

*Ab initio* study of  $M_2\text{AlN}$  ( $M = \text{Ti, V, Cr}$ )

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## LETTER TO THE EDITOR

***Ab initio* study of  $M_2AlN$  ( $M = Ti, V, Cr$ )**Zhimei Sun<sup>1,4</sup>, Denis Music<sup>1</sup>, Rajeev Ahuja<sup>2</sup> and Jochen M Schneider<sup>1,3</sup><sup>1</sup> Materials Chemistry, RWTH Aachen, Kopernikusstrasse 16, D-52074 Aachen, Germany<sup>2</sup> Department of Physics, Condensed Matter Theory Group, Uppsala University, Box 530, S-751 21 Uppsala, Sweden<sup>3</sup> Department of Physics, Materials Physics, Uppsala University, Box 530, S-751 21, Uppsala, Sweden

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Online at [stacks.iop.org/JPhysCM/17/L15](http://stacks.iop.org/JPhysCM/17/L15)**Abstract**

We have studied  $M_2AlN$  phases, where  $M = Ti, V$ , and  $Cr$ , by means of *ab initio* total energy calculations. The bulk modulus of  $M_2AlN$  increases as  $Ti$  is replaced with  $V$  and  $Cr$  by 19.0% and 26.5%, respectively, which can be understood on the basis of the increased number of valence electrons filling the  $p$ - $d$  hybridized bonding states. The bulk modulus of  $M_2AlN$  is generally higher than that of the corresponding  $M_2AlC$  phase, which may be explained by an extra electron in the former phases contributing to stronger chemical bonding. This work is important for fundamental understanding of elastic properties of these ternary nitrides and may inspire future experimental research.

$M_2AX$  phases (space group  $P6_3/mmc$ , prototype  $Cr_2AlC$ ), where  $M$  is an early transition metal,  $A$  is a group IIIA or IVA element, and  $X$  is either  $C$  or  $N$ , have attracted great attention due to their unusual properties associated with metals and ceramics (for details see [1] and the references cited therein). While there are approximately 50 experimentally known  $M_2AX$  phases, only a very limited number of  $M_2AN$  phases have been synthesized. In our previous paper [2], we have investigated the effect of valence electron population on bonding and elastic properties of  $M_2AlC$  phases, where  $M = Ti, V$ , and  $Cr$ , by means of *ab initio* total energy calculations. The bulk modulus of  $M_2AlC$  increases as  $Ti$  is replaced with  $V$  and  $Cr$  by 19% and 36%, respectively, which is associated with an extensive increase in the  $M$ - $Al$  and  $M$ - $C$  bond energy [2]. In this letter, using *ab initio* total energy calculations, we systematically study  $M_2AlN$  phases ( $M = Ti, V, Cr$ ).  $Ti_2AlN$  has already been synthesized [1], while the other two phases have not been experimentally investigated. The main aim of this letter is to correlate the chemical bonding and elastic properties of  $M_2AlN$  phases as a function of valence electron population in order to gain insight into this fascinating class of materials.

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**Table 1.** The calculated lattice parameters  $a$  and  $c$  (in Å), equilibrium volume  $V_0$  (Å<sup>3</sup>), energy of formation  $E_f$  (in eV/atom), bulk modulus  $B$  (in GPa), and optimized free internal parameters  $z(M)$  for  $M_2\text{AlN}$ , where  $M = \text{Ti}, \text{V},$  and  $\text{Cr}$ .

	$E_f$	$a$	$c$	$V_0$	$B$	$z(M)$
Ti <sub>2</sub> AlN	-1.201	2.998	13.625	106.05	181	0.086
Exp. <sup>a</sup>		2.989	13.614	105.33		
Cal. <sup>b</sup>					175	
Cal. <sup>c</sup>					163	
V <sub>2</sub> AlN	-0.823	2.866	13.166	93.65	215	0.086
Cr <sub>2</sub> AlN	-0.375	2.847	12.689	89.07	229	0.082

<sup>a</sup> Reference [13].

<sup>b</sup> Reference [12].

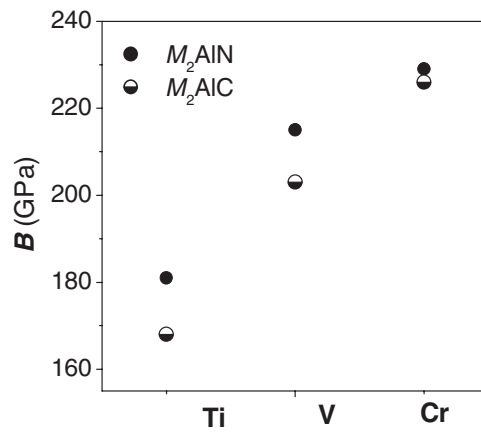
<sup>c</sup> Reference [9].

Our calculations are based on the density functional theory, using the VASP code [3], in conjunction with the generalized gradient approximations [4] and projector augmented wave potentials [5]. The calculation details have been given in previous letter [2]. The input structure for Ti<sub>2</sub>AlN was from [6], while those of V<sub>2</sub>AlN and Cr<sub>2</sub>AlN were from V<sub>2</sub>AlC [7] and Cr<sub>2</sub>AlC [7], respectively, since neither of the two phases has been reported experimentally. The structures were first fully relaxed, i.e. the cell shape, volume, and atomic position were relaxed. We have also optimized the  $c/a$  ratios and the free internal parameters ( $z$ ). The total energy was calculated at various cell volumes to obtain the equilibrium volume ( $V_0$ ) and the bulk modulus ( $B$ ) from a least-squares fit of the calculated  $V-E$  curves to the integrated form of the third-order Birch–Murnaghan equation of states [8]. In this letter we have assumed the paramagnetic configuration of Cr in Cr<sub>2</sub>AlN, since the effect of spin polarization resulted in comparatively small differences in cohesive energy. The energy differences between antiferromagnetic and paramagnetic as well as ferromagnetic and paramagnetic configurations were 0.37 and  $-3.28$  meV/atom, respectively. The total density of states (DOS) was obtained using the relaxed structures at  $V_0$ . The energy of formation ( $E_f$ ) was calculated using the following equation:

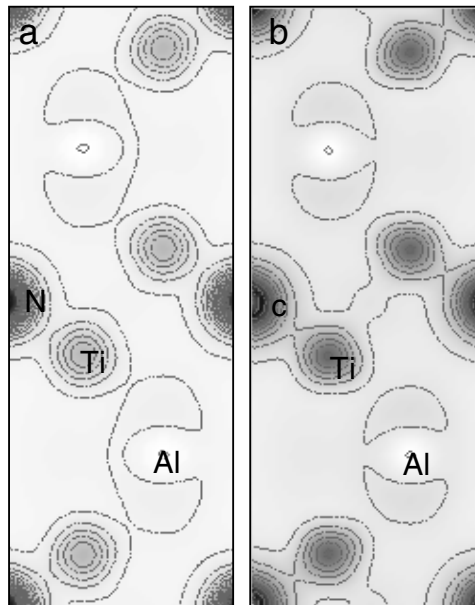
$$E_f(M_2\text{AlN}) = \frac{E(M_2\text{AlN}) - 2E(M) - E(\text{Al}) - E(\text{N}_2)}{8}, \quad (1)$$

where  $M$  designates a metal with Ti crystallizing in the hexagonal structure (space group  $P6_3/mmc$ , prototype Mg), V and Cr are body-centred cubic metals (space group  $Im\bar{3}m$ , prototype W), Al is a face-centred cubic metal (space group  $Fm\bar{3}m$ , prototype Cu), and  $\text{N}_2$  is a gas. There are two atoms in the unit cell for every metal.

The calculated results are given in table 1, wherein the energy of formation, equilibrium volume, lattice parameters  $a$  and  $c$ , bulk modulus, and the optimized free internal parameters for  $M_2\text{AlN}$ , with  $M = \text{Ti}, \text{V},$  and  $\text{Cr}$ , are listed. On the basis of the calculated energy of formation, it appears that these three phases may be observed experimentally. Furthermore, the values of  $C_{44}$  for V<sub>2</sub>AlN and Cr<sub>2</sub>AlN, which were calculated to be 158 and 128 GPa respectively, indicate that these structures may be stable against shear deformation. Among the herein investigated  $M_2\text{AlN}$  phases, only Ti<sub>2</sub>AlN has been studied both theoretically [9–12] and experimentally [12, 13]. The calculated equilibrium volumes of Ti<sub>2</sub>AlN are in agreement with the experimental result [13], differing by 0.7%. In terms of the bulk modulus for Ti<sub>2</sub>AlN, the deviation is within 3.3% and 9.9%, respectively [9, 12], which is due to the different calculation methods. The bulk modulus increases by 19.0% and 26.5% as Ti is replaced with V and Cr. For comparison, figure 1 shows the calculated bulk modulus for both  $M_2\text{AlN}$  and  $M_2\text{AlC}$  [2, 14, 15], where  $M = \text{Ti}, \text{V},$  and  $\text{Cr}$ . The behaviour of the bulk modulus of  $M_2\text{AlN}$

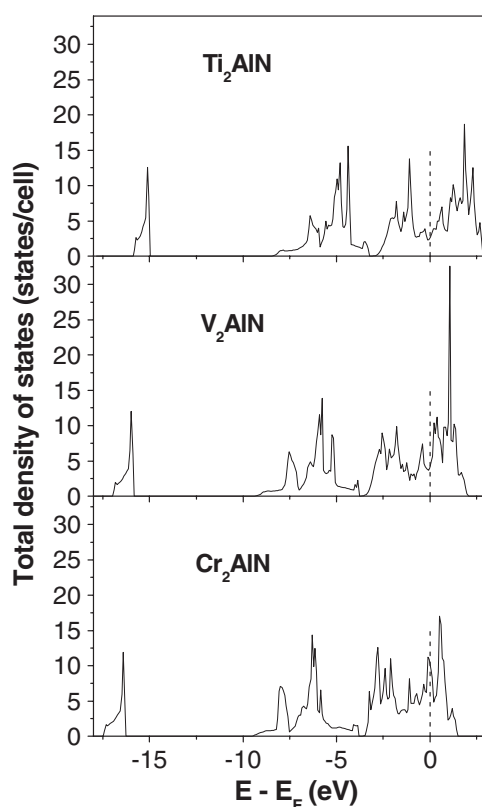


**Figure 1.** The calculated bulk modulus ( $B$ ) for  $M_2AlN$  ( $M = Ti, V,$  and  $Cr$ ). The previous results [2] for  $M_2AlC$  are included for comparison.



**Figure 2.** Charge density distribution in the  $(11\bar{2}0)$  plane for (a)  $Ti_2AlN$  and (b)  $Ti_2AlC$ . The density values vary from 0 (white) to  $3.5 \text{ electron } \text{\AA}^{-3}$  (dark grey).

is similar to that of the bulk modulus of  $M_2AlC$  [2], and the magnitude of the bulk modulus of  $M_2AlN$  ranges from 8.3% to 1.3%, higher than that of the  $M_2AlC$  phase, as Ti is replaced with V and Cr. This indicates that an extra electron in the  $M_2AlN$  phases may contribute to stronger chemical bonding and thus larger bulk moduli than that of the corresponding  $M_2AlC$  phase. This is consistent with the comparison of the charge density distribution in the  $(11\bar{2}0)$  plane as shown in figure 2(a) for  $Ti_2AlN$  and figure 2(b) for  $Ti_2AlC$ . As C is replaced with N, the uniform charge density region between the MX layers is extended, which may be responsible for the larger bulk modulus, as discussed above.



**Figure 3.** The total density of states of  $M_2\text{AlN}$  ( $M = \text{Ti}, \text{V},$  and  $\text{Cr}$ ), where the Fermi level is set to zero and marked by a vertical dashed line.

In order to gain better understanding of the chemical bonding in  $M_2\text{AlN}$ , we have calculated the total DOS (see figure 3). The total DOS of  $\text{Ti}_2\text{AlN}$  agrees qualitatively with that given in [9]. The Fermi level moves from a lower energy level to a higher energy level with the substitution of the transition metal Ti with V and with Cr, which indicates that the increased extra valence electrons fill the p-d hybridized bonding states of M-Al and M-N. This band filling is responsible for the increase of the bulk modulus. The Fermi levels of  $\text{Ti}_2\text{AlN}$  and  $\text{V}_2\text{AlN}$  are located in pseudogaps (see figure 3), which are similar to those for  $\text{Ti}_2\text{AlC}$  [2] and  $\text{V}_2\text{AlC}$  [2], respectively. The Fermi level of  $\text{Cr}_2\text{AlN}$  (see figure 3) is positioned at a DOS peak, unlike the case for  $\text{Cr}_2\text{AlC}$  [2], suggesting that  $\text{Cr}_2\text{AlN}$  may have the lowest stability of the three herein investigated phases. This is consistent with the energy of formation given in table 1. The calculated number of states at the Fermi level is  $\sim 2.6$  and  $\sim 4.2$  states/cell for  $\text{Ti}_2\text{AlN}$  and  $\text{V}_2\text{AlN}$ , respectively, which is less than that for  $\text{Ti}_2\text{AlC}$  ( $\sim 3.2$  states/cell) [2] and that for  $\text{V}_2\text{AlC}$  ( $\sim 4.7$  states/cell) [2]. The result from the calorimetric measurements [12] at liquid He temperatures for  $\text{Ti}_2\text{AlN}$  is 2.69 states/cell, rather close to our calculated value. Fewer states at the Fermi level for both  $\text{Ti}_2\text{AlN}$  and  $\text{V}_2\text{AlN}$ , as compared to the corresponding carbides, and the fact that the Fermi level is located in a pseudogap may contribute to stronger chemical bonding and hence result in larger bulk moduli. In the case of  $\text{Cr}_2\text{AlN}$ , the number of states at the Fermi level is  $\sim 10.9$  states/cell, but due to the above-discussed misalignment, more electrons are likely to occupy non-bonding states. On the other hand, these extra states

in  $\text{Cr}_2\text{AlN}$  may also contribute to conduction of electrons and heat, a well-known feature of MAX phases [1].

In summary, we have studied  $\text{M}_2\text{AlN}$ , where  $\text{M} = \text{Ti}, \text{V},$  and  $\text{Cr}$ , using *ab initio* total energy calculations. The bulk modulus of  $\text{M}_2\text{AlN}$  increases as Ti is replaced with V and Cr by 19.0% and 26.5%, respectively. This can be understood on the basis of the increased number of valence electrons filling the p-d hybridized bonding states. Furthermore, the bulk modulus of  $\text{M}_2\text{AlN}$  is higher than that of the corresponding  $\text{M}_2\text{AlC}$  phase, which may be explained by there being an extra electron in these nitrides, contributing to stronger chemical bonding. This work is important for basic understanding of elastic properties of these phases and may encourage future experimental research.

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## References

- [1] Barsoum M W 2000 *Prog. Solid State Chem.* **28** 201
- [2] Sun Z, Ahuja R, Li S and Schneider J M 2003 *Appl. Phys. Lett.* **83** 899
- [3] Kresse G and Hafner J 1993 *Phys. Rev. B* **48** 13115
- [4] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
- [5] Kresse G and Hafner J 1994 *Phys. Rev. B* **49** 14251
- [6] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 1198
- [7] Jeitschko W, Nowotny H and Benesovsky F 1963 *Monatsh. Chem.* **94** 672
- [8] Birch F 1978 *J. Geophys. Res.* **83** 1257
- [9] Holm B, Ahuja R, Li S and Johansson B 2002 *J. Appl. Phys.* **91** 9874
- [10] Zhou Y C and Sun Z M 2000 *Phys. Rev. B* **61** 12570
- [11] Hug G and Fries E 2002 *Phys. Rev. B* **65** 113104
- [12] Lofland S E, Hettinger J D, Harrell K, Finkel P, Gupta S, Barsoum M W and Hug G 2004 *Appl. Phys. Lett.* **84** 508
- [13] Gamarhik M Y, Barsoum M W and El-Raghy T 2000 *Powder Diff.* **15** 241
- [14] Sun Z, Li S, Ahuja R and Schneider J M 2004 *Solid State Commun.* **129** 589
- [15] Sun Z, Music D, Ahuja R, Li S and Schneider J M 2004 *Phys. Rev. B* **70** 092102