Electronic, thermal, and elastic properties of Ti$_3$Si$_{1-x}$Ge$_x$C$_2$ solid solutions

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In this paper we report on the electronic, elastic, and thermal properties of Ti$_3$Si$_{1-x}$Ge$_x$C$_2$. The conductivities, Hall coefficients, and magnetoresistances are analyzed within a two-band framework assuming temperature-independent charge carrier concentrations. In this framework, Ti$_3$Si$_{1-x}$Ge$_x$C$_2$ is shown to be a compensated material, i.e., the concentration of electrons is nearly equal to that of the holes. Aside from effects of solid solution scattering at low temperature, there appears to be surprisingly little effect on any of the physical properties due to Ge substitution, with the exception of the thermal expansion, which is smallest in $x=1$.

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I. INTRODUCTION

Thermodynamically stable nanolaminates, so called MAX phases, with chemical formula $M_{n\times1}AX_n$ where $n=1$ to 3, $M$ an early transition metal, $A$ an $A$-group element, and $X$ is C and/or N, are of considerable interest because of their unusual combination of properties: they are readily machinable, relatively stiff, pseudo ductile at room temperature, and electrically and thermally conductive.$^1$ These remarkable features are thought to be attributed to the relative weakness in shear of the hexagonal nets of the $A$-group elements interleaved with $M_{n\times1}X_n$ layers. To date the most studied materials of the MAX family are Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$. While these materials exhibit qualitatively similar elastic and electrical properties, interpreting the differences between compounds is difficult since Al and Si belong to different $A$ groups. As a result, there is a change in both atomic size, as well as electronic structure, which could have complementary or offsetting effects. One distinct difference between the two compounds is the fact that the $c$ axis lattice constant of Ti$_3$AlC$_2$ is more than 5% larger than that of Ti$_3$SiC$_2$. $^1$

The only other known $M_{3}AX_2$ phase is Ti$_3$GeC$_2.$$^2$ While Ge is larger than Si, it is isoelectronic. However, there has been little work done on the physical properties of Ti$_3$GeC$_2$ or substitutions of Ge for Si in Ti$_3$SiC$_2$. We attempt to investigate the impact of the atomic radius of the $A$-group element on the elastic and electronic properties. Since substitutions on the $X$ site$^3$ apparently do not affect the conductivity, and since substitutions on the $M$ sites give rise to classic solid solution scattering,$^4$ it is reasonable to assume, as a first approximation, that the current flows through the $d$-$d$ bands of the $M$ atoms. This conclusion is consistent with the fact that the density of states at the Fermi level is substantial ($\approx 0.6-0.8$ eV per Ti atom)$^{-1}$ and is dominated by $d$ orbitals of the $M$ element.$^5$ While one may therefore anticipate that substitution of Ge for Si may have little impact on the electronic transport properties of these materials, it must be kept in mind that the electrical and thermal conductivities of the MAX phases are larger than those of the binary carbides, and one thus cannot totally discount the role of the $A$-group element.

In this paper we report the results of a systematic investigation of the magnetoresistance, Hall effect, thermopower, electrical and thermal conductivities, the density of states at the Fermi level $N(E_F)$, elastic moduli and thermal expansion coefficients of fully dense samples of Ti$_3$Si$_{1-x}$Ge$_x$C$_2$ with $x=0$, 0.25, 0.5, and 1. We compare the measured values for the elastic moduli and $N(E_F)$ to those obtained from ab inito calculations. This is an important step toward understanding the nature of the MAX phases as it is the presence of the $A$-group layers that give rise to the unusual characteristics which set them apart from the binary carbides.

II. EXPERIMENTAL DETAILS

The sample fabrication details are described elsewhere.$^6$ In general, bulk polycrystalline samples of $x=0.25$ and $x=0.5$ were fabricated by mixing Ti, C, SiC, and Ge powders in order to yield the desired stoichiometry. The mixed powders were hot isostatically pressed at 1873 K under 172 MPa pressure for 8 h in vacuum-sealed glass tubes. The main impurity in each case was TiC≈2 vol.%. However, for the $x=0.5$ sample a Si-Ti rich phase was observed (~3 vol.%) with a Si:Ti:Ge molar percentages determined by electron dispersive x-ray spectroscopy to be $\approx 48\pm 4:40\pm 3.5:12\pm 1.4$. The $x=1$ samples were prepared by hot pressing the appropriate stoichiometric composition at 1873 K for
6 h with an applied pressure of ~45 MPa. The samples were then annealed at 1873 K for 48 h in an argon atmosphere. Optical microscopy revealed the main impurity to be ~3 vol. % TiO₂. All samples were >99% dense.

The room-temperature elastic constants were determined with an ultrasonic echo-pulse technique using a RAM 10000 system from Ritec. The time of flight of a 10-MHz tone burst produced by a lithium niobate transducer was measured by heterodyne phase sensitive detection. For the ultrasonic measurements \(8 \times 8 \times 8 \text{ mm}^3\) cubes of \(x=0.5\) and \(x=0\) were used. The \(x=1\) sample was cylindrical (10 mm in diameter and 16 mm long). In all cases Salol was used as the ultrasonic transducer-bonding compound. Room temperature Young’s \(E\) and shear \(G\) moduli were calculated from independent measurements of the longitudinal \(v_l\) and shear \(v_s\) sound velocities, assuming an isotropic media. These results were then used to calculate the bulk moduli \(B\) and Poisson’s ratio.

Several bar shaped specimen with dimensions 1 \(\times\) 1 \(\times\) 12 mm\(^3\) and 1.5 \(\times\) 2 \(\times\) 12 mm\(^3\) were cut for the transport measurements. The Hall effect, resistivity and magnetoresistance MR, were measured as a function of temperature \(T\) in the 5 – 300 K range and in magnetic fields up to 9 T with a Quantum Design Physical Properties Measurement System (PPMS) using four and/or five probes. The voltage sensitivity was roughly 5 nV, and no contact heating was observed for currents up to 300 mA. The MR component of the transverse voltage and the extraction of the Hall signal were achieved by either a balancing potentiometer or by magnetic field reversal and subtraction of the measured voltages. Thermal voltages were eliminated by use of a low-frequency ac current technique. The low-temperature thermal conductivities, Seebeck coefficients and heat capacities were also measured with the PPMS.

The thermal coefficient of expansion (TCE) was measured from 323 to 1473 K under Ar in an Anter Corporation Unitherm dilatometer. The measurements were carried out on heating and cooling at a rate of 3 °C/min.

### III. CALCULATIONAL DETAILS

Our calculations are based on density functional theory with the so-called VASP (Refs. 8 and 9) program package, wherein ultrasoft pseudopotentials within generalized-gradient approximations (GGA) are explored. The following parameters were used in the calculations: a relaxation convergence for ions of \(1 \times 10^{-4}\) eV and an electronic relaxation convergence of \(1 \times 10^{-5}\) eV. We employed conjugate gradient optimization of the wave functions, using reciprocal-space integration with a Monkhorst-Pack scheme. The energy cutoff was 500 eV with a \(k\)-points grid of \(7 \times 7 \times 7\) and the tetrahedron method with Blöchl corrections for the energy. Once the equilibrium configuration was reached, the \(a\) and \(c\) lattice parameters and the elastic constants were calculated. More details about the elastic constant calculations can be found in previous work. In addition to the elastic constants, we also calculated the density of states at the Fermi level and the Debye temperature.

![FIG. 1. Resistivity as a function of temperature for Ti₃SiGeC₂. Also included are previous results for Ti₃SiC₂ (Ref. 16).](image1)

![FIG. 2. The Seebeck coefficient as a function of temperature for the Ti₃Si₁₋ₓGeₓC₂ samples. Also included are the results for single crystal Ti (Ref. 17).](image2)
The temperature dependencies of the Hall coefficients $R_H$ for the various compounds are plotted in Fig. 3. The $R_H$ values are negative and small at the lowest temperatures and become more negative with increasing temperature. As found for Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$, the magnetoresistance $MR$ of all phases could be well fitted by the expression $MR = f(r_s B - r_s 0^d / r_s 0^d) = aB^2$, where $a$ is a quadratic coefficient and $B$ is the magnetic field. The temperature dependence of $a$ for $x=0.5$ and 1 is plotted in Fig. 4.

The room-temperature thermal conductivity $\kappa$ of all phases is about 40 W/m K range (Fig. 5). The end members show clear maxima in $\kappa$ in the temperature range of 40 to 75 K. These maxima are absent for the solid solution compositions.

The thermal expansion of $x=0.5$ and the end members are compared in Fig. 6 (the curves are shifted to the right from room temperature for clarity). Least squares fits of the curves results in a temperature coefficient of expansion (TCE) for $x=0.5$ (9.3 $\times$ 10$^{-6}$ K$^{-1}$) that is slightly higher than that of $x=0$ (8.9 $\times$ 10$^{-6}$ K$^{-1}$). At 7.8 $\times$ 10$^{-6}$ K$^{-1}$, the TCE of $x=1$ is the lowest of the three. Note the excellent agreement between the heating and cooling curves, suggesting no microcracks or phase transitions.

The room-temperature longitudinal and shear sound velocities together with the various elastic constants determined in this work are listed in Table I. The moduli of $x=0.5$ were $\approx$10\% lower than those of the end members.
TABLE I. The Young’s, shear, and bulk moduli of Ti$_3$Si$_{1-x}$Ge$_x$C$_2$. Also listed are the longitudinal $v_l$ and shear $v_s$ sound velocities and Poisson ratio $\nu$. The Debye temperature is calculated from the mean sound velocity and estimated from the low-temperature heat capacity.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>$B$ (GPa)</th>
<th>$G$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>$v_l$ (m/s)</th>
<th>$v_s$ (m/s)</th>
<th>$\nu$</th>
<th>$\Theta_D^v$ (K)$^a$</th>
<th>$\Theta_D^c$ (K)$^b$</th>
<th>$N(E_F)$ (eV/unit cell)$^{-1}$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0$</td>
<td>4.5 ± 0.10</td>
<td>138 ± 4</td>
<td>330 ± 10</td>
<td>9100</td>
<td>5570</td>
<td>0.20</td>
<td>715–780</td>
<td>715</td>
<td>5.0$^c$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td>4.5</td>
<td>206</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x=0.5$</td>
<td>5.02</td>
<td>169</td>
<td>130</td>
<td>310</td>
<td>8262</td>
<td>0.20</td>
<td>728</td>
<td>724</td>
<td>5.1</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td>4.4</td>
<td>183 ± 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x=1$</td>
<td>5.56</td>
<td>186</td>
<td>142</td>
<td>340</td>
<td>8230</td>
<td>0.19</td>
<td>725</td>
<td>670</td>
<td>5.4</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td>5.36</td>
<td>191</td>
<td>144</td>
<td>345</td>
<td>8451</td>
<td>0.20</td>
<td>736</td>
<td>4.73</td>
<td>This work</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$e=elastic.
$^b*=low temperature heat capacity.
$^c$Ref. 19

Table I also lists Debye temperature $\Theta_D^v$ values calculated from the mean sound velocity$^2$ as well as $N(E_F)$ and Debye temperature $\Theta_D^c$ determined from the low-temperature heat capacity $c_p$ fitting by $c_p = \gamma T + \beta T^3$ with the electronic and phonon contributions described by $\gamma$ and $\beta$, respectively. The agreement among all the values is quite satisfying.

The elastic constants for $x=0$ and 1 obtained from the ab initio calculations are listed in Table II. For comparison purposes, all moduli, sound velocities, and $\Theta_D^v$ were calculated from the elastic constants derived in turn from the ab initio calculations. Those values and the calculated $N(E_F)$ are given in Table I. The measured $a$ and $c$ lattice parameters of 3.090±0.002 Å and 17.764±0.002 Å (Ref. 6), respectively, are in good agreement with the corresponding calculated values of 3.075 and 17.687 Å. The calculated $z$ parameter for the Ti atoms is 0.134 and for C atoms is 0.572; the latter have not been measured.

V. DISCUSSION

Not surprisingly all compositions show metallic-like conduction down to 5 K (Fig. 1). Similar to Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ (Refs. 16 and 18) the temperature dependence of $R_H$ (Fig. 3), the positive quadratic, nonsaturating magnetoresistance (MR~$aB^2$) and the relatively small Seebeck coefficients (Fig. 2) require a two-band model to analyze the experimental results. In the low-field limit of the two-band model, the following applies:

\[ \sigma = \frac{1}{\rho} e(n\mu_n + p\mu_p), \]  
\[ \alpha = \frac{\mu_n\mu_p p(n + p)^2}{(\mu_n n + \mu_p p)^2}, \]  
\[ R_H = \frac{(\mu_n^2 p - \mu_p^2 n)}{e(\mu_p p + \mu_n n)^2}. \]

where $n$ and $p$ are electron and hole carrier densities, respectively; $\mu_n$ and $\mu_p$ are the respective mobilities. There are three equations but four unknowns. Thus, we can solve for $p$ as a function of $n$. Parametrically plotting $p$ as a function of $n$ for different temperatures [inset, Fig. 7(a)] indicates that the curves are identical. It is unlikely that there is any significant temperature dependence to either $n$ or $p$ since previous work has shown that the magnetic susceptibilities of these compounds are weak functions of temperature.$^{16,18}$

From the inset of Fig. 7(a), one finds that a given value of $n$ yields a value for $p$ that is the same at all temperatures. Based on the fact that the thermopower is negligible (Fig. 2), it seems reasonable to choose $n=p$, as is done in the inset of Fig. 7(a). From this, we can therefore deduce the values of $n$ and $p$ as a function of $x$ [inset, Fig. 7(b)]. There is little variation in the carrier concentration with $x$, although it appears that in retrospect, based on this work, our previously derived values for $n$ and $p$ for Ti$_3$SiC$_2$ (Ref. 16) were off by a factor of $\approx 2$.

The electron and hole mobilities deduced assuming $n=p$ as a function of $x$ and $T$ are plotted in Figs. 7(a) and 7(b), respectively. Not surprisingly the mobilities of the end members are higher than those for the solid solutions. This effect is indeed consistent with the fact that the $\alpha$‘s for the solid solutions are also lower than those for either end members (Fig. 4). Also note that $R_H < 0$ because $\mu_n > \mu_p$. The increasingly negative $R_H$ with increasing $T$ is due to the fact that the holes scatter more easily at high $T$ than the electrons do.
The thermal conductivity (Fig. 5) of all compositions is found to be high at 300 K and does not change appreciably with the substitution of Ge for Si. At room temperature, all the thermal conductivities converge, similar to the resistivities. The absence of a maximum in \( k \) associated with the phonon conductivity in the mixtures is presumably due to a combination of solid solution and grain boundary scattering. This result is supported by the fact the residual electrical resistivities of the solid solutions are also higher than those for the end members. In any case, the fact that the room temperature value for \( k \) scales with \( \rho \), independent of whether there is sizable phonon contribution to \( k \), strongly suggests that nearly all of the entropy transport takes place through the charge carriers, in agreement with a Wiedemann-Franz analysis of the electrical and thermal conductivities.

Remarkably, the substitution of Si by the Ge atom does not impact the elastic properties. Based on the results shown in Table I, it is obvious that substitution of Ge for Si in Ti\(_3\)Si\(_{1-x}\)Ge\(_x\)C\(_2\) has a small effect: only minor (<10%) solid solution softening is observed. The agreement between the bulk modulus at \( x=0.5 \) measured in this work (169 GPa) and that measured by x-ray diffraction in an anvil cell (183±4 GPa) is good.\(^{23}\) Furthermore, the agreement between the values of the elastic constants for \( x=1 \) derived from our \textit{ab initio} calculations and experiment (last two rows in Table I) is quite gratifying. The value of \( B \) is also in good agreement with the 198 GPa value predicted by Zhou \textit{et al.}\(^{24}\)

Interestingly, while the calculations indicate that \( c_{11} \) and \( c_{13} \) are smaller in \( x=1 \) than in \( x=0 \), \( c_{12}, c_{33}, \) and \( c_{44} \) are larger (Table II).

On the other hand, the TCE of Ti\(_3\)GeC\(_2\) is one of the lowest measured for a MAX phase to date. This lower value is consistent with the fact that the calculated value for \( c_{33} \) in Ti\(_3\)GeC\(_2\) is larger than in Ti\(_3\)SiC\(_2\) (Table II). It is also noteworthy that the \( c \) axis lattice constant of \( x=1 \) is only 0.5\% bigger than that of \( x=0 \) even though Ge has a significantly larger radius than both Si and Al, again suggesting that Ge may be more tightly bound.

**VI. SUMMARY AND CONCLUSIONS**

We have completed systematic measurements of the electronic, thermal, and elastic properties of Ti\(_3\)Si\(_{1-x}\)Ge\(_x\)C\(_2\). Surprisingly the substitution of Ge for Si in Ti\(_3\)SiC\(_2\) has little effect on the properties. From the conductivity, magnetoresistance and the Hall effect, utilizing a two-band model, we find a temperature-independent charge carrier density wherein \( n=p=2\times10^{27} \text{ m}^{-3} \). The reduction in thermal conductivity and higher residual resistivity demonstrates the role of the defect scattering in the solid solutions. Finally, the calculated elastic properties are in very good agreement with the experiment.

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