess, viz., $\Delta c_p(T) = c_p^{\text{exp}} - c_p^{\text{cal}}$, was plotted versus $T$ in the 3–17 K temperature range (lower inset of Fig. 3). The result is a Schottky-like peak, with a $T_{\text{MAX}}$ of 4.5 K and $\Delta c_{\text{MAX}} = 1.9 \times 10^{-2}$ J/mol K. The question arises: What kind of phenomenon is responsible for this contribution?

According to their respective temperature range of importance, the following typical contributions can be considered: (i) nuclear, which is usually recognized by a $T^2$ dependence for $T > 0.5$ K; (ii) spin fluctuation, or paramagnons, characterized by a $T^2$ ln $T$ term; (iii) magnons, which are related to some magnetic transition or anomalies; (iv) heavy fermion quasiparticles, Kondo effect, spin glass, and finally atomic disorder, like that in a glass matrix. Most of these contributions are either negligible or can be safely ignored because some of them would be detectable only well below the low-temperature limit of our measurements or have different statistics of the thermal populations of the excited state than observed here.

We suggest that the anomalous variation of $c_p$ displayed in insets (a) and (b) of Fig. 3 is due to the disorder in the Ti$_2$SC atomic structure resembling the disorder in glasses. The existence of glasslike properties in nonglassy materials has been found in many crystalline materials that have been strongly irradiated with high-energy neutrons or in fast ionic conducting solids for example.$^{39}$ The principal, anomalous low-temperature properties of glasses can be understood in the framework of the two-level system (TLS), which has become the conventional approach in this area.$^{40}$ According to this model, an atom or group of atoms moves in a double-well potential by tunneling (at the lowest temperatures) or by activation processes at relatively higher temperatures.

To describe the TLS contribution to $c_p$, we must assume that activation processes dominate over tunneling in the 3–14 K temperature region. In this case the atom excitations within the TLS interlevels are described by Boltzmann statistics, while their contributions to $c_p$ are described by a Schottky-like function described by

\[
\Delta c_p(T) = c_p^{\text{exp}} - c_p^{\text{cal}} = \frac{1}{1 + \left(\frac{T}{\Theta_D}\right)^2}.
\]
where $\Delta$ is the energy separation measured in Kelvins, and $g_i$ and $g_o$ are the degeneracies of the energy levels. When $g_i = g_o$, and for $k_B T \ll \Delta$, then $c_{Sch} = R \frac{(\Delta / T)^2 e^{(\Delta / T)}}{1 + g_o e^{(\Delta / T)}}$, whereas at higher temperatures a typical $T^{-2}$ tail appears.\(^{41}\) The full line in the lower inset of Fig. 3 describes a Schottky contribution for $g_i/g_o = 1$, with an average $\Delta$ of 11 K, assuming a con-
centration of TLS defects of $\approx 3 \times 10^{21}$/mole. While better agreement between theoretical and calculated curves could be obtained if a reasonable distribution of $\Delta$ values is assumed, such agreement would add little to the discussion. Note that the agreement shown in Fig. 3 does not prove the existence of a TLS but is consistent with it.

Several structural models have appeared recently, which attempt to describe the origin of TLS. Here we adopt the Phillips model for Ge$_{1-x}$S$_x$, who assumed that the TLS phenomenon can be realized in layered solids. Fluctuations of interlayer distances caused by structural defects—in our case most likely on the $S$-sublattice—lead to the deformation of interlayer bonds such that some of them behave as two well potentials. Such lattice defects are also evidenced by an increase in resistivity at the lowest temperatures.

D. High-temperature and ab initio results

Figures 4(a) and 4(b) plot the temperature dependencies of $c_p$ for Cr$_2$GeC and Ti$_2$SC, respectively, over the 3–300 K (open triangles) and the 300–1600 K range (solid circles) temperature regimes. The solid lines in the figure are the lattice contributions to the heat capacity calculated from density-functional theoretical simulations, some of the results of which are shown in Fig. 5. Note the acoustic-like modes in all three compounds in Fig. 5. The dashed lines present the calculated lattice contribution plus $\gamma T$ term, where $\gamma$ is the experimental value reported in Table I. From these results it is clear that when viewed over the entire temperature range, the agreement between theory plus $\gamma T$ and experiment is quite good.

The agreement in the case of Ti$_2$SC is almost excellent over the 4–1000 K range [Fig. 4(b)]. At higher temperatures the experimental $c_p$ values are higher than theory for reasons that are not entirely clear but may be due to one or more of the following: (i) at higher temperatures, the $c_p \approx \gamma T$ approximation is no longer a good one, (ii) anharmonic effects that are not accounted for in the density-functional theory (DFT) calculations, and (iii) to the incipient dissociation of the Ti$_2$SC at higher temperatures.

IV. SUMMARY AND CONCLUSIONS

Herein we report on and analyze $c_p$ of Ti$_2$SC and Cr$_2$GeC in the 3–1500 K temperature range and Ta$_2$AlC in the 3–260 K range. By also comparing the results with other MAX phases we reach the following conclusions.

(i) The substitution of Ta for V or Nb atoms in $M_2$AlC-type compounds has little effect on the electronic properties. The DOS at the Fermi level of Ta$_2$AlC is 6.0 (eV uc)$^{-1}$, 7.5 for V$_2$AlC, and 5.06 (eV uc)$^{-1}$ for Nb$_2$AlC, respectively. The high atomic number (atomic mass) of Ta, however, alters the lattice dynamics and results in significantly lower Debye temperatures.

(ii) For reasons that are unclear, the increase of $c_p$ in Cr$_2$GeC at $T > 170$ K is so large that we were not able to adequately describe it by the Debye, Einstein, and/or a combination of the two models. A similar problem was encountered for Cr$_2$AlC, where the agreement between the experimental and calculated $c_p$ values was good only up to about 180 K. At 26.12 mJ/mol K$^2$, $\gamma$ for Cr$_2$GeC is by far the highest for any MAX phase measured to date. This value, which corresponds to a DOS at the Fermi level of 22 (eV unit cell)$^{-1}$, is $\approx 50\%$ higher than the previous record of 14.6 (eV UC)$^{-1}$ reported for another Cr-containing MAX phase, viz., Cr$_2$AlC.

In Ti$_2$SC, a clear visible upturn in $c_p/T$ at the lowest temperatures clearly indicates that, in addition to an ordinary electronic term, additional low-energy thermal excitations must exist. We suggest that these excitations are due to disorder in the Ti$_2$SC atomic structure reminiscent of a TLS disorder in glasses. To include the TLS contributions to $c_p$ we assumed that in the 3–14 K temperature region, thermally activated processes dominate over tunneling ones, in which case the atom excitations within the TLS interlevels are described by Boltzmann statistics, while their contributions to $c_p$ are described by a Schottky-like function.

(iv) The agreement between the DFT-calculated and experimental results for Ti$_2$SC is quite good over the 4–1000 K temperature range. The agreement for Cr$_2$GeC, particularly, at lower temperatures, is less good and is partially related to the larger than expected $c_p$ for Cr$_2$GeC alluded to above.

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32Procedure SETARAM, SETSOFT 2000, V.1.2.
34Materials Design, MEDEA software, Version 2.2.1, Materials Design, Angel Fire, NM.