Electronic structures, bonding natures and defect processes in Sn-based 211 MAX phases

M.A. Hadi, 1,2 N. Kelaidis, 3,4 S. H. Naqib, 1 A. Chronneos, 2,4* A. K. M. A. Islam 1,5

1Department of Physics, University of Rajshahi, Rajshahi 6205, Bangladesh
2Faculty of Engineering, Environment and Computing, Coventry University, Priory Street, Coventry CV1 5FB, UK
3Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinous 48, GR-11635 Athens, Greece
4Department of Materials, Imperial College, London SW7 2AZ, UK
5International Islamic University Chittagong, Kumira, Chittagong-4318, Bangladesh

Abstract

The electronic structure, bonding natures, and defect processes of the new superconducting MAX phase Lu2SnC are investigated by using density functional theory, and are compared to other existing M2SnC phases. The formation of M2SnC MAX phases is exothermic and these compounds are intrinsically stable in agreement with experiment. The finite value of DOS, in addition to the d-resonance at the vicinity of the Fermi level, indicates a metallic nature and conductivity of M2SnC MAX phases. The strength of the covalent M–C bond is higher than that of the covalent M–Sn bond. The calculated effective valence charge also indicates the dominance of covalency in the chemical bonding in the studied compounds. The charge transfer in M2SnC phases indicates the ionic nature of their chemical bonds. The ionic character of their chemical bonds can also be understood from the spherical nature of charge distribution in their contour maps of electron charge density. Therefore, the overall bonding nature in the studied M2SnC MAX phases is a combination of metallic, covalent, and ionic. The bond length is directly proportional to the crystal radius, while bond covalency is inversely proportional to the crystal radius. Additionally, the Fermi surface topology is also investigated. Considering the intrinsic defect processes it is calculated that Nb3SnC is the material that is predicted to have better radiation tolerance.

Key-words: Sn-based 211 MAX phase; Electronic structure; Bonding nature; Defect process

1. Introduction

MAX phases, a new class of ternary layered carbide and nitride materials, are potentially technologically important as they exhibit unique physical properties due to the combination of metallic and ceramic natures [1]. In the mid-sixties of the last century, Nowotny et al. first discovered some members of this family, now known as the ‘211’ MAX phases, and named them ‘H’ phases [2]. After re-synthesizing a phase pure dense Ti3SiC2 and its characterizing study in 1996 by Barsoum and El-Raghy, a renewed interest of scientific community has grown on MAX phases [3]. Following this study, Barsoum et al. also discovered the carbide phase Ti4AlN3 and understood that they were dealing with a larger family of compounds with similar properties [4–6]. This realization led to the nomenclature “Mn+1AXn” (later shortened to MAX) phases, which also stands for the chemical formula for this class of solids [1,7]. In this formula, M represents a transition metal, A refers to an A-group element, and X is carbon and/or nitrogen. The MAX phases are categorized into different sub-families, namely 211, 312, and 413 phases depending on n = 1, 2, and 3, respectively.

MAX phases possesses a diverse combination of some of the best physical, chemical, electrical, and mechanical properties, showing both metallic and ceramic physiognomies. In the meantime, a tremendous progress has been made in understanding the properties of these layered compounds [1,3–23]. The MAX phases have been characterized having properties found commonly in metals such as high thermal and electrical conductivities, thermal shock resistance, damage tolerance, machinability and plasticity at high temperature [1,14–17]. Remarkably, ceramic-like properties are also present by such as light weight, elastic rigidity, fatigue, oxidation and corrosion resistant, and maintaining the strength to high temperature [18–23]. Due to these technologically important properties. MAX phases are potentially used as tough, machinable and thermal shock refractories, high temperature heating elements, coatings for electrical contacts, neutron irradiation resistant parts for nuclear applications, precursors for synthesis of carbide-derived carbon and MXenes, the latter being a family of two-dimensional transition metal carbides, nitrides, and carbonitrides [24–28].

* Corresponding author: A. Chronneos (ab8104@coventry.ac.uk)

Corresponding author: M.A. Hadi (hadipab@gmail.com)
MAX phases crystallize in the layered hexagonal structures with space group P6\textsubscript{3}/mmc (no. 194). These materials comprise of alternate near-close-packed layers of M\textsubscript{6}X octahedra interpolated with pure A-atomic layers. The M\textsubscript{6}X octahedra, similarly to those materializing in the corresponding MX binary phases, are linked to each other by edge sharing [29]. The number of M-layers separating every two A-layers leads to the basic difference in the structures of 211, 312, and 413 MAX phases. In fact, in the 211, 312, and 413 phases, two, three, and four M-layers exist in the middle of every two A-layers. Such atomic arrangements in the MAX phases give them a characteristic layered structure, which accumulates both metallic and ceramic properties in these solids. For this reason, the MAX phases are sometimes termed as ‘metallic ceramics’. These compounds are also termed as ‘nanolaminates’ due to their effective laminated monolayers [30].

A large number of MAX phases have been predicted very recently [12]. The list of existing MAX phases is expanding day by day by synthesizing the new members [31–34]. Recently, a new MAX phase Lu\textsubscript{2}SnC, out of any prediction, is synthesized by Kuchida et al. [35]. It is not only new but also exceptional as it contains Lu belonging to lanthanide series instead of transition metals. Kuchida et al. [35] applied the arc melting method to prepare a polycrystalline sample of Lu\textsubscript{2}SnC. Powder X-ray diffraction (PXRD) pattern is employed to index the unit cell. The cell is identified as a hexagonal system with Cr\textsubscript{2}AlC-type structure and with the space group of P6\textsubscript{3}/mmc, which belongs to the MAX phase. They also reported the occurrence of superconductivity at 5.2 K for Lu\textsubscript{2}SnC on the basis of their magnetic susceptibility and electrical resistivity measurements. The new phase Lu\textsubscript{2}SnC should belong to the type-II superconductors according to the obtained superconducting parameters.

In our previous paper [36], the structural, elastic, mechanical and thermal properties of Lu\textsubscript{2}SnC are investigated along with other existing M\textsubscript{6}SnC (M = Ti, Zr, Hf, Nb) phases and the obtained results are compared with those found in literatures. It is mentioned that the early existing phase Nb\textsubscript{2}SnC is also superconductor and its superconducting transition temperature is 7.8 K. The electronic structure and bonding nature of Lu\textsubscript{2}SnC are still unexplored. The defect processes in existing M\textsubscript{6}SnC phases have yet to be studied. The knowledge of electronic structure is important to understand many physical properties of crystals. The investigation of defect processes is important to provide a primary selection criterion for radiation tolerance on the basis of Schottky or Frenkel pair formation energies. Motivated by this we have done the present study.

2. Computational methods

The CASTEP code [37] embodied with planewave pseudopotential density functional theory (DFT) [38,39] is employed to carry out the present investigation. Generalized gradient approximation (GGA) simplified by Perdew–Burke–Ernzerhof (PBE) is used to treat the electronic exchange and correlation potential [40]. The interactions of electrons with ion cores are evaluated with the Vanderbilt type ultrasoft pseudopotential [41] with 2\textsuperscript{s}\textsuperscript{2}2\textsuperscript{p}\textsuperscript{5}, 5\textsuperscript{s}\textsuperscript{2}5\textsuperscript{p}\textsuperscript{2}, 5\textsuperscript{d}\textsuperscript{2}6\textsuperscript{s}, 5\textsuperscript{p}\textsuperscript{5}5\textsuperscript{d}\textsuperscript{4}6\textsuperscript{s}, 5\textsuperscript{p}\textsuperscript{6}5\textsuperscript{d}\textsuperscript{3}6\textsuperscript{s}, and 4\textsuperscript{p}\textsuperscript{6}4\textsuperscript{d}\textsuperscript{4}5\textsuperscript{s}\textsuperscript{2} as the basis set of the valence electron states for C, Sn, Hf, Lu, Nb, Ti, and Zr, respectively. A \Gamma-centered k-point mesh of 15\times15\times3 grid in Monkhorst-Pack (MP) scheme [42] is applied in the reciprocal space for sampling the first Brillouin zone of hexagonal unit cell for MAX phase. A planewave basis with a cutoff energy of 700 eV is used to expand the eigenfunctions of the valence and nearly valence electrons. To minimize the total energy and internal forces the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm is used in the geometry optimization [43]. The convergence tolerance for total energy, residual force, maximum ionic displacement, and maximum stress are set to 5\times10\textsuperscript{5} eV/atom, 0.01 eV/Å, 5\times10\textsuperscript{4} Å, and 0.02 GPa, respectively. For self-consistent field calculations, the tolerance is chosen 5\times10\textsuperscript{7} eV/atom. To obtain smooth Fermi surfaces a \k\textsuperscript{-point mesh of 15\times15\times3 grid in MP scheme is used. DFT is an appropriate method to describe the electronic structure of crystalline solids [30,36,44–65].

To carry out the population analysis using the CASTEP code, a projection of the planewave states onto a localized (LCAO) basis is used through a scheme proposed by Sanchez-Portal et al. [66]. Population analysis of the resulting projected states is then implemented with the Mulliken formalism [67]. The defect calculations are carried out with a 108-atomic site supercell using a 3 \times 3 \times 1MP k-point mesh under constant pressure. Considering all possible interstitial sites, we performed an intensive computational search to identify the potential interstitial sites. The defect energies are defined as effectively energy differences (refer to defect reactions in section 3.4) between isolated defects. The effectiveness of the technique to determine the defect properties and the convergence as compared to experiment has been discussed in a recent study [68].
3. Results and discussion

3.1. Optimized Geometry and energy

The optimized geometry of newly synthesized Lu$_2$SnC as a structural model of M$_2$SnC 211 MAX phases is shown in Fig. 1. The calculated lattice constants $a$ and $c$ along with experimental [35, 69, 70] and other theoretical [71–73] values are plotted in Fig. 2. It is observed that the present values are very close to the experimental ones. The deviation of present values from the experimental values for $a$ and $c$ of Lu$_2$SnC is 0.91% and 1.08%, respectively. For other M$_2$SnC phases, the deviation of $a$ and $c$ is calculated to be within 0.27–1.66% and 0.71–1.12%, respectively. These ensure the reliability of the present calculations. The GGA-trend, overestimation in lattice constants, is also observed in the present CASTEP-GGA and previous VASP-GGA [71] calculations. All results for lattice constants of M$_2$SnC phases including Lu$_2$SnC show increasing trend following the sequence of M-elements as Ti→Nb→Hf→Zr→Lu, excepting the results due to Bouhemadou [73]. Both the lattice parameters $a$ and $c$ and consequently the unit cell volume $V$ are largest for Lu$_2$SnC among all existing M$_2$SnC phases. In our previous paper, we showed that the crystal radius of M-element plays the role for this trend [36].

![Geometry of Lu$_2$SnC as a structural model of M$_2$SnC.](image1)

![Lattice constants $a$ and $c$ of M$_2$SnC as a function of M-elements.](image2)
Fig. 3. Unit cell volume and hexagonal ratio of M$_2$SnC as a function of M-elements.

The calculated unit cell volume and hexagonal ratio are shown in Fig. 3 together with other literature values. The cell volume also exhibits the similar trend as observed in lattice constants. This trend actually follows the increasing trend of crystal radius of M-elements [36]. Though the hexagonal ratio $c/a$ lies within the range 3.5–4.6 for 211 MAX phases, the literature values found in Ref. [73] scatter randomly. As the present lattice constants are consistent with the experimental values, the present volume and hexagonal ratio also show the closeness to the measured ones. The internal energy, $E(V)$ for M$_2$SnC crystal systems are calculated with the equation of state [74] and shown in Fig. 4.
The formation energy $\Delta E_f$ is calculated from the total energy of an examined phase minus the sum of the energies of its pure constituent elements. The calculated formation energies of Ti$_2$SnC, Nb$_2$SnC, Hf$_2$SnC, Zr$_2$SnC and Lu$_2$SnC are found to be -3.18, -2.05, -2.77, -3.47 and -2.31 eV/fu, respectively. These values are compared in Fig. 5 with those found in literatures [72, 75]. Negative sign in these values imply that the materialization of M$_2$SnC MAX phases is exothermic and these compounds are intrinsically stable in covenant with the experiment [35, 69, 70]. Evidently, Zr$_2$SnC is the most stable phase. Between two superconducting phases, Lu$_2$SnC is more stable than Nb$_2$SnC.

3.2. Electronic band structure and density of states

Electronic band structures of five Sn-containing M$_2$SnC MAX phases are investigated with high symmetry points in the first Brillouin zone and shown in Fig. 6. The energy scale is defined with $E-E_F$ and the Fermi surfaces are set at zero in this scale. No band gap arises in the energy band structures as a large number of valence bands cross over the Fermi level and overlap with the conduction bands. As a result, all the studied M$_2$SnC phases should attain metallic conductivity. Though the band profiles of M$_2$SnC are almost similar [44], a distinct difference is observed for M$_2$SnC. The position of Fermi surface in Ti$_2$SnC is just below the valence band maximum near the $\Gamma$-point. In Nb$_2$SnC, it lies above the valence band maximum at the same point. The $\Gamma$-point, where the maximum valence bands meet together, situates above the Fermi level of Hf$_2$SnC, Zr$_2$SnC and Lu$_2$SnC MAX phases. The upward distances of these points from Fermi levels follow the order Zr$_2$SnC < Hf$_2$SnC < Lu$_2$SnC. A large number of valence bands accumulate around the energy levels of -4.3 eV in Lu$_2$SnC and leads to a large peak in the total DOS. Such accumulations are not found in the other M$_2$SnC phases although similar features in the band profiles are observed in Hf$_2$SnC and Zr$_2$SnC phases.
Fig. 6. Energy band structures for M$_2$SnC MAX phases.

Fig. 7. Total and partial density of states of M$_2$SnC MAX phases.

The electronic density of states (DOS) provides more insights into the chemical bonding in crystals. The calculated total and partial DOS for M$_2$SnC including newly synthesized Lu$_2$SnC are shown in Fig. 7. The Fermi level $E_F$ of Lu$_2$SnC lies near a pseudogap at the left similar to the other M$_2$SnC MAX phases, indicating their structural stability. The DOS has finite value at the Fermi level of each examined Sn-containing 211 MAX phases. Contribution to this finite value mainly comes from d-orbitals of each transition metal M. The finite value of DOS as well as d-resonance at the vicinity of the Fermi level is responsible for the metallic conductivity of these nanolaminates. The DOS at Fermi level is calculated to be 3.93, 3.62, 2.84, 3.25, and 2.35 states/eV-uc for Ti, Nb, Hf, Zr, and Lu based M$_2$SnC compounds. These values are compared with the literature values in Fig. 8. It is evident that the new phase Lu$_2$SnC has the lowest DOS at $E_F$, which is two-third of that of superconducting phase Nb$_2$SnC. Surprisingly, the $T_c$ of Lu$_2$SnC (5.2 K) [35] is almost two-third of that of Nb$_2$SnC (7.8 K) [76]. To the best of our knowledge, presently there is no direct correlation between DOS at the Fermi surface and the superconducting transition temperature $T_c$. Whether it is a coincidence or an inherent relationship- more data should be examined for being sure. In a next paper we will examine for all superconducting MAX phases.
The valence band of M₂SnC phases studied here consists of main two parts. A low flat-type valence band arises between these two parts owing to s-electrons of the Sn-atoms similar to the M₁SnC₂ compounds [44]. The lower part with a single peak arises due to the hybridization between M d and C s electrons, indicating covalent M-C bonding in M₂SnC compounds. This part shifts towards the Fermi level as M-atom varies from Ti to Lu following the route Ti → Nb → Hf → Zr → Lu, which means that the covalency of M-C bonding i.e., M₂SnC phases, decreases following this order. Accordingly, Lu-based Lu₂SnC should be softer than other studied M₂SnC phases, which is consistent with the prediction based on mechanical properties of these crystals [36].

The higher valence band consists of several distinct peaks, in which the smallest peak at the left in M₂SnC excluding Lu₂SnC originates as a result of weak interaction of d-orbitals of M atoms and p-orbitals of C and Sn atoms. At the similar energy position, an extra-large peak (also shown in inset) is observed in the higher valence band of Lu₂SnC, which is responsible for a wide flat band in the band structure. The next peak in Ti, Nb, Hf and Zr based M₂SnC phases is their highest peak and arises due to the hybridization between M d and C p orbitals. This hybridization strengthens the covalent M-C bonding. In the last one, the main contribution comes from M d and Sn p states of all the studied phases. In Lu₂SnC phase, the C p states contribute equally. This interaction leads to weaker covalent M-Sn bonding owing to proximity of the peak to the Fermi level. Therefore, the overall bonding nature in the studied M₂SnC MAX phases should be a combination of metallic, covalent, and, due to the difference in electronegativity between the constituent atoms, ionic.

![Mulliken atomic population analysis](image)

**Fig. 8.** Total density of states (TDOS) at Fermi level of M₂SnC MAX phases.

### 3.2 Mulliken atomic population analysis

Mulliken atomic population analysis is the most common and simplest method for analyzing the atomic population. This method assigns charges to wave functions represented in LCAO basis sets and gives an effective way to quantify the atomic charge, effective valence, charge transfer, etc. Mulliken atomic charge on the anion species facilitates the calculation of the effective valence from the formal ionic charge. The effective valence of an atomic species defined as the difference between formal ionic charge and Mulliken atomic charge can quantify the degree of covalency or ionicity of a chemical bond. Small values of effective valence correspond to an ionic bond, while a purely ionic bond assigns with a zero value. Actually, the increase of effective valence from zero value leads to decrease of ionicity and increase of covalency. The calculated effective valence for newly synthesized Lu₂SnC and its analogues M₂SnC (M = Ti, Nb, Hf, Zr) is presented in Table 1, indicating the dominant covalency in their chemical bonding.

Mulliken charge analysis also estimates the charge transfer from one atom to another. In the Ti₂SnC crystal, the amount of charge transferred to the C and Sn from Ti is 0.74 and 0.11e, respectively. Likewise, the charge transfer from Zr to C and Sn is 0.78 and 0.07e, respectively for Zr₂SnC. In the case of Lu₂SnC, the electron charge of 0.43 and 0.46 is transitioned to the C and Sn from Lu, respectively. In Nb₂SnC and Hf₂SnC, Sn takes part in charge transferring instead of charge receiving. Only C atoms receive 0.68 and 0.86e charges from M (Nb/Hf) and Sn atoms, respectively in these two ternary carbides. The charge transferring in M₂SnC phases is responsible for their ionic nature in chemical bonding.
Bond length is another measure of bond strength. The shorter the bond length, the stronger the chemical bond. The calculated bond length is shown in Table 2. Evidently, the strength of M–C bond is much stronger than that of M–Sn bond. M–C bond is more covalent than M–Sn bond. Considering both the covalent bonds, the covalency in M₂SnC crystals follows the order Ti₂SnC > Nb₂SnC > Hf₂SnC > Zr₂SnC > Lu₂SnC. This order is opposite to the order of crystal radius of M₂SnC solids. Therefore, it can be concluded that the bond length is proportional to the crystal radius (see Fig. 9), while bond covalency is inversely proportional to the crystal radius.

### Table 1. Effective valence, Mulliken charge and atomic populations for M₂SnC MAX phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Species</th>
<th>No. of ions</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
<th>Total Charge (e)</th>
<th>Effective valence (e)</th>
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</thead>
<tbody>
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<td>Ti</td>
<td>4</td>
<td>2.19</td>
<td>6.68</td>
<td>2.71</td>
<td>0.00</td>
<td>11.58</td>
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<tr>
<td></td>
<td>Sn</td>
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<td>1.54</td>
<td>2.57</td>
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<td>0.00</td>
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<tr>
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<td>2.23</td>
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<td></td>
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<td>0.00</td>
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<td>0.00</td>
<td>4.68</td>
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<td>14.25</td>
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### Table 2. Calculated bond lengths for M₂SnC with (M = Ti, Nb, Hf, Zr, and Lu).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>M–C</th>
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<th>M–Sn</th>
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<td>This Calc.</td>
<td>Calc. [72]</td>
<td>This Calc.</td>
</tr>
<tr>
<td>Ti₂SnC</td>
<td>2.14139</td>
<td>2.126</td>
<td>3.90027</td>
</tr>
<tr>
<td>Nb₂SnC</td>
<td>2.20031</td>
<td>2.193</td>
<td>3.95511</td>
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<tr>
<td>Hf₂SnC</td>
<td>2.31581</td>
<td>2.270</td>
<td>4.12331</td>
</tr>
<tr>
<td>Zr₂SnC</td>
<td>2.31179</td>
<td>2.302</td>
<td>4.16312</td>
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<tr>
<td>Lu₂SnC</td>
<td>2.42779</td>
<td>-----</td>
<td>4.34473</td>
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</tbody>
</table>

**Fig. 9.** Bond length in M₂SnC as a function of crystal radius of M-atoms. Filled and open symbols respectively represent the values obtained in present study and literature [72].
3.3 Electron charge density and Fermi surface

The contour maps of electron charge density for Sn-containing five 211 MAX phases are investigated to further understand their chemical bonding and presented in Fig. 10. The charge distributions around M atoms are almost spherical and their intensity indicates the amount of charge accumulation. Evidently, the lowest charge is accumulated around the Hf atom (0.28e), while the highest charge is deposited around the Lu atom (0.45e). The amount of Mulliken charge on M-atoms follow the order, Lu > Zr > Ti > Nb > Hf. This charge fairly overlaps with the C-charge and slightly edges with the Sn-charge, indicating stronger M–C and weaker M–Sn bonds, respectively. The spherical nature of charge distributions also indicates some ionic characters in chemical bonds in M$_2$SnC MAX phases, fairly Sn–C bond.

**Fig. 10.** Electron charge density map of M$_2$SnC MAX phases

**Fig. 11.** Fermi surfaces of M$_2$SnC MAX phases
Fermi surface, a conceptual geometrical presentation of all the available electronic states, aids in characterizing a material and its thermal, electrical, and magnetic properties. To develop a material with desired functionality, the knowledge of Fermi surface can help the material scientists. The calculated Fermi surfaces of newly synthesized Lu₂SnC and its isostructural existing M₂SnC (M = Ti, Nb, Hf and Zr) 211 MAX phases are presented in Fig. 11.

The Fermi surface topologies of Ti₂SnC, Hf₂SnC and Zr₂SnC look like almost identical. They are also comparable with those of their 312 MAX phase counterparts [44]. These topologies contain different sheets. First four sheets are seen to be centered along the Γ-A direction and reveal the electron characteristics. The first sheet is cylindrical and the other three sheets are prismatic-like with hexagonal cross sections. There are two hole-like sheets with complex topology at the corners of the Brillouin zone around the H-K directions.

Among the five studied M₂SnC phases, Nb₂SnC and Lu₂SnC are superconducting compounds. So, we would expect that the features of the Fermi surfaces of these two MAX superconductors will be identical. It is surprising that there is no common feature in the Fermi surfaces of these compounds. It can be assumed that the different origin of superconductivity in Nb₂SnC and Lu₂SnC leads to form their dissimilar Fermi surfaces. The properties of superconducting state are strongly dependent on the synthesis method [76]. The Fermi surface topology of Lu₂SnC is quite different from those of the non-superconducting phases Ti₂SnC, Hf₂SnC and Zr₂SnC. There is no prismatic sheet in the Fermi surface of Lu₂SnC. The Fermi surface topology of Lu₂SnC is most simple compared to those of other M₂SnC phases.

3.4. Defect processes

Table 3 reports the intrinsic defect processes (in Kröger–Vink notation [78], in this notation V_C and C_i represent a C vacancy and C interstitial atom respectively) and the relative energies for the M₂SnC phases considered. The first three reactions are the Frenkel defects and these can be deemed as important particularly for nuclear applications. This is because low Frenkel energies can be linked to higher concentrations of persistent defects. The lowest energy Frenkel process is the carbon Frenkel (reaction 3, Table 3). For these MAX phases the Schottky defect processes are significantly higher in energy as compared to the C-Frenkel process (refer to Table 3).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Defect energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lu₂SnC</td>
</tr>
<tr>
<td>1. M_M → V_M + M_i</td>
<td>6.61</td>
</tr>
<tr>
<td>2. Sb_Sb → V_Sb + Sb_i</td>
<td>3.57</td>
</tr>
<tr>
<td>3. C_C → V_C + C_i</td>
<td>2.23</td>
</tr>
<tr>
<td>5. M_M + C_C → M_C + C_M</td>
<td>11.79</td>
</tr>
<tr>
<td>6. Sb_Sb + C_Sn → Sb + C_Sn</td>
<td>7.75</td>
</tr>
<tr>
<td>7. Sb_i + V_M → Sb_M</td>
<td>-3.61</td>
</tr>
<tr>
<td>8. C_i + V_M → C_M</td>
<td>-0.13</td>
</tr>
<tr>
<td>9. M_i + V_Sn → M_Sn</td>
<td>-2.90</td>
</tr>
<tr>
<td>10. C_i + V_Sn → X_Sn</td>
<td>1.56</td>
</tr>
<tr>
<td>11. M_i + V_C → M_C</td>
<td>3.08</td>
</tr>
<tr>
<td>12. Sb_i + V_C → Sb_C</td>
<td>0.39</td>
</tr>
<tr>
<td>13. M_i + Sb_Sb → M_Sn + Sb_i</td>
<td>0.67</td>
</tr>
<tr>
<td>14. M_i + C_C → M_C + C_i</td>
<td>5.31</td>
</tr>
<tr>
<td>15. Sb_i + M_M → Sb_M + M_i</td>
<td>3.01</td>
</tr>
<tr>
<td>16. Sb_i + C_C → Sb_C + C_i</td>
<td>2.62</td>
</tr>
<tr>
<td>17. C_i + M_M → C_M + C_i</td>
<td>6.49</td>
</tr>
<tr>
<td>18. Sb_Sb + X_Sn → X_Sn + Sb_i</td>
<td>5.13</td>
</tr>
<tr>
<td>Schottky reaction</td>
<td>9.99</td>
</tr>
</tbody>
</table>
Antisite defects are common defects in these materials and can have non-negligible concentrations particularly in a radiation environment. Typically, in a radiation environment the non-equilibrium point defects can either recombine or occupy alternative lattice sites to form antisites [79, 80]. Low antisite formation energies are indicative that an important proportion of antisites will remain in the host lattice [79, 80]. The common antisite formation mechanisms are relations 4–6 in Table 3. The antisite defect formation reactions 5 and 6 have very high energies and are not relevant. Reaction 4 with energies ranging from 3.67 eV (Lu₂SnC) to 5.12 (Nb₂SnC) may become significant particularly for Ti₂SnC, Zr₂SnC and Nb₂SnC for which it is lower in energy than the Frenkel processes. Interestingly, for Hf₂SnC and Nb₂SnC the antisite and C-Frenkel reactions have very similar energies and these processes will both play a role simultaneously.

Reactions 7–12 (Table 3) reveal whether interstitial defects will associate with vacant sites to form antisite defects or remain as isolated defects. For all the MAX phases considered here Sn will associate with Vₘ to form Snₘ (reaction 7) and M will interact with Vₙ to form Mₙ (reaction 9). For the other reactions there is no clear trend but Table 3 can serve as a guide of the possible defects that can form.

Finally, we considered the displacement of lattice atoms by interstitials to form antisite defects (reactions 13–18). This is particularly relevant under irradiation, where a non-equilibrium concentration of interstitials can exist. This route for the formation of antisite defects in the M₂SnC MAX phases is deemed to be energetically unfavourable (refer to Table 3). Nb₂SnC has a higher energy for its lowest energy defect process (i.e. Schottky or Frenkel) as compared to the other MAX phases considered here. Therefore, Nb₂SnC should have better radiation tolerance among studied M₂SnC phases.

4. Conclusions

DFT calculations were performed in order to calculate the electronic structure, bonding nature, and energetics of the intrinsic defect processes of M₂SnC (M = Lu, Ti, Zr, Hf, Nb) MAX phases. The calculated formation energies of M₂SnC are negative, signifying that these compounds are intrinsically stable in accordance with the experiment. The bond profiles of M₂SnC are distinctive in shape though all they indicate the metallic conductivity. The covalency in M₂SnC decreases as the M atom moves from Ti to Lu following the order Ti → Nb → Hf → Zr → Lu. Lu₂SnC is predicted to be softer than other studied M₂SnC phases. The charge transfer in M₂SnC as well as the spherical nature of charge distributions in contour maps of electronic charge indicates the ionic character of chemical bonds. Basically, the chemical bonds in studied M₂SnC phases are a combination of ionic, metallic and covalent in nature. The bond length and bond covalency are directly and inversely proportional to the crystal radius, respectively. The dissimilar Fermi surfaces of Nb₂SnC and Lu₂SnC indicate the different origin of superconductivity in these two MAX phases. For Ti₂SnC, Zr₂SnC and Nb₂SnC the dominant intrinsic disorder mechanism was calculated to be the antisite mechanism (reaction 4, Table 3), whereas for Lu₂SnC and Hf₂SnC the C Frenkel (reaction 4, Table 3). Other intrinsic defect processes are less significant. Based on the intrinsic defect processes Nb₂SnC is the material that should have the better radiation tolerance of the M₂SnC MAX phases (M = Lu, Ti, Zr, Hf, Nb) considered here.

Data Availability: Supplementary data will be made available on request.

Author Contributions:

M.A.H. and N.K. performed the first-principles calculations. M.A.H. and A.C. wrote the manuscript and discussed the results. S.H.N. designed the project and supervised along with A.C. and A.K.M.A.I. All authors revised the manuscript.

Reference

