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## Abstract

We have investigated the structural properties and electronic structure of the recently discovered
layered ternary Ti₃SnC₂ using the first-principles all-electron full-potential augmented plane
wave method within the generalized-gradient approximation and the local density
approximation. The lattice constants obtained after geometry optimization are in good
agreement with experiment data and the bulk modulus is predicted. The band structure shows
that the electrical conductivity is metallic and anisotropic with a high density of states at Fermi
level. The analysis of the projected local density of states shows that the major hybrids come
from Ti d and C p states.

## 1. Introduction

Discovered in the sixties in Vienna [1–5], a group of nanolayered compounds with chemical formula $M_{n+1}AX_n$ (hence named MAX phases) with $n = 1$, 2, or 3, where M is an early transition metal, A an A-group element (mostly IIIA and IVA), and $X = C$ or N, has become the subject of renewed interest and of numerous studies both experimentally and theoretically [6–19]. Indeed, these layered ternary compounds exhibit remarkable physical properties, such as high strength and modulus, good electrical conductivity, exceptional shock resistance and damage tolerance, high loss factor, fully reversible plasticity, and high thermal conductivity [6, 7, 11, 12, 15]. This unique set of properties makes them potentially interesting for applications. If the chemical formula of most MAX compounds is $M_2AX$ (211, in short) [10], however much attention has been paid to Ti₃SiC₂ which is the prototype member for MAX phases with formula $M_3AX_2$ (312, in short). Although 211's are more numerous, more 312's remain to be explored because one can expect they have superior physical properties than the former. Recently Dubois *et al* [20] have successfully synthesized for the first time Ti₃SnC₂, a new 312 phase, by using the hot isostatic pressing (HIP) method starting with pure titanium, tin and carbon powders. Its lattice parameters have been deduced from Rietveld analysis of the related x-ray diffraction pattern. However, the sample contains about 22% of TiC and one may ask if such an amount of minority phase does not affect the measured lattice parameters. To support the experimental findings quoted in [20], we report the results of the first-principles calculations for this ternary compound. Our theoretically computed lattice constants obtained from structural relaxation are found to be in reasonable agreement with the experimental ones. We predict the bulk modulus, electronic structure and bonding properties of this 312 MAX phase by using a full-potential linearized plane wave method within the density functional theory.

## 2. Calculations details

Theoretical calculations were carried out using the full-potential (linearized) augmented plane waves plus local orbitals (FP-L/APW + lo) method [21], which is a first principle calculation based on the density functional theory (DFT) [22]. In the FP-L/APW + lo method, no approximation on the shape of the potential is made. The muffin-tin radii ($R_{MT}$) are considered to be equal to 1.85, 2.44 and 1.7 a.u. (Bohr units) for Ti, Sn and C atoms, respectively. The maximum value $\ell$ for the wavefunction expansion inside the atomic spheres is confined to $\ell_{max} = 10$. To achieve the energy eigenvalues convergence, the wavefunctions in 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 1000 points in the first Brillouin

zone. The convergence has been followed with respect to the energy and the density. The influence of the exchange and correlation potential has been tested using either the local density approximation (LDA) or the generalized-gradient approximation (GGA). In the latter case, we use for exchange–correlation the most popular scheme of Perdew, Burke and Ernzerhof (PBE) [23] and the new one of Wu and Cohen (WC) [24]. This latter is a nonempirical density functional GGA based on a diffuse radial cutoff for the exchange hole in the real space that satisfies the known [25] analytic gradient expansion of the exchange energy for small gradients. Since solids can have a diffuse tail around the exchange–correlation hole, to use a diffuse radial cutoff factor, instead of a sharp one like in the GGA-PBE, leads to a smaller exchange energy for large gradients. Thus the GGA-WC keeps the behavior of the GGA-PBE for small gradients, retaining cancelation of gradient correction of exchange and correlation as the gradient goes to zero, while it is smaller for large gradient values. It has been shown to give significant improvements for lattice constants [24], a point of highest interest for the present study.

Like all MAX phases, $Ti_3SnC_2$ belongs to $P6_3/mmc$ space group. The unit cell of the layered ternary $Ti_3SnC_2$ is shown in figure 1. This hexagonal structure can be considered as a nearly close-packed stacking of titanium carbide layers interleaved with a pure tin layer every fourth layer. The atoms are located at the following Wyckoff positions: two inequivalent Ti atoms—denoted Ti1 and Ti2 in the following—at 2a and 4f ($Z_{Ti2}$), respectively, Sn at 2b and C at 4f ($Z_C$). The coordinates $Z_{Ti2}$ and $Z_C$ are the only internal free parameters in the crystal structure. For the atoms in 4f positions, the ideal values of the two internal dimensionless parameters $Z$ are $1/8 = 0.125$ and $1/16 = 0.0625$ for Ti2 and C, respectively. The geometry has been optimized for the considered structure following the procedure described by Hug [26]. 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 parameters $Z_{Ti2}$ and $Z_C$ are allowed to vary for optimization. The energy curves as 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 volume in which all other parameters are optimized. In a last step, this energy versus volume curve is fitted using the third-order Birch–Murnaghan equation of state [27–29] to find the optimized parameters.

## 3. Results and discussion

Our calculated values for $a$, $c$, $Z_{Ti2}$, $Z_C$ and $c/a$ within the LDA, GGA-PBE and GGA-WC frameworks are gathered in table 1 as well as the experimental data [20] for comparison. The deviations from experimental values for $a$ and $c$ lattice parameters were underestimated by the LDA about 1.47% and 1.53%, and overestimated by the GGA-PBE about 0.37% and 0.78%, respectively. The GGA-WC scheme improves $a$ and $c$ significantly over the LDA and the GGA-PBE calculations despite it underestimates them slightly compared to the experiment (0.05% and 0.06%, respectively). For all
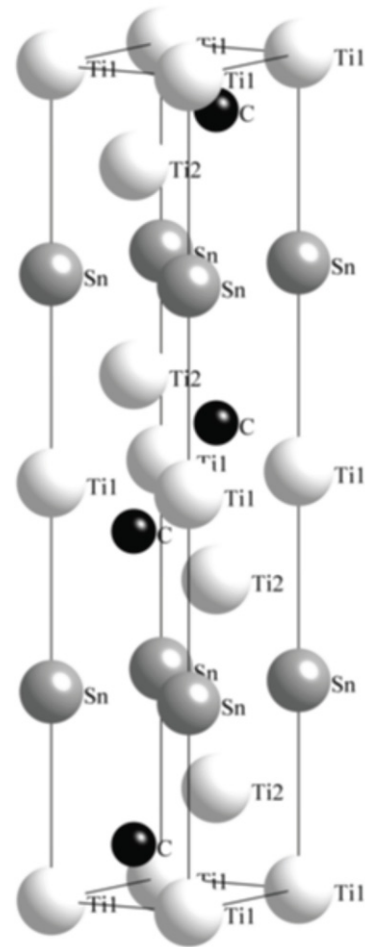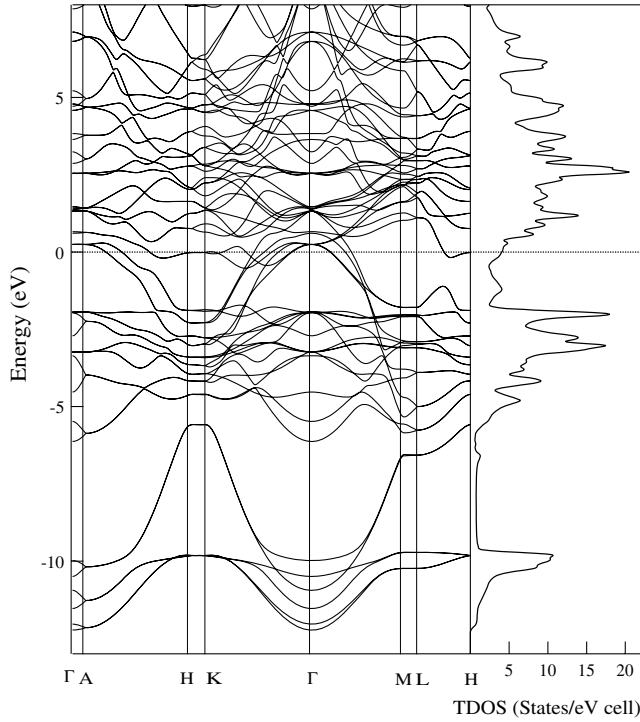


**Figure 1.** Crystal structure of $Ti_3SnC_2$.

calculation schemes, the relaxed structure is found to depart from the ideal stacking as it is observed in the experiment (see table 1): $Z_{Ti2}$ is smaller and $Z_C$ is higher than their respective ideal values. However, the magnitude of the absolute deviations of these two internal free parameters is underestimated in the theory compared to the experiment. This slight discrepancy is likely to be due to C vacancies in the real material, C vacancies we do not consider in the present calculations [30, 31]. The predicted bulk modulus was found to be 208 and 178 GPa by LDA and GGA-PBE calculations, respectively. The GGA-WC bulk modulus value is in between (192 GPa) and significantly higher than the one already predicted (167 GPa [26]) for the 211 $Ti_2SnC$ compound. Looking at the unit cell shown in figure 1, we see that the $Ti_3SnC_2$ structure is composed of three nearly close-packed Ti layers interleaved with Sn layers, with C atoms filling the octahedral sites between the former. The Sn atoms are located at the centers of trigonal prisms that are larger than the octahedral sites to accommodate the quite large Sn atoms. The $Ti_6C$ octahedra are edge sharing and identical to those found in the rock salt corresponding binary TiC. This already noted [10] resemblance in structure between the MAX phases and their corresponding binaries MX explains that they share
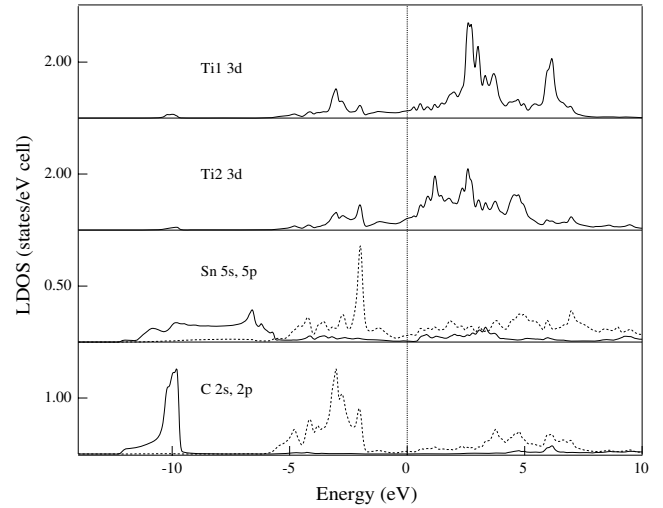
**Table 1.** Lattice constants, $c/a$ ratio, $Z_{Ti2}$ and $Z_C$ internal position parameters, bulk modulus $B$ and pressure derivative $B'$ of the bulk modulus for $Ti_3SnC_2$ from FP-L/APW calculations.

|                | $a$ (pm) | $c$ (pm) | $c/a$ | $Z_{Ti2}$ | $Z_C$ | $B$ (GPa) | $B'$ |
|----------------|----------|----------|--------|-----------|--------|-----------|-------|
| Experiment [20] | 313.66   | 1865.0   | 5.9459 | 0.1204    | 0.0720 | —         | —     |
| LDA            | 309.04   | 1836.4   | 5.9422 | 0.1240    | 0.0677 | 208       | 4.45  |
| GGA-PBE        | 314.85   | 1879.6   | 5.9698 | 0.1236    | 0.0675 | 178       | 4.30  |
| GGA-WC         | 312.0    | 1853.4   | 5.9404 | 0.1234    | 0.0671 | 192       | 4.13  |



**Figure 2.** Band structure and TDOS of $Ti_3SnC_2$.



**Figure 3.** LDOS for $Ti_3SnC_2$. For C and Sn atoms are presented s (full lines) and p (dashed lines) LDOS. The origin for energy is at the Fermi level.

many properties. In general, the MAX phases are elastically quite stiff, the stiffness increasing with N: it increases with the fraction of M–X bonds [10]. In $Ti_3SnC_2$ it exists two layers of $Ti_6C$ octahedra between the Sn layers and only one in $Ti_2SnC$, and so a larger fraction of Ti–C bonds in the former than in the latter. Thus, it is fair to conclude that $Ti_3SnC_2$ is stiffer than $Ti_2SnC$ in agreement with the above reported calculated values for the bulk modulus.

The electronic band structure (BS) at different high symmetry points within the first Brillouin zone of the hexagonal lattice and the total density of states (TDOS) of $Ti_3SnC_2$ calculated within the GGA-WC scheme are presented in figure 2. Contrarily to what is observed for lattice parameters determination (table 1), we found like other authors [32] that these quantities do not depend significantly of the used exchange–correlation scheme for calculating them. It can be assessed from figure 2 that there is no gap at the Fermi level $E_F$ in which vicinity it exists a strong overlapping of bonding and anti bonding states: thus the conductivity of $Ti_3SnC_2$ is of metallic nature. The second point of interest of the BS is its strongly anisotropic character with less $c$-axis energy dispersion. This can be seen from the reduced dispersion

along the short $H–K$ and $M–L$ directions, the bands being then quite flat. The anisotropy of the band structure near and below $E_F$ indicates that the conductivity is also anisotropic. These conclusions, not surprisingly, are quite similar to those predicted to occur for $Ti_2SnC$ [33].

The local $\ell$-projected densities of states (LDOS) are presented in figure 3 to show the hybridization between the electronic states of elements Ti, Sn and C. These LDOS shows several interesting features. At the bottom of the valence band, i.e. between $-13$ and $-8$ eV, the width the Sn 5s state is much larger than that of the C 2s state and there are quite a few peaks in the Sn 5s state. In the energy range from $-6$ to $-1.8$ eV, the C p LDOS has the same shape as the d electronic states of Ti1 atoms located between C layers, but also to the Ti2 d LDOS in the range from $-6$ to $-2.5$ eV. It is indicative of an hybridization between Ti1-2 d and C p states and thus of a covalent interaction. In turn, in the energy window from $-2.5$ to $-0.6$ eV, the Sn 5p states interact mainly with the Ti2 d states. But these Sn p–Ti d hybrids are higher in energy than the C p–Ti d ones (i.e. closer to the Fermi level) suggesting that Ti–C bonds are stronger than Ti–Sn bonds. It is this strong C p–Ti d hybridization which stabilizes the structure of $Ti_3SnC_2$, a general trend in MAX phases [8, 13]. The TDOS at the Fermi level $E_F$ is equal to 4.07 states $eV^{-1}$ per unit cell, a value slightly higher than the one predicted [26] for $Ti_2SnC$ (3.71 states $eV^{-1}$ per unit cell). Assuming a single carrier model for the conductivity, and in analogy to the free

electron model, the concentration $n$ of electron is proportional to the cube of $N(E_F)$ expressed on a per unit volume basis. Thus, in this crude assumption, and for same defect density levels [34], the 312 compound will be more conductive than the 211 one, a behavior originating from the increased number of $Ti_6C$ octahedra layers, and thus of Ti atoms per unit cell, in the former. Indeed, the largest contribution to the conduction bands near $E_F$ comes mainly from 3d states of Ti2 atoms located in the vicinity of Sn layers and from Ti1 atoms which do not exist in the 211's. In return, the contributions of Sn 5p and C 2p states is quite low around the Fermi level. The same situation occurs above the Fermi level: anti bonding Ti2 and Ti1 3d states dominate with less contributions from Sn 5p and C 2p states. However it remains to perform experimental resistivity and Hall coefficient measurements on these tin based MAX phases because it is well documented ([10] and references therein) that defects like vacancies and carriers (electrons *and* holes) mobilities contribute strongly to the conductivity.

## 4. Conclusion

Full-potential linearized augmented plane wave calculations have been performed to investigate the structure and properties of the layered ternary $Ti_3SnC_2$. It has been shown that the structural parameters obtained after relaxation are in good agreement with the experimental ones when using the GGA-WC approximation which is a significant improvement over the LDA and GGA-PBE schemes. The calculated band structure shows that $Ti_3SnC_2$ is metallic and anisotropic. It is suggested that this material will exhibit better mechanical and conduction properties than the corresponding 211 member $Ti_2SnC$ because two layers of $Ti_6C$ octahedra are intercalated between Sn layers in the former instead of one in the latter. Like all MAX phases known to date, the density of state indicates that Ti 3d states are strongly hybridized with the C 2p states while the Ti 3d–Sn 5p bonds are in comparison weaker.

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