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Possible monoclinic distortion of Mo₂GaC under high pressure

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Abstract

In this work, we present a high-pressure diffraction results of the Mo-based MAX phase, Mo₂GaC. A diamond anvil cell was used to compress the material up to 30 GPa, and X-ray diffraction was used to determine the structure and unit cell parameters as a function of pressures. Somewhat surprisingly, we find that at 295±25 GPa, the bulk modulus of Mo₂GaC is the highest reported of all the MAX phases measured to date. The *c/a* ratio increases with increasing pressure. At above 15 GPa, a splitting in the (1 0 0) reflection occurs. This result, coupled with new DFT calculations, show that a second order phase transition to possibly a mixture of a hexagonal and monoclinic structures may explain this splitting. Such experimentally and theoretically supported phase transition was not predicted in previously published calculations.

I. Introduction

With over 150 members, the $M_{n+1}AX_n$ (MAX) phases with $n=1-3$ are a large class of layered, machinable, hexagonal, nanolaminated materials, where M is an early transition metal, A is the main group element, and X is C or N [1-5]. They are characterized by carbide or nitride slabs ($M_{n+1}X_n$) separated by pure A monolayers. Having this layered structure, the MAX phases exhibit a combination of the beneficial properties of both ceramic and metallic compounds, making them attractive for many technological applications [4], such as machinable thermal shock resistance refractories [6], high temperature heating elements [7], neutron irradiation resistant parts for the nuclear industry [8]. Moreover, with the discovery of MXenes [9], MAX phases' 2D derivatives, the variety of possible applications vastly increased to the fields of energy storage [10], electronics, sensors, and more [11].

Out of this large family of compounds, Mo_2GaC is one of few having Mo as the sole occupant of the M-site [12,13]. It was first synthesized in 1967 and found to be superconducting below ~ 4 K [14]. Some theoretical studies were published in recent years regarding its physical properties at ambient pressure with the goal of linking the observed superconductivity to calculated electronic properties [15-17]. When compared to the isostructural Ga-containing phases (Nb_2GaC and V_2GaC) it is predicted to have the highest bulk, B, and lowest shear, G, modulus, and that its compressibility along the c axis is smaller than along the a axis [15]. When compared to five other superconducting MAX phases (Nb_2AC with $A = S, Sn, As,$ and In , and Ti_2InC) Mo_2GaC was predicted to have the highest bulk modulus (~ 249 GPa) and the second largest shear modulus (~ 96 GPa) [16]. The combination of high bulk modulus, machinability, and interesting electronic properties makes Mo_2GaC a worthy candidate for further study and characterization.

Quite recently, the elastic properties and structural evolution under pressure of Mo_2GaC were calculated by first-principles [18]. As in Ref. [15], a substantial difference in the compressibilities along the different axes was found with the a axis predicted to be significantly softer than the c axis. Moreover, it was shown that internal coordinate shifts of the Mo atoms is closely reflected by the c axis compressibility anomaly that showed three different slopes within 0–15 GPa, 20–60 GPa, and 70–100 GPa, respectively [18]. Importantly, no phase transition as a function of pressure is reported. *Ab initio* calculations in Zr_2InC above 70 GPa [19] and in Ti_2GaC between 350 GPa and 600 GPa [20] show a similar abnormal c axis behavior. In the first example, as oppose to Mo_2GaC , the c axis is softer than the a axis, apart from the anomaly. In the later example the anomaly is much broader, and the c/a ratio is extremely large, compared to other examples in this review. In both cases this abnormal behavior only occurs at very large pressures, beyond the scope of this work. These behaviors were found to be as a result of a similar coordinate shifts in the corresponding M-site in the M_2AX phase.

In recent experimental work, Hu et al. described a method for the rapid synthesis of Mo_2GaC , shortening its preparation time from 4 weeks to about a day [12]. During the course of that work, $\text{Mo}_2\text{Ga}_2\text{C}$ was discovered and later characterized [21,22]. With two Ga layers between the Mo_2C layers, the $\text{Mo}_2\text{Ga}_2\text{C}$ structure is quite similar to that of Mo_2GaC with only one Ga layer.

The interest in high-pressure properties of the MAX phase family of compounds resulted in various measurement campaigns in the past decade. A summary of such previously published studies is given in Table 1.

Table 1: Summary of response of different MAX phases to hydrostatic pressure. The table includes the bulk moduli, B , and their derivatives as a function of pressure, the maximal pressure reached in the experiment and the trends of the ratios between the c and a axes with increasing pressure. The measurement technique was X-ray diffraction (XRD) for all entries.

Phase [ref.]	Fitted Bulk modulus [GPa]	Fitted Bulk Modulus derivative	Max. pressure [GPa]	c/a ratio
Zr_2InC [23]	127±5	4.3±0.3	52	Decreases
Ti_2InC [24]	148±3	4.20±0.04	53	Decreases
Ti_2SnC [24]	152±3	3.90±0.06	49	*
Nb_2SnC [24]	180±5	4 (fixed)	49	*
Hf_2SnC [24]	169±4	4 (fixed)	50	Decreases
Ti_2AlC [25,26]	186±2	4.0±0.1	54	*
Ti_2AlN [26]	169±3	3.5±0.2	45	Decreases
V_2AlC [25]	201±3	4.0±0.1	46	*
Cr_2AlC [25]	165±2	4.1±0.1	50	Increases
V_2GeC [27]	165±2	4 (fixed)	50	*
Cr_2GeC [27]	182±2	4 (fixed)	50	*
Nb_2AlC [25]	209±2	3.9±0.1	36	Increases
Ta_2AlC [25]	251±2	4.5±0.2	45	Approx. 1
Cr_2GaC [28]	188±5	3.6±0.3	50	Approx. 1
Ti_2GaC [28]	189±4	3.5±0.3	46	Decreases
Ta_4AlC_3 [29]	261±2	3.8±0.2	47	Approx. 1
Ti_4AlN_3 [30]	216±2	3.84±0.06	55	Decreases
Ti_3GeC_2 [31]	197±2	3.4±0.1	51	Decreases
$(\text{Ti}_{0.5}\text{V}_{0.5})_2\text{AlC}$ [32]	183±3	4 (fixed)	47	Approx. 1
$(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$ [32]	181±3	4 (fixed)	53	Decreases
$\text{Ti}_3(\text{Si}_{0.5}\text{Ge}_{0.5})\text{C}_2$ [33]	183±4	3.4±0.2	53	Decreases

$\text{Ti}_3\text{Al}(\text{C}_{0.5}\text{N}_{0.5})_2$ [34]	219 ± 4	3.7 ± 0.3	50	Decreases
$\text{Ti}_3(\text{AlSn}_{0.2})\text{C}_2$ [34]	226 ± 3	4 (fixed)	50	Decreases
$(\text{Ti}_{0.5}\text{Zr}_{0.5})_2\text{InC}$ [24]	131 ± 3	3.80 ± 0.05	50	Decreases

* The behavior of the c axis changes as the pressure increases while the a axis remains more or less unchanged. At lower pressures the c/a ratio decreases (Ti_2InC , Nb_2InC , V_2GeC , V_2AlC and Ti_2AlC) or remains the same (Cr_2GeC) and above a certain pressure the c/a ratio increases.

Close examination of Table 1 leads to several general conclusions regarding the behavior of MAX phases under pressure. First and foremost, no symmetry changes have been reported up to the highest (mostly ~ 50 GPa) studied pressures. Second, from the fitted results, the B values seem to differ quite substantially between different MAX phases from a low of ~ 127 GPa for Zr_2InC , to a high of ~ 261 GPa for Ta_4AlC_3 . The pressure derivatives, on the other hand, were more or less constant at ≈ 4 for all phases. Third, in the overwhelming majority of the studied cases, the c axis is softer than the a axis, especially at lower pressures. Importantly, as noted above, Gao *et al.* [18] predicted the opposite for Mo_2GaC as found below.

Herein, we report on the high-pressure XRD measurement of Mo_2GaC up to 30 GPa. Moreover, we theoretically re-examine the high-pressure behavior predicted in previous theoretical work for Mo_2GaC . The experimental and theoretical results are then compared.

II. Methods

A detailed description of sample preparation is given elsewhere [12]. In short, it was fabricated by heating a 1:1.4 molar ratio of Mo_2C and pure Ga to 900 °C for 24 h under flowing argon, Ar. Excess Ga was dissolved using HCl. A small sample of that powder was remeasured at ambient conditions using a low noise Bruker D8 – advanced type diffractometer at the Nuclear Research Centre – Negev (NRCN), Israel. Using $\text{CuK}\alpha$ radiation, an angular range from 20° to 100° was covered in steps of 0.01°. For the high-pressure measurements, the same powder was loaded into a 301 steel gasket placed in a Tel-Aviv design Diamond Anvil Cell (DAC) [35] with a pair of 500 μm culet sized diamond anvils. A Brilliant cut and a Bohler-Almax design (BA) anvils were used [36]. Ar was cryogenically loaded into the cell to act as a pressure medium and ruby spheres were placed on the sample to be used as a pressure calibrant. A Bruker micro-focus X-ray source ($\text{I}\mu\text{S}$ 3.0) at the NRCN, with a Mo anode, created a 0.7107 Å monochromatic X-ray beam that was focused on the sample. The beam FWHM, at the focal point, was 110 μm . A 2D-CMOS detector was used to measure the diffraction pattern, and the DAC was placed with the BA anvil facing the detector to obtain a 70° aperture (*i.e.* a 2θ range of 0-35°). The entire setup was held on a 2θ stage. For

comparison purposes one ambient pressure run without DAC was undertaken on the I μ S 3.0 at a 2θ range of 0~60°.

The systematic uncertainties in determining lattice parameters and pressure were evaluated using several standards (LaB₆, Al₂O₃ and Au) runs in 0 to 95 GPa range, resulting in typical values of ~0.1%, and ~5%, respectively, for the entire pressure range. Instrument resolution functions were also determined in these runs. The peak profile was chosen to be Thompson-Cox-Hastings pseudo-voigt convolution where the contribution of the instrument is a constant width of the Gaussian and no cosine contribution to the Lorentzian [37]. The Mo₂GaC powder was measured during both compression (7 pressure points) and decompression (20 pressure points), with a wait of at least 0.3 h at each pressure point. Each measurement took 10 minutes. The diffraction pattern did not change as a function of time. In this work the maximum pressure reached was 30 GPa. All diffraction patterns were analyzed by the Rietveld method [38], using the FULLPROF code [39].

All first-principles calculated energies were obtained using the Vienna Ab initio Simulation Package (VASP 5.4.4) [40] implementation of density functional theory (DFT), using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation [41] description of the exchange–correlation energy. The plane wave energy cutoff was set at 520 eV, k -point grids with a spacing of 0.05 Å⁻¹ according to the Monkhorst-Pack method [42]. The electronic energy convergence threshold is set to 10⁻⁶ eV/atom for energy and 10⁻² eV/Å for force.

Two different approaches were used to calculate the possible structures; (a) relaxation of structures at various volumes, and (b) relaxation at a given applied pressure. In the first approach we allow complete relaxation of lattice parameters, unit cell shape, and internal coordinates at a static volume. In the second approach we applied an isostatic pressure while relaxing the lattice parameters, unit cell shape, and internal coordinates to the various considered symmetries.

III. Results

Rietveld analysis of the XRD pattern at ambient conditions measured using the Bruker D8 diffractometer (Figure 1a) showed that most reflections agree with a hexagonal symmetry (space group $P6_3/mmc$) and lattice parameters $a \sim 3$ Å, and $c \sim 13$ Å. All the major peaks are attributable to the Mo₂GaC phase. Additional reflections were observed, which agree with the existence of two minor phases, Mo₂C, and Mo₂Ga₂C. A model containing the above mentioned three phases was fit to the data using the Rietveld analysis method. The major Mo₂GaC phase was assumed to have the $P6_3/mmc$ hexagonal structure with Mo, Ga, and C positioned in the $4f(1/3, 2/3, z \approx 0.58)$, $2c(1/3, 2/3, 1/4)$, and $2a(0, 0, 0)$, respectively. The refined weight percentages of the phases were ~78 wt.% Mo₂GaC, ~15 wt.% Mo₂C [43], and ~7 wt. % Mo₂Ga₂C.

The a and c lattice parameters of Mo_2GaC were refined as $3.0328(4)\text{\AA}$, and $13.194(2)\text{\AA}$, respectively. We note the small difference in the XRD results between what is presented here and in Ref. [12]. In their work, Hu *et al.* did not refine the XRD pattern with $\text{Mo}_2\text{Ga}_2\text{C}$ as an additional impurity phase, which is the most probable reason for this discrepancy (see Figure 3 in Ref. [12]). A similar measurement is shown in figure 1b taken with the 17KeV Bruker XRD I μ S at ambient pressure. With $a = 3.028(3)\text{\AA}$ and $c = 13.195(2)\text{\AA}$ the lattice parameters of Mo_2GaC determined by the I μ S instrument are in excellent agreement with the ones determined using the high-resolution diffractometer. A small difference is observed in the impurity weight percentages determined by the I μ S instrument were Mo_2C was found to amount for $\sim 12\text{ wt.}\%$ and $\text{Mo}_2\text{Ga}_2\text{C} \sim 6\text{ wt.}\%$. This small difference is probably due to the higher background of the latter instrument were the sample size is much smaller.

XRD patterns as a function of pressure in the range ambient to 30 GPa are presented in Figure 2. From ambient and up to $15.7(8)\text{ GPa}$, a stable hexagonal structure ($P6_3/mmc$) with a clear compression of the unit cell (Figure 2) is identified. For these patterns, Rietveld refinement analysis was performed assuming the major Mo_2GaC MAX phase has the ambient $P6_3/mmc$ hexagonal structure, with starting values of a , c , and z as in the ambient XRD analysis described above. Structural parameters of the two minor impurity phases, Mo_2C , and $\text{Mo}_2\text{Ga}_2\text{C}$, were also refined, using their structural models from Refs. [43], and [22], respectively, as the starting ones. α -Fe and ϵ -Fe, resulting from the steel gasket of the DAC, were also considered, before and after the Fe phase transition. Their previously published structures as a function of pressure were fixed in the analysis [44]. XRD patterns as a function of pressure above $15.7(8)\text{ GPa}$ clearly show splitting of the $(1\ 0\ 0)$ reflection of the major phase (Figure 2). This splitting increases with pressure, suggesting a deviation from the typical MAX phase hexagonal structure.

Figure 1: Rietveld analysis of the XRD pattern of Mo_2GaC at ambient pressure using the hexagonal ($P6_3/mmc$) structure (see text). The ambient pressure diffractograms are obtained using the (a) Bruker D8 – advanced type diffractometer with $\text{CuK}\alpha$ radiation, and (b) Bruker I μ S diffractometer with $\text{MoK}\alpha$ radiation. Data (black circles) are taken from experiment performed; the red line represents the calculated pattern that included the major MAX phase (red indices) as well as the Mo_2C (blue indices) and $\text{Mo}_2\text{Ga}_2\text{C}$ (green indices) impurity phases. The blue line represents the residual curve between the measured data and the fitted model.

Figure 2: Effect of hydrostatic pressure on XRD patterns of $\text{Mo}_2\text{Ga}_2\text{C}$. Main reflections are denoted by their Miller indices. A splitting of the (1 0 0) reflection is clearly observed at around 16° above 15.7 GPa and develops as the pressure increases. Reflections belonging to $\text{Mo}_2\text{Ga}_2\text{C}$, Fe α and ϵ phases are marked with daggers, dots, and double dagger, respectively. Of note is the splitting of reflections that occurs in the $\text{Mo}_2\text{Ga}_2\text{C}$ phase, similar to that of the major phase. The maximum pressure reached was 30 GPa. The inset depicts the area of the (1 0 0) split between 14° and 18° .

IV. DFT Calculations

Following the clear evidence of splitting of the original hexagonal (1 0 0) line, as well as the evidence for the relative similarity of the low-pressure and high-pressure structures, it was assumed that the best candidate structures to describe the high-pressure range of $\text{Mo}_2\text{Ga}_2\text{C}$ should either be the orthorhombic, or monoclinic structures that are related to the original $P6_3/mmc$ structure by isomorphic super-group/sub-group relation [45]. Eleven different symmetries were considered (Figure 3). They include the following: The typical MAX phase with $P6_3/mmc$ (α) symmetry depicted in Figure 3a, denoted α to distinguish it from β in Figure 3b [46]; additional monoclinic and hexagonal symmetries (Figure 3c-g); and symmetries

retrieved by combining the $P6_3/mmc$ (α) with $P6_3/mmc$ (β) where the notation in parenthesis indicates the stacking sequence of α and β symmetries within the unit cell (Figure 3 h-k).

Figure 3: Considered crystal symmetries for Mo_2GaC where the unit cells are indicated by black quadrangle. (a) shows the common hexagonal MAX phases structure $P6_3/mmc$; (b) the modified hexagonal structure $P6_3/mmc(\beta)$. (d), and (g) show trigonal structures, (h), (i), and (k) orthorhombic, and (c), (e), and (j) monoclinic.

The results for the volume relaxation method are shown in Figure 4. Figure 4a depicts the calculated total energy as a function of volume per atom for the eleven considered symmetries shown in Figure 3. All are very close in energy despite the various stacking symmetries. For the volume range considered, the structures with $C2/c$ and $P2_1/m$ symmetries, (e) and (f) in Figure 3, relaxes to the original MAX phase $P6_3/mmc$ symmetry. Figure 4b shows the relative enthalpy change ΔH , with respect to $P6_3/mmc$ (α), as function of pressure, p , using:

$$\Delta H = H - H(P6_3/mmc (\alpha)), \quad (1)$$

where H is given by:

$$H(V) = E(V) + pV = E(V) + \frac{\delta E}{\delta V} V, \quad (2)$$

and $E(V)$ is the calculated energy at volume V .

Up to ~ 9 GPa, the initial $P6_3/mmc$ symmetry possesses the lowest enthalpy. Above 12 GPa $P6_3/mmc$ (β) is favored. In between there is a structure which has C-Mo-Ga-Mo-C subunits with alternating α and β symmetries. This intermediate structure is thus a hybrid of the structures below 9 GPa and above 12 GPa.

Figure 4: (a) Calculated energy as function of volume and (b) enthalpy change with respect to $P6_3/mmc$ (α) as function of pressure for the considered symmetries in Figure 3.

In the pressure relaxation approach very similar results were obtained, qualitatively and quantitatively. The results of the enthalpy change as a function of pressure for the pressure relaxation method are shown in Figure 5.

Figure 5: Enthalpy change with respect to $P6_3/mmc (\alpha)$ as function of pressure for the considered symmetries in figure 3 in the pressure relaxation method.

The calculated structural parameters for the nine inequivalent symmetries considered are shown in Figure 6, together with previously calculated results [18]. To allow clear comparison between the various symmetries having different out-of-plane extensions, we chose to present a normalized lattice parameter extending over two Mo_2C layers as in Figure 3(a). As the pressure increases both a and c decrease for all considered symmetries. Compressibility ratio in Figure 6(c) demonstrates that the compressibility of the a axis is higher than the c axis in agreement with previous calculations [18]. Note that for $P6_3/mmc$, the decrease in c is less within 15 to 20 GPa, while a decrease more within the same pressure range. Correspondingly, the compressibility ratio for $P6_3/mmc$ thus show an increased slope within this pressure range. Of note is the generally good agreement between our results and those published previously in the case of the $P6_3/mmc (\alpha)$ structure [18].

Figure 6. Calculated structural parameters (a) a , (b) c , (c) ratio between normalized – by values at ambient pressure - of c and a axes, volume per atom, and (f) volume normalized by values at ambient pressure for considered symmetries in Figure 3. Cited data (pentagons) were reproduced from [G. Qing-He, X. Zhi-Jun, T. Ling, L. Jin, D. An, G. Yun-Dong, and Y. Ze-Jin, Journal of Applied Physics 119, 015901 (2016).], with the permission of AIP Publishing.

V. Analysis and Discussion

V. a. Analysis using $P6_3/mmc$

At low-pressures, the results show good agreement with the known hexagonal model fitted with three added impurity phases, Mo_2C , $\text{Mo}_2\text{Ga}_2\text{C}$ and $\alpha\text{-Fe}$. At 5.6 GPa, the lowest measured pressure point upon compression, the fit reached agreement factors with values of $\chi^2 = 95.8$, $R_{\text{wp}} = 9.2$, and $R_{\text{exp}} = 0.94$ (Figure 7). Attempting to evaluate the impurity concentration results in much lower values than expected from the ambient pressure measurements for both Mo_2C ($0.99 \pm 0.01 \text{ wt\%}$) and $\text{Mo}_2\text{Ga}_2\text{C}$ ($1.31 \pm 0.23 \text{ wt\%}$). This could be explained by the high-pressure peak broadening of the main Mo_2GaC phase and the minor phases, as well as to the limited measured Q range ($Q = \sin\theta/\lambda$). Moreover, as the pressure increases the ability to fit the impurity models is more difficult. The compression and decompression measured cell

parameters up to ~ 16 GPa coincide and show that the compressibility of the a axis is higher than the c axis in agreement with calculations both in the present work (figure 8) and previously published [18].

Figure 7: Rietveld analysis of Mo_2GaC at 5.6 GPa. The model (red line) fitted to the data (black circles) consisted of the main Mo_2GaC phase (of which main reflections are indexed) with three added impurity phases, Mo_2C (not marked), $\text{Mo}_2\text{Ga}_2\text{C}$ (dagger), and $\alpha\text{-Fe}$ (black dot). The residual between the measured data and the fit is presented by the blue line at the bottom.

Figure 8: Ratio between normalized – by values at ambient pressure - of c and a axes. The measured data (black spheres and circles) were obtained by Rietveld refinement of the XRD patterns under pressure, assuming the hexagonal $P6_3/mmc$ (α) structure and normalized using the ambient pressure lattice parameters assuming the same structure (see text). The measured results are compared to selected calculated results from Figure 6c (solid lines with symbols). From the results, it is clear that the a axis is more compressible than the c axis, as predicted.

An attempt to refine the same hexagonal model, used for pressures $\leq 15.7(8)$ GPa to higher pressure values resulted in increasingly worse agreement factors reaching values of $\chi^2 = 1290$, $R_{wp} = 27.3$, and $R_{exp} = 0.76$ at 30 GPa. The most serious discrepancy between data and model resulted from the splitting of the hexagonal (1 0 0) reflection (Figure 9). A demonstration of attempts to refine the hexagonal model to the angle range of the original hexagonal (1 0 0) reflection at 20 and 30 GPa is shown in Figure 9(c)&(d). They are clearly poor.

Figure 9: Analysis of diffraction patterns as a function of pressure using the $P6_3/mmc$ (194) symmetry. (a) a lattice parameter and, (b), c lattice parameter. Rietveld analyses of results at (c) 20 GPa and (d) 30 GPa assuming no change in symmetry. The vertical line in (a) and (b) represents the pressure after which refinement using the hexagonal symmetry gives poor fit agreement factors.

Of note is the apparent reversibility of this symmetry distortion. Upon decompression, the lattice symmetry returns to the low-pressure hexagonal phase at approximately 15 GPa. In addition, when we closely examine the lattice parameters when fitting the hexagonal model to the entire pressure range (Figure 9), no noticeable change of slope is observed at ~15 GPa, within the accuracy of our analysis. Moreover, as will be shown below, the lattice parameters values for pressures > 16 GPa, resulting from the analysis using the hexagonal structure, agree well with the average of the lattice parameters values that resulted from analyses using lower symmetries. These two observations indicate that the structure at high-pressure, is a slightly distorted symmetry of the original hexagonal one, which in turn, suggests a second order phase transition.

An additional important observation that stands out from Figure 8 is the quantitative agreement between the measured lattice parameters ratio and the calculated one using *Amm2* ($\alpha\beta\beta\beta$) for pressures above ~8 GPa. It is clear that the lattice parameters ratio favors a lower than hexagonal crystal symmetry, which is also predicted to be more stable at higher pressures.

V. b. Analysis using lower symmetries

Following the DFT calculations, that show possible lower (than hexagonal) symmetry for pressures above 15 GPa, the data in this pressure region was analyzed using each one of the eleven calculated symmetries including the monoclinic symmetries, *P2₁/m* and *C2/c*, that were found in the calculations to relax back to the *P6₃/mmc* structure. As starting models, the structures in Figure 3 with their corresponding calculated values are used. Even though the β -*P6₃/mmc* structure (Figure 3b) was found to be the most stable structure among those calculated it was dismissed as it failed to explain the splitting at high-pressure. Refinement of all other structures was attempted. However, full atomic positions refinement of the structures presented in Figure 3f-i was impossible due to the large number of degrees of freedom in their atomic sites. Out of the three remaining structures (Figure 3c-e) the only symmetry that was fully refined in the entire high-pressure range was *C2/m*. Albeit these limitations, that probably rise from the broadening of the peaks at high pressures and Q-range limits of the instrument used, it is important to compare the results of these three relatively similar structures to those achieved assuming hexagonal symmetry. The fitted structural parameters of the *C2/m*, *C2/c* and *P2₁/m* models to the 30 GPa data (see Figure 10 for *C2/m*, and *C2/c*) are summarized in Table 2. The fitted structural parameters of the hexagonal model to the same data is also given for comparison.

Table 2: Rietveld refined structural parameters of four different candidate models to the 30 GPa XRD pattern of Mo₂GaC.

	P6 ₃ /mmc (194)	P2 ₁ /m (11)	C2/c (15)	C2/m (12)
a (Å)	2.941(2)	2.972(7)	2.913(1)	2.967(5)
b (Å)	-	2.929(5)	5.145(1)	5.036(1)
c (Å)	12.95(2)	12.83(2)	12.989(7)	12.87(3)
β/γ (Degrees)	-	119.9(2)	89.9(4)	90.4(3)
Volume/atom (Å ³)	12.12(3)	12.11(5)	12.17(4)	12.03(6)

By comparing the fitted parameters of the three monoclinic phases to the original hexagonal phase, there is no obvious difference in the relative uncertainties. The results for the monoclinic phases seem to partly explain the splitting of the (1 0 0) peak at pressures < 20 GPa, but at higher pressures, closer to 30 GPa, attempting to fit either one of the *P2₁/m*, *C2/m* or the *C2/c* models to the data, results again in poor agreement (Figure 10). From the three candidates, the best fit at 30 GPa is the *C2/c* structure even though none of the proposed structures fully resolve the structure of the high-pressure phase. In all cases, the values of the angles β for *P2₁/m* or γ for *C2/c* and *C2/m* do not change from their original values above the calculated uncertainty, meaning that the angle of the monoclinic structure barely changes with increasing pressure.

The most prominent change seen for all attempts to refine with monoclinic symmetry is the obvious split between lattice parameters; a change in the a and b axes lengths. While one parameter seems to barely change its value, the other parameter rapidly decreases with increasing pressure. Moreover, as we refine the results using the monoclinic structures at lower pressures, closer to 15 GPa, the values of the a and b axes converge back to a single axis, similar to the hexagonal phase.

Overall, the calculated atomic volumes seem to behave similarly in all the phase candidates and the behavior as a function of pressure also remains the same during the phase transition. The fitted a, b and c parameters of the *C2/c* and *C2/m* phases are shown in Figure 11.

Figure 10: Fitted XRD patterns zoomed in on the (1 0 0) reflection splitting at 15 GPa, 20 GPa and 30 GPa displayed from left to right. Top row is a fit to the C2/c structure and the bottom row is a fit to C2/m structure.

Figure 11: a, b, and c unit cell parameters as a function of pressure, refined by fitting the C2/c structure (left column), and C2/m (right column) to the XRD patterns. The vertical lines represent the pressure after which refinement using the hexagonal symmetry gives poor fit agreement factors.

One could possibly argue that the (1 0 0) splitting is an artifact of the $\text{Mo}_2\text{Ga}_2\text{C}$ contamination. Yet, attempting to fit the diffraction at 30 GPa to the Mo_2GaC hexagonal phase and the $\text{Mo}_2\text{Ga}_2\text{C}$ low-pressure hexagonal phase did not result in a good fit as the splitting is too large for a 10 % contamination. Moreover, $\text{Mo}_2\text{Ga}_2\text{C}$ was reported to have a phase transition to a $P\bar{3}m1$ symmetry above 22 GPa [47], and this structure was attempted to fit to the result as well, with even less success compared to when the original symmetry used for that impurity. Another possible explanation is the coexistence of both the monoclinic and the low-pressure hexagonal structures. Figure 12 depicts the fitted diffraction pattern to a mixed phase structure of both the monoclinic $C2/m$ phase and the hexagonal phase, the refinement factors achieved from the Rietveld analysis are $\chi^2 = 255$, $R_{\text{wp}} = 11.9$, and $R_{\text{exp}} = 0.75$. This analysis did not include any of the impurities, but the iron. With the impurities the refinement did not converge. Attempting to fit the hexagonal phase with the $C2/c$ phase or the $P2_1/m$ phase did not converge either with, or without, impurities. This mixture is the best candidate for the HP structure of Mo_2GaC , but due to the peak broadening at high pressures it is impossible to conduct a full analysis as a function of pressure, especially around the transition point where the differences between the phases are practically negligible (Figure 11).

Figure 12: Rietveld analysis of the XRD pattern of Mo_2GaC at 30 GPa using a mixture of hexagonal ($P6_3/mmc$, blue indices) and monoclinic ($C2/m$, red indices) structures with iron (dagger) as the only impurity. Data (black circles) are taken from experiment performed; the red line represents the calculated pattern. The blue line represents the residual curve between the measured data and the fitted model.

V. c. Structural variations

Following the above-mentioned evidence for possible monoclinic distortion in the Mo_2GaC structure as a function of pressure above ~ 15 GPa, an attempt was made to identify the cause of this distortion. To that end we calculated the major lattice distances and angles as a function of pressure for the original hexagonal ($P6_3/mmc$ (α)) structure, as well as for the three most possible structures that may exist after the transition according to our calculation and measurements, namely, $P6_3/mmc$ (β), $C2/m$, $Amm2$ ($\alpha\beta$) (Figures S1, and S2 in the supplemental material). In general, all studied parameters change smoothly with pressure, and do not differ much between structures. This is in contrast with the clear jump in structural parameters observed for $\text{Mo}_2\text{Ga}_2\text{C}$ at much higher pressure (~ 48 GPa) [48]. Moreover, no significant change of slope or discontinuity in the bond lengths is observed unlike what was previously observed for $\text{Mo}_2\text{Ga}_2\text{C}$ at ~ 22 GPa [47]. It is worth noting here that the significant change observed in $\text{Mo}_2\text{Ga}_2\text{C}$ resulted when the Ga layers change their stacking from top-packed double layer to close-packed stacking without changing the Mo_2C layer ($\alpha\text{-Mo}_2\text{Ga}_2\text{C}$ to $\beta\text{-Mo}_2\text{Ga}_2\text{C}$ transition [47]). Clearly, such a transition is impossible in the original structure of the $n=1$ MAX phases.

However, an indication for behavioral change in the Mo-Ga-Mo angle (across layers) is observed for the original $P6_3/mmc$ structure, and therefore was further studied (Figure 13). It is clear from these additional calculations, that at ~ 12 GPa it is more energetically favorable for the Mo-Ga-Mo angle in the $P6_3/mmc$ structure to start increase with pressure rather than to decrease with the latter increase. This pressure is in excellent agreement with the pressure from which the structural transition is observed experimentally. In the case of the other structures this angle either continues to decrease or reaches a plateau. A closer look on the $P6_3/mmc$ structure, with its single free position parameter z_{Mo} , reveals that the most significant structural value that correlates with changes in c/a is the Mo-Ga-Mo angle. As the pressure increases c/a can either decrease or increase. An increase in this value, as is the case for Mo_2GaC , will either force the Mo-Ga-Mo angle to increase or z_{Mo} to increase to accommodate for the change. However, an increase in z_{Mo} will cause an increase in the Mo-Mo bond length *within* the Mo_2C carbide layer. Obviously, for the case of Mo_2GaC it becomes unfavorable energetically above ~ 12 GPa, and the Mo-Ga-Mo angle therefore must increase with increase in pressure (Figure 13). This effect is also accompanied by relatively large increase in c/a as a function of pressure, which is much higher than the observed one (Figure 6c). One possible way to both decrease the Mo-Ga-Mo angle (or keep it constant) and keep the Mo_2C layer from expanding too much with pressure is to change to monoclinic symmetry and open more structural degrees of freedom. This effect should be further studied experimentally.

Figure 13: Relative and absolute values of the Mo-Ga-Mo angle (Figure S3) as a function of pressure for the four possible Mo_2GaC structure discussed in the text.

V. d. Equation of state (EOS)

A universal equation of state (EOS) was fitted to the results and from it we estimated the bulk modulus, B , and its derivative. The equation was fitted to the data between 0 and 30 GPa both in compression and decompression as no sign of change between both was seen. The result is shown in Figure 14. The data above 15.7 GPa was calculated using the monoclinic $C2/c$ phase, even though fitting the results up to 15.7 GPa or using the monoclinic $P2_1/m$ or $C2/m$ above 15.7 GPa did not change the results above the fit uncertainties. Due to the large uncertainties of the measured volume values, and the relatively low maximum pressure of the experiment, a well-defined equation of state was nearly impossible to obtain, because nearly every possible combination of B and its derivative, B' , gave similarly acceptable fits. Confining B' to a range of values that previous work has, viz. between 3 and 6, always resulted in a fit where B was larger by at least 20 GPa than the stiffest experimentally known MAX phase to date, viz. Ta_4AlC_3 [29]. Assuming B' to be 4, which is similar to most MAX phases (see Table 1) resulted in a bulk modulus of 295 ± 25 GPa. This means that Mo_2GaC is the stiffest MAX phase measured under high pressure. The same result is achieved when attempting to fit the results to the hexagonal phase up to 15.7 GPa.

Figure 14: Average volume per atom as a function of pressure. There is no evidence of a change in the volume during the second order phase transition at ≈ 15.7 GPa. A universal EOS [49] was fitted to the results.

VI. Conclusions

In this work, we measured the compressibility, up to a hydrostatic pressure of 30 GPa, of the Mo₂GaC MAX phase, using the DAC method. In accordance with a recent DFT study, we show that the a-axis is more compressible than the c-axis. Somewhat surprisingly, at 295±25 GPa, the bulk modulus of Mo₂GaC is the highest reported of all the MAX phases measured to date.

Above 15 GPa, a splitting in the (1 0 0) reflection occurs suggesting the occurrence of a second order phase transition in which the symmetry of the material decreases from the initial hexagonal structure to a new, and yet unknown, high-pressure phase. The possibility of an impurity in the DAC explaining the high-pressure splitting of the (1 0 0) reflection was ruled out, and the best possible explanation found was a transition to a monoclinic structure or even a mixture of both monoclinic and hexagonal phases.

Our theoretical calculations reinforce this hypothesis as they show quite small enthalpy differences (0.005eV/atom at 30 GPa) between the monoclinic structure and the ambient pressure hexagonal phase. Comparing the experimental results to the calculations clearly show that the experimental lattice dimension favor dimensions of lower than hexagonal symmetry, or, at least strongly disagree with the expected dimensions of the original hexagonal structure. The exact structure of this new phase is still unknown as well as the position of the atoms, but it is most likely that the phase transition involves a relative change in the a and b cell parameters. A possible origin of this structural transition can be found within the behavior of the Mo-Ga-Mo angle across layers as a function of pressure.

Among studied structures, the two best candidates for the high-pressure phase were C2/c and C2/m. The former was found to be the best fit for the results when attempting to fit the XRD results using Rietveld analysis of a single phase, while the latter produced the best fit at 30 GPa when mixed with the hexagonal phase. DFT calculations of the C2/c phase quickly collapse back to the hexagonal phase, while the C2/m phase was found to be stable, and at lower enthalpy than the hexagonal phase above 15 GPa. Future work needs to take a closer examination at the high-pressure structure.

Supplementary Material

A comparison of three different bond lengths and two bond angles calculated for four selected structures (P6₃/mmc(α), P6₃/mmc(β), C2/m, and Amm2($\alpha\beta$)) on a relative (to 0 GPa), and absolute scales.

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