The compression behavior of the hexagonal $MAX$ phases $M_2AX$ ($M=\text{Ti, V, Cr, Nb, and Ta}$)—selected because they represent two series; a horizontal series in which the atomic number of the $M$ element increases from 23 to 25 and a vertical series where the $M$ element ($V$, $Nb$, or $Ta$) belongs to the VA group—were measured as a function of quasi-hydrostatic pressure up to 55 GPa, using a synchrotron radiation source and a diamond-anvil cell. No phase transformations were observed in any of these compounds. The contractions for the Ti- and V-containing compositions were higher along the $c$ axis than along the $a$ axis; the opposite was true for Cr$_2$AlC and Nb$_2$AlC. In Ta$_2$AlC, the shrinkages in both directions are almost identical. For V$_2$AlC the bulk modulus $K_0$ is 201±3 GPa. As V is substituted by Nb, $K_0$ increases by 4%. The $K_0$ of Ta$_2$AlC, 251 GPa, is the highest reported for any $MAX$ phase to date. For Ti$_2$AlC, $K_0$ is 186±2 GPa. As Ti is substituted by V, $K_0$ increases by 8%. Surprisingly, the substitution of Ti by V or Cr leads to a reduction in $K_0$ to 165±2 GPa. With the notable exception of Cr$_2$AlC, the agreement between experimental and calculated $K_0$ values is acceptable. The presence of C in these structures appears to have a stabilizing effect on the $M$-Al bonds, presumably by attracting electrons to the $M$-X bonds.

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also predicted that, as V is substituted by Nb or Ta, $K_0$ would increase by 5 and 13 %, respectively.

The combination of easy machinability, relative low densities (in some of the phases) and high elastic constants, together with the possibility of extremely high damping\(^8,15\) is one that to date had not been possible. Thus one motivation for this work was to identify compositions of potential technological interest. The second motivation was to directly measure the bulk moduli of experimental results with the theoretical work. As noted above, we chose to measure the bulk moduli of $M_2$AlC ($M$ =Ti, V, Cr, Nb, and Ta) phases. These compounds were selected because they represent two series; a horizontal series in which the atomic number of the $M$ element increases from 23 to 25; and a vertical series where the $M$ elements (V, Nb, and Ta) belong to the VA group. We were also interested in exploring the stability of these phases at high pressures.

II. EXPERIMENTAL DETAILS

The processing details can be found elsewhere. In short, fully dense, predominantly single phase samples of Ti$_2$AlC,\(^20\) V$_2$AlC,\(^21\) and Nb$_2$AlC,\(^22\) were prepared by reaction hot isostatic pressing (HIP) the appropriate stoichiometric mixtures of powders of the constituent elements and/or appropriate carbides.

To fabricate the Ta$_2$AlC samples Ta, C, and Al powders (99% pure, −325 mesh, Alfa Aesar, Ward Hill, MA) were mixed in stoichiometric proportions, ball milled, cold pressed and placed in a graphite die in a vacuum hot press. The latter was evacuated and heated to 650 °C for 6 h, and then to 1600 °C. The sample was held at the maximum applied uniaxial pressure (≈30 MPa) and temperature for 8 h. The Cr$_2$AlC samples were fabricated by reactive HIPing of Cr, Al, and graphite powders (99.9% and −325 mesh, Alfa Aesar, Ward Hill, MA). The powders were mixed in stoichiometric proportions and ball milled in a plastic container with alumina balls for 1 h. The mixed powders were sealed in borosilicate glass tubes, under mechanical vacuum and heated to 650 °C for 10 h. This procedure led to the collapse of the glass tubes and allowed the powders to prereact. The collapsed tubes were placed in the HIP, heated at 10 °C/min to 650 °C, followed by a rate of 2 °C/min to 750 °C. The chamber was then pressurized with Ar gas to 70 MPa. Once pressurized, the heating resumed at 10 °C/min to 1200 °C, held at temperature for 12 h and furnace cooled. The pressure at 1200 °C was ≈100 MPa.

An online image plate recorded the angle-dispersive diffraction patterns of V$_2$AlC and Ti$_2$AlC; the measurements were conducted at room temperature using synchrotron radiation at the High Pressure Collaborating Access Team (HP-CAT) beam line at the Advanced Photon Source (Chicago). A monochromatic beam—with a wavelength $\lambda=0.4066$ Å for V$_2$AlC and $\lambda=0.3678$ Å for Ti$_2$AlC—was focused to a 10 μm spot size on the sample. For Nb$_2$AlC and Ta$_2$AlC, the x-ray diffraction patterns—using a $\lambda=0.496$ Å of a monochromatic beam focused down to a 35 μm spot size—were collected at CHESS (Cornell University Ithaca, NY). Diffraction rings were recorded between 2$\theta$=1° and 35°.

For Cr$_2$AlC the diffraction patterns were collected using energy dispersive mode at the bending magnet beamline of the Cornell High Energy Synchrotron Source (CHESS). A solid-state Ge detector, used to detect the diffracted energy, was calibrated with fluorescence standards of $^{57}$Fe and $^{133}$Ba, while the 2$\theta_0$ of 11° was attuned taking diffraction patterns of a gold standard.

Measurements were conducted at room temperature; powdered samples were pressurized using a gasketed diamond-anvil cell (DAC) with a 300 to 400 μm culet. A 250 μm initial thickness rhenium gasket, was indented to about 40–50 μm. Since high purity Al does not undergo structural phase transition at high pressure, has low shear strength, as in our previous work,\(^10,12,23,24\) it was the pressure-transmitting medium of choice. Also since its pressure-volume relation is well established\(^25\) it also acted as a pressure marker. Powdered samples were placed between two pieces of Al foil (≈15 μm thickness) and packed in the 100–150 μm hole.

TABLE I. Ambient pressure lattice parameters and unit cell volumes of $M_2$AlC compounds measured herein. Also listed are previous results. The space group adopted for all phases is P6$_3$/mmc.

<table>
<thead>
<tr>
<th>$M_2$AlC</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Nb</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.065±0.004</td>
<td>2.914±0.003</td>
<td>2.857±0.002</td>
<td>3.103±0.004</td>
<td>3.086±0.006</td>
</tr>
<tr>
<td></td>
<td>3.058$^a$</td>
<td>2.909$^b$</td>
<td>2.854$^b$</td>
<td>3.106$^a$</td>
<td>3.07$^a$</td>
</tr>
<tr>
<td></td>
<td>3.052$^b$</td>
<td>2.925$^d$</td>
<td>2.848$^d$</td>
<td>3.107$^c$</td>
<td>3.099$^f$</td>
</tr>
<tr>
<td></td>
<td>3.062$^d$</td>
<td>3.129$^f$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>13.71±0.03</td>
<td>13.19±0.03</td>
<td>12.81±0.02</td>
<td>13.93±0.03</td>
<td>13.85±0.04</td>
</tr>
<tr>
<td></td>
<td>13.624$^a$</td>
<td>13.127$^b$</td>
<td>12.82$^b$</td>
<td>13.888$^a$</td>
<td>13.8$^c$</td>
</tr>
<tr>
<td></td>
<td>13.64$^b$</td>
<td>13.105$^d$</td>
<td>12.72$^d$</td>
<td>13.888$^c$</td>
<td>13.89$^f$</td>
</tr>
<tr>
<td></td>
<td>13.673$^d$</td>
<td></td>
<td></td>
<td>13.895$^f$</td>
<td></td>
</tr>
<tr>
<td>$V_0$ (Å$^3$)</td>
<td>111.6±0.6</td>
<td>97.0±0.7</td>
<td>90.6±0.5</td>
<td>116.2±0.7</td>
<td>114.4±0.7</td>
</tr>
</tbody>
</table>

$^a$Reference 28.  
$^b$Reference 29.  
$^c$Reference 22.  
$^d$Reference 16.  
$^e$Reference 6.  
$^f$Reference 30.
The FIT2D software\textsuperscript{26,27} was employed to convert the image plate records into 2\theta's and intensities. All cell parameters were determined using least squares refinement on individually fitted peaks.

III. RESULTS AND DISCUSSION

The x-ray powder diffraction patterns collected at 1 atm for Cr\textsubscript{2}AlC, V\textsubscript{2}AlC, Ti\textsubscript{2}AlC, Nb\textsubscript{2}AlC, and Ta\textsubscript{2}AlC are shown in Fig. 1. For all but Ta\textsubscript{2}AlC, all major peaks were assigned to the hexagonal structure \textit{P}6\textsubscript{3}/mmc. A few low intensity impurity peaks, which were not identified, were also observed in Nb\textsubscript{2}AlC and Cr\textsubscript{2}AlC. Figure 2 shows typical high-pressure x-ray diffraction spectra for Cr\textsubscript{2}AlC. Note that upon compression, most peaks remain visible until the highest pressure reached in this study.

In general the agreement between the unit cell parameters measured in this study, those previously reported,\textsuperscript{6,22,26–30} and those predicted from the \textit{ab initio} calculations\textsuperscript{16} is acceptable (Table I). The XRD spectra of the Ta\textsubscript{2}AlC sample, contained extra and overlapping peaks of another phase that we tentatively identified as a new MAX phase. The details of that study will be reported elsewhere.

Figure 3 plots the variations in lattice parameters versus applied quasihydrostatic pressure \(P\). Second order polynomial least square fits resulted in the coefficients listed in Table II. From the results we note that (i) the contraction along the \(a\) direction with pressure is greater than along the \(c\) direction for Nb\textsubscript{2}AlC and Cr\textsubscript{2}AlC, (ii) the opposite is true for Ti\textsubscript{2}AlC and V\textsubscript{2}AlC, and (iii) Ta\textsubscript{2}AlC is unique in that the variations along the two orthogonal directions are almost identical.

Figure 4 plots the axial ratios \((c/c_0)/(a/a_0)\) as a function of pressure. From this figure it is clear that for Ti\textsubscript{2}AlC and

![Intensity graph](image)

FIG. 1. (Color online) Ambient pressure x-ray powder diffraction patterns of \(M_2\)AlC phases studied in this work. Except for Ta\textsubscript{2}AlC, all major peaks were assigned to the hexagonal structure \((P6_3/mmc)\). A few low intensity impurity peaks, which were not identified, were also observed in Nb\textsubscript{2}AlC (arrows) and Cr\textsubscript{2}AlC (the impurity peaks have very low intensity and can not be seen at this scale). The XRD spectrum of the Ta\textsubscript{2}AlC sample, contained extra and overlapping peaks of another phase that we tentatively identified as a new MAX phase.

![X-ray spectra](image)

FIG. 2. X-ray diffraction patterns of Cr\textsubscript{2}AlC MAX phase to pressures up to 50.7 GPa. The 111 aluminum peak was removed for clarity. “UNP” stands for unidentified peak.
V₂AlC the axial ratio decreases before increasing slightly at pressures above ≈30 GPa. For Cr₂AlC and Nb₂AlC, the axial ratio increases with pressure, before leveling out at higher pressures. For Ta₂AlC, the axial ratio hovers around unity before decreasing slightly.

From relative unit cell volume versus pressure plots (Fig. 5) it is clear that Cr₂AlC possesses the lowest bulk modulus, Ta₂AlC the highest, with those of V₂AlC, Nb₂AlC, and Ti₂AlC in between. Least squares fit of these data yield the results listed in Table III. Fitting the same results to the Birch-Murnaghan equation yields

\[ P = 3/2K_0[(V/V_0)^{7/3} - (V/V_0)^{5/3}] \times \left[1 + 3/4(K_0' - 4)[(V/V_0)^{-2/3} - 1]\right] \]

yields \( K_0 \) values that vary from a low of 165±2 GPa for Cr₂AlC, to a high of 251±3 GPa for Ta₂AlC, with the others in between (Table III). The calculated pressure derivative values \( K_0' \) are also listed in Table III. For V₂AlC, \( K_0 \) is 201±3 GPa. As V is substituted by Nb, \( K_0 \) increases by 4%; for Ti₂AlC, \( K_0 \) is 186±2 GPa. As Ti is substituted by V, \( K_0 \) increases by 8%. Surprisingly, the substitution of Ti by Cr leads to reduction in \( K_0 \) to 165±2 GPa.

Based on this work it is clear that the nature of the \( M \) element has a large effect on the bulk moduli of the MAX phases. In a recent paper, Music et al., using \textit{ab initio} calculations, showed that, in Sc₂AlC with \( A=\text{Al}, \text{Ga}, \text{In}, \text{and Ti} \), the bulk modulus was not affected much by the \( A \) substitution. This is also true in Ti₃C₂ phases (\( A=\text{Si, Ge, Al} \)) where the \( A \) element did not have much effect on the bulk modulus, which varied from 206 for Ti₃SiC₂ (Ref. 14) to 226 for Ti₃AlC₂.

The \( K_0 \) values reported herein are in line with previous MAX phase results in that these solids are elastically quite stiff. At this time, Ta₂AlC has the highest bulk modulus of any MAX phase. Also in line with previous work is the stability of these phases under quasihydrostatic pressure. To date all MAX phases have been stable up to ≈50 GPa.

The results obtained in this work are useful in shedding important light on the bonding in these phases. As noted above, the only MAX phase to date for which the pressure contraction along the \( a \) direction was greater than the \( c \) direction was Nb₂AsC. However, since Nb₂AlC and Cr₂AlC (Fig. 3, Table II) behave in the same way, this is no longer the case. From a bonding point of view, this result implies

<table>
<thead>
<tr>
<th>( M₂AIC )</th>
<th>Pressure range</th>
<th>( a/a₀=1+\beta P/P₀+\gamma(P/P₀)^2 )</th>
<th>( c/c₀=1+\beta P/P₀+\gamma(P/P₀)^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1 atm–55 GPa</td>
<td>1−0.0011P/P₀+7×10⁻⁷(P/P₀)²</td>
<td>1−0.00024P/P₀+2×10⁻⁵(P/P₀)²</td>
</tr>
<tr>
<td>Cr</td>
<td>1 atm–51 GPa</td>
<td>1−0.0021P/P₀+2×10⁻⁵(P/P₀)²</td>
<td>1−0.0017P/P₀+1×10⁻⁵(P/P₀)²</td>
</tr>
<tr>
<td>V</td>
<td>1 atm–47 GPa</td>
<td>1−0.0010P/P₀−7×10⁻⁷(P/P₀)²</td>
<td>1−0.0022P/P₀+2×10⁻⁵(P/P₀)²</td>
</tr>
<tr>
<td>Nb</td>
<td>1 atm–38 GPa</td>
<td>1−0.0014P/P₀+3×10⁻⁶(P/P₀)²</td>
<td>1−0.0014P/P₀+9×10⁻⁶(P/P₀)²</td>
</tr>
<tr>
<td>Ta</td>
<td>1 atm–47 GPa</td>
<td>1−0.0012P/P₀+6×10⁻⁶(P/P₀)²</td>
<td>1−0.0012P/P₀+5×10⁻⁶(P/P₀)²</td>
</tr>
</tbody>
</table>
that contraction of the $M$-$X$ bonds (along the $a$ direction) is higher than along the $M$-$Al$ bonds. In other words, the latter are more resistant to deformation than the former. Based on these results it appears that the Nb-Al bonds are stronger than the Nb-C bonds. This is a noteworthy result because—based on the melting points of the early transition metal binary carbides—the $M$-$C$ bonds are believed to be some of the strongest known. For example, the melting point of NbC is 3600 °C. Those of Nb$_2$Al and Nb$_3$Al on the other hand, are ~2000 °C. Similar arguments can be made concerning the Ta-Al bonds in comparison to the Ta-C bonds. According to Fig. 3, they must be quite comparable; again a somewhat surprising conclusion given that the melting point of TaC is 3985 °C, while that of Ta$_2$Al is ~2100 °C. Note that since the $MAX$ phases are near closed packed, the arguments about relative bond strengths and their relationships to melting points, are more tenable than in more open or complex structures.

It thus appears that the presence of C in the interstitial sites of the $M$ octahedra has a stabilizing effect on the $M$-$Al$ bonds. One explanation is that the X atoms attract electrons, that would otherwise go into antibonding $M$-$Al$ orbitals. This not only would explain the stability of the $M$-$Al$ bonds in the ternaries, but also their relative weakness in the binary $M$ aluminides. This conclusion is bolstered by recent $ab$ $initio$ calculations that have shown that in the $M_2$AlC phases of the first transition metal series, as well as Nb$_2$AlC, the C atoms always carry a negative charge. Along the same lines Music $et$ $al.$, using $ab$ $initio$ calculations, showed that the antibonding states in the vicinity of the Fermi level for Sc$_2$AC (where $A$=Al, Ga, In, and Ti), result in a weakening of the overall bonding. These comments notwithstanding, it is hereby acknowledged that more work is needed to explore the validity of some of these arguments.

The results also show that $K_0$ increases as Nb replaces V and Ta replaces Nb. The agreement between our results and those deduced from recent $ab$ $initio$ calculations (Fig. 6) is mixed. (For completeness, Fig. 6 includes previous results for other $MAX$ phases.$^{10,11,14,34}$) For V$_2$AlC and Nb$_2$AlC the agreement is excellent; for Ti$_2$AlC it is within 10%. The $ab$ $initio$ calculations (Ref. 17) underestimate the bulk modulus of Ta$_2$AlC by ~15%, and overestimate the bulk modulus of Cr$_2$AlC by almost 40%. The symbols are data generated in this paper; the square symbols are those for Zr$_2$InC (Ref. 10), Ti$_3$SiC$_2$ (Ref. 14), and Ti$_3$AlN$_3$ (Refs. 11 and 34).

![FIG. 5.](Image)

**FIG. 5.** (Color online) Relative volume of $M_2$AlC phases studied in this work as a function of pressure. Clearly, Cr$_2$AlC possesses the lowest bulk modulus, Ta$_2$AlC the highest, with those of V$_2$AlC, Nb$_2$AlC, and Ti$_2$AlC in between. Lines shown are least square fits of the data points.

![FIG. 6.](Image)

**FIG. 6.** Theoretical versus experimental bulk moduli. The agreement between our results and those deduced from recent $ab$ $initio$ calculations is mixed. Also included are previous results for other $MAX$ phases (Refs. 10, 11, 14, and 34). For V$_2$AlC and Nb$_2$AlC the agreement is excellent; for Ti$_2$AlC it is within 10%. The $ab$ $initio$ calculations (Ref. 17) underestimate the bulk modulus of Ta$_2$AlC by ~15%, and overestimate the bulk modulus of Cr$_2$AlC by almost 40%. The symbols are data generated in this paper; the square symbols are those for Zr$_2$InC (Ref. 10), Ti$_3$SiC$_2$ (Ref. 14), and Ti$_3$AlN$_3$ (Refs. 11 and 34).

**TABLE III.** Relative unit cell volume changes with pressure and summary of experimental and calculated bulk moduli. The pressure derivatives $K'_0$ are also given. All correlation coefficient values were >0.995. Also included are $ab$ $initio$ total energy calculation results by Sun $et$ $al.$ (Ref. 17).

<table>
<thead>
<tr>
<th>$M_2$AlC</th>
<th>$V/V_0=\alpha+\beta P/P_0+\gamma (P/P_0)^2$</th>
<th>$K_0$ (GPa)</th>
<th>$K'_0$ (GPa)</th>
<th>$K_0$ (GPa)</th>
<th>Ref. 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>$1-0.0045P/P_0+2\times10^{-5}(P/P_0)^2$</td>
<td>186.2</td>
<td>4.0±0.1</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>$1-0.0043P/P_0+2\times10^{-5}(P/P_0)^2$</td>
<td>201±3</td>
<td>4.05±0.13</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>$1-0.0058P/P_0+4\times10^{-5}(P/P_0)^2$</td>
<td>165±2</td>
<td>4.1±0.1</td>
<td>226</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>$1-0.0041P/P_0+2\times10^{-5}(P/P_0)^2$</td>
<td>209±2</td>
<td>3.95±0.15</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>$1-0.0036P/P_0+2\times10^{-5}(P/P_0)^2$</td>
<td>251±3</td>
<td>4.5±0.2</td>
<td>221</td>
<td></td>
</tr>
</tbody>
</table>
of Ta$_2$AlC by $\approx 14\%$, while overestimating the bulk modulus of Cr$_2$AlC by $\approx 37\%$. The latter is the most surprising result of this work. However, in line with the aforementioned discussion, it is possible that Cr$_2$AlC has too many electrons compared to the Al$_3$Ta compound. This work. However, in line with the aforementioned discussion, it is possible that Cr$_2$AlC has too many electrons compared to the Al$_3$Ta compound. This work. However, in line with the aforementioned discussion, it is possible that Cr$_2$AlC has too many electrons compared to the Al$_3$Ta compound.

Previously high thermal expansion coefficient of Cr$_2$AlC is confirmed by its relatively low—1450 °C—peritectic decomposition temperature and a relatively high thermal expansion coefficient ($\approx 12 \times 10^{-6} \text{°C}^{-1}$). This structural destabilization is also clearly seen 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 Cr$_2$AlC relative to the Ti and V containing structures.

Lastly we note that at $\approx 14$ GPa, a shoulder—centered at $\approx 1.207 \text{Å}$—to the left of the (116) diffraction peak of V$_2$AlC appeared. With increasing pressure the intensity of the peak increases, up to 36.1 GPa when it starts decreasing again. The reason for the extra peak and its behavior is unclear at this time. However, at $\approx 18.5$ GPa the Al peak intensity was found to decrease dramatically, probably as a result of one of the Al disks leaking out and therefore the sample may start bridging the anvil. Whether the two events are correlated is, again, unclear and more work is required to understand this response.

**IV. CONCLUSIONS**

Using a synchrotron radiation source and a diamond-anvil cell, we measured the pressure dependencies of the lattice parameters of selected M$_2$AlC phases. Up to a pressure of 55 GPa, no phase transformations were observed. The contractions in Ti$_2$AlC and V$_2$AlC compounds were higher along the c than along the a axes; the opposite was true for Cr$_2$AlC and Nb$_2$AlC. For Ta$_2$AlC, the shrinkages in both directions were almost identical. Going down the VA group results in a systematic increase in $K_0$. The $K_0$ of Ta$_2$AlC of 251 GPa, is the highest reported for any MAX phase to date. Going across the row of M elements, the bulk modulus decreases before decreasing. This reduction in modulus of Cr$_2$AlC relative to V$_2$AlC, was not predicted, and is possibly a reflection of the fact that Cr$_2$AlC may have too many electrons, that, in turn are pushed into antibonding orbitals. Furthermore, the presence of C in the structure has a stabilizing effect on the M-Al bonds, presumably by pulling electrons away from those bonds into the M-X bonds.

**ACKNOWLEDGMENTS**

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