New ordered MAX phase Mo_2TiAlC_2: Elastic and electronic properties from first-principles

M A Hadi[1,†] and M S Ali[2]

[1] Department of Physics, University of Rajshahi, Rajshahi-6205, Bangladesh
[2] Department of Physics, Pabna University of Science and Technology, Pabna 6600, Bangladesh

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First-principles computation on the basis of density functional theory (DFT) is executed with the CASTEP code to explore the structural, elastic, and electronic properties along with Debye temperature and theoretical Vickers' hardness of newly discovered ordered MAX phase carbide Mo_2TiAlC_2. The computed structural parameters are very reasonable compared with the experimental results. The mechanical stability is verified by using the computed elastic constants. The brittleness of the compound is indicated by both the Poisson's and Pugh's ratios. The new MAX phase is capable of resisting the pressure and tension and also has the clear directional bonding between atoms. The compound shows significant elastic anisotropy. The Debye temperature estimated from elastic moduli (B, G) is found to be 413.6 K. The electronic structure indicates that the bonding nature of Mo_2TiAlC_2 is a mixture of covalent and metallic with few ionic characters. The electron charge density map shows a strong directional Mo–C–Mo covalent bonding associated with a relatively weak Ti–C bond. The calculated Fermi surface is due to the low-dispersive Mo 4d-like bands, which makes the compound a conductive one. The hardness of the compound is also evaluated and a high value of 9.01 GPa is an indication of its strong covalent bonding.

Keywords: new ordered MAX phase, density functional theory calculations, Debye temperature, Vickers hardness

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1. Introduction

The MAX phases are a class of compounds that have a common formula $M_{n+1}AX_n$ with $n = 1, 2, 3$, etc. Here M denotes an early transition metal from group 3–6, A is an A-group element that comes from columns 12–16 in the periodic table, and X represents C and/or N. The MAX phases are the materials with laminated layered structures having thickness values of the individual layers on a nanometer scale. This family of ternary layered carbides and nitrides are promising materials carrying the merits of both metals and high-performance ceramics.[1] These metallic ceramics were first discovered in the 1960s by Nowotny *et al.*[2–8] All the studies completed over the past six decades have confirmed that these nanolaminates exhibit an uncommon arrangement of properties, which put together the high specific stiffness and lubricity with assuagement of machinability and good oxidation resistance including expedient high-temperature properties. In addition, the MAX phases possess surprisingly good electrical and thermal conductivities, exceptional damage tolerance, excellent thermal shock resistance, and reversible plasticity, high resistance to oxidation and corrosion and ability to maintain the strengths to high temperature.[9–15] This rare collection of metallic and ceramics properties of the MAX compounds makes them aspirant materials for a series of applications ranging from catalysis to aerospace.[16]

At present, we have more than 70 synthesized MAX phases amongst which there is only the Mo_2GaC phase containing Mo as M element. Very recently, Anasori *et al.*[17] reported on the synthesis of a new Mo-containing ordered MAX phase, Mo_2TiAlC_2 having structure similar to Ti_3SiC_2.[10,18] In this phase, the Ti atoms are pressed between two Mo-layers like a layer pressed between two others of a different kind in a sandwich form that in turn are contiguous to the Al planes resulting in an Mo–Ti–Mo–Al–Mo–Ti–Mo stacking order. The C-atoms take positions in between the Mo and Ti layers. In the present study, the first-principles method is used to predict the elastic and electronic properties along with Debye temperature and theoretical hardness of this new member of the MAX family. Very recently, we became aware of a report on various properties of newly discovered Mo_2TiAlC_2 with first-principles calculations by the projector augmented wave method as implemented within the Vienna *ab-initio* simulation package (VASP).[19] The present results are compared with those found in this report.

2. Method

The structural, elastic, and electronic properties of the newly synthesized MAX phase Mo_2TiAlC_2 are calculated by using the plane wave pseudopotential approach within the density functional theory (DFT) that is used in the Cambridge Serial Total Energy Package (CASTEP) code.[20] The generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional[21] is used to evaluate the exchange–correlation energy. The Vanderbilt-type ultrasoft

†Corresponding author. E-mail: hadipab@gmail.com

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pseudopotential is taken for the treatment of electron–ion interactions.[22] The energy cut-off is set to be 550 eV to expand the plane wave functions. The first Brillouin zone of the unit cell is sampled by using the Monkhorst–Pack scheme[23] of k-points with $17 \times 17 \times 2$ mesh. The structure is fully optimized with respect to atomic positions and lattice parameters by means of the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.[24] The tolerances of convergence for the energy, maximum force, maximum stress, and maximum atomic displacement are set to be 5×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa, and 5×10^{-4} Å, respectively. To achieve good convergences in total energy, geometry, and elastic moduli, the parameters set above cover the required adequacy. To obtain the smooth Fermi surface, $30 \times 30 \times 4$ k-point mesh is used.

The structure of Mo_2TiAlC_2 is first optimized. The elastic constants are calculated from the first-principles via the finite-strain theory as implemented in the CASTEP code. In the finite-strain theory, a set of finite identical deformations is applied and the resulting stress is computed to find the elastic constants by solving the equation, $\sigma_i = C_{ij}\varepsilon_j$. The detailed procedures can be found in Ref. [25]. The polycrystalline elastic properties namely, bulk modulus B and shear modulus G are calculated from the single-crystal elastic constants C_{ij} using the well-known Voigt–Reuss–Hill approximation.[26–28] In addition, the Young's modulus Y, Poisson's ratio v, and shear anisotropy factor A are derived by using the equations $Y = (9GB)/(3B+G)$, $v = (3B-2G)/(6B+2G)$, and $A = 4C_{44}/(C_{11}+C_{33}-2C_{13})$, respectively.

The Debye temperature, θ_D, is calculated by using one of the standard methods, depends on the elastic constants such as bulk modulus and shear modulus.[29] Within this method, the Debye temperature can be estimated from the average sound velocity v_m by the following equation:

$$\theta_D = h/k_B[(3n/4\pi)N_A\rho/M]^{1/3}v_m,$$

where h is the Planck's constant, k_B is the Boltzmann's constant, n is the number of atoms per formula unit, M is the molar mass, N_A is the Avogadro's number, and ρ is the mass density of the polycrystalline solid. The average sound velocity in the polycrystalline material is given by $v_m = [1/3(1/v_l^3 + 2/v_t^3)]^{-1/3}$. Here v_l and v_t denote the longitudinal and transverse sound velocities in crystalline solids and are determined as $v_l = [(3B+4G)/3\rho]^{1/2}$ and $v_t = [G/\rho]^{1/2}$.

The theoretical Vickers' hardness for crystal with metallic bonding is evaluated from the empirical formula:[30,31]

$$H_v = \left[\sum^{\mu}(H_v^{\mu})^{n^{\mu}}\right]^{1/\sum n^{\mu}}$$

with individual bond hardness,

$$H_v^{\mu} = 740(P^{\mu} - P^{\mu'})(v_b^{\mu})^{-5/3}.$$

Here P^{μ} is the Mulliken population of the μ-type bond; $P^{\mu'}$, known as metallic population, is the number of free electrons in unit volume in a cell:

$$P^{\mu'} = \frac{1}{V}\int_{E_P}^{E_F} N(E)\,dE,$$

v_b^{μ} is the bond volume of μ-type bond:

$$v_b^{\mu} = (d^{\mu})^3/\sum_{\nu}[(d^{\mu})^3 N_b^{\mu}]$$

with d^{μ} being the bond length, N_b^{μ} the number of bonds of type ν per unit volume.

3. Results and discussion

3.1. Structural properties

Mo_2TiAlC_2 crystallizes in a hexagonal structure with a space group of $P6_3/mmc$ and is isostructural with Ti_3SiC_2. Figure 1 gives an idea about the crystal structure of Mo_2TiAlC_2. In Mo_2TiAlC_2 there are 12 atoms in one unit cell ($Z = 2$). The calculated lattice constants a and c as well as equilibrium unit cell volume V along with atomic positions for Mo_2TiAlC_2 are listed in Table 1. The present theoretical results show the closeness to the experimental and theoretical data. The deviations from the data obtained via the Rietveld analysis of the powder x-ray pattern in the experiment[17] for the lattice constants and unit cell volume are within 0.48% and 0.55%, respectively. On the other hand, the deviations of theoretical data obtained in previous VASP calculation[19] are more than 0.50% and 1.25%, respectively. Therefore, the present first-principles calculations are highly reliable.

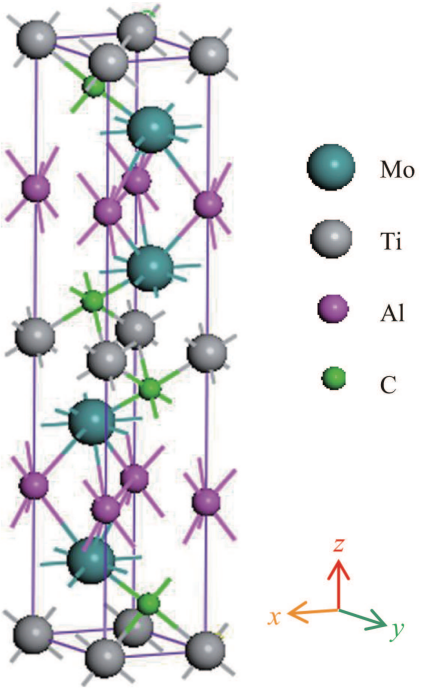


Fig. 1. (color online) Crystal structure of layered ordered new MAX compound Mo_2TiAlC_2.

Table 1. Structural properties obtained by using the DFT-based first-principles calculations together with corresponding experimental data.

Structural properties	Experimental data		Theoretical data	
	SAED[17]	Rietveld[17]	CASTEP Calc.[this]	VASP Calc.[19]
a/Å	2.933	2.997	2.998	3.0082
c/Å	18.970	18.661	18.751	18.757
V/Å^3	141.326	145.157	145.955	147.00
Space group $P6_3/mmc$				
Atomic position (Rietveld)				
Mo	$4f$	(2/3, 1/3, 0.13336)	(2/3, 1/3, 0.13316)	
Ti	$2a$	(0, 0, 0)	(0, 0, 0)	
Al	$2b$	(0, 0, 1/4)	(0, 0, 1/4)	
C	$4f$	(1/3, 2/3, 0.06875)	(1/3, 2/3, 0.06857)	

3.2. Elastic properties

The elastic properties are directly related to the crystal structure and the nature of bonding between atoms within the system. These in turn largely determine the phonon spectrum and the Debye temperature of the compound. The predicted single crystal elastic constants C_{ij} under 0 GPa are presented in Table 2.

Table 2. Calculated values of single crystal elastic constants C_{ij} (in unit GPa), polycrystalline bulk modulus B (in unit GPa), shear modulus G (in unit GPa), Young modulus Y (in unit GPa), Pugh's ratio G/B, Poisson's ratio v, and shear anisotropy factor A of Mo_2TiAlC_2.

Single crystal elastic properties			Polycrystalline elastic properties		
	CASTEP Calc.[this]	VASP Calc.[19]		CASTEP Calc.[this]	VASP Calc.[19]
C_{11}	393	386	B	217	220
C_{12}	132	143	G	140	131
C_{13}	133	140	Y	346	329
C_{33}	371	367	G/B	0.65	0.60
C_{44}	160	150	v	0.23	0.25
C_{66}	131	131	A	1.29	1.27

The polycrystalline elastic properties such as bulk modulus B, shear modulus G, Young's modulus Y, Pugh's ratio G/B, Poisson's ratio v, and shear elastic anisotropy factor A derived from C_{ij} are also listed in Table 2 along with available results converted into aggregate values using Hill approximation.[28] The positive values of C_{11}, C_{44}, $(C_{11}-C_{12})$ and $\{(C_{11}+C_{12})C_{33}-2(C_{12})^2\}$ justify the mechanical stability[32] of newly discovered nanolaminate Mo_2TiAlC_2. The comparatively large Young's modulus of Mo_2TiAlC_2 suggests that it should have a high resistance to pressure and tension in the range of elastic deformation. The directional bonding between atoms in this new compound should also be stronger due to having the large value of G. Generally, the large shear modulus of a material is an indication of its well-defined directional bonding between atoms. Pugh[33] suggested G/B ratio as an index of the plastic behavior of a material and proposed the value ~ 0.57 as the critical threshold value for separating the brittle and ductile nature of a material. A polycrystalline material would bear its mechanical property dominated by brittleness if $G/B > 0.57$, otherwise it would behave as a ductile material. In addition, the Frantsevich's rule[34] related to Poisson's ratio recommends the value ~ 0.33 as the border line between the ductile and brittle nature of a material. If the Poisson's ratio is over 0.33, the material would show the nature of ductility. Otherwise, it would exhibit the characteristics of a brittle material. The present calculated results are evident that the new compound Mo_2TiAlC_2 like most of the MAX phases[35–37] is brittle in nature in accordance with both the Pugh's criterion and Frantsevich's rule. Indeed, the brittleness is the inherent trend of MAX materials. It is seen that the new ordered MAX phase Mo_2TiAlC_2 possesses relatively low value of Poisson's ratio and it is indicative of its high level of directional covalent bonding.

Elastic anisotropy of a crystal reflects a characteristic feature of bonding in different directions. Inherently, most of the known crystals are elastically anisotropic, and a precise depiction of such an anisotropic character has, therefore, an essential implication in crystal physics and science of engineering. It shows a relationship with the possibility of existence of microcracks in the crystals. For hexagonal crystals, a shear anisotropy factor associated with the (100) shear plane between the $\langle 011\rangle$ and $\langle 010\rangle$ directions is defined as $A = 4C_{44}/(C_{11}+C_{33}-2C_{13})$. For an isotropic crystal, A is found to be unity. The deviation of A from unity assesses the elastic anisotropy possessed by the crystal and the amount of deviation measures the level of elastic anisotropy. The shear anisotropic factor for Mo_2TiAlC_2 is given in Table 2, which deviates from unity by $\sim 28\%$. It means that both the in-plane and out-of-plane inter-atomic interactions differ from each other significantly. Another anisotropic factor for hexagonal crystal is defined as the ratio between the linear compressibility coefficients along the c and a axes and expressed as $k_c/k_a = (C_{11}+C_{12}-2C_{13})/(C_{33}-C_{13})$. This factor is also evaluated. The present (previous) value of 1.09 (1.10) discloses that the compressibility along the c axis is slightly

greater than that along the a-axis for this new MAX compound.

The Debye temperature θ_D is an influential parameter directly related to various physical properties including melting temperature and specific heat, and is used to make a distinction between high- and low-temperature regions for a solid material. The Debye temperature well determines a demarcation between quantum and classical behavior of phonons. When the temperature T of a solid is raised over θ_D, all modes of vibrations are expected to have energy equal to $k_B T$. At $T < \theta_D$, the high-frequency modes are found to be stationary. The vibrational excitations at low temperature appear only from acoustic vibrations. Consequently, the Debye temperature calculated from elastic constants is seen to be the same as that estimated from measured specific heat.[38] The Debye temperature along with the related quantities including longitudinal, transverse and average sound velocities calculated within the present formalism is listed in Table 3. The high Debye temperature is an indication of strong covalent bonding in Mo_2TiAlC_2.

Table 3. Calculated density (ρ in units gm/cm^3), longitudinal, transverse and average sound velocities (v_l, v_t, and v_m in units km/s) and Debye temperature (θ_D in unit K) of Mo_2TiAlC_2.

ρ	v_l	v_t	v_m	θ_D
6.297	8.006	4.715	3.196	413.6

3.3. Electronic and bonding properties

A proper depiction of electronic structure is essential to explain many physical phenomena such as optical spectra of materials. The calculated electronic energy band structure of Mo_2TiAlC_2 at equilibrium lattice parameters along the high-symmetry lines in the first Brillouin zone is shown in Fig. 2(a). The new MAX carbide keeps its Fermi surface just below the valence band maximum around the Γ point. The occupied valence bands extend broadly from -8.7 eV to the Fermi level E_F. A lot of valence bands cross the Fermi level and partly cover the conduction bands. Accordingly, no band gap appears at the Fermi level and Mo_2TiAlC_2 should behave as a metallic compound.

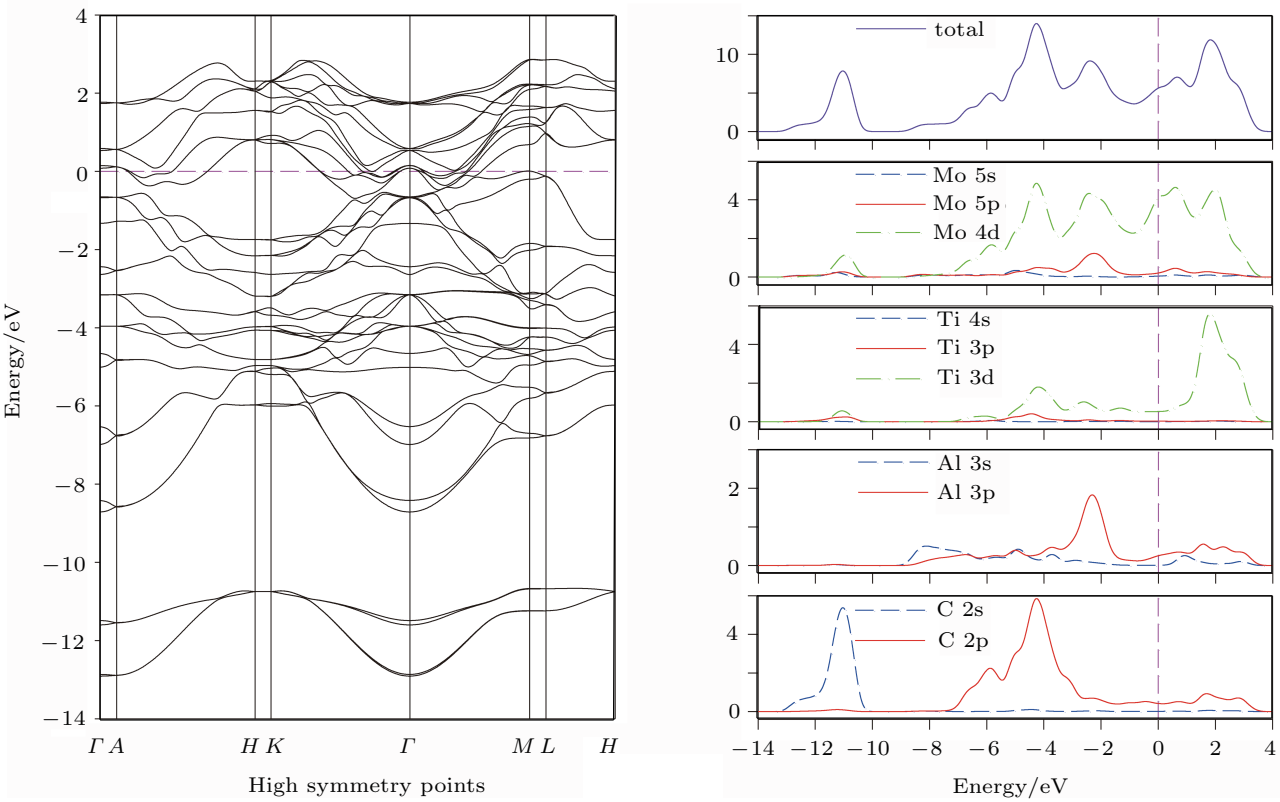


Fig. 2. (color online) Electronic structure of Mo_2TiAlC_2. (a) Band structure at optimized cell parameters along with the high symmetry lines. (b) Total and partial DOSs. The Fermi level is set to be 0 eV.

To give a clear view of the nature of the electronic band structure, the total and partial energy density of states (DOS) are also calculated and explained as indicated in Fig. 2(b). A large value of total DOS is observed at the Fermi level and estimated as 5.6 states per eV per unit cell, which originates mainly from Mo 4d and Ti 3d states, indicating that the metallic bond is existent in Mo_2TiAlC_2 and it is electrically conductive. It is seen that several distinct peaks form the wide valence band in total DOS. The lowest lying valence band from -13.1 eV to -10.2 eV originates from C 2s electron with hybridization of Mo 4d and Ti 3d electrons. The next lowest peak structure situated between -8.8 eV and -7.1 eV is mainly composed of Al 3s states and shows the hybridization with Al 3p electrons. The peak on the left side of the highest

peak ranges from –7.1 eV to –5.4 eV and arises due to C 2p states with hybridization of Mo 4d states. The highest peak located between –5.4 and –3.3 eV is derived from the strong hybridization of C 2p with Mo 4d and Ti 3d states. The intense peak on the right side of the highest peak consists of the dominant contributions from Mo 4d and Al 3p states with a small contribution from Mo 5p states. In the lowest valence band, the peaks due to Ti 3d and C 2s states are weaker than those of Mo 4d and C 2s states. Hence, the Mo–C bond is stronger than the Ti–C bond. It is seen that the hybridization of Al 3p states with Mo 4d/5p states appears in the highest energy range. Therefore, Mo-Al bond is weaker than both Mo–C and Ti-C bonds. The overall picture of electronic structure suggests that the new MAX compound Mo_2TiAlC_2 should appear to have strong covalent character and heavy metallic conductivity. Also some ionic natures would be expected due to the difference in electronegativity between the constituent atoms as predicted in most of the MAX phases.[36,37,39] Strong covalent bonding in Mo_2TiAlC_2 as predicted from high Debye temperature is again verified now. The general features of the electronic structures obtained in the present and previous studies are almost similar.

Table 4. Population analysis of Mo_2TiAlC_2.

Species	Mulliken atomic populations					Effective valence Charge (e)
	s	p	d	Total	Charge (e)	
C	1.45	3.19	0.00	4.64	–0.64	–
Al	0.91	1.79	0.00	2.70	0.30	2.70
Ti	2.04	6.45	2.64	11.12	0.88	2.12
Mo	2.23	6.70	5.02	13.95	0.05	3.95

The charge transfer and Mulliken atomic populations are also calculated in order to obtain the bonding characters in Mo_2TiAlC_2. Listed in Table 4 are the atomic populations along with effective valence. The effective valence is a measure of the difference between the formal ionic charge and the Mulliken charge on the anion species in the crystal and identifies a bond as being either covalent or ionic. The zero value of effective valence indicates an ideal ionic bond while a value greater than zero refers to an increasing level of covalency. The calculated effective valence listed in the last column in Table 4 signifies the remarkable covalency in bonding within Mo_2TiAlC_2. The results also show that C carries the negative charge and the positive charge is carried by the other three metal atoms. These suggest two possible paths for electron transfer. The one guides to s-d hybridized covalent bonding between Mo and C as well as Ti and C atoms, and the other one makes the metallic or weak covalent bonding between Mo and Al atoms. The calculated bond overlap population shown in Table 5 also predicts that a high overlap population implies a high level of covalency, whereas, a low value signifies the potency of ionicity in the chemical bonds. A value of zero population suggests that there is no significant interaction between the electronic populations of the two atoms. Positive and negative values refer to bonding and antibonding states, respectively.

Therefore, it can be seen that the Mo–C bond is more covalent than the Ti–C bond, and Ti–C bond holds stronger covalent bonding than the Mo–Al bond. The values of degree of metallicity[31,40] defined as $f_m = P^{\mu'}/P^{\mu}$ for Mo–C, Ti–C, and Mo–Al bonds are 0.021, 0.033, and 0.063, respectively. Hence, the metallicity ranking of the bonds is Mo–Al > Ti–C > Mo–C; the Mo–Al bond has the highest metallicity, yielding strong metallic bonding. Thus, based on the above discussion, one can determine that the bonding nature of the new compound is dominated by the covalent and metallic bonds. The calculated theoretical hardness is also listed in Table 5. The hardness of a material is closely related to its crystal structure and chemical bonding. The higher hardness value of 9.01 GPa ensures the strong covalent bonding within Mo_2TiAlC_2. Moreover, the bond-length of Mo–C bond is shorter than those of Ti–C and Mo–Al bonds. Thus considering the general relationship between bond-length and hardness, it is expected that Mo–C bond is harder than the other two bonds Ti–C and Mo–Al. It is observed that the lowest bond volume causes the highest hardness of the bond.

Table 5. Calculated values of Mulliken bond number n^{μ}, bond length d^{μ}, bond overlap population P^{μ}, bond volume v_b^{μ}, and bond hardness H_v^{μ} of μ-type bond and metallic population $P^{\mu'}$ and Vickers hardness H_v of Mo_2TiAlC_2.

Bond	n^{μ}	d^{μ}/Å	P^{μ}	$P^{\mu'}$	v_b^{μ}/Å^3	H_v^{μ}/GPa	H_v/GPa
Mo–C	4	2.1124	1.21	0.025	8.3452	25.54	9.01
Ti–C	4	2.1560	0.76	0.025	8.8727	14.30	
Mo–Al	4	2.7921	0.40	0.025	19.2709	2.00	

To further clarify the nature of chemical bonding in Mo_2TiAlC_2, the electron charge density distribution is investigated and the contour of electron charge density in $(11\bar{2}0)$ plane is given in Fig. 3. In the adjacent scale the blue and red color indicate the low and high electron density, respectively. An atom with large electronegativity (electronic charge) attracts electron density towards itself.[41] Due to the large differences in electronegativity and radius between atoms, the electronic charges around C (2.55) and Mo (2.16) are greater than those around Ti (1.54) and Al (1.61). The higher electronegativities of C and Mo show strong accumulation of electronic charges whereas the relatively low charge density indicates weak charge accumulation of the other elements.

The contour of electron charge density reveals a strong directional Mo–C–Mo covalent bond chain with each pair of the chains linked by a relatively weak Ti–C bond. Because of a large difference in electronegativity, the electronic charge around Mo atoms is attracted towards C atoms and a strong covalent–ionic bonding along Mo and C direction is induced. The hybridized Mo 4d–C 2p states are, in fact, responsible for the forming of these bonds. Additionally, the electron charge density of Mo just overlaps with that of Al, which is an indication of a relatively weak bonding between Mo and Al. The

present results are in good agreement with the findings that MAX phases characteristically have the remarkably strong M–X bonds and rather weak M–A bonds.[1]

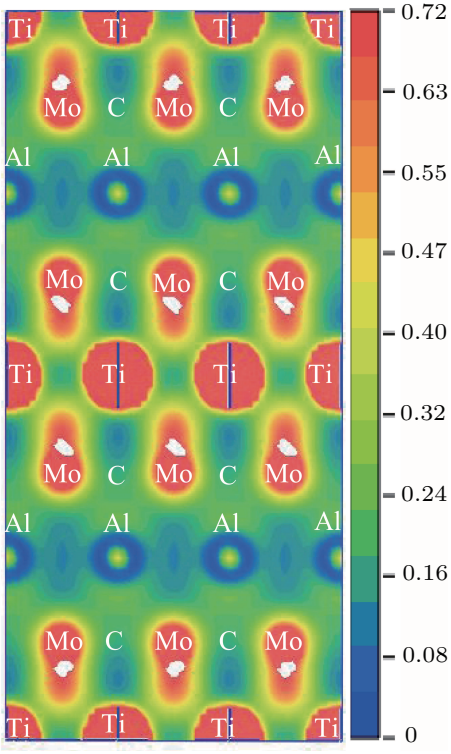


Fig. 3. (color online) Electronic charge density in $(11\bar{2}0)$ plane of Mo_2TiAlC_2.

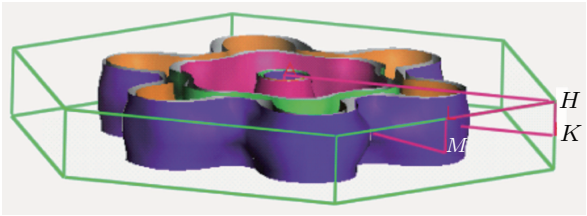


Fig. 4. (color online) Fermi surface of new ternary MAX phase carbide Mo_2TiAlC_2.

Figure 4 shows the Fermi surface of Mo_2TiAlC_2 in the equilibrium structure at $P = 0$. The Fermi surface consists of both electron and hole-like sheets centered along the Γ–A direction of the Brillouin zone. The inner sheets are completely cylindrical with circular cross section and give rise to three-dimensional Fermi pockets. The outer sheets expand along Γ–K direction and shrink along Γ–M directions. No additional sheets appear at the corners of the Brillouin zone The Fermi surface is formed mainly by the low-dispersive Mo 4d-like bands, which is responsible for the conductivity in the compound.

4. Conclusions

The structural, elastic, and electronic properties of Mo_2TiAlC_2 are studied by the DFT-based first-principles pseudopotential total energy method. The calculated structural parameters agree fairly with both the experimental and theoretical data. The single crystal elastic constants ensure the mechanical stability of the new MAX nanolaminate by satisfying the Born criteria. The Poisson's and Pugh's ratios suggest that Mo_2TiAlC_2 should behave as a brittle material. The new ordered MAX carbide has the ability to resist the pressure and tension. The compound is characterized by significant elastic anisotropy. The shear modulus and Debye temperature as well as bond overlap population and Vickers' hardness indicate the strong directional bonding between atoms in the compound. The chemical bonding is seen to be a combination of covalent, metallic and ionic nature. The electron charge density map reveals that the electronic charge around Mo atoms is attracted towards C atoms and a strong covalent–ionic bonding along Mo and C direction is observed The investigated Fermi surface originates mainly from the low-dispersive Mo 4d-like bands, which is responsible for the conductivity of Mo_2TiAlC_2. Finally, we hope that these theoretical results inspire experimental research to measure the elastic properties, Debye temperature and Vickers' hardness of the newly discovered layered MAX phase.

References

[1] Barsoum M W 2000 *Prog. Solid State Chem.* **28** 201
[2] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 672
[3] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 844
[4] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 1198
[5] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 1201
[6] Jeitschko W, Nowotny H and Benesovsky F 1964 *Monatsh. Chem.* **95** 178
[7] Jeitschko W, Nowotny H and Benesovsky F 1964 *Monatsh. Chem.* **95** 431
[8] Jeitschko W, Holleck H, Nowotny H and Benesovsky F 1964 *Monatsh. Chem.* **95** 1004
[9] Sun Z M, Hashimoto H, Zhang Z F, Yang S L and Tada S 2006 *Mater. Trans.* **47** 170
[10] Barsoum M W and El-Raghy T 1996 *J. Am. Ceram. Soc.* **79** 1953
[11] Yoo H, Barsoum M W and El-Raghy T 2000 *Nature* **407** 581
[12] Barsoum M W, Farber L and El-Raghy T 1999 *Metall. Mater. Trans. A* **30** 1727
[13] El-Raghy T, Barsoum M W, Zavaliangos A and Kalidindi S R 1999 *J. Am. Ceram. Soc.* **82** 2855
[14] Sundberg M, Malmqvist G, Magnusson A and El-Raghy T 2004 *Ceram. Inter.* **30** 1899
[15] Jovic V D, Barsoum M W, Jovic B M, Gupta S and El-Raghy T 2006 *Corr. Sci.* **48** 4274
[16] Lofland S E, Hettinger J D, Harrell K, Finkel P, Gupta S, Barsoum M W and Hug G 2004 *Appl. Phys. Lett.* **84** 508
[17] Anasori B, Halim J, Lu J, Cooper A, Voigt, Hultman L and Barsoum M W 2015 *Scr. Mater.* **101** 5
[18] Jeitschko W and Nowotny H 1967 *Monatsh. Chem.* **98** 329
[19] Anasori B, Dahlqvist M, Halim J, Moon E J, Lu J, Hosler B C, Caspi E N, May S J, Hultman L, Eklund P, Rosén J and Barsoum M W 2015 *J. Appl. Phys.* **118** 094304
[20] Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M I J, Refson K and Payne M C 2005 *Z. Kristall* **220** 567
[21] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[22] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
[23] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
[24] Fischer T H and Almlof J 1992 *J. Phys. Chem.* **96** 9768
[25] Murnaghan F D 1951 *Finite Deformation of an Elastic Solid* (New York: Wiley)

[26] Voigt W 1928 *Lehrbuch der Kristallphysik* (Leipzig: Taubner)
[27] Reuss A 1929 *Z. Angew. Math. Mech.* **9** 49
[28] Hill R 1963 *Proc. Phys. Soc. A* **65** 349
[29] Anderson O L 1963 *J. Phys. Chem. Solids* **24** 909
[30] Gao F M 2006 *Phys. Rev. B* **73** 132104
[31] Gou H Y, Hou L, Zhang J W and Gao F M 2008 *Appl. Phys. Lett.* **92** 241901
[32] Born M 1940 *Math. Proc. Camb. Philos. Soc.* **36** 160
[33] Pugh S F 1954 *Philos. Mag.* **45** 823
[34] Frantsevich I N, Voronov F F and Bokuta S A 1983 *Elastic constants and elastic moduli of metals and insulators handbook* (Kiev: Naukova Dumka) pp. 60–180
[35] Ching W Y, Mo Y, Aryal S, and Rulis P 2013 *J. Am. Ceram. Soc.* **96** 2292
[36] Hadi M A, Roknuzzaman M, Parvin F, Naqib S H, Islam A K M A and Aftabuzzaman M 2014 *J. Sci. Res.* **6** 11
[37] Nasir M T, Hadi M A, Naqib S H, Parvin F, Islam A K M A, Roknuzzaman M and Ali M S 2014 *Int. J. Mod. Phys. B* **28** 1550022
[38] Ravindran P, Fast L, Korzhavyi P A, Johansson B, Wills J and Eriksson O 1998 *J. Appl. Phys.* **84** 4891
[39] Li C, Wang B, Li Y and Wang R 2009 *J. Phys. D: Appl. Phys.* **42** 065407
[40] Hadi M A, Ali M S, Naqib S H and Islam A K M A 2013 *Int. J. Comp. Mater. Sci. Eng.* **2** 1350007
[41] UPAC 1997 *Compendium of Chemical Technology*, 2nd edn. (the "Gold Book"), 2006 online corrected version