Electrical and Thermal Transport Properties of

\( \text{M}_2\text{AlC}, \text{where } M = \text{Ti, Cr, Nb and V} \)


* Department of Physics and Astronomy, Rowan University, Glassboro, NJ 08028
‡ Department of Materials Engineering, Drexel University, Philadelphia, PA 19104
‡‡ 3ONE2, Voorhees, NJ

Abstract

In this paper we report on a systematic investigation, in the 5 to 300 K temperature regime, of the electronic, magneto-transport, thermoelectric, thermal and elastic properties of four \( \text{M}_2\text{AlC} \) phases: \( \text{Ti}_2\text{AlC}, \text{V}_2\text{AlC}, \text{Cr}_2\text{AlC} \) and \( \text{Nb}_2\text{AlC} \). The electrical conductivity, Hall coefficient and magnetoresistances are analyzed within a two-band framework assuming a temperature-independent charge carrier concentration. As with other MAX-phase materials, these ternaries are nearly compensated, viz. the densities and mobilities of electrons and holes are almost equal over the temperature regime explored. There is little correlation between the Seebeck and Hall coefficients. With Young’s and shear moduli in the 270 GPa and 120 GPa range, respectively, the phases studied herein are reasonably stiff. With room temperature thermal conductivities in the 25 W/m K range (45 W/m K for \( \text{V}_2\text{AlC} \)) they are also good thermal conductors.

PACS Nos. 72.15.Eb, 72.15.Gd, 71.20.Be
*) Current address: Thomson TWW Lancaster R&D Center, Lancaster, PA 17601
I. INTRODUCTION

Recent interest in an unusual class of 50+ layered ternary carbides and nitrides has been generated as a result of the densification and characterization of phase-pure samples with the general chemical formula: $M_{n+1}AX_n$ where $n = 1$ to $3$, M is an early transition metal, A is an A-group element (mostly IIIA and IVA) and X is either C and or N. Most of these ternaries were first synthesized in powder form more than 35 years ago, yet little was known about their properties until recently. Partially because these materials are comprised of $M_{n+1}X_n$ layers interleaved with pure A layers, and partially because of how they deform they are best described as nanolaminates. As a result of this layered structure they are readily machinable, despite the fact that some of them are elastically quite stiff, as well as lightweight. They are also excellent electric and thermal conductors. When combined with the low friction coefficients associated with their basal planes, and the excellent oxidation resistances of some of them, their potential in applications such as rotating contacts at elevated temperatures becomes obvious.

To date, by far the most studied of this group of materials is Ti$_3$SiC$_2$. Some work has been geared toward understanding the properties of Ti$_3$AlC$_2$ and Ti$_4$AlN$_3$ and, to a lesser extent, Ti$_3$GeC$_2$. Yet much of the interesting physics leading to the properties of these materials can best be evaluated and understood through systematic investigations of the materials where the elemental constituents can be varied, while maintaining the same crystallographic structure. One way to undergo such a systematic study is to investigate several different phases from the M$_2$AX group of MAX-phase materials. Over 40 M$_2$AX phases are known to exist: they include 11 different A-group elements and 9 different early transition metals. In fact, the structures more extensively studied, M$_4$AX$_3$,
and M₃AX₂, are much more of an exception, consisting of only four known compounds. Recently we reported also on some elastic and electronic properties of some select MAX phases.¹²

In this paper - which is a continuation of our efforts in understanding the chemistry/physical property relationships in these compounds - we report on the 5 to 300 K electrical resistivities, Hall and Seebeck voltages, magnetoresistances, thermal and elastic properties of the Al-containing phases: Ti₂AlC, V₂AlC, Cr₂AlC and Nb₂AlC. Investigating this series allowed us to look for systematic trends when adding electrons across three columns of the periodic table (viz. Ti, V, Cr), while also attempting a comparison between elements in a single column (V and Nb).

II. EXPERIMENTAL DETAILS

Polycrystalline bulk samples of these phases were fabricated by reactively hot isostatically pressing a stoichiometric mixture of powders of the constituent elements. Details of the V₂AlC and Nb₂AlC syntheses are given elsewhere.¹³,¹⁴ The Ti₂AlC and Cr₂AlC samples were obtained from 3ONE2, Voorhees, NJ. The latter were made by pressureless sintering of pre-reacted powders. X-ray diffractometry indicated that the materials were predominantly phase pure. All samples were greater than 99 % of their theoretical density.

Polycrystalline parallelepiped shaped specimens with approximate dimensions 1 × 1 × 10 mm³ were cut from the bulk samples. The electrical resistivity ρ, Hall voltage VH, and magnetoresistance MR = [ρ(B)- ρ(0)]/ρ(0) were measured for temperatures T ranging between 5 and 300 K and magnetic fields B, up to 9 T with a Quantum Design
Physical Properties Measurement System (PPMS). A specially designed sample holder - with spring-loaded gold-coated contacts - was used to mount the samples for electrical transport measurements. The voltage sensitivity was roughly 5 nV, and no contact heating was observed for currents up to 300 mA. Measurements were performed by a four-probe method to eliminate contact resistance for these low-resistivity materials. This configuration allowed a simultaneous measurement of the transverse and longitudinal magnetic-field-dependent voltages. The magnetoresistive component of the measured voltage and extraction of the Hall signal were achieved by magnetic field reversal and subtraction of the measured voltages to separate those components even and odd in magnetic field. Thermal voltages were eliminated from the measured values by use of a low-frequency ac current technique.

The Seebeck voltages were also measured using the PPMS configured with the thermal transport option (TTO) from 5 to 300 K in zero magnetic field. The TTO allows sequential measurements of the thermal conductivity, Seebeck voltage, and electrical resistivity at each temperature. This measurement was made by attaching four leads, each with a large thermal conductance, to the sample with conducting silver epoxy. A temperature gradient was established by applying heat at one end of the specimen while holding the other end at constant temperature by maintaining good thermal contact with a low-temperature reservoir. Calibrated Cernox thermometers are attached to the sample between 4 and 7 mm apart. The temperature difference is monitored and the voltage measured at the same positions along the sample.

Ultrasonic measurements of elastic moduli were carried out using a RAM 10000 (Ritec) utilizing an echo-pulsed phase-sensitive detection technique for determining the
time-of-flight (TOF) of the ultrasonic wave. This system was able to provide absolute and relative sound velocity measurements with a precision of 5 ppm. TOF of 10- and 15 MHz tone bursts produced by a lithium niobate transducer were measured on 8×8×8 mm³ cubes cut from M₂AlC samples. In all cases Salol was used as the ultrasonic transducer-bonding compound. Ultrasonic velocities were then used to calculate the bulk moduli, \( B \), and Poisson’s ratio, \( \nu \), assuming the medium is isotropic.

### III. RESULTS

*Electronic properties*

Figure 1 presents the measured resistivities as a function of temperature. The slopes of the curves for the V and Nb-containing materials are similar, with Nb₂AlC having a slightly higher overall resistivity. The Cr and the Ti-containing materials have somewhat stronger temperature dependences. Of the materials measured, V₂AlC has the largest residual resistance ratio \([\text{RRR} = \rho(300 \text{ K})/\rho(5 \text{ K})]\) of about 6.5.

The Hall number, \( R_H \), is plotted in Fig. 2 as a function of temperature. With the exception of Cr₂AlC for which \( R_H \) is slightly positive, \( R_H \) for the rest is negative. Although results for only one sample are shown for clarity, three samples of Cr₂AlC were measured all showing a small positive Hall number. Also observed in Fig. 2 are the temperature dependences of \( R_H \). Note that some tend toward zero as the temperature is lowered, while Nb₂AlC becomes more negative as the temperature is decreased.

Figure 3a is a plot of \( \alpha \) which is related to the relative change in resistivity with applied magnetic field, \( B \) (see Eq. 2, below). The temperature dependencies of the
Seebeck voltages are shown in Fig. 4. In general they are low and tend to fluctuate around zero and change sign with increasing temperatures.

The thermal conductivity results are shown in Fig. 5a. The conductivities rise rapidly in the 5-100 K temperature range and then tend to plateau. At $\approx 22$ W/m K, the room temperature conductivity $\kappa$ of Cr$_2$AlC is the lowest measured; at $\approx 48$ W/m K, V$_2$AlC is the highest, with Ti$_2$AlC and Nb$_2$AlC in between. Figure 5b plots the temperature dependence of the Lorenz number $L = \rho \kappa / T$. Note that at higher temperatures, the Lorenz number for Nb$_2$AlC asymptotically approaches the horizontal line drawn at $L_0 = 2.45 \times 10^{-8}$ W$\Omega$/K$^2$, which represents the value of the Lorenz number when the phonon contribution to the total thermal conductivity is negligible.

IV. DISCUSSION

The resistivities for all materials investigated herein drop linearly with decreasing temperatures (Fig. 1). This metal-like behavior, characteristic of all MAX phases explored to date,$^{15,10}$ results from the large density of states at the Fermi level $N(E_F)$ of these solids.$^{12,16}$

To shed further light on the mechanisms of electronic conduction in these solids, it is useful to analyze the magneto- and electro-transport results. A temperature-dependent Hall number requires at least a two-band model to explain the results. Within a two-band framework, the expression used to describe the Hall number $R_H$ is:

$$R_H = \frac{(\mu_p^2 p - \mu_n^2 n)}{e(\mu_p p + \mu_n n)^2}$$

(1)
This expression contains four unknowns: $\mu_p$, $\mu_n$, $p$, and $n$ which are the hole and electron mobilities and the hole and electron concentrations, respectively. To solve completely for each unknown, three additional constraints are required. In the two-band model the magnetoresistance $\Delta \rho/\rho = [\rho(H) - \rho(H=0)/\rho(H=0)]$ and the electrical conductivity $\sigma$ are described by:

$$\frac{\Delta \rho}{\rho} = aB^2 = \frac{\mu_n \mu_p np(\mu_n + \mu_p)^2}{(n\mu_n + p\mu_p)^2} B^2 \quad (2)$$

$$\sigma = \frac{1}{\rho} = e(n\mu_n + p\mu_p) \quad (3)$$

To solve the problem an additional constraint is required. Given the small Seebeck and Hall coefficients it is reasonable to choose carrier concentrations that are temperature independent (a reasonable assumption for metals) and, as important based on previous work, roughly equal numbers for the densities of the electrons and holes.

Thus solving the above expressions, assuming the $n = p$, we find that at all temperatures, for the three materials with negative Hall coefficients, $\mu_p \sim 0.8-0.9 \mu_n$. In Cr$_2$AlC, with its positive $R_H$, $\mu_p \sim 1.02 \mu_n$. The temperature dependence of $R_H$ is imbedded in the mobility. The required temperature dependent mobilities are shown in Fig. 3b.

The carrier concentrations for Ti$_2$AlC and Cr$_2$AlC are $1.0 \times 10^{27}$ and $1.2 \times 10^{27}$ m$^{-3}$, respectively; those for V$_2$AlC and Nb$_2$AlC are identical at $2.7 \times 10^{27}$ m$^{-3}$. These values are quite reasonable and are comparable with those determined for the M$_3$AX$_2$ compounds, Ti$_3$SiC$_2$ and Ti$_3$GeC$_2$ ($\approx 2.0 \times 10^{27}$ m$^{-3}$)$^{10}$ and Ti$_3$AlC$_2$ ($\approx 1.5$ to $2 \times 10^{27}$ m$^{-3}$).$^9$ Not surprisingly, there is no correlation between $n$ and $p$ and $N(E_F)$.$^{12,18}$
The results to date strongly suggest that the electronic properties of the MAX phases are dominated by the $d$ orbitals of the $M$-elements and that these properties are, in turn, comparable to those of the transition metals. With this in mind, it is thus useful to briefly summarize what is known about the transition metal electronic transport. According to Kulikov, the resistivity of transition metals can be written in a fashion similar to the Bloch-Grüneisen by:

$$\rho \propto \frac{1}{n\tau} \frac{N(E_F)\lambda\Theta}{n} \left(\frac{T}{\Theta}\right)^5 \varphi_5(\Theta/T)$$  \hspace{1cm} (4)

where $\tau$ is the scattering time, $N(E_F)$ the density of states at the Fermi level, $\lambda$ the electron-phonon coupling factor, and $\Theta$ the Debye temperature. According to Eq. (4) and assuming Matthieusen’s rule, $\mu(T=0) \propto \lambda\left(RRR-1\right)/N(E_F)$ where $(RRR-1)$ relates to the intrinsic resistivity. Plotting the electronic mobilities at 5 K as a function of $(RRR-1)/N(E_F)$ (Fig. 3c) for the compounds tested in this work, together with previously reported corresponding values of other MAX phases, we find that there is a linear relationship, indicating that the electron-phonon coupling is more or less constant for all materials.

The sign of the Seebeck voltage is often used to qualitatively determine the sign of the dominant charge carrier. With this in mind, it may be expected that the Seebeck voltages should roughly reflect the sign and shape of $R_H$ as a function of temperature. Comparing the Hall (Fig. 2) and the Seebeck (Fig. 4) coefficients it is clear there are no obvious correlations between them. Three of the materials have clearly changing signs of
the Seebeck voltage with no corresponding changes in $R_H$, again providing evidence that these compounds are nearly compensated.

**Thermal Properties:**

In agreement with previous work, the MAX phases are good thermal conductors, because they are good electronic conductors. However, the results shown in Fig. 5b, demonstrate that the total thermal conductivity has electronic and phonon contributions, $\kappa_{el}$ and $\kappa_{ph}$, respectively. Since phonons are easily scattered by defects, especially in transition metal carbides and nitrides, $\kappa_{ph}$ should be sensitive to sample quality. One measure of defects in a metal is the $RRR$. In Fig. 5c we plot $\kappa_{ph} = (\kappa - L_0T/\rho)$ calculated at room temperature as a function of $RRR$. It is clear that the differences in the thermal conductivities can be attributed to differences in the resistivities, which in turn are related to the density of states, and the defect density, which scatter both the phonons and charge carriers. To a lesser extent, the stiffness also plays a role, but only in compounds where $\kappa_{ph}$ is large; viz. materials with high resistivities where $\kappa_{el}$ is small or very clean materials, which provide a long phonon mean free path.

**Elastic Properties**

Whereas the differences in the $\kappa_{ph}$ values are more dependent on defect density than on the elastic properties, there are clear differences between the measured sound velocities in these compounds (Table I). They range from a high of $\approx 8500$ m/s for Ti$_2$AlC to about 7000 m/s for Nb$_2$AlC. Most of these variations can be attributed to
differences in density. The bulk moduli calculated in this work (column 8, Table 1) are \( \approx 25 \% \) lower than those recently directly measured in a diamond anvil cell.\textsuperscript{20}

Also included in Table 1 are recent \textit{ab initio} calculations on the same compounds. With the notable exception of \( \text{Cr}_2\text{AlC} \), the agreement between the calculated and measured elastic constants is quite good. This structural destabilization of \( \text{Cr}_2\text{AlC} \) was thus unexpected. It is in line, however, other recent observations. As noted above it is seen in direct measurements of \( B \).\textsuperscript{20} It is also manifested in a 7\% drop in the energy of the highest energy Raman vibrational mode – involving the motion of the A and M atoms along the \( c \) axis - of \( \text{Cr}_2\text{AlC} \) relative to the Ti and V-containing structures. Lastly, at \( \approx 12 \times 10^{-6} \text{ K}^{-1} \), the thermal expansion coefficient of \( \text{Cr}_2\text{AlC} \)\textsuperscript{21} is \( \approx 50 \% \) higher than that of either \( \text{Ti}_2\text{AlC} \)\textsuperscript{22} or \( \text{Nb}_2\text{AlC} \).\textsuperscript{23}

\textbf{V. Conclusions:}

By measuring the electrical and thermal conductivities, Hall and Seebeck coefficients between 5 and 300 K of the Ti, V, Cr and Nb-containing \( M_2\text{AlC} \) phases, we have shown that, like other MAX phases, the electrical conductivities in these solids is compensated, with \( n \approx p \approx 2 \times 10^{27} \text{ m}^{-3} \), and \( \mu_n \approx \mu_p \) over the entire temperature range examined. Examining the mobility at 5 K, it was shown that the electron-phonon coupling of all studied MAX phases is more or less the same, irrespective of \( d \) element or structure. On the other hand, the phonon contribution to the total thermal conductivity was shown to be proportional to the defect concentration. We also measured the longitudinal and shear velocities of sound in these materials and shown them to be elastically quite stiff.

\textbf{Acknowledgements}
Partial support for this work from the National Science Foundation (DMR 0072067) is gratefully acknowledged. SEL and JDH acknowledge support from the New Jersey Commission on Higher Education and NSF Grant DMR 0114073.
References:

Table 1. Young’s, $E$, shear, $G$, and bulk $B$, moduli of the M$_2$AlC phases. $B$ and $B^*$ are determined from velocity of sound and directly from diamond anvil cell. Also listed are the longitudinal $v_l$ and shear $v_s$ sound velocities and Poisson ratio, $\nu$. $\Theta_D^e$ corresponds to the Debye temperature calculated from the mean sound velocity, while $\Theta_D^T$ to that determined from low temperature heat capacity measurements.

<table>
<thead>
<tr>
<th>Solid</th>
<th>Density g/cm$^3$</th>
<th>$v_l$ (m/s)</th>
<th>$v_s$ (m/s)</th>
<th>$G$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
<th>$B$ (GPa)</th>
<th>$B^*$ (GPa)</th>
<th>$\Theta_D^e$ (K)</th>
<th>$\Theta_D^T$ (K)</th>
<th>$N(E_F)$ (1/eV.unit cell)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$AlC Theory</td>
<td>4.1</td>
<td>8525</td>
<td>5298</td>
<td>118</td>
<td>277</td>
<td>0.19</td>
<td>144</td>
<td>186$^a$</td>
<td>732</td>
<td>672$^b$</td>
<td>619$^c$</td>
<td>4.9$^b$</td>
</tr>
<tr>
<td>V$_2$AlC Theory</td>
<td>4.81</td>
<td>7989</td>
<td>4913</td>
<td>116</td>
<td>277</td>
<td>0.20</td>
<td>152</td>
<td>201$^a$</td>
<td>696</td>
<td>625$^b$</td>
<td>658$^c$</td>
<td>7.5$^b$</td>
</tr>
<tr>
<td>Cr$_2$AlC Theory</td>
<td>5.24</td>
<td>7215</td>
<td>4450</td>
<td>102</td>
<td>245</td>
<td>0.20</td>
<td>138</td>
<td>166$^a$</td>
<td>644</td>
<td>589$^b$</td>
<td>673$^c$</td>
<td>14.5$^b$</td>
</tr>
<tr>
<td>Nb$_2$AlC Theory</td>
<td>6.34</td>
<td>7125</td>
<td>4306</td>
<td>117</td>
<td>286</td>
<td>0.21</td>
<td>165</td>
<td>208$^a$</td>
<td>577</td>
<td>NA</td>
<td>540$^c$</td>
<td>NA</td>
</tr>
<tr>
<td>a Ref. 20.</td>
<td>b Ref. 18.</td>
<td>c Ref. 12.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure Captions:

Figure 1: Temperature dependence of resistivity.

Figure 2: Temperature dependence of Hall coefficients.

Figure 3: a) Semi-log plot of $\alpha$ as a function of temperature for several M$_2$AlC materials. The parameter $\alpha$ was extracted assuming $\Delta \rho/\rho(B=0) = \alpha B^2$. b) Temperature dependence of electron (solid symbols) and hole (open symbols) mobilities. c) Mobilities at 4 K versus $(RRR-1)/N(E_F)$. The linear relationship indicates the electron-phonon coupling is similar in all studied MAX phases.

Figure 4: Plot of Seebeck coefficients as a function of temperature.

Figure 5: a) Temperature dependence thermal conductivities, $\kappa$. b) Temperature dependence of Lorenz number. Note line near $2.5 \times 10^{-8} \text{ W}\Omega/\text{K}^2$, is theoretical value for thermal conduction by charge carriers only. c) Phonon conductivity, $\kappa_{ph} = (\kappa - L_0 T/\rho)$ versus residual resistivity ratio, indicating that $\kappa_{ph}$ is dominated by scattering.
Figure 1:
Figure 2:
Figure 3:
Figure 4

Seebeck Coef. (µV/K) vs. Temperature (K) for V$_2$AlC, Ti$_2$AlC, Nb$_2$AlC, and Cr$_2$AlC.
Figure 5a:
Lorenz Number ($\Omega/\kappa$)

Temperature (K)

Cr$_2$AlC

V$_2$AlC

Ti$_2$AlC

Nb$_2$AlC
Figure 5c