Electrical transport, thermal transport, and elastic properties of $M_2AIC$ ($M=$Ti, Cr, Nb, and V)


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In this paper we report on a systematic investigation, in the 5 to 300 K temperature regime, of the electronic, magnetotransport, thermoelectric, thermal, and elastic properties of four $M_2AIC$ phases: Ti$_2$AIC, V$_2$AIC, Cr$_2$AIC, and Nb$_2$AIC. 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. 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 V$_2$AIC) they are also good thermal conductors.

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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 proper-

In this paper—which is a continuation of our efforts in understanding the chemistry and/or physical property relationships in these compounds—we report on the 5 to 300 K electrical resistivities, Hall and Seebeck voltages, magnetoresistances, and thermal and elastic properties of the Al-containing phases: Ti$_2$AIC, V$_2$AIC, Cr$_2$AIC, and Nb$_2$AIC. 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 V$_2$AIC and Nb$_2$AIC syntheses are given elsewhere. The Ti$_2$AIC and Cr$_2$AIC samples were made by pressureless sintering of prereacted 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 $1 \times 1 \times 10$ mm$^3$ were cut from the bulk samples. The electrical resistivity $\rho$, Hall voltage $V_H$, and magnetoresistance $MR=[(\rho(B)-\rho(0))/\rho(0)]$ were measured for temperatures $T$ ranging between 5 and 300 K and magnetic fields $B$, up to 9 T with Quantum Design’s Physical Properties Measurement System (PPMS). A specially de-

d signed 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 the 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 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 a 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-MHz and 15-MHz tone bursts produced by a lithium niobate transducer were measured on $8 \times 8 \times 8$ mm$^3$ cubes cut from $M_2$AlC samples. In all cases phenyl salicylate was used as the ultrasonic transducer-bonding compound. Ultrasonic velocities were then used to calculate the bulk modulus, $B$, and Poisson’s ratio, $\nu$, assuming that the medium is isotropic.

III. RESULTS

Figure 1 presents the measured resistivities as a function of temperature. The slopes of the curves for the V-containing and Nb-containing materials are similar, with Nb$_2$AlC having a slightly higher overall resistivity. The Cr-containing and the Ti-containing materials have somewhat stronger temperature dependences. Of the materials measured, V$_2$AlC has the largest residual resistance ratio (RRR) [$\text{RRR} = \rho(300 \text{ K})/\rho(5 \text{ K})$] of about 6.5.

The Hall number, $R_H$, is plotted in Fig. 2 as a function of temperature. With the exception of Cr$_2$AlC for which $R_H$ is slightly positive, $R_H$ is negative. Although results for only one sample are shown for clarity, three samples of Cr$_2$AlC 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 Nb$_2$AlC becomes more negative as the temperature is decreased.

Figure 3(a) 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. 5(a). The conductivities rise rapidly in the 5–100 K temperature range and then tend to plateau. At $=22$ W/m K, the room temperature conductivity $\kappa$ of Cr$_2$AlC is the lowest measured; at $=48$ W/m K, that of V$_2$AlC is the highest, with those of Ti$_2$AlC and Nb$_2$AlC in between. Figure 5(b) plots the temperature dependence of the Lorenz number $L = \rho e/kT$. Note that at higher temperatures, the Lorenz number for Nb$_2$AlC asymptotically approaches the horizontal line drawn at $L_0 = 2.45 \times 10^{-8}$ V$^2$/K$^2$, which represents the value of the Lorenz number when the phonon contribution to the total thermal conductivity is negligible.

IV. DISCUSSION

A. Electronic properties

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, results from the large density of states at the Fermi level $N(E_F)$ of these solids.

To shed further light on the mechanisms of electronic conduction in these solids, it is useful to analyze the magnetotransport and electrotransport 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
This expression contains four unknowns: $\mu_\text{p}$, $\mu_\text{n}$, $p$, 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.

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 that $n = p$, we find that at all temperatures for the three materials with negative Hall coefficients, $0.8–0.9 \times 10^{27}$ m$^{-3}$. The temperature dependence of $R_H$ is imbedded in the mobility. The required temperature-dependent mobilities are shown in Fig. 3.

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 $M_2AX_2$ compounds, Ti$_3$SiC$_2$ and Ti$_3$GeC$_2$ (=2.0 $\times 10^{27}$ m$^{-3}$) (Ref. 10) and Ti$_3$AlC$_2$ (=1.5 to $2 \times 10^{27}$ m$^{-3}$). Not surprisingly, there is no correlation between $n$ and $p$ and $N(E_F)$. The linear relationship indicates the electron-phonon coupling is similar in all studied MAX phases.

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
versus residual resistivity ratio, indicating that scattering.

The Fermi level, \( n \), and the Grüneisen integral, and \( \Theta \) the Debye temperature. According to Eq. (4) and assuming Matthiessen’s rule, \( \mu(T = 0) \propto \lambda(\text{RRR} - 1)/N(E_F) \) where (RRR - 1) relates to the intrinsic resistivity. Plotting the electronic mobilities at 5 K as a function of \( (\text{RRR} - 1)/N(E_F) \) [Fig. 3(c)] for the compounds tested in this work, together with previously reported corresponding values of other MAX phases,\(^9,10\) 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 \( R_{H} \), providing additional evidence that these compounds are nearly compensated.

### B. Thermal properties

In agreement with a previous work, the MAX phases are good thermal conductors, because they are good electronic conductors. However, the results shown in Fig. 5(b), 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,\(^9,10\) \( \kappa_{ph} \) should be sensitive to sample quality. One measure of defect density in a metal is the RRR. In Fig. 5(c), we plot \( \kappa_{ph} = (k - L_0T/\rho) \) 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.

### C. 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 \( \approx 8500 \text{ m/s} \) 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 I) are \( \approx 25\% \) lower than those recently directly measured in a diamond-anvil cell.\(^20\)

Also included in Table I are recent \( \textit{ab initio} \) calculations on the same compounds. With the notable exception of Cr\(_2\)AlC, the agreement between the calculated and measured elastic constants is quite good. This structural destabilization of Cr\(_2\)AlC was thus unexpected. It is in line, however, with other recent observations. As is noted above, it is seen in direct measurements of \( B \).\(^20\) It is also manifested in a 7% drop in the energy of the highest energy Raman vibrational

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**FIG. 5.** (a) Temperature dependence of the thermal conductivity, \( \kappa \). (b) Temperature dependence of Lorenz number. Note that the line near \( 2.5 \times 10^{-8} \text{ V}^2/\text{K}^2 \) is theoretical value for thermal conduction by charge carriers only. (c) Phonon conductivity, \( \kappa_{ph} = (k - L_0T/\rho) \) versus residual resistivity ratio, indicating that \( \kappa_{ph} \) is dominated by scattering.
mode—involving the motion of the A and M atoms along the c axis—of Cr2AlC relative to the Ti-containing and V-containing structures. Lastly, at ≈12 × 10^6 K^−1, the thermal expansion coefficient of Cr2AlC is ≈50% higher than that of either Ti2AlC (Ref. 22) or Nb2AlC.

### 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 M2AlC phases, we have shown that, like other MAX phases, the electrical conductivities in these solids are compensated, with \( n ≈ p ≈ 2 \times 10^{27} \text{ m}^{-3} \), and \( \mu_s ≈ \mu_p \) 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 have shown them to be elastically quite stiff.

### ACKNOWLEDGMENTS

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TABLE I. Young’s E, shear G, and bulk B moduli of the M2AlC 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 \( \Theta_D^T \) is that determined from low-temperature heat-capacity measurements.

<table>
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<th>Solid</th>
<th>Density (g/cm³)</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>
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\(^a\)Reference 20.
\(^b\)Reference 18.
\(^c\)Reference 12.

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References:
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