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Steric effect on the M site of nanolaminate compounds M_2SnC ($M = Ti, Zr, Hf$ and Nb)

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Abstract

In this paper we report calculations based on an all electron *ab initio* full-potential linearized augmented plane-wave method using the generalized gradient approximation within the density functional theory to determine the structures of Ti_2SnC , Zr_2SnC , Hf_2SnC and Nb_2SnC . The lattice constants obtained after geometry optimization are in good agreement with experimental data. It is observed from these results that there exists a steric effect on the M site. For M atoms with atomic radius (Zr, Hf) larger than that of tin, the polyhedra (octahedron and trigonal prism) constituting the unit cell are less distorted compared to those related to M atoms with atomic radius (Ti, Nb) similar to that of tin. The computed values for the bulk modulus of these ternary carbides are predicted to be about 69% of those of the corresponding binary carbides MC. The analysis of the projected local density of states shows that the major hybrids come from M ($M = Ti, Zr, Hf, Nb$) d and C p states.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

$M_{n+1}AX_n$ phases ($n = 1-3$), where M is an early transition metal, A being mostly a IIIA or IVA group element and X is either carbon (C) and/or nitrogen (N), have recently drawn a lot of attention due to their unique combination of properties which mix those usually associated with metals and ceramics [1]. In these phases, M_6X blocks are interleaved with A layers and are hence referred to as nanolaminates. Generally, the $M_{n+1}AX_n$ phases are machinable [2], exhibit good damage tolerance [3], have excellent thermal shock resistance [4], good corrosion resistance [5], and they are good thermal and electrical conductors [6, 7]. These materials have gained renewed interest since Barsoum and co-workers [8] succeeded in synthesizing single phase, bulk dense samples of Ti_3SiC_2 . Afterward, many of the roughly 60 $M_{n+1}AX_n$

phases known to date have been studied both experimentally and theoretically [9–11].

It has been suggested from *ab initio* calculations [12] that M_2AC ($M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W$ and $A = Al, Ga, Ge$ and Sn) can be classified into two groups: one where the bulk modulus of the binary MC is conserved and the other for which the bulk modulus is decreased. However, the same authors [13] have questioned their own results, the description of the binary carbides MC being very sensitive to the choice of the projector augmented wave (PAW) potentials they used. More recently, Hug [14] has studied Ti_2AC compounds with $A = Al, Si, P, S, Sn, Ga, In, Ge, As, Pb$ and Tl . All these phases are shown, except for $A = Si, P$ and As , to be stable, a behavior originating from the particularities of the hybridization scheme in these compounds (Ti d– A p

and Ti d–C p hybrids). Motivated by these works and in the quest for MAX phases with interesting properties, we explored the structure, bulk modulus and formation energy of M_2SnC ($M = Ti, Zr, Hf$ and Nb), compounds that have been synthesized by Barsoum *et al* [15]. Our computed lattice constants obtained from structural relaxation are found to be in reasonable agreement with the experimental ones. From steric arguments, a connection between the lattice constants and the atomic radii of M and Sn is discussed. Moreover we predict that M_2SnC ($M = Ti, Zr, Hf$ and Nb) bulk moduli are approximately 69% of those of their corresponding binary carbides.

2. Description of crystal structure and method of calculation

Our calculations were carried out using an all electron full-potential (linearized) augmented plane waves plus local orbitals (FP-L/APW + lo) method [16], based on density functional theory (DFT) [17]. The influence of the exchange and correlation potential has been tested within the generalized gradient approximation (GGA-WC) using the scheme of Wu and Cohen [18] for exchange and correlation. The muffin-tin radii (R_{MT}) are set to 2.0, 2.21, 2.1, 2.12, 2.5 and 1.9 a.u. (Bohr units) for Ti, Zr, Hf, Nb, Sn and C atoms, respectively. The maximum value l_{max} for the wavefunction expansion inside the atomic spheres is limited to 10. To achieve the energy eigenvalues convergence, the wavefunctions inside the interstitial region are expanded in plane waves with a cutoff $R_{MT} \times K_{max} = 8$, where K_{max} is the maximum modulus for the reciprocal lattice vector. Moreover, local orbitals have been added for all atoms and valence states. The self-consistency cycle was achieved taking 1500 points in the first Brillouin zone. The convergence has been followed with respect to the energy and the density.

Like all MAX phases, M_2SnC belongs to the $P6_3/mmc$ space group. In such a hexagonal structure, the atoms are located at the following Wyckoff positions: M atoms in 4f (Z_M), Sn in 2d and C in 2a. The coordinate Z_M is the only internal free parameter in the crystal structure. For atoms in 4f positions, the ideal value of the internal dimensionless parameter Z_M is 1/12. The geometry has been optimized for the considered structures following the procedure described by Hug [14]. A set of different predefined volumes are chosen and for each of these volumes different calculations are made for several c/a ratio values. During each step, the free parameter Z_M is allowed to vary for optimization. The energy curves as a function of the c/a ratio are then fitted with a polynomial function. This allows us to find a minimum in energy as a function of the c/a ratio for each selected volume. These minima give a set of energies as a function of the volume in which all other parameters are optimized. In the last step, these energy versus volume curves are fitted using the third-order Birch–Murnaghan equation of state [19–21] to find the optimized parameters.

3. Structure and steric effect

Our calculated values for a , c and Z_M are gathered in table 1 as well as the experimental data [15] for comparison. Compared

Table 1. Equilibrium theoretical and experimental lattice parameters a , c and relaxed atomic parameter Z_M . The bulk modulus B (GPa), total density of states at the Fermi level $N(E_F)$ (states/eV/Cell) and formation energy (ΔE_f) for M_2SnC are also shown.

| | | a (nm) | c (nm) | Z_M | B | $N(E_F)$ | ΔE_f |
|---------------------|------------|----------|----------|--------|-----|----------|--------------|
| Ti ₂ SnC | This work | 0.3136 | 1.3641 | 0.0817 | 170 | 3.30 | −1.032 |
| | Exp. [15] | 0.3163 | 1.3679 | — | — | — | — |
| | Calc. [14] | 0.3171 | 1.3857 | 0.0807 | 167 | — | −2.32 |
| Zr ₂ SnC | This work | 0.3352 | 1.4681 | 0.0850 | 156 | 2.71 | −1.269 |
| | Exp. [15] | 0.3357 | 1.457 | — | — | — | — |
| Hf ₂ SnC | This work | 0.3308 | 1.445 | 0.0850 | 165 | 2.97 | −1.189 |
| | Exp. [15] | 0.332 | 1.4388 | — | — | — | — |
| Nb ₂ SnC | This work | 0.3244 | 1.3754 | 0.0830 | 206 | 3.71 | −1.071 |
| | Exp. [15] | 0.3241 | 1.3802 | — | — | — | — |

to the experiment, the calculated a and c lattice parameters were underestimated by about 0.85% and 0.28%, respectively, for Ti₂SnC. For Zr₂SnC, the calculated values depart from the experimental ones by 0.15% and 0.76%, while for Hf₂SnC the discrepancies are 0.36% and 0.43%, respectively. For Nb₂SnC, a and c deviate from the experiment by about 0.09% and 0.34%, respectively. It should be remarked that our results for Ti₂SnC are closer to the experimental data than those reported in [15]. This slight difference probably originates from the fact that we have used for the exchange–correlation the new scheme of Wu and Cohen [18] instead of the most popular one of Perdew *et al* [22] as in [14]. Indeed, we have found [11] that it gives improved lattice parameters for Ti₃SnC₂, a 312 compound successfully synthesized by Dubois *et al* quite recently [23]. The formation energies ΔE_f of these MAX phases, calculated from the difference between their total energies and the sum of the isolated atomic energies of the pure constituents, are also reported in table 1. The values for ΔE_f are always negative, indicating that the formation of these MAX phases is exothermic and that they are intrinsically stable in agreement with the experiment [15].

Following previous works [14, 24], it is of interest to consider the MAX crystal unit cell as constituted of $[M_6X]$ octahedra and $[M_6A]$ trigonal triangular prisms (figure 1). The stacking of these two polyhedra allows us to describe the 211 phases, while it needs two (three) octahedra units and one trigonal prism unit to obtain the 312 (413) MAX phases. It should be mentioned that a cubic octahedron is the unit block of the binary MX, but it loses its fourfold axis in the ternary MAX and it results in a relaxation owing to this reduced symmetry. This noncubic distortion of the octahedron can be estimated from the parameter o_d defined as [24]:

$$o_d = \frac{\sqrt{3}}{2\sqrt{4Z_M^2(\frac{c}{a})^2 + 1/12}}. \quad (1)$$

Concerning the trigonal prism, the distortion parameter p_d is given by [14]:

$$p_d = \frac{1}{\sqrt{\frac{1}{3} + (\frac{1}{4} - Z_M)^2(\frac{c}{a})^2}}. \quad (2)$$

For 211 MAX phases like M_2SnC , an ideal packing of hard spheres of equal diameter leads to a ratio $c/a = 2\sqrt{6}$

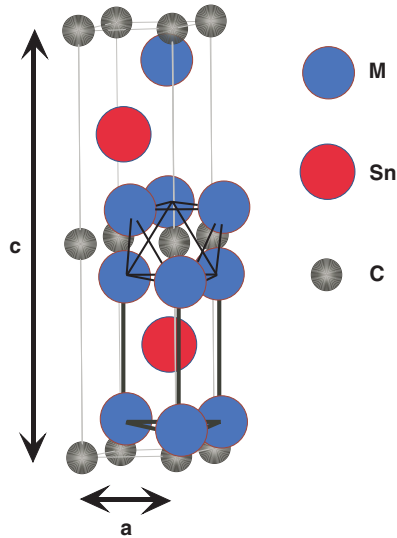


Figure 1. Unit cell of M_2SnC ($M = Ti, Zr, Hf, Nb$) phase. A $[M_6C]$ octahedron and a $[M_6Sn]$ trigonal prism are outlined.

Table 2. Octahedron o_d (equation (1)) and trigonal prism p_d (equation (2)) distortions, as well as their ratio. Also reported are the c/a ratio and atomic radius of M elements [24].

| | o_d | p_d | o_d/p_d | c/a | R_M (nm) |
|-----------|----------|----------|-----------|-------|------------|
| Ti_2SnC | 1.128 42 | 1.072 72 | 1.052 | 4.35 | 0.143 |
| Zr_2SnC | 1.084 48 | 1.081 11 | 1.003 | 4.38 | 0.155 |
| Hf_2SnC | 1.086 42 | 1.083 06 | 1.003 | 4.38 | 0.155 |
| Nb_2SnC | 1.138 79 | 1.094 45 | 1.041 | 4.24 | 0.145 |

≈ 4.89 and $o_d = p_d = 1$ for an ideal octahedron (cubic) and trigonal prism. In table 2 are reported the values for these parameters deduced from the results quoted in table 1 as well as the atomic radii R_M of the M elements [25] (note here that $R_{Sn} = 0.145$ nm). From these values, it can be concluded that, as expected, both polyhedra are distorted. Looking at the elements of the IVB group (Ti, Zr, Hf), it is for those for which the atomic radius is the larger (Zr, Hf) that the distortion of the two constituting polyhedra is minimum. Moreover, the octahedra and the trigonal prism's distortions are then quite similar (the ratio o_d/p_d departs from unity only by 3×10^{-3}). This behavior can be interpreted as a steric effect: the big M atoms dominate the topology of the crystal structure. This effect is also traduced by the fact that lattice parameters a and c are then observed to be both larger for Zr and Hf based alloys compared to Ti_2SnC and Nb_2SnC (table 1). For these two compounds, the c/a ratios are equal and of maximum magnitude (table 2), their values being nevertheless far from the ideal value 4.86. Finally, it is interesting to note that the internal free parameter Z_M is pretty close to its ideal value (0.0833) for Nb_2SnC , a compound for which $R_{Nb} = R_{Sn}$. It is also a kind of steric effect: despite their distortion being quite large (table 2), the trigonal prisms $[Nb_6Sn]$ are then at, or close to, the ideal position with respect to the C planes. To know if this observation is a general trend needs additional studies.

On figure 2 are plotted the calculated bulk moduli we obtain for the ternary carbides M_2SnC ($M = Ti, Zr, Hf$ and Nb)

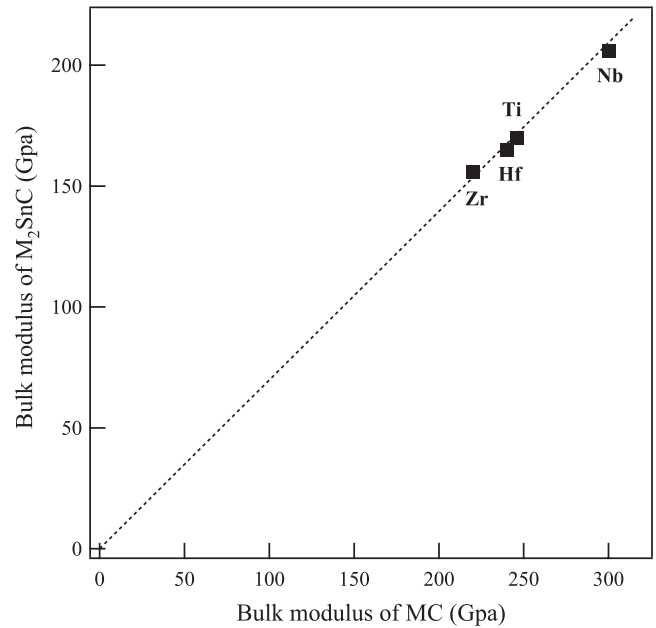


Figure 2. The bulk moduli of M_2SnC ($M = Ti, Zr, Hf, Nb$) versus the bulk moduli of the corresponding MC.

versus those of the corresponding binary carbides MC. It shows that there is a linear relationship between these ternaries and the corresponding binaries: almost 69% of the bulk modulus of the MC is retained in M_2SnC . This is in agreement with the results obtained by Music *et al* [13] for M_2AC ($M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W$ and $A = Al, Ga, Ge$ and Sn). In turn, our results do not support those reported by Sun *et al* [12] for Nb_2SnC who predict that the bulk modulus of NbC is preserved for this alloy. In our case, whatever the valence electron concentration (VEC) is, the bulk modulus of the tin based ternary carbides is reduced by about 69% compared to the corresponding binaries. It is interesting to compare this result with those obtained by Fang *et al* [26] for the 312 M_3SiC_2 ($M = V, Cr, Zr, Nb, Mo, Hf, Ta$ and W) MAX phases. These authors have found from their calculations that the bulk moduli of these 312 ternaries are reduced by about 75% with respect to the bulk moduli of the corresponding binary carbide MC. Such behavior can be understood from the structure of $M_{n+1}AC_n$ compared to the binary carbides MC: every $n + 1$ single monolayer of C atoms in MC is replaced by an A layer, resulting in an under stoichiometric $M_{n+1}C_n$ carbide (M_2C for 211, M_3C_2 for 312 and M_4C_3 for 413 MAX phases). Indeed, a MAX phase $M_{n+1}AC_n$ can be viewed as composed of $M_{n+1}C_n$ slabs twinned with respect to the separating A monolayers that are mirror planes [1], resulting in an increasing number of M–C bonds when n increases. Such an intercalation of A monolayers into the MC matrix needs to break strong MC bonds that are replaced by weaker M–A bonds [27]. Therefore, when going from the binary carbides MC to the ternaries M_2SnC , some ‘strong’ M–C bonds are replaced with ‘softer’ M–Sn bonds and this results in reduced elastic properties for the ternaries compared to the binaries as evidenced from figure 2.

These close similarities of the structures of the M_2SnC and MC phases are also reflected by the correlation between a and c

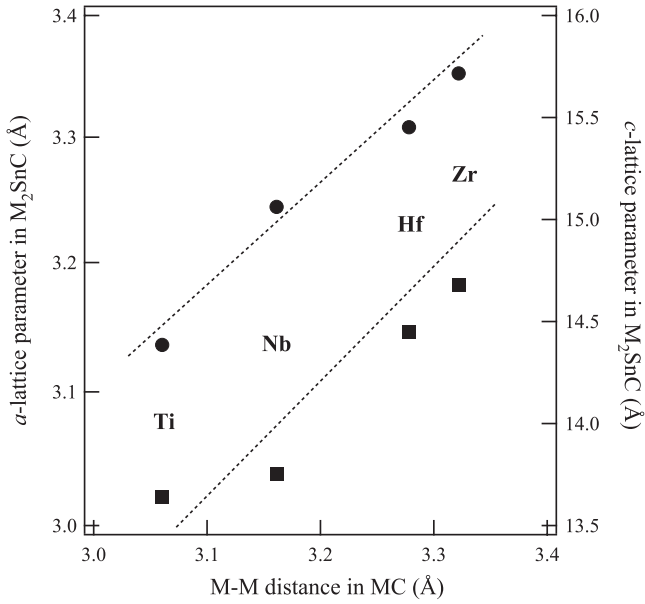


Figure 3. Dependence of the a (circles, left hand scale) and c (squares, right hand scale) lattice parameters in M_2SnC ($M = Ti, Zr, Hf, Nb$) compounds on $M-M$ distance in the corresponding MC.

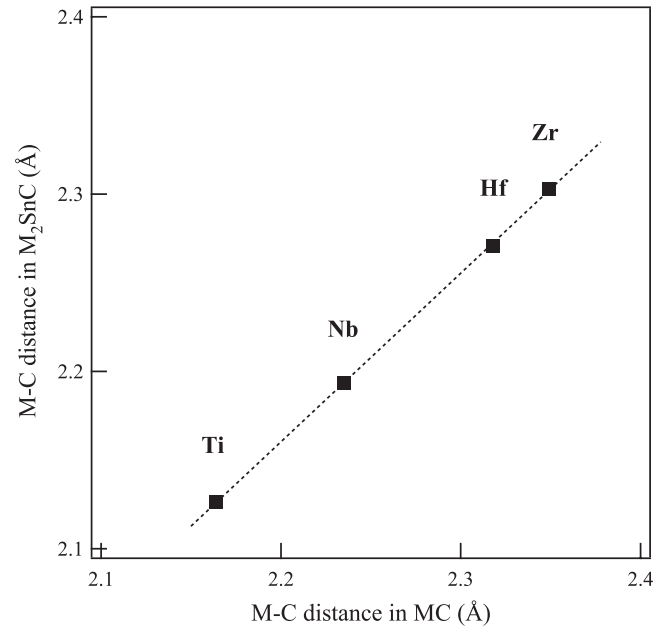


Figure 4. Dependence of the $M-C$ distance in M_2SnC ($M = Ti, Zr, Hf, Nb$) versus the $M-C$ distance in the corresponding MC.

lattice parameters of the former, and the first near-neighboring $M-M$ distances in the corresponding MC binaries. As shown in figure 3, both increase linearly with increasing $M-M$ binary carbide distances. We have also calculated the interatomic distances $M-C$ for the ternary carbides M_2SnC and compared them to those related to the corresponding binaries MC. For the 211 phases, the interatomic distance $M-C$ is related to the structural parameters a , c and Z_M according to the following relation:

$$d_{M-C} = \sqrt{\frac{a^2}{3} + c^2 Z_M^2}. \quad (3)$$

From the examination of figure 4, it is clear that the $M-C$ distances in M_2SnC vary linearly with those of the MC binaries (the slope of the dotted line in figure 3 is unity), $M-C$ distances being, however, about 2% larger in the latter than in the former.

4. Density of states study

Obviously, all these results reflect the underlying electronic structure of the alloys under investigation. The electronic structure of the MAX phases has been widely investigated theoretically (see [27] and references therein) and is now quite well established. From the literature [27], the bonding scheme in 211 MAX phases can be summarized as follows: relatively weak $M d-A p$ bonding just below the Fermi level E_F and stronger (e.g. deeper in energy) $M d-X p$ and $M d-X s$ bondings. These trends are confirmed from the examination of the local l -projected LDOS of the selected compounds M_2SnC ($M = Ti, Zr, Hf$ and Nb) displayed in figure 5. Indeed, on the one hand, in the energy range from -6 to -1.8 eV, the $C p$ LDOS has the same shape as the d states of the M atoms located each side of the C layers. It is indicative of a hybridization between $M d$ and $C p$ states and thus of a

covalent interaction. On the other hand, in the energy window from -2.5 to -0.6 eV, the $Sn 5p$ states interact mainly with the $M d$ states. But these $M d-Sn p$ hybrids are higher in energy than the $M d-C p$ ones (e.g. closer to the Fermi level) suggesting that $M-C$ bonds are stronger than $M-Sn$ bonds. It is this strong $M d-C p$ hybridization which stabilizes the structure of M_2SnC . These strong $M-C$ hybrids are, however, in competition with the weaker $M-Sn$ ones which results in the noncubic distortions for octahedra and trigonal prisms evoked previously. From figure 5, one also observes that when going from the IVB group (s^2d^2 configuration: Ti, Zr, Hf) to the VB group (s^2d^3 configuration: Nb), both $M-C$ and $M-Sn$ hybrids shift towards lower energies with respect to E_F . It is fair to conclude that bonds are stronger in Nb_2SnC than in M_2SnC ($M = Ti, Zr, Hf$). It reflects the better elastic properties for the former than for the latter owing to a strengthening of both ‘soft’ $Nb-Sn$ and ‘hard’ $Nb-C$ bonds due to an increased VEC at the M site. Finally, from the total DOS values at the Fermi level (E_F) reported in table 1, it is obvious that all alloys have a metallic character. Hence it is tempting to conclude that Nb_2SnC is more conducting than Ti_2SnC, Zr_2SnC and Hf_2SnC . However, this assumption is not supported by experiment [15]: for example the conductivity of Ti_2SnC ($14 \times 10^6 (\Omega m)^{-1}$) is about six times higher than the Nb_2SnC one ($2.4 \times 10^6 (\Omega m)^{-1}$). This trend is general for all MAX phases except for Ti_4AlN_3 : as stated by Barsoum [28], the mobilities of charge carriers (electrons and holes) are not proportional to the DOS at the Fermi level in these materials.

5. Conclusion

In summary, we have carried out *ab initio* calculations of the structural properties of M_2SnC , with $M = Ti, Zr, Hf$ and Nb using a hybrid all electron full-potential linearized

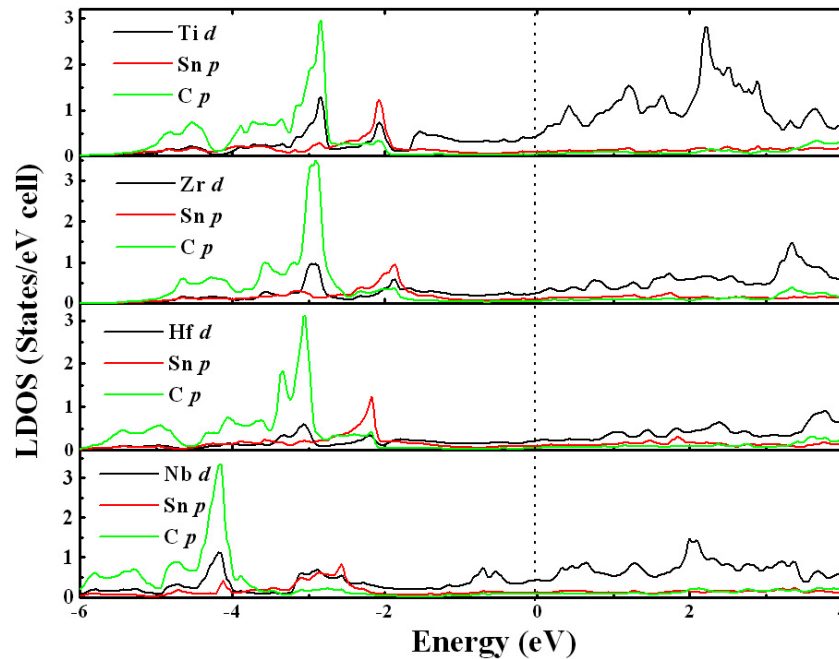


Figure 5. Local density of states (LDOS) as a function of energy for M_2SnC ($M = Ti, Zr, Hf, Nb$). The vertical dotted line denotes the Fermi level.

augmented plane-wave method within the GGA-WC and the DFT approaches. It has been shown that the structural parameters obtained after relaxation are in good agreement with the experimental ones. We have evidenced the existence of a steric effect on the M site in the M_2SnC 211 MAX phases. For M elements with atomic radius (Zr, Hf) larger than the tin one, the distortions of the polyhedra (octahedron and trigonal prism) constituting the hexagonal unit cell are minimum. We have found that the 211 M_2SnC ($M = Ti, Zr, Hf$ and Nb) MAX phases hold back about 69% of the bulk modulus of the corresponding binary carbides, a value close to $\frac{2}{3}$. Knowing that the bulk moduli of M_3SiC_2 is $\frac{3}{4}$ of the corresponding MC, it is curious to remark that the bulk moduli of $M_{n+1}AC_n$ are pretty close to $\frac{n+1}{n+2}$ of the corresponding binary carbides for $n = 1$ and 2. Such a phenomenological relation will give $\frac{4}{5}$ for the bulk moduli of M_4AC_3 compared to the related MC ones. To know if the relationship $B_{M_{n+1}AC_n} = \frac{n+1}{n+2} B_{MC}$ is only due to chance or to some deeper underlying physics needs further study that is out of the scope of the present paper. However, it is reasonable to think that the elastic properties of MC will be inherited more in 413 phases than in 312 and 211 because the number of M–C bonds per unit cell is higher. Like all MAX phases experimentally or theoretically studied so far, the 211 M_2SnC are found to be conducting alloys, the DOS at the Fermi level being for all of them below four states eV^{-1} per cell. As already known [12, 27, 29–32], the origin of the stability of the M_2SnC phases is related to M d–Sn p and especially M d–C p bonds.

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