Article

Structural Stability, Electronic, Mechanical, Phonon, and Thermodynamic Properties of the $M_2$GaC ($M = Zr, Hf$) MAX Phase: An ab Initio Calculation

Muhammad Waqas Qureshi $^{1,2}$*, Xinxin Ma $^{1,2}$*, Guangze Tang $^2$ and Ramesh Paudel $^3$

1. Introduction

A new class of nanolayered transition metal carbides and/or nitrides was first discovered by H. Nowotny and coworkers, which were called H-phases in 1960, now known as MAX phases [1]. The general formula $M_{n+1}AX_n$ typically represents these ternary compounds (where M is an early transition metal, A is an IIIA- or IVA-group element, and X is either C or N, $1 \leq n \leq 3$). MAX phase crystallizes in the hexagonal crystal structure (space group P6$_3$/mmc) in which MX$_6$ octahedral crafted with a pure A-group atom layer grown in c-direction, which bring forth a mixture of a strong covalent M-X bond and a relatively weak metallic M-A bond [2,3]. Due to a unique layered structure, MAX phases possess hybrid properties of both metals and ceramics, such as low density, machinability, thermal and electrical conductivity, damage and irradiation tolerance, oxidation, and corrosion resistance [4–7]. These remarkable properties make MAX phases suitable for versatile applications from microelectronics to aerospace [8–11]. Moreover, these ternary compounds can be exfoliated into...
2D nanocrystals (MXene) by the selective etching of A-elements, applicable in Li-ion and sodium-ion batteries and supercapacitors, which further broaden the area of interest for researchers [12–14].

Over the past few years, extensive work has been devoted to investigating the properties of MAX phases materials experimentally and theoretically. More than 70 different thermodynamically stable $M_{n+1}AX_n$ materials have been synthesized experimentally in bulk form and some of them as a thin-film. Experimental results proved that Al-based MAX phase materials are thermally stable due to the formation of a continuous protective $Al_2O_3$ layer [15,16]. Recently, among the $M_2AC$ MAX phases, $Zr_2AlC$ and $Hf_{n+1}AlC_n$ ($n = 1, 2$) have already been synthesized, and their lattice parameter was in good agreement with first-principle investigations [17,18]. As far as theoretical research is concerned, density functional theory (DFT) [19] calculations have provided valuable information related to MAX phases. For $M_2GaC$ MAX phases, X.-X. Pu et al. [20] calculated the structural, electronic, and thermodynamic properties of $Ti_2GaC$, Thore et al. [21] studied the electronic, elastic, and vibrational properties of $Mn_2GaC$, and Shein et al. [22,23] investigated the structural, elastic, and electronic properties of $Mo_2GaC$. At the same time, Qing-He et al. [24] found the extraordinary structural evolution while calculating the mechanical properties of $Mo_2GaC$ at different pressures. In addition, A. Petruhins et al. [25] predicted the phase stability, and the magnetic state of $Cr_2GaC$ and thin film of $Cr_2GaC$ was also prepared using the magnetron sputtering technique. In particular, Ga-containing $M_{n+1}GaC_n$ phases (where $M = Ti, Cr,$ and $n = 1, 3$) were synthesized by J. Etzkorn et al. in 2009 [26].

Similarly, many computed data can be found in the literature for $M_2AC$ ($M = Zr, Hf$) MAX phases [27–30]. For example, A. Bouhemadou et al. investigated the structural, electronic, and elastic properties of a wide range of $M_2AC$ MAX phases [31], B. Ghebouli, et al. [32] computed the structural, elastic, and thermal properties of $M_2SiC$, and Fen Luo et al. [33] studied the thermodynamic properties of $Zr_2AlC$ MAX phase under high pressure and temperature respectively. Despite numerous theoretical investigations, the computed data related to $M_2GaC$ ($M = Zr$ and $Hf$) is lacking. To the authors’ best knowledge, only limited information about the elastic properties of $M_2GaC$ ($M = Zr$ and $Hf$) has been reported by Sun Zhimei et al. [34]. Furthermore, thermodynamic properties of $M_2GaC$ MAX phases at higher temperature and pressure have not been studied yet. So, our results can serve as a reference for upcoming theoretical and experimental studies.

In the present study, density functional theory and the quasiharmonic Debye model were utilized to study the electronic, structural, and mechanical properties of $M_2GaC$ MAX phase materials along with their thermodynamic properties at pressure ranging 0–50 GPa and temperature ranging 0-1600 K. The Debye temperature ($\theta_D$), heat capacity ($C_v$), thermal expansion ($\alpha$) coefficient, and Grüneisen parameter ($\gamma$) were calculated in the described pressure and temperature ranges. This article is organized as follows: there are detailed computational methods in Section 2; the obtained results and discussion of $M_2GaC$ are presented in Section 3; in Section 4, thermodynamic properties are discussed; and in Section 5, a summary of this research is given.

2. Computational Details

The ab initio estimation was performed based on density functional theory (DFT) using the Cambridge Serial Total Energy Package (CASTEP) [35] in which plane wave ultrasoft pseudopotential is used. The exchange-correlation was treated within the generalized gradient approximation (GGA) of Perdew–Wang (GGA-PW91) [36], Perdew–Burke–Ernzerhof (PBE) [37], and local density approximations developed by Ceperly and Alder and parametrized by Perdew and Zunger (LDA-CA-PZ) [38] for comparison. GGA-PBE was implemented to calculate the different properties in each system. A total energy convergence test was performed carefully at additional cutoff energies and the k-point mesh for the $M_2GaC$ ($M = Zr$ and $Hf$) system. For all cases, the plane waves’ cut off energy, and the Monkhorst-pack [39] scheme k-point were set at 600 eV and $15 \times 15 \times 3$, respectively. The ground state structural parameters were determined using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) [40] minimization technique while the self-consistent convergence parameters were total energy
tolerance less than $5 \times 10^{-6}$ eV/atom, stress component less than 0.02 GPa, maximum force tolerance 0.01 eV/A, and maximum displacement of atom during the geometric optimization less than 0.0005 Å.

To investigate the thermodynamic properties of Zr$_2$GaC and Hf$_2$GaC, the quasiharmonic Debye model using the GIBBS program [41, 42] was applied in the temperature ranges 0–1600 K and pressure in the range 0–50 GPa. Finally, the phonon dispersion was computed using a finite displacement method implemented in Material Studio [43].

3. Results and Discussion

3.1. Structural Properties

As mentioned earlier, MAX phase materials crystallize in hexagonal crystal structures with space group P6$_3$/mmc (No. 194) in which an edge-shared octahedral of transition metal carbide M$_6$X is sandwiched between a pure A-element. The stimulated unit cell is shown in Figure 1. The Wyckoff positions in the M$_2$GaC (M = Zr and Hf) system are as follows: C 2a(0, 0, 0), Ga 2d(2/3, 1/3, 1/4), and M 4f(1/3, 2/3, $Z_M$) where the internal parameter $Z_M$ is about 0.08. The quest for stable structure and optimized geometry of the crystalline structure is the first step in any ab initio calculation. For this purpose, the total energy versus volume for each structure in the M$_2$GaC (M = Zr and Hf) system is plotted in Figure 2, and the data were fitted according to the equation of energy of state (EOS) due to Birch–Murnaghan [44]. For comparison, we have obtained lattice parameters for the M$_2$GaC MAX phase by GGA-PW91, LDA-CA-PZ, along with GGA-PBE functionals, and the results are shown in Table 1. Moreover, there is no experimental data available in the literature related to M$_2$GaC (M = Zr and Hf), so as a reference, theoretical and experimental results of other Ga-containing MAX phases, i.e., Ti$_2$GaC, Cr$_2$GaC, and Sc$_2$GaC by other researchers are also cited in Table 1 for comparison.
Table 1. Calculated lattice parameters (a) and (c) in Å, c/a, bulk modulus (GPa), no. of density of states (DOS) at E\(_{\text{F}}\) (states/eV/unit cell), and formation energy \(E_{\text{for}}\) (eV/atom) for \(M_2\text{GaC}\) MAX phase (\(M = \text{Zr, Hf}\)) obtained by generalized gradient approximation (GGA) and local density approximation (LDA).

| \(M_2\text{GaC}\) | Functional | a (Å) | c (Å) | v (Å\(^3\)) | c/a (Å) | \(B^*\) (GPa) | N(E\(_{\text{F}}\)) (states/eV/u.c) | \(E_{\text{for}}\) (eV/atom) | \(E_{\text{coh}}\) (eV/atom) | \(f_m\) (×10\(^{-3}\)) | Ref |
|-------------------|------------|-------|-------|-------------|--------|--------------|-------------------------------|-----------------|-----------------|-----------------|-----|
| \(\text{Zr}_2\text{GaC}\) | GGA-PBE    | 3.330 | 14.257| 136.92      | 4.28  | 121.8        | 3.002                         | −7.59           | −6.328          | 5.20            | This work |
|                   | GGA-PW91   | 3.330 | 14.245| 136.88      | 4.27  |              |                               |                 |                 |                 |       |
|                   | LDA-CA-PZ  | 3.276 | 13.956| 129.73      | 4.26  |              |                               |                 |                 |                 |       |
| \(\text{Hf}_2\text{GaC}\) | GGA-PBE    | 3.324 | 14.025| 134.20      | 4.22  | 141.9        | 2.475                         | −7.45           | −6.162          | 4.29            | This work |
|                   | GGA-PW91   | 3.325 | 14.003| 134.11      | 4.21  |              |                               |                 |                 |                 |       |
|                   | LDA-CA-PZ  | 3.268 | 13.716| 126.93      | 4.19  |              |                               |                 |                 |                 |       |
| \(\text{Ti}_2\text{GaC}\) | GGA-PBE    | 3.083 | 13.397|            | 4.34  |              |                               |                 |                 |                 | Calc [20] |
|                   |            | 3.066 | 13.312|            |       |              |                               |                 |                 |                 | Exp [26] |
| \(\text{Cr}_2\text{GaC}\) |            | 2.900 | 12.632|            |       |              |                               |                 |                 |                 | Exp [26] |
| \(\text{Sc}_2\text{GaC}\) | LDA-CA-PZ  | 3.236 | 14.394|            | 4.44  |              |                               |                 |                 |                 | Calc [45] |

\(B^*\) is the bulk modulus obtained from the Birch–Murnaghan equation of energy of state (EOS).
Figure 1. The unit cell of the $M_2GaC$ MAX phase ($M = Zr, Hf$). An edge-shared $[M_6X]$ octahedra, and a $M_6A$ trigonal prism are outlined.

![Unit Cell Diagram](image)

Figure 2. The total energy as a function of unit cell volume for the $M_2GaC$ MAX phase (a) $Zr_2GaC$; (b) $Hf_2GaC$.

The computed equilibrium volume for $Zr_2GaC$ and $Hf_2GaC$ is 136.92 Å³ and 134.20 Å³, and lattice parameters ($a$, $c$) are 3.33 Å, 14.25 Å for $Zr_2GaC$, and 3.32 Å, 14.02 Å for $Hf_2GaC$, respectively. The study made by Sun Zhimei et al. [34] on Ga-containing MAX Phases $M_2GaC$ (where $M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W$) did not contain useful information related to optimized lattice parameters or volume, and there is no experimental data available in the literature so far. Hence, we predict the physical properties of the $M_2GaC$ MAX phase for the very first time.

The effect of pressure on the equilibrium volume of $M_2GaC$, ranging from 0–50 GPa with a step of 10 GPa, is shown in Figure 3, where $V_0$ is the volume at the zero-pressure equilibrium structural parameter. It is noticed that the volume ratio $(V/V_0)$ was reduced in the order of $(V/V_0)_{Zr_2GaC} = 9\% > (V/V_0)_{Hf_2GaC} = 7\%$ with an increase in pressure. Therefore, the compressibility of the $M_2GaC$ MAX phase system is strong, and the change of external pressure has a more significant impact on $Zr_2GaC$. 

![Pressure Volume Graph](image)
Figure 3. Calculated dependence of volume change $V/V_0$ on pressure for $M_2GaC$ MAX phase ($M = Zr, Hf$).

The energy of formation per atom ($E_{for}$) was calculated to investigate the phase stability of the researched $M_2GaC$ MAX phase, which is defined as follows [46]:

$$E_{for}^{M_2GaC} = \frac{E_{total}^{M_2GaC} - (xE_{solid}^M + yE_{solid}^{Ga} + zE_{solid}^{C})}{x + y + z} M = Zr, Hf$$

where: $x, y, z$ is the number of atoms for $M$, Ga, and C element in the unit cell, i.e., $x = 4$, $y = 2$, and $z = 2$ and $E_{total}^{M_2GaC}$, $E_{solid}^M$, $E_{solid}^{Ga}$, and $E_{solid}^{C}$ are the total energy of $M_2GaC$ MAX phase, $M$, Ga, and C atoms in the solid form respectively in their stable structures. The calculated formation energy for $Zr_2GaC$ and $Hf_2GaC$ is $-7.59$ eV/atom and $-7.45$ eV/atom, respectively, given in Table 1.

Cohesive energy ($E_{Coh}$) is defined as the energy required to break the crystal into an isolated atom and used to identify the structural stability of the $M_2GaC$ MAX phases. The $E_{Coh}$ is computed using Equation (2).

$$E_{Coh}^{M_2GaC} = \frac{E_{total}^{M_2GaC} - \left( 2E_{iso}^{M} + E_{iso}^{Ga} + E_{iso}^{C} \right)}{4} M = Zr, Hf$$

where: $E_{Coh}^{M_2GaC}$, $E_{iso}^{M}$, $E_{iso}^{Ga}$, and $E_{iso}^{C}$ are the total energy of the $M_2GaC$ MAX phase and the energies of isolated $M$, Ga, and C atoms, respectively. The calculated $E_{Coh}$ for $Zr_2GaC$ and $Hf_2GaC$ is $-6.328$ eV/atom and $-6.162$ eV/atom, respectively (see Table 1). It is worth noticing that the formation and cohesive energies for $M_2GaC$ are negative, indicating that these MAX phases are energetically favorable from the thermodynamic point of view. Moreover, these structures can be experimentally formed by different synthesis methods.

3.2. Electronic Properties

3.2.1. Band Structure

Based on optimized lattice parameters, the band structure for $M_2GaC$ ($M = Zr, Hf$) was calculated and obtained. Figure 4 shows the band structure from $-15$ eV to $6$ eV energy range along the high symmetry lines of the Brillouin zone. The appearance of the obtained band structure for both $Zr_2GaC$ and $Hf_2GaC$ MAX phases is similar to the other metallic MAX phases, such as $Cr_2AlC$ [47] and $Ti_2AlC$ [48] because of considerable overlapping of bands without having bandgap in the vicinity of the Fermi level. It can also be assessed that there is a strong anisotropic behavior with less c-axis energy dispersion. In other words, less energy dispersion was observed along the short H-K and M-L directions for both MAX phase compounds indicating the electronic anisotropic nature of $M_2GaC$ MAX.
phases (see Figure 4), which means conductivity will be lower along the c-axis as compared to their basal planes. The electronic anisotropic behavior of M$_2$GaC MAX phases is in good agreement with the available data of other MAX phases [21,49]. This is a consequence of the nanolaminated structure of M$_2$GaC MAX phases. Vincent et al. [50] investigated the electronic anisotropy of Ti$_2$AlC MAX phase and found that resistivity ($\rho = 1/\sigma$) along the c-axis is much higher than polycrystalline bulk material or thin-film along the (0001) orientation.

![Graph of Zr$_2$GaC and Hf$_2$GaC band structures](image)

**Figure 4.** The calculated band structure as obtained from GGA-PBE of M$_2$GaC MAX phase (a) Zr$_2$GaC; (b) Hf$_2$GaC.

### 3.2.2. Density of States (DOS)

To investigate the nature of chemical bonding in the M$_2$GaC (M = Zr, Hf) MAX phases, the density of states (DOS) was calculated and studied. The total and partial density of states is shown in Figures 5 and 6 and the results obtained are tabulated in Table 1. It is observed that the total DOS at $E_F$ for Zr$_2$GaC and Hf$_2$GaC are 3.002 states/eV/unit cell and 2.475 states/eV/unit cell, respectively, suggesting that the both Zr$_2$GaC and Hf$_2$GaC MAX phases are metallic and the metallicity of M$_2$GaC MAX phase compounds can be measured by DOS at $E_F$. The metallicity of Zr$_2$GaC and Hf$_2$GaC phases at ambient temperature is investigated by:

$$f_m = \frac{n_m}{n_e} = \frac{k_B T \times N(E_F)}{n_e} = 0.026 \times N(E_F)$$

(3)

where $n_m$ and $n_e$ are the thermally excited number of electrons and the total number of valence electron in the unit cell while $k_B$, $T$ and $N(E_F)$ are the Boltzmann constant, temperature, and value of DOS at $E_F$ in unit states/eV/unit cell, respectively. The calculated values of $f_m$ are listed in Table 1. Moreover, the conductivity of the M$_2$GaC MAX phase is investigated from the DOS at $E_F$ as follows:

$$\nu_F = \sqrt{\frac{2E_F}{m}}$$

(4)

where $\nu_F$ and $m$ are the velocity of electrons near the Fermi level and mass of electrons, respectively. From $\nu_F$, the conductivity ($\sigma$) of material is estimated as:

$$\sigma = \frac{ne^2\tau}{m} = \frac{ne^2l}{m\nu_F\tau} = \frac{l}{\nu_F}$$

(5)
where: \( n, e, \) and \( l \) are the number of electrons, electrons’ charge, and mean free path of electrons, respectively. \( \tau \) is the time between two collisions. In Equation (5), \( e, I, \) and \( m \) are constants; thus, conductivity mainly depends upon the \( n/\tau \) ratio. It is observed that the \((n/\tau)_{Zr_{2}GaC} > (n/\tau)_{Hf_{2}GaC}\); we may conclude that the conductivity of the \( M_2GaC \) MAX phase is in the order of \( Zr_2GaC > Hf_2GaC \). However, the values for total density of states (TDOS) obtained for \( M_2GaC \) (\( M = Zr, Hf \)) is much smaller than that of \( Cr_2AlC \) (6.46 states/eV/unit cell) [43], the maximum TDOS measured among the MAX phases so far. It is noted that the main contribution in the DOS at \( E_F \) is from the M-4d electrons in both cases, indicating that d bands of transition metal mainly contribute to the conduction properties during the electrical transport. These results are consistent with the previous studies on MAX phases [46].

![Figure 5](image_url)

**Figure 5.** The total and partial density of states (PDOS) obtained from GGA-PBE for \( M_2GaC \) MAX phase). Fermi level is set to 0 eV. (a) \( Zr_2GaC \); (b) \( Hf_2GaC \).

![Figure 6](image_url)

**Figure 6.** The total density of states obtained from GGA-PBE for \( M_2GaC \) MAX phase (\( M = Zr, Hf \)). Fermi level is set to 0 eV.
For Zr$_2$GaC, the total and partial density of states (TDOS and PDOS) from Figure 5a shows that the lowest states range from −10.85 eV to −9.11 eV of the TDOS is formed by C-s with Zr-d, Zr-p along with a small portion of Zr-s. The valence band in the range −5 eV to −1.90 eV is formed by the strong hybridization of C-s and Zr-d states. The highest valance band is related to the relatively weak hybridization of Zr-d, Zr-p, and Ga-p, which shows the covalent interaction between the Zr-d and Ga-p. The TDOS and PDOS for Hf$_2$GaC shown in Figure 5b is similar to that of Zr$_2$GaC with two common sharing features: Firstly, as M from Hf to Zr, the hybridization peaks of C-s and C-p with M-d states shifts from right to left towards the lower energy level and C-s, C-p peaks become narrow (See Figure 6). This expresses that as M from Hf to Zr, the hybridization peaks of C-s and C-p with M-d states is stronger than that of the M-d and Ga-p states.

### 3.3. Mechanical Properties

A brief knowledge about the elastic constants of the crystalline materials helps to predict its behavior under the application of external stress. It contributes to a critical understanding of the many solid-state properties, i.e., ductility, brittleness, stiffness, structural stability, and anisotropy. The elastic constants ($C_{ij}$) of M$_2$GaC (M = Zr, Hf) were calculated from the PBE, PW91, and LDA, and the obtained results are tabulated in Table 2. The hexagonal structure of MAX phases has six independent elastic constants ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$, $C_{55}$, and $C_{66}$), but five of them are listed since $C_{66} = \frac{(C_{11} - C_{12})}{2}$ [51]. Moreover, it is observed that the obtained elastic constants ($C_{ij}$) are positive and satisfy the mechanical stability criteria known as Born stability ($C_{11} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0$) [52] showing that the M$_2$GaC MAX phase is mechanically stable. In order to comprehend the mechanical properties further, the bulk modulus (B), shear modulus (G), Young’s modulus (E), G/B or B/G (Pugh ratio), elastic anisotropy (A), and Poisson’s ratio (ν) are calculated from the obtained elastic constants and results are given in Table 3. The Voigt (V) [53], Russ (R) [54,55], and Voigt–Russ and Hill (VRH) [56,57] approximation scheme were used to determine the parameters concerning properties. The following equations are used to calculate these quantities:

\[ B = \frac{1}{2}(B_V + B_R) \] (6)

and

\[ G = \frac{1}{2}(G_V + G_R) \] (7)

where $B_V$, $G_V$ and $B_R$, $G_R$ are the B and G in terms of the Voigt and Russ approximation respectively and calculated by given Equations (8)–(11)

\[ B_V = \frac{1}{9}(2(C_{11} + C_{12}) + 4C_{13} + C_{33}) \] (8)

\[ G_V = \frac{1}{30}(C_{11} + C_{12} + 2C_{33} + 4C_{13} + 12C_{44} + 12C_{66}) \] (9)

and

\[ B_R = \frac{((C_{11} + C_{12})C_{33} - 2C_{13}^2)}{(C_{11} + C_{12} + 2C_{33} - 4C_{13})} \] (10)

\[ G_R = \frac{5}{4}\left[\frac{((C_{11} + C_{12})C_{33} - 2C_{13}^2)}{C_{55}C_{66}}\right]^2 \] (11)
Table 2. The elastic constants (in GPa) for $M_2$GaC ($M = \text{Zr and Hf}$) obtained from GGA and LDA.

| $M_2$GaC | Functional | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $B_v$ | $B_r$ | $G_v$ | $G_r$ |
|----------|------------|----------|----------|----------|----------|----------|-------|-------|-------|-------|
| Zr$_2$GaC | PBE        | 266.78   | 59.35    | 59.91    | 217.99   | 91.07    | 123.32 | 122.33 | 95.33 | 94.66 |
|          | PW91       | 281.03   | 67.30    | 76.23    | 218.78   | 81.24    | 135.60 | 134.28 | 91.27 | 89.39 |
|          | LDA        | 296.52   | 70.35    | 75.63    | 244.41   | 94.46    | 142.30 | 141.42 | 101.45| 100.46|
| Hf$_2$GaC | PBE        | 305.81   | 65.32    | 72.60    | 251.48   | 112.85   | 142.68 | 141.84 | 112.69| 111.87|
|          | PW91       | 305.71   | 66.90    | 73.44    | 249.97   | 111.07   | 143.21 | 142.28 | 111.49| 110.66|
|          | LDA        | 340.36   | 75.95    | 88.05    | 284.29   | 126.99   | 163.23 | 162.55 | 124.77| 123.76|

Table 3. The calculated bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$), Pugh’s ratio ($B/G$ and $G/B$), anisotropic index ($A$), and Poisson’s ratio for $M_2$GaC MAX phase ($M = \text{Zr, Hf}$).

| $M_2$GaC | Functional | $B$ (GPa) | $G$ (GPa) | $E$ (GPa) | $B/G$ | $G/B$ | $A$ | $\nu$ |
|----------|------------|-----------|-----------|-----------|-------|-------|-----|-----|
| Zr$_2$GaC | Ref [34]   | 146       |           |           |       |       |     |     |
|          | PBE        | 122.827   | 94.99     | 226.57    | 1.29  | 0.77  | 0.99| 0.192|
|          | PW91       | 134.938   | 90.33     | 221.56    | 1.49  | 0.67  | 0.94| 0.226|
|          | LDA        | 141.857   | 100.96    | 244.80    | 1.40  | 0.71  | 0.97| 0.212|
| Hf$_2$GaC | Ref [34]   | 158       |           |           |       |       |     |     |
|          | PBE        | 142.260   | 112.28    | 266.68    | 1.26  | 0.79  | 1.09| 0.187|
|          | PW91       | 142.749   | 111.06    | 264.58    | 1.28  | 0.77  | 1.08| 0.191|
|          | LDA        | 162.893   | 124.27    | 297.21    | 1.31  | 0.76  | 1.13| 0.195|

Young’s modulus can be calculated by

$$E = \frac{9BG}{3B + G} \quad (12)$$

To calculate the anisotropy index ($A$) following expression is used

$$A = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (13)$$

The Poisson’s ratio can be calculated by:

$$\sigma = \frac{3B - 2G}{2(3B + G)} \quad (14)$$

Generally, the calculated parameters $B$, $G$, and $E$ measure the material’s resistance to fracture, resistance to plastic deformation, and stiffness of the material, respectively. The bulk modulus ($B$) calculated in terms of elastic constants is in good agreement with the bulk modulus ($B^*$) obtained from the Birch–Murnaghan equation of state (EOS), indicating that our estimated elastic constants for Zr$_2$GaC and Hf$_2$GaC are accurate and precise. Moreover, the calculated bulk modulus obtained from LDA is in good agreement with the available study [34]. Furthermore, $B$, $G$, and $E$ for Hf$_2$GaC > Zr$_2$GaC, which means the effect to resist the deformation of Hf$_2$GaC is better than that of Zr$_2$GaC. Therefore, the reduction of volume ratio ($V/V_0$) for Zr$_2$GaC is higher than Hf$_2$GaC (See Figure 3).

Another parameter, the Pugh’s ratio ($B/G$ and $G/B$) [58], separates the ductile to brittle nature of the material. It is known that if $B/G > 1.75$ and $G/B < 0.5$, the material will be ductile; otherwise, it will be brittle [59]. In our cases (Zr$_2$GaC and Hf$_2$GaC), the $B/G < 1.75$ and $G/B > 0.5$; consequently, the compounds under this study are predicted to be brittle like Ta$_2$GaC [20]. The anisotropy index ($A$) gives the knowledge about the anisotropic nature of the materials. If the value of A is equal to 1,
then the material is said to be isotropic; otherwise, material will be anisotropic if the value of $\sigma$ is higher or lower than 1. Our calculated results from Table 3 showed that the M$_2$GaC MAX phases are anisotropic.

One of the most essential elastic parameters is Poisson’s ratio ($\sigma$), defined as the ratio between the transverse strain to longitudinal strain under the applied tensile stress. It gives knowledge about the material’s chemical bonding and is linked to its stability against the shear stress. Whether the material is brittle or ductile can be predicted from the Poisson’s ratio ($\sigma$) value, and the 0.33 value is set for ductile material; otherwise, the material is called brittle if $\sigma < 0.33$. In the results of both investigated Zr$_2$GaC and Hf$_2$GaC MAX phases, the Poisson’s ratio ($\sigma$) value is smaller; consequently, both compounds are predicted to be brittle.

For the phase stability of M$_2$GaC MAX phases, the calculated phonon dispersion curves along the high-symmetry directions in the Brillouin zone are shown in Figure 7. The M$_2$GaC MAX phases have eight atoms in the unit cell; therefore, the phonon dispersion curve shows twenty-four branches (three acoustic and twenty-one optical). The optical frequencies (longitudinal optical (LO) and transverse optical (TO)) at $\Gamma$ are 14.58 THz and 16.00 THz for Zr$_2$GaC and 16.56 THz and 18.32 THz for Hf$_2$GaC. We have not observed any negative or imaginary frequency in the phonon dispersion curves of both MAX phases indicating that M$_2$GaC MAX phases are dynamically stable. To the best of the authors’ knowledge, phonon dispersion for Zr$_2$GaC and Hf$_2$GaC have not yet been investigated theoretically and experimentally.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** The phonon dispersion curve for M$_2$GaC MAX phase (a) Zr$_2$GaC; (b) Hf$_2$GaC.

4. Thermodynamic Properties

The thermal properties of Zr$_2$GaC and Hf$_2$GaC are computed in the temperature ranges 0–1600 K and the pressure in the range 0–50 GPa with the step of 10 GPa, whereas the quasiharmonic Debye model remains valid [41,42] in this temperature range. This model has been successfully applied to calculate the thermodynamic properties of other MAX phases as well. The Debye temperature ($\theta_D$) is calculated from elastic constants and it depends on the mean propagation sound velocity ($v_m$). A couple of equations are used to calculate the $\theta_D$ which are given below: [61–63]

$$\theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi V_a} \right]^{\frac{1}{2}} v_m \tag{15}$$

where

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_1^3} + \frac{1}{v_2^3} \right) \right]^{-\frac{1}{2}} \tag{16}$$
with

\[ v_t = \left( \frac{G}{\rho} \right)^{\frac{1}{2}} \]  

(17)

and

\[ v_l = \left( \frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}} \]  

(18)

where \( h \) is Planck’s constant, \( k_B \) is Boltzmann’s constant, \( n \) represents the number of atoms per unit cell, \( V_a \) is the atomic volume while \( v_m, v_t, \) and \( v_l \) are mean sound velocity, transverse and longitudinal sound velocities respectively.

The calculated relationship between volume and temperature, heat capacity and temperature, Debye temperature and temperature, Grüneisen parameter (\( \gamma \)) and temperature, and thermal expansion coefficient and temperature for \( \text{Zr}_2\text{GaC} \) and \( \text{Hf}_2\text{GaC} \) is given in Figures 8–12. The calculated \( v_m, v_t, v_l, \) Debye temperature (\( \theta_D \)), thermal expansion coefficient CTE (\( \alpha \)), and heat capacity at constant volume (\( C_V \)) and constant pressure (\( C_P \)) for \( \text{Zr}_2\text{GaC} \) and \( \text{Hf}_2\text{GaC} \) at 300 K are presented in Tables 1–4.

Figure 8. Temperature effect on lattice parameters at different pressures for \( M_2\text{GaC} \) MAX phase (a) \( \text{Zr}_2\text{GaC} \); (b) \( \text{Hf}_2\text{GaC} \).

Figure 9. The dependence of Debye temperature on temperature at different pressures for \( M_2\text{GaC} \) MAX phase (a) \( \text{Zr}_2\text{GaC} \); (b) \( \text{Hf}_2\text{GaC} \).
Figure 10. Temperature effect on heat capacity $C_v$ and $C_p$ at different pressures for $M_2GaC$ MAX phase (a) $Zr_2GaC$; (b) $Hf_2GaC$.

Figure 11. Temperature effect on Grüneisen parameters at different pressures for $M_2GaC$ MAX phase (a) $Zr_2GaC$; (b) $Hf_2GaC$. 
Figure 12. The effect of temperature on thermal expansion coefficient at different pressures for M$_2$GaC MAX phase (a) Zr$_2$GaC; (b) Hf$_2$GaC.

Table 4. The calculated transverse elastic wave velocity ($v_t$), longitudinal elastic wave velocity ($v_l$), the average wave velocity ($v_m$), Debye temperature ($\theta_D$), thermal expansion coefficient ($\alpha$), and heat capacities at constant volume and constant pressure (Cv and Cp) at 300 K for M$_2$GaC MAX phase (M = Zr, Hf).

| M$_2$GaC | $v_t$ ($\times 10^5$ m/s) | $v_l$ ($\times 10^5$ m/s) | $v_m$ ($\times 10^5$ m/s) | $\theta_D$ (K) | $\alpha$ ($\times 10^{-5}$ K$^{-1}$) | Cv (J/mol·K) | Cp (J/mol·K) |
|----------|----------------|----------------|----------------|---------------|----------------|----------------|----------------|
| Zr$_2$GaC | 3.85 | 6.24 | 4.24 | 787.91 | 1.1432 | 72.33 | 72.77 |
| Hf$_2$GaC | 3.21 | 5.18 | 3.54 | 720.78 | 0.8427 | 76.00 | 76.34 |

From Figure 8, it is noticed that a small change in volume takes place from the temperature 0 to 100 K at a given pressure, and volume linearly increases with the rise in temperature while a decrease in volume is observed at high pressure at a given temperature. The relationship between the Debye temperature and temperature is shown in Figure 9. The linear decline in Debye temperature could be seen with the increase in temperature and increases with pressure. For both Zr$_2$GaC and Hf$_2$GaC MAX phase, the value of $\theta_D$ at a given temperature and pressure is in the order of $(\theta_D)_{Zr_2GaC} > (\theta_D)_{Hf_2GaC}$. Many physical properties of solidity such as hardness, thermal expansion [60], and heat capacity depend on Debye temperature. The hardness of the Zr$_2$GaC and Hf$_2$GaC MAX phase in terms of Debye temperature is in the order of Zr$_2$GaC > Hf$_2$GaC because the $\theta_D$ value for Zr$_2$GaC and Hf$_2$GaC is 787.91 K and 720.78 K, respectively, at 0 GPa and ambient temperature.

The effect of temperature on heat capacity (Cv, Cp) of Zr$_2$GaC and Hf$_2$GaC MAX phase is depicted in Figure 10. The heat capacity is the ability of the material to absorb heat from the surroundings, and one can get useful information about the density of states, lattice vibration, energy band structure, etc., from heat capacity. It is observed that both Cv and Cp increase abruptly with temperature when temperature limit T ≤ 300 K, beyond the 300 K, Cv and Cp increases slowly and finally get converged at higher temperature to obey the Dulong–Petit limit. The effect of temperature and pressure on heat capacity is the opposite; however, temperature change has a more significant impact than pressure. The obtained heat capacity values of Zr$_2$GaC and Hf$_2$GaC MAX phase at constant volume corresponding to ambient temperature and 0 GPa are 72.33 J/mol·K and 76.00 J/mol·K, respectively.

The Grüneisen parameter ($\gamma$) is used to calculate the thermal state and is a dimensionless quantity. The trend for $\gamma$ is almost similar to that of volume. As shown in Figure 11 that $\gamma$ decreases with an increase in pressure while increasing linearly with temperature. However, $\gamma$ remains constant in the temperature range from 0–100 K. The obtained $\gamma_0$ values for Zr$_2$GaC and Hf$_2$GaC are 1.76 and 1.74 at 0 GPa, respectively. Finally, the dependence of the thermal expansion coefficient ($\alpha$) on temperature is depicted in Figure 12. At a given temperature, $\alpha$ decreases with the increase in pressure; this may
be due to reduced unit cell volume. The results of $\alpha$ at ambient temperature and 0 GPa for $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ are $1.14 \times 10^{-5}$ K$^{-1}$ and $0.84 \times 10^{-5}$ K$^{-1}$, respectively. However, in the range 0–300 K, $\alpha$ increases rapidly and reaches a plateau at higher temperature, indicating that the temperature effect is more important at lower temperature.

5. Conclusions
In this study, electronic, structural, elastic, phonon, thermodynamical, and mechanical properties of the $\text{M}_2\text{GaC}$ MAX phase ($\text{M} = \text{Zr, Hf}$) were comprehensively investigated by employing first-principle calculations based on GGA and LDA exchange-correlation functional. The thermodynamic properties were computed using the quasiharmonic Debye model in the pressure ranges 0–50 GPa, and temperature in the range 0–1600 K. The results showed that the formation and cohesive energies for both $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ are found to be negative, i.e., $-7.59$ eV/atom and $-6.32$ eV/atom for $\text{Zr}_2\text{GaC}$ and $-7.45$ eV/atom and $-6.16$ eV/atom for $\text{Hf}_2\text{GaC}$. The PDOS revealed that the main contribution in electric transport at $E_F$ was by transition metal M-4d electrons and hybridizations between M-d and C-p states is stronger than M-d and Ga-p states. The DOS at $E_F$ for $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ was 2.96 states/eV/unit and 2.47 states/eV/unit, respectively, indicating that these MAX phases are predicted to be electrical conductors while band structures pointed out their anisotropic nature. Moreover, the formation and cohesive energies, elastic constants, and phonon calculations showed that both compounds are thermodynamically, mechanically, and dynamically stable. Furthermore, the values of $E$, $B$, and $G$ in terms of elastic constants are in the order of $\text{Hf}_2\text{GaC} > \text{Zr}_2\text{GaC}$. From the $B/G$, Poisson’s ratio, and anisotropy index, it is concluded that the MAX phases investigated in this study are brittle and anisotropic. As far as thermodynamic properties of the $\text{M}_2\text{GaC}$ MAX phase are concerned, the volume and Grüneneisen parameter increases linearly with an increase in temperature and decreases with an increase in pressure while the Debye temperature has an inverse trend compared to them. The heat capacities ($C_v$ and $C_p$) and the thermal expansion co-efficient increases rapidly up to the temperature ranges 0–300 K and then reaches a plateau at higher temperature. To the best of the authors’ knowledge, no data related to the electronic, structural, phonon, and thermodynamic properties in the literature exist so far. Hence, the results about the $\text{M}_2\text{GaC}$ ($\text{M} = \text{Zr, Hf}$) MAX phase can serve as a reference for future theoretical and experimental research.

Author Contributions: Conceptualization, M.W.Q. and X.M.; methodology, M.W.Q. and R.P.; software, X.M.; validation M.W.Q., X.M., G.T., and R.P.; formal analysis, M.W.Q., X.M., and R.P.; investigation, M.W.Q., G.T.; writing—original draft preparation, M.W.Q., and X.M.; writing—review and editing, M.W.Q., X.M., and R.P.; supervision, X.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the National Science and Technology Major Project (No. 2017-VII-0003-0096) and the National Natural Science Foundation of China (NSFC No. 51971084 and No. 52031003).

Acknowledgments: The authors express their sincere gratitude to Zhu Jingchuan from the School of Material Science and Engineering, Harbin Institute of Technology, for providing the computing facility.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Nowotny, V.H. Strukturchemie einiger Verbindungen der Übergangsmetalle mit den elementen C, Si, Ge, Sn. Prog. Solid State Chem. 1971, 5, 27–70. [CrossRef]
2. Barsoum, M.W. MAX Phases: Properties of Machinable Ternary Carbides and Nitrides; Wiley-VCH: Weinheim, Germany, 2013. [CrossRef]
3. Eklund, P.; Rosen, J.; Persson, P.O.Å. Layered ternary Mn + 1AXn phases and their 2D derivative MXene: An overview from a thin-film perspective. J. Phys. D Appl. Phys. 2017, 50. [CrossRef]
4. Eklund, P.; Beckers, M.; Jansson, U.; Högborg, H.; Hultman, L. The Mn + 1AXn phases: Materials science and thin-film processing. Thin Solid Films 2010, 518, 1851–1878. [CrossRef]
5. Barsoum, M.W.; El-Raghy, T. The MAX phases: Unique new carbide and nitride materials: Tertiary ceramics are soft and machinable, yet heat-tolerant, strong and lightweight. Am. Sci. 2001, 89, 334–343. [CrossRef]
6. Barsoum, M.W.; El-Raghy, T. Synthesis and characterization of a remarkable ceramic: Ti$_2$SiC$_2$. *J. Am. Ceram. Soc.* 1996, 79, 1953–1956. [CrossRef]

7. Tzenov, N.V.; Barsoum, M.W. Synthesis and Characterization of Ti$_3$AlC$_2$. *J. Am. Ceram. Soc.* 2004, 83, 825–832. [CrossRef]

8. Li, C.; Wang, B.; Li, Y.; Wang, R. First-principles study of electronic structure, mechanical and optical properties of V$_4$AlC$_3$. *J. Phys. D. Appl. Phys.* 2009, 42. [CrossRef]

9. Nappé, J.C.; Grosseau, P.; Audubert, F.; Guilhot, B.; Beauvy, M.; Benabdesselam, M.; Monnet, I. Damages induced by heavy ions in titanium silicon carbide: Effects of nuclear and electronic interactions at room temperature. *J. Nucl. Mater.* 2009, 385, 304–307. [CrossRef]

10. Shi, S.; Zhang, L.; Li, J. High frequency electromagnetic interference shielding behaviors of Ti$_3$SiC$_2$/Al$_2$O$_3$ composites. *J. Appl. Phys.* 2008, 103. [CrossRef]

11. Barsoum, M.W. MN + 1AXN phases: A new class of solids; thermodynamically stable nanolaminates. *Prog. Solid State Chem.* 2000, 28, 201–281. [CrossRef]

12. Sun, D.; Hu, Q.; Chen, J.; Zhang, X.; Wang, L.; Wu, Q.; Zhou, A. Structural Transformation of MXene (V$_2$C, Cr$_2$C, and Ta$_2$C) in comparison with O Groups during Lithiation: A First-Principles Investigation. *ACS Appl. Mater. Interfaces* 2016, 8, 74–81. [CrossRef][PubMed]

13. Lin, Z.; Barbara, D.; Taberna, P.L.; van Aken, K.L.; Anasori, B.; Gogotsi, Y.; Simon, P. Capacitance of Ti$_3$C$_2$Tx MXene in ionic liquid electrolyte. *J. Power Sources* 2016, 326, 575–579. [CrossRef]

14. Wang, Y.; Ma, C.; Ma, W.; Fan, W.; Sun, Y.; Yin, H.; Shi, X.; Liu, X.; Ding, Y. Enhanced low-temperature Li-ion storage in MXene titanium carbide by surface oxygen termination. *2D Mater.* 2019, 6. [CrossRef]

15. Wang, Q.M.; Renteria, A.F.; Schroeter, O.; Mykhaylonka, R.; Leyens, C.; Garkas, W.; Baben, M. Fabrication and oxidation behavior of Cr$_2$AlC coating on Ti6242 alloy. *Surf. Coat. Technol.* 2010, 204, 2343–2352. [CrossRef]

16. Hajas, D.E.; Baben, M.T.; Hallstedt, B.; Ikandar, R.; Mayer, J.; Schneider, J.M. Oxidation of Cr$_2$AlC coatings in the temperature range of 1230 to 1410 °C. *Surf. Coat. Technol.* 2011, 206, 591–598. [CrossRef]

17. Lapauw, T.; Tunca, B.; Cabioc’h, T.; Lu, J.; Persson, P.O.Å.; Lambrinou, K.; Vleugels, J. Synthesis of MAX Phases in the HF-Al-C System. *Inorg. Chem.* 2016, 55, 10922–10927. [CrossRef][PubMed]

18. Lapauw, T.; Lambrinou, K.; Cabioc’h, T.; Halim, J.; Lu, J.; Pesach, A.; Rivin, O.; Ozeri, O.; Caspi, E.N.; Hultman, L.; et al. Synthesis of the new MAX phase Zr$_2$AlC. *J. Eur. Ceram. Soc.* 2016, 36, 1847–1853. [CrossRef]

19. Perdew, J.P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* 1986, 33, 8822–8824. [CrossRef]

20. Pu, X.X.; Long, X.J.; Zhang, L.; Zhu, J. The structure, elastic and thermodynamic properties of Ti$_2$GaC from first-principles calculation. *Int. J. Mod. Phys. B* 2019, 33, 1–17. [CrossRef]

21. Thore, A.; Dahlqvist, M.; Alling, B.; Rosén, J. First-principles calculations of the electronic, vibrational, and elastic properties of the magnetic laminate Mn$_2$GaC. *J. Appl. Phys.* 2014, 116. [CrossRef]

22. Shein, I.R.; Ivanovskii, A.L. Elastic properties of superconducting MAX phases from first-principles calculations. *Phys. Status Solidi Basic Res.* 2011, 248, 228–232. [CrossRef]

23. Shein, I.R.; Ivanovskii, A.L. Structural, elastic, electronic properties and Fermi surface for superconducting Mo$_2$GaC in comparison with V$_2$GaC and Nb$_2$GaC from first principles. *Phys. C Supercond. Appl.* 2010, 470, 533–537. [CrossRef]

24. Qing-He, G.; Zhi-Jun, X.; Ling, T.; Jin, L.; An, D.; Yun-Dong, G.; Ze-Jin, Y. Origin of the c-axis ultraincompressibility of Mo$_2$GaC above about 15 GPa from first principles. *J. Appl. Phys.* 2016, 119. [CrossRef]

25. Petruhins, A.; Ingason, A.S.; Dahlqvist, M.; Mockute, A.; Junaid, M.; Birch, J.; Lu, J.; Hultman, L.; Persson, P.O.A.; Rosen, J. Phase stability of Cr$_n$+1GaCn MAX phases from first principles and Cr$_2$GaC thin-film synthesis using magnetron sputtering from elemental targets. *Phys. Status Solidi Rapid Res. Lett.* 2013, 7, 971–974. [CrossRef]

26. Etzkorn, J.; Ade, M.; Kotzott, D.; Kleczek, M.; Hillebrecht, H.; Ti$_2$GaC, Ti$_4$Ga$_3$C and Cr$_2$GaC-Synthesis, crystal growth and structure analysis of Ga-containing MAX-phases Mn + 1GaCn with M = Ti, Cr and n = 1, 3. *J. Solid State Chem.* 2009, 182, 995–1002. [CrossRef]

27. Aydin, S.; Tatar, A.; Ciftci, Y.O. Some new members of MAX family including light-elements: Nanolayered Hf$_2$XY (X = Al, Si, P and YCombining double low lineB, C, N). *Solid State Sci.* 2016, 53, 44–55. [CrossRef]

28. Ghebouli, B.; Ghebouli, M.A.; Fatmi, M.; Louail, L.; Chihi, T.; Bouhemadou, A. First-principles calculations of structural, electronic, elastic and thermal properties of phase M$_2$SiC (M = Ti, V, Cr, Zr, Nb, Mo, Hf, Tà and W). *Trans. Nonferrous Met. Soc. China (English Ed.)* 2015, 25, 915–925. [CrossRef]
29. Bouhemadou, A. Calculated structural and elastic properties of M$_2$InC (M = Sc, Ti, V, Zr, Nb, Hf, Ta). *Mod. Phys. Lett. B* 2008, 22, 2063–2076. [CrossRef]

30. Islam, A.K.M.A. Remarkable Class of Materials: Band Structures and Optical Properties of Non-Superconducting and Superconducting MAX Phases. 2015. Available online: https://www.researchgate.net/publication/291354284 (accessed on 3 October 2020).

31. Bouhemadou, A. Calculated structural, electronic and elastic properties of M$_2$GeC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W). *Appl. Phys. A Mater. Sci. Process.* 2009, 96, 959–967. [CrossRef]

32. Luo, F.; Guo, Z.C.; Zhang, X.L.; Yuan, C.Y.; Cai, L.C. Ab initio predictions of structural and thermodynamic properties of Zr$_2$AlC under high pressure and high temperature. *Chin. J. Chem. Phys.* 2015, 28, 263–268. [CrossRef]

33. Brik, M.G.; Avram, N.M.; Avram, C.N. Ab initio calculations of the electronic, structural and elastic properties Nb$_2$InC. *Comput. Mater. Sci.* 2012, 63, 227–231. [CrossRef]

34. Sun, Z.; Music, D.; Ahuja, R.; Li, S.; Schneider, J.M. Bonding and classification of nanolayered ternary carbides. *Phys. Rev. B Condens. Matter Mater. Phys.* 2004, 70, 1–3. [CrossRef]

35. Payne, M.C.; Teter, M.P.; Allan, D.C.; Arias, T.A.; Joannopoulos, J.D. Iterative minimization techniques for ab initio total-energy calculations: Molecular dynamics and conjugate gradients. *Rev. Mod. Phys.* 1992, 64, 1045–1097. [CrossRef]

36. Perdew, J.P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* 1992, 45, 13244–13249. [CrossRef] [PubMed]

37. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868. [CrossRef] [PubMed]

38. Perdew, J.P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* 1981, 23, 5048–5079. [CrossRef]

39. Fischer, T.H.; Almlöf, J. General methods for geometry and wave function optimization. *J. Phys. Chem.* 1992, 96, 9768–9774. [CrossRef]

40. Otero-De-La-Roza, A.; Abbasi-Perez, D.; Luana, V. Gibbs2: A new version of the quasiharmonic model code. II. Models for solid-state thermodynamics, features and implementation. *Comput. Phys. Commun.* 2011, 182, 2232–2248. [CrossRef]

41. Blanco, M.A.; Francisco, E.; Luaña, V. GIBBS: Isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model. *Comput. Phys. Commun.* 2004, 158, 57–72. [CrossRef]

42. Payne, M.C.; Teter, M.P.; Allan, D.C.; Arias, T.A.; Joannopoulos, J.D. Iterative minimization techniques for ab initio total-energy calculations: Molecular dynamics and conjugate gradients. *Rev. Mod. Phys.* 1992, 64, 1045–1097. [CrossRef]

43. Mauchamp, V.; Yu, W.; Gence, L.; Piraux, L.; Cabioc-H, T.; Gauthier, V.; Eklund, P.; Dubois, S. Anisotropy of the resistivity and charge-carrier sign in nanolaminated Ti$_2$AlC: Experiment and ab initio calculations. *Phys. Rev. B Condens. Matter Mater. Phys.* 2013, 87, 1–7. [CrossRef]

44. Hadi, M.A.; Kelaidis, N.; Naqib, S.H.; Islam, A.K.M.A.; Chronoos, A.; Vovk, R.V. Insights into the physical properties of a new 211 MAX phase Nb$_2$CuC. *J. Phys. Chem. Solids* 2021, 149, 109759. [CrossRef]

45. Hadi, M.A.; Kelaidis, N.; Naqib, S.H.; Islam, A.K.M.A.; Chronoos, A.; Vovk, R.V. Insights into the physical properties of a new 211 MAX phase Nb$_2$CuC. *J. Phys. Chem. Solids* 2021, 149, 109759. [CrossRef]

46. Huang, Z.W.; Zhao, Y.H.; Hou, H.; Han, P.D. Electronic structural, elastic properties and thermodynamics of Mg$_{17}$Al$_{12}$, Mg$_2$Si and Al$_2$Y phases from first-principles calculations. *Phys. B Condens. Matter.* 2012, 407, 1075–1081. [CrossRef]

47. Cui, S.; Wei, D.; Hu, H.; Deng, W.; Gong, Z. First-principles study of the structural and elastic properties of Cr$_2$AlX (X = N, C) compounds. *J. Solid State Chem.* 2012, 191, 147–152. [CrossRef]

48. Tan, J.; Han, H.; Wickramaratne, D.; Liu, W.; Zhao, M.; Huai, P. A comparative first-principles study of the electronic, mechanical, and acoustic properties of Ti$_2$AlC and Ti$_3$AlC. *J. Phys. D Appl. Phys.* 2014, 47, 215301. [CrossRef]

49. Hadi, M.A.; Kelaidis, N.; Naqib, S.H.; Islam, A.K.M.A.; Chronoos, A.; Vovk, R.V. Insights into the physical properties of a new 211 MAX phase Nb$_2$CuC. *J. Phys. Chem. Solids* 2021, 149, 109759. [CrossRef]

50. Mauchamp, V.; Yu, W.; Gence, L.; Piraux, L.; Cabioc-H, T.; Gauthier, V.; Eklund, P.; Dubois, S. Anisotropy of the resistivity and charge-carrier sign in nanolaminated Ti$_2$AlC: Experiment and ab initio calculations. *Phys. Rev. B Condens. Matter Mater. Phys.* 2013, 87, 1–7. [CrossRef]

51. Li, H.; Sun, G.; Deng, J.; Zhang, W.; Xu, L.; Jiang, W.; Feng, Y.; Li, K. Phonon and electronic properties of Ti$_2$SiC from first-principles calculations. *Solid State Commun.* 2015, 204, 37–40. [CrossRef]
52. Schäfer, K.; Duane, C. Wallace: Thermodynamics of Crystals. XVIII u. 484 S. mit 57 Abb. John Wiley & Sons Ltd. Chichester, New York, Sydney, Tokio, Mexiko 1972. Preis: £ 8,85. *Ber. Bunsenges. Phys. Chem.* 1972, 76, 1211. [CrossRef]

53. Mouhat, F.; Coudert, F.X. Necessary and sufficient elastic stability conditions in various crystal systems. *Phys. Rev. B Condens. Matter Mater. Phys.* 2014, 90, 224104. [CrossRef]

54. Reuss, A. Berechnung der Fließgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle. *ZAMM J. Appl. Math. Mech. Z. Angew. Math. Mech.* 1929, 9, 49–58. [CrossRef]

55. Brazhkin, V.V. High-pressure synthesized materials: Treasures and hints. *High Press. Res.* 2007, 27, 333–351. [CrossRef]

56. Hill, R. The elastic behaviour of a crystalline aggregate. *Proc. Phys. Soc. Sect. A* 1952, 65, 349–354. [CrossRef]

57. Johnson, D.D. Electronic Basis of the Strength of Materials. *Phys. Today* 2004. [CrossRef]

58. Pugh, S.F. XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *Lond. Edinb. Dublin Philos. Mag. J. Sci.* 1954, 45, 823–843. [CrossRef]

59. Chen, X.Q.; Niu, H.; Li, D.; Li, Y. Modeling hardness of polycrystalline materials and bulk metallic glasses. *Intermetallics* 2011, 19, 1275–1281. [CrossRef]

60. Haines, J.; Léger, J.; Bocquillon, G. Synthesis and Design of Superhard Materials. *Annu. Rev. Mater. Res.* 2001, 31, 1–23. [CrossRef]

61. Schreiber, E. *Elastic Constants and Their Measurement*; McGraw-Hill: New York, NY, USA, 1974.

62. Sun, Z.; Li, S.; Ahuja, R.; Schneider, J.M. Calculated elastic properties of M₂AlC (M = Ti, V, Cr, Nb and Ta). *Solid State Commun.* 2004, 129, 589–592. [CrossRef]

63. Jasiukiewicz, C.; Karpus, V. Debye temperature of cubic crystals. *Solid State Commun.* 2003, 128, 167–169. [CrossRef]

**Publisher’s Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).