Ab Initio Calculations for Properties of MAX Phases Ti_2GaN, V_2GaN, and Cr_2GaN

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Abstract

Using *ab initio* calculations we have computed the lattice constants, bulk moduli, and local and total density of states of the MAX phases, Ti_2GaN, V_2GaN, and Cr_2GaN in the hexagonal $P6_3/mmc$ space group. The results for lattice constants are in reasonable agreement with experiments. The bulk moduli are predicted to be 158, 170, and 180 GPa respectively, thus showing a monotonic increase as we go across the fourth period from Ti to Cr. The electronic density of states shows that all three materials are conducting. The local electronic density of states shows that the transition metal, M d and nitrogen p orbital bonding is stronger than M d and Ga p orbital bonding (M = Ti, V, Cr).

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1. Introduction

$M_{n+1}AX_n$ phases were discovered about 35 years ago by Nowotny and his coworkers.[1]   In the chemical formula, M is an early transition metal, A is an A-group element, and X is either carbon (C) or nitrogen (N). When n=1 these phases are called 211 MAX phases, signifying the ratio of the constituent elements. These structures are unique in that they have attributes of metals and ceramics, allowing for some fascinating possibilities for these materials as conductors at very high temperatures.[1] More recently these studies gained renewed interest by the production of a single phase of Ti_3SiC_2 by Barsoum and co-workers.[2]   Subsequently, many of these phases have been studied experimentally and theoretically.[3,4]

In this report we study the structural and electronic properties of M_2GaN, with M = titanium (Ti), vanadium (V) or chromium (Cr). These three early transition metal-MAX phases have been synthesized by Nowotny and co-workers.[5,6] Our theoretically computed lattice constants are in reasonable agreement with experiment.[5,6] We predict the bulk modulus (B), local- and total- electronic density of states for these MAX phases. Our computations suggest that all three materials are electrically conducting.

2. Crystal Structure

The three MAX phases studied in this paper are 211 phases with a layered hexagonal, close-packed structure. They belong to the space group $P6_3/mmc$.[7]   In each unit cell as shown in Fig. 1 there are 8 atomic layers. All the even numbered layers are M layers (M= Ti, V, Cr), the first and fifth layers are nitrogen and third and seventh layers are gallium. The nitrogen (N) atoms fill the octahedral locations between the M layers.[1]

The repeating structure of the planes in the unit cell can be further defined by the $A_N C_M B_{Ga} C_M A_N B_M C_{Ga} B_M$ close-pack stacking along the c-axis.[7,8,9] The letters A, B, and C stand for the three distinct positions for atoms to occupy, in the close-packed $\langle 0001 \rangle$ plane.[10] The subscripts denote the type of atom that sits at the site, e.g. B_M means the metal atom M sits at a B site. The Z- coordinate increases as we go from left to right. Table I gives a precise description of the specific positions of each atom in the unit cell corresponding to this type of stacking.

3. Computation Method

We performed first-principles total energy calculations within the generalized gradient approximation (GGA) to density functional theory[11] (DFT) using the suit of codes VASP.[12,13,14,15] Core electrons are implicitly treated by ultra soft Vanderbilt type pseudopotentials[16] as supplied by G. Kresse and J. Hafner.[17] For each calculation, irreducible k-points are generated according to the Monkhorst-Pack scheme.[18] The convergence is achieved with 60 k- points in the irreducible part of Brillouin zone for the eight atom unit cell described in Table I. The single-particle wave functions have been expanded in a plane-wave basis using a 300 eV kinetic energy cutoff. All atoms are allowed to relax until a force tolerance of 0.01 eV/Å is reached for each atom. The calculations for the total density of states (DOS) were performed with the tetrahedron method with Blöchl corrections[19] for the energy. Tests using a higher plane-wave cutoff and a larger k-point sampling indicate that a numerical convergence better than ±1.0 meV is achieved for relative energies.

To obtain the absolute minimum in total energy for each crystal structure, the equilibrium lattice constants a and c were varied independently. Once the equilibrium constants and volume V_0 were established for each structure, external strains δ of $\pm 1\%$, and $\pm 2\%$ were applied to the structure, while allowing full relaxation of the ions. This ionic relaxation allowed the value of z_M to change with the strain. We thus obtained the total minimum energies E(V) at these strained volumes V, corresponding to each value of δ. These energies and strains were fit with the corresponding parabolic equation

$$\Delta E = \frac{9}{2} V_0 B \delta^2, \text{ where } \Delta E \equiv E(V) - E(V_0).$$

5. Results

Our calculated values for the constants a, c, z_M, and c/a are shown in Table II. The deviation from the experimental values of c and a for Ti_2GaN was 0.67% and 0.15%, respectively. For Cr_2GaN, the change from experimental values was 1.0% and 4.0%, while for V_2GaN[20] it was 3.0% and 3.6%, respectively. Although the bulk moduli have not been experimentally measured, the values increase across the table, very similar to the trend in theoretical bulk moduli calculated by Sun et al. [21], for Ti_2GaC, Cr_2GaC, and V_2GaC. Though this trend is similar to the carbides, the nitrides have lower bulk moduli, ranging from 158 to 188 GPa, while the carbides range from 166 to 226 GPa, showing that replacing the nitrogen with carbon in these structures makes them more able to resist isotropic external strains.[21]

The calculated density of states (DOS) is shown in Fig. 2. At the fermi level E_f, the DOS for Ti_2GaN, V_2GaN, and Cr_2GaN, were 2.5, 7, and 11 states per unit cell per eV, respectively. Thus there is a clear increasing trend in the DOS at E_f with increasing

valence electrons of the transition metal (M). A similar trend is found in Ti_2AlC, V_2AlC, and Cr_2AlC experimentally[3] and theoretically.[3,9,22] From these trends one is tempted to conclude that Cr_2GaN is more conducting than V_2GaN and V_2GaN is more conducting than Ti_2GaN. However as stated by Barsoum[23], the mobilities of charge carriers for all MAX phases except for Ti_4AlN_3 are inversely proportional to the DOS at Fermi level.

The local density of states (LDOS) is shown in Fig. 3. The hybridization of the (i) M d orbitals with nitrogen p orbitals and (ii) M d orbitals with gallium p orbitals is seen from their common peaks lying between -7 to -4 eV for the former and -4 to -1 eV for the latter. Thus the bonding between M and N is stronger than that between M and Ga. Two clear trends in bonding are evident from the LDOS plots. With the increase in the valence electrons of M from Ti to Cr, there is a shift towards lower energy (compared to their respective Fermi levels E_f) of the (i) hybridized peaks of M d orbitals with nitrogen p orbitals and (ii) hybridized peak of M d orbitals with gallium p orbitals. These two observations are not unique to our data. We find similar correlations in the data of Sun *et al.*,[21] from their Fig. 3 which shows LDOS for Ti_2AlC, Cr_2AlC and Cr_2GeC MAX phases.

In summary we have performed *ab initio* computations of the structural, elastic, and electronic properties of M_2GaN, M = Ti, V, Cr. The structural properties are in reasonable agreement with experimental measurements. The bulk moduli B increase as we substitute Ti with V and V with Cr. All three materials are found to be conducting. The transition metal, M d hybridization with nitrogen p orbitals is stronger than that with gallium p orbitals. We hope our calculations will spur further experimental interest in these materials.

Atom Type	Atom Number	Position Vector
X	1	0
M	2	$c_1(\mathbf{a_1} + 2\mathbf{a_2}) + z_M\mathbf{a_3}$
A	3	$c_1(2\mathbf{a_1} + \mathbf{a_2}) + c_2\mathbf{a_3}$
M	4	$c_1(\mathbf{a_1} + 2\mathbf{a_2}) + (2c_2 - z_M)\mathbf{a_3}$
X	5	$2c_2\mathbf{a_3}$
M	6	$c_1(2\mathbf{a_1} + \mathbf{a_2}) + (2c_2 + z_M)\mathbf{a_3}$
A	7	$c_1(\mathbf{a_1} + 2\mathbf{a_2}) + 3c_2\mathbf{a_3}$
M	8	$c_1(2\mathbf{a_1} + \mathbf{a_2}) + (1 - z_M)\mathbf{a_3}$

Table I. The table lists the 8 atom basis for a unit cell of M_2AX phase[7,8,9] with M = Ti, Cr, or V.   X=N and A=Ga. The lattice vectors of this hexagonal unit cell with lattice constants a and c are: $\mathbf{a}_1 = 2c_2 a(1, -c_3, 0)$, $\mathbf{a}_2 = 2c_2 a(1, c_3, 0)$, and $\mathbf{a}_3 = c(0, 0, 1)$. The constants are $c_1 \equiv \dfrac{1}{3}$, $c_2 \equiv \dfrac{1}{4}$, and $c_3 \equiv \dfrac{1}{\sqrt{c_1}}$. The constant "$z_M$" corresponding to the internal degree of freedom is given in Table II for each phase. The atoms corresponding to the numbers given in the table are shown in Fig. 1.

Property	Ti$_2$GaN		V$_2$GaN		Cr$_2$GaN	
	Theory	Expt.[1,5]	Theory	Expt.[1,20]	Theory	Expt.[1,6]
a (Å)	3.02	3.00	2.91	3.00	2.91	2.88
c (Å)	13.28	13.30	12.82	13.30	12.26	12.77
z$_M$ (Å)	0.0869		0.0861			0.0860
c/a	4.40	4.42	4.41	4.42	4.22	4.43
$V = \left(\dfrac{\sqrt{3}}{2}\right) a^2 c$ (Å^3)	104.59	103.35	93.91	103.35	89.72	91.65
B (GPa)	158		170		180	

Table II. Equilibrium values of the hexagonal unit cells in Table I: the lattice constants a and c, their ratio c/a, z$_M$, equilibrium volume V, and bulk modulus B for the three phases calculated with GGA, compared with experimental values. The internal degree of freedom z$_M$ in the unit cells is defined in Table I.
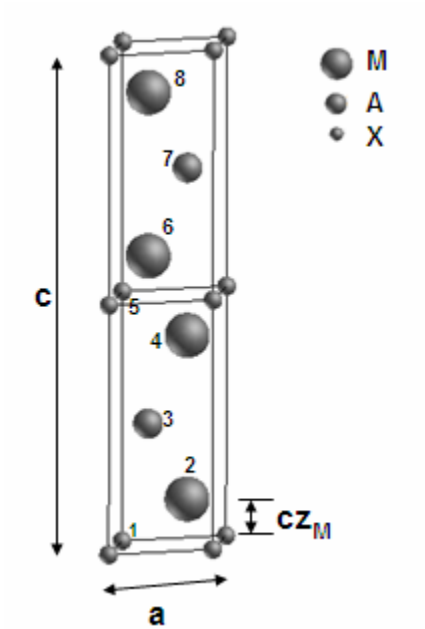
Fig. 1. Unit cell of a 211 MAX phase. The positions of all the 8 atoms numbered in unit cell are given in Table I. The lattice constants are a and c and z_M is the paramenter corresponding to the internal degree of freedom.
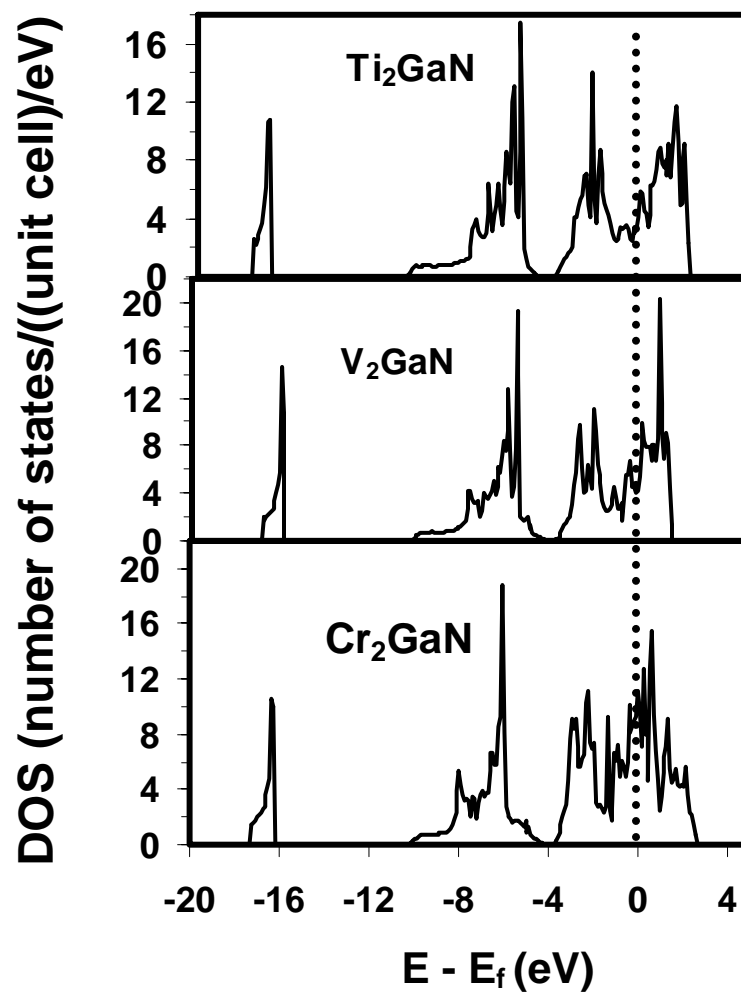
Fig. 2 The total density of states (DOS) is shown as a function of energy for the three phases studied. The zero of the energy is taken at the Fermi energy E_f shown by a dotted line.
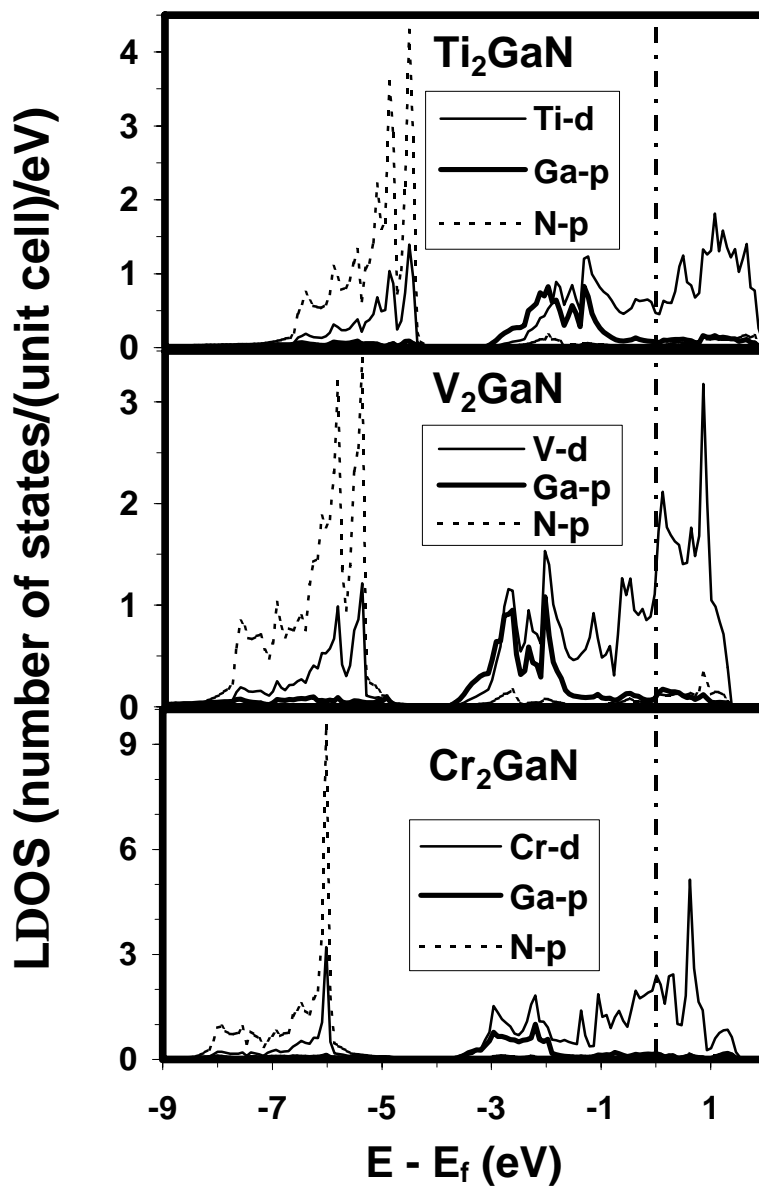
Fig. 3 Local density of states (LDOS) for M_2GaN (M = Ti, V, Cr). The LDOS for the s states are not shown since they do not contribute much to bonding.

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