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# Optimization of Criteria for an Efficient Screening of New Thermoelectric Compounds: The TiNiSi Structure-Type as a Case-Study

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1 Optimization of criteria for an efficient screening  
2 of new thermoelectric compounds: the TiNiSi  
3 structure-type as a case-study

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7 ABSTRACT

8 High-throughput calculations can be applied to a large number of compounds, in order to  
9 discover new useful materials. In the present work, ternary intermetallic compounds are  
10 investigated, to find new potentially interesting materials for thermoelectric applications. The  
11 screening of stable non-metallic compounds required for such applications is performed by  
12 calculating their electronic structure, using DFT methods. In the first section, the study of the  
13 density of states at the Fermi level, of pure elements, binary and ternary compounds, leads to  
14 empirically chose the selection criterion to distinguish metals from non-metals. In the second  
15 section, the TiNiSi structure-type is used as a case-study application, through the investigation  
16 of 570 possible compositions. The screening leads to the selection of 12 possible  
17 semiconductors. The Seebeck coefficient and the lattice thermal conductivity of the selected

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18 compounds are calculated in order to identify the most promising ones. Among them, TiNiSi,  
19 TaNiP or HfCoP are shown to be worth a detailed experimental investigation.

20 KEYWORDS: Thermoelectricity, DFT calculations, Semiconductors, Intermetallic

## 21 INTRODUCTION

22 Thermoelectricity may be used as an interesting technology able to reduce the energy  
23 consumption through the recycling of waste heat. The conversion efficiency of thermoelectric  
24 devices is related to the dimensionless figure of merit  $ZT$  of their constituting materials, which  
25 is defined as

$$26 \quad ZT = S^2 \sigma T / \kappa \quad (1)$$

27 where:  $S$  represents the Seebeck coefficient;  $\sigma$  the electrical conductivity;  $\kappa$  the thermal  
28 conductivity and  $T$  the absolute temperature. Even though efficient thermoelectric devices exist,  
29 they are limited to niche markets because of their quite high cost compared to their conversion  
30 yield. One way to improve this technology is to find new materials based on more abundant,  
31 less toxic and less expensive elements. These limitations led us to define a set of elements, we  
32 could investigate to search for new interesting compounds<sup>1</sup>. For this set of elements, hundreds  
33 of compounds have already been reported in crystallographic databases, and even if some of  
34 them are known to be good thermoelectric compounds, there is still a very large number of  
35 possibly unknown compounds. In order to screen more efficiently the possible combinations,  
36 we use high-throughput calculations. We will present an efficient method to screen ternary  
37 intermetallic compounds in order to find new promising thermoelectric compounds. In this  
38 article, we will focus on the equimolar compounds and use the orthorhombic TiNiSi structure  
39 type as a case-study. We choose the TiNiSi structure-type because even though it is a large  
40 family with more than 70 compounds already reported in the crystallographic databases<sup>2-3</sup>, it

41 has been less subject of investigations compared with other equimolar structure-types. In  
42 contrast, numerous high-throughput calculations and screenings have already successfully  
43 shown very promising results for the equimolar half-Heusler family <sup>4-8</sup>.

44 Before estimating the thermoelectric properties of the compounds pertaining to the TiNiSi  
45 family, the main goal of the present work is to define an efficient method to discriminate among  
46 the investigated compounds those, which might be both stable and semiconducting. In our  
47 previous investigation <sup>1</sup>, we compared the enthalpy of formation of the same combination of  
48 elements in four structure types to determine the most stable one. In the present work, for the  
49 compounds stable in the TiNiSi structure-type, investigation of the electronic band structure  
50 will be carried out, to exclude the metallic compounds and keep only the possible  
51 semiconductors and semi-metals. A definition and the application of our exclusion criterion  
52 will be presented in this article. For the most remarkable compounds, the Seebeck coefficient  
53 and the thermal conductivity will be estimated using calculations based on the BoltzTrap  
54 package <sup>9-10</sup> and the Slack equation <sup>11-12</sup> respectively. All the results will be compared with the  
55 literature and the selected compounds will be highlighted.

## 56 COMPUTATIONAL DETAILS AND METHODOLOGY

57 In our previous work <sup>1</sup>, a combinatorial approach has been implemented to screen all possible  
58 *T-M-X* combinations with the 1:1:1 stoichiometry generated within a restrained set of chemical  
59 elements. In this set of elements, *T* is a transition metal from the Ti, V, and Cr columns or Sr,  
60 Ba, Y and La. *M* is an element from the first line of transition metals and *X* a *sp* element (Al, P,  
61 Si, Sn, and Sb). All *T-M-X* combinations have been calculated in four different structure-types:  
62 the orthorhombic TiNiSi (*Pnma*), the cubic MgAgAs (*F-43m*, half-Heusler), the two hexagonal  
63 ZrNiAl (*P-62m*) and BeZrSi (*P6<sub>3</sub>/mmc*). The 570 possible configurations have been calculated  
64 in these 4 structure-types by systematically assigning an unique element from our *T-M-X*

65 nomenclature to each crystallographic site, discarding “inverse” configurations or site mixing,  
66 yielding 2280 different compounds.

67 The calculations of the stability and ground-state properties are based on the density functional  
68 theory (DFT). This technique allows us to obtain the enthalpy of formation at 0 K for each  
69 compound (by total energy difference with the elemental reference state) as well as its electronic  
70 structure. The calculations were conducted using the projector augmented wave (PAW)  
71 method, implemented in the Vienna *Ab initio* Simulation Package (VASP)<sup>13-16</sup>. The exchange  
72 correlation was described by the generalized gradient approximation modified by Perdew,  
73 Burke, and Ernzerhof (GGA-PBE)<sup>17</sup>. An energy cut-off of 600 eV was used for the plane wave  
74 basis set. A high-density *k*-points meshing was employed for Brillouin zone integrations in the  
75 TiNiSi structure-type ( $7 \times 11 \times 6$ ), MgAgAs ( $21 \times 21 \times 21$ ), ZrNiAl ( $19 \times 19 \times 37$ ) and BeZrSi  
76 ( $21 \times 21 \times 10$ ). These parameters ensured robust results in the total energy within convergence  
77 tolerance for the calculations set within  $10^{-6}$  eV of difference. We performed volume and ionic  
78 relaxation steps for each structure-type, and we considered spin polarization for all the  
79 configurations. Blöchl correction was applied in a final step calculation<sup>18</sup>. Phonon dispersion  
80 bands were obtained by computing the atomic forces for different, finite atomic displacements  
81<sup>19</sup> and a subsequent calculation and integration over the corresponding phonon frequencies,  
82 within the harmonic approximation. i.e. without any volume dependence, using the Phonopy  
83 code<sup>20-21</sup>. The phonon calculations were carried out within a  $1 \times 2 \times 1$  supercell (24 atoms)  
84 with 12 atomic displacements for the TiNiSi structure-type.

85 The Seebeck coefficient was calculated from the Boltzmann transport theory<sup>22</sup> as implemented  
86 in the BoltzTrap simulation package (v2)<sup>9-10</sup>. The BoltzTrap code uses the electronic structure  
87 calculated with a dense *k*-mesh ( $12 \times 20 \times 10$ ) from VASP as an input data and assumes a  
88 constant relaxation time for the electrons.

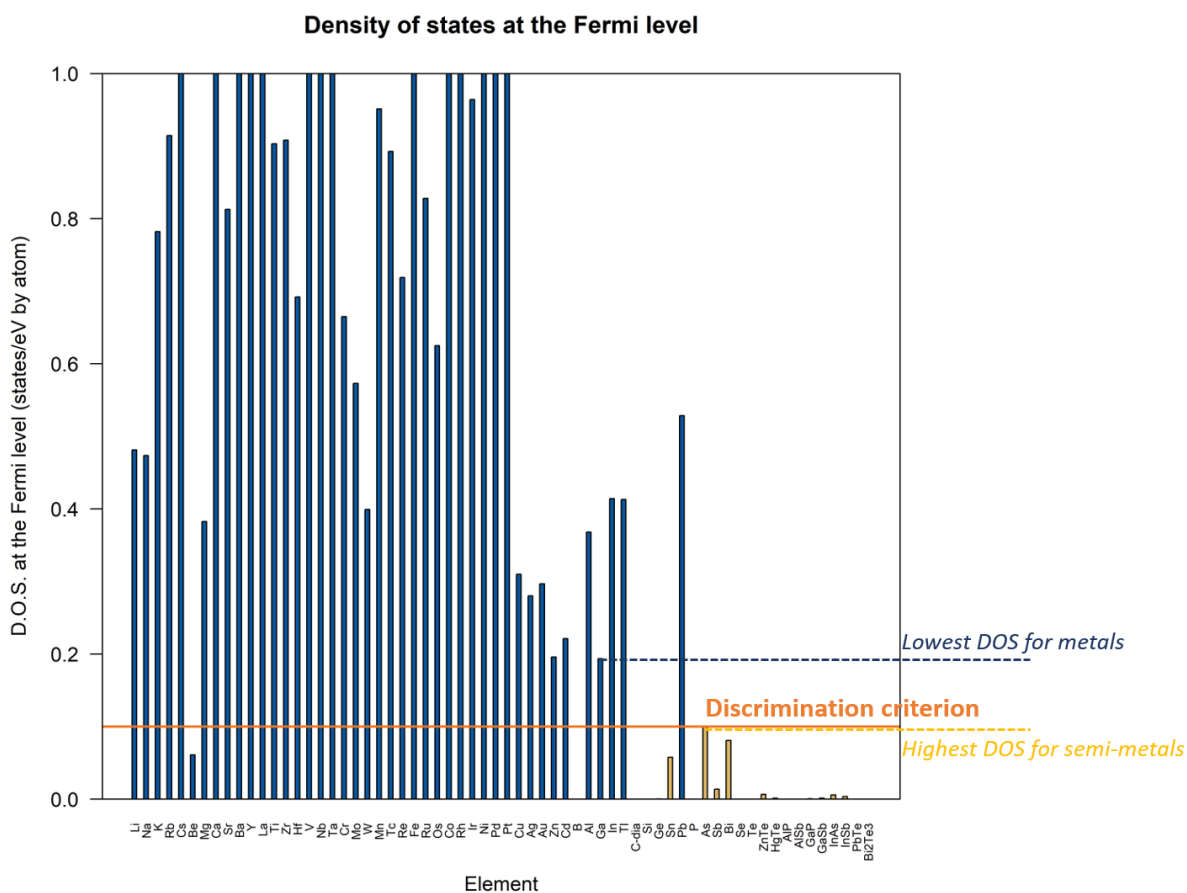
89 The first step of our selection concerns the stability of the calculated compounds. A positive  
90 enthalpy of formation leads to the exclusion of the combination, as it is obvious that the ternary  
91 compound is unstable toward the decomposition into its pure elements. In the second step, the  
92 most negative enthalpy of formation of the four-competing structure-types at the same  
93 composition, allows the selection of the most probable stable structure. Comparison with the  
94 literature and the crystallographic database has confirmed the robustness of our model <sup>1</sup>.

#### 95 Definition of the non-metallic criterion

96 In addition to the stability criterion, it is important to find a simple and robust way to exclude  
97 metallic compounds for thermoelectric application. For this purpose, we decided to focus our  
98 screening method on the density of states (DOS) at the Fermi level ( $E_F$ ). By definition, when  
99 the DOS is zero at the  $E_F$ , a semiconducting or insulating ground-state is expected. However,  
100 DFT-PBE is known <sup>23-24</sup> to not only systematically underestimate the gap magnitude but also  
101 to provide a non-zero DOS for known semiconductors. To compensate for this spurious effect,  
102 a non-zero discrimination criterion to select semiconductors is thus required to assess an  
103 unknown ground state (not too strict so as to miss interesting compounds and not too high for  
104 being efficiently selective). To estimate this value, preliminary calculations have been  
105 performed on the chemical elements in their stable structure (table S1) at 0 K and on known  
106 semiconducting binary compounds. Most of the elements of the periodic table have been  
107 investigated, except the  $4f$  elements and the noble gas, whereas the investigated binary  
108 compounds have been chosen among known semiconductors or semi-metals.

109 The calculated DOS are presented in Fig. 1. As expected, all the metallic elements ( $s$ ,  $d$  blocks)  
110 have a non-zero DOS at  $E_F$ , consistent with their metallic ground-state. In group **III**, (B, Al,  
111 Ga, In), the last three elements present a non-zero DOS at  $E_F$  in agreement with their metallic  
112 ground-state whereas B has a zero DOS consistent with its semiconducting ground-state <sup>25</sup>.

113 When looking at the first elements from group *IV* (C, Si, Ge), it is obvious that all the DOS at  
 114  $E_F$  exhibit a zero value. The last two elements of this group, Sn and Pb, have a non-zero DOS  
 115 at  $E_F$ , 0.05 state  $eV^{-1}$  by atom and 0.5 state  $eV^{-1}$  by atom, respectively. This very low DOS at  
 116  $E_F$  for Sn agrees with previous results <sup>26</sup> which have shown that “gray tin”, the  $\alpha$  form of Sn  
 117 (*A4*), which is the stable allotrope at low temperature <sup>27</sup>, is semiconducting. Elemental Pb  
 118 displays a DOS at  $E_F$  similar to the metals of the block *d*. In group *V* (P, As, Sb, Bi), P has a  
 119 zero DOS at  $E_F$  whereas As, Sb, and Bi have a DOS smaller than 0.1 state  $eV^{-1}$  by atom. This  
 120 confirms the semi-metallic ground-state of these last three elements, while elemental P is a  
 121 semiconductor as reported in reference <sup>28</sup>. In group *VI* with Se and Te, the DOS at  $E_F$  is zero as  
 122 these elements are reported as semiconductors <sup>29-30</sup>. In addition, all the binary compounds  
 123 presented in Figure 1 exhibit a zero DOS or a very low DOS at  $E_F$ , smaller than 0.005 state  $eV^{-1}$   
 124 <sup>1</sup> by atom, which is consistent with their semiconducting ground states.



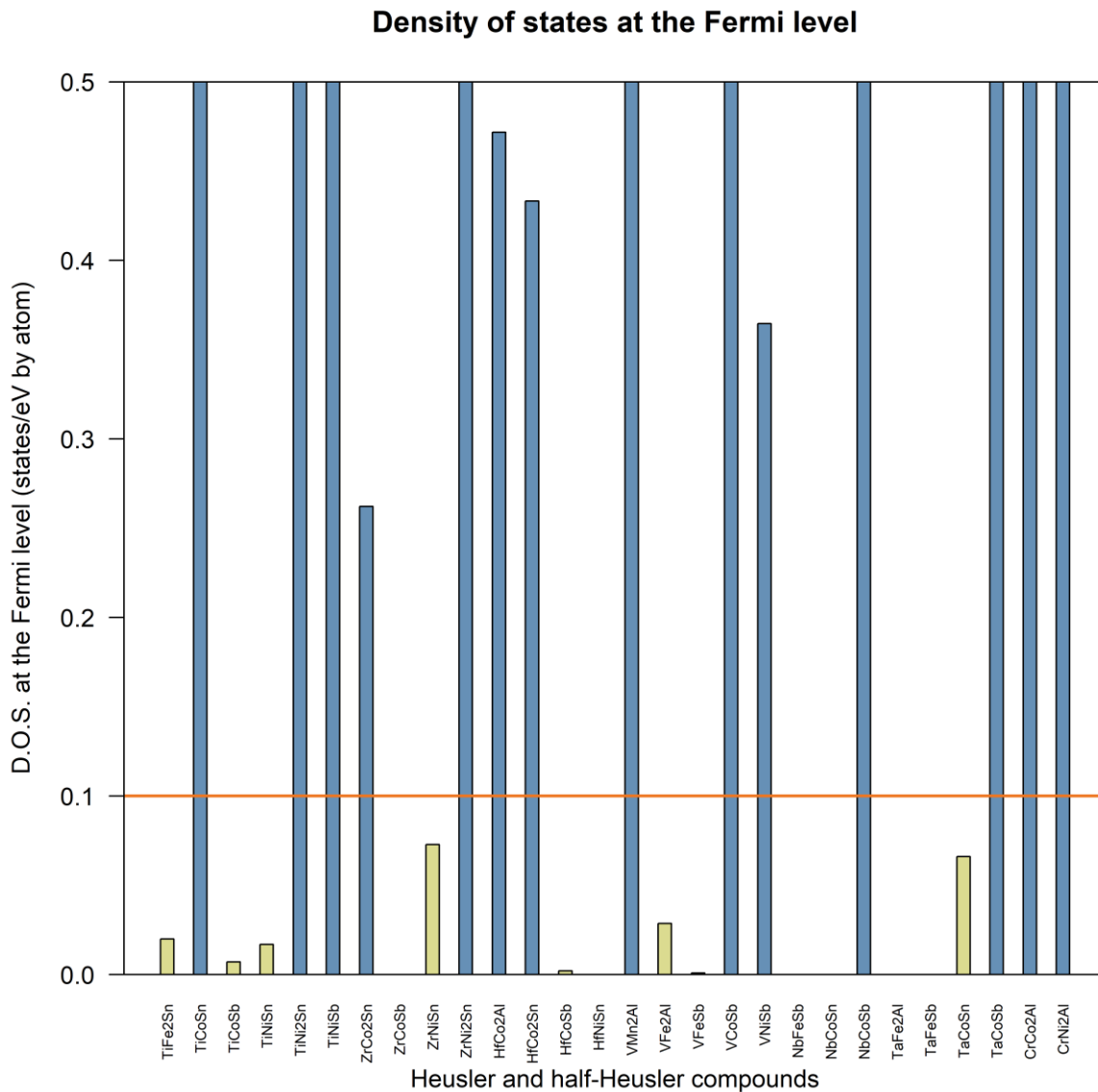
125

126 **Figure 1.** Density of states (DOS) at  $E_F$  for a selection of pure elements and binary compounds;  
127 reported semiconductors and semi-metals are in yellow and metals are in blue.

128 Reported results in Figure 1 allow to show an interval between the DOS at  $E_F$  for known  
129 semiconductor or semi-metallic elements such as Sn or As and these of Ga and Zn, two metallic  
130 elements. Thus, with a selection limit set at 0.1 state  $eV^{-1}$  by atom for the DOS at  $E_F$ ,  
131 semiconductors, as well as elements with a semi-metallic ground state such as As or Sb, are  
132 kept whereas metals are excluded. Only one exception to this criterion is found: with this limit,  
133 Be, which is known as a metal is also selected. However, Be is known to exhibit a very low  
134 DOS at  $E_F$ , despite its metallic behaviour<sup>31-34</sup>. Overall, this limit ensures a judicious selection  
135 with a very small number of ambiguous results.

136 These calculations on elemental and known binary semiconductors allowed to establish an  
137 empirical discrimination criterion. However, before using it to screen unknown compounds, an  
138 additional test has been made on reported compounds from the Heusler family (full and half-  
139 Heusler). This family has been chosen because it has already been the object of several studies  
140<sup>4-5, 35</sup>, Heusler compounds are very similar chemically to our screened compounds and metallic,  
141 semi-metallic and semiconductors compounds are reported in this family. The results are  
142 presented in the figure 2 with the DOS at  $E_F$  for the considered ternary intermetallic compounds.





143

144 **Figure 2** : Density of states (DOS) at  $E_F$  for a selection of half-Heusler and Heusler compounds;  
 145 reported semiconductors and semi-metals are in yellow and metals are in blue.

146 As presented in **Figure 2**, our discrimination criterion is efficient to sort metals for

147 semiconductors. Most of the reported semiconductors in the Heusler family exhibit a zero DOS

148 at  $E_F$ . However, some reported semiconductors or semi-metals do not and would be excluded

149 without our criterion, even though, according to the literature, they are promising thermoelectric

150 compounds. This is the case for ZrNiSn, TaCoSn or Fe<sub>2</sub>VAl<sup>36-39</sup>. Indeed, ZrNiSn is a very good

151 example of both the necessity and the relevance of our discrimination criterion. As presented

152 **Figure 2**, the DOS( $E_F$ ) is equal to 0.07 states/eV by atom, which is not strictly zero, however

153 when looking at the density of states as a function of the energy, it is clear that the value falls  
154 down to zero in the vicinity of the Fermi energy (see figure 4 in reference <sup>1</sup>). A non-zero  
155 criterion is therefore essential to get rid of the calculation errors and uncertainties on both the  
156 density of states and the position of the Fermi level. Finally, our criterion allows to screen  
157 efficiently the Heusler family by excluding only metallic compounds. The robustness of our  
158 model being proven, another intermetallic family can be investigated.

### 159 **Twelve selected compounds in the TiNiSi structure type**

160 Among the 570 unique configurations calculated in the 4 structures type, 317 compounds are  
161 more stable in the TiNiSi structure-type than in any other structure type. But only 12 compounds  
162 are found to be non-metallic, according to the electronic criterion set at 0.1 state eV<sup>-1</sup> by atom  
163 for the DOS at  $E_F$ . They are reported in Table 1. All of these compounds are mechanically stable  
164 (no imaginary frequency is observed in their phonon bands, figure S2).

165 Half-metals<sup>40</sup>, which can be interesting for spintronic applications have also been searched. For  
166 these compounds, the majority-spin electrons are metallic whereas the minority-spin electrons  
167 are semiconducting. The criterion was applied to each spin directions. Eleven compounds  
168 complied with this criterion but only four are stable in the TiNiSi structure-type: CrNiSi,  
169 SrTiSn, BaVSb and BaCrSn (the DOS of these compounds are presented in figure S3 and  
170 phonon bands in figure S4). Nonetheless, these compounds are not interesting for  
171 thermoelectricity since they display a metallic total DOS and will not be investigated in detail  
172 in the following.

173 **Table 1** *Non-metallic compounds in the TiNiSi structure type.*

<b><i>TMX</i> Compounds</b>	<b>Crystal databases</b>	<b>Enthalpy of formation (kJ mol<sup>-1</sup>)</b>	<b>DOS at the Fermi level (state. eV<sup>-1</sup> by atom)</b>
<b>TiCuSb</b>	Unreported	-20.90	0.092

<b>ZrZnSi</b>	Unreported	-62.22	0.098
<b>HfMnSb</b>	Unreported	-26.15	0.098
<b>HfCuSb</b>	Unreported	-27.12	0.015
<b>HfZnSi</b>	Unreported	-52.84	0.098
<b>TaCuSi</b>	Unreported	-44.15	0.043
<b>MoZnSi</b>	Unreported	-15.53	0.062
<b>TiMnSb</b>	BeZrSi	-23.06	0.071
<b>TiCoP</b>	TiNiSi	-109.95	0.068
<b>TiNiSi</b>	TiNiSi	-88.47	0.061
<b>HfCoP</b>	TiNiSi	-109.99	0.032
<b>TaNiP</b>	TiNiSi	-73.48	0.062

174

175 We will first review the existence and structure of each selected compound. Then, for each  
176 candidate, a more specific study of the electronic structure will be presented. Finally, to assess  
177 their thermoelectric properties, the calculated values of the Seebeck coefficient and the thermal  
178 conductivity, will be examined.

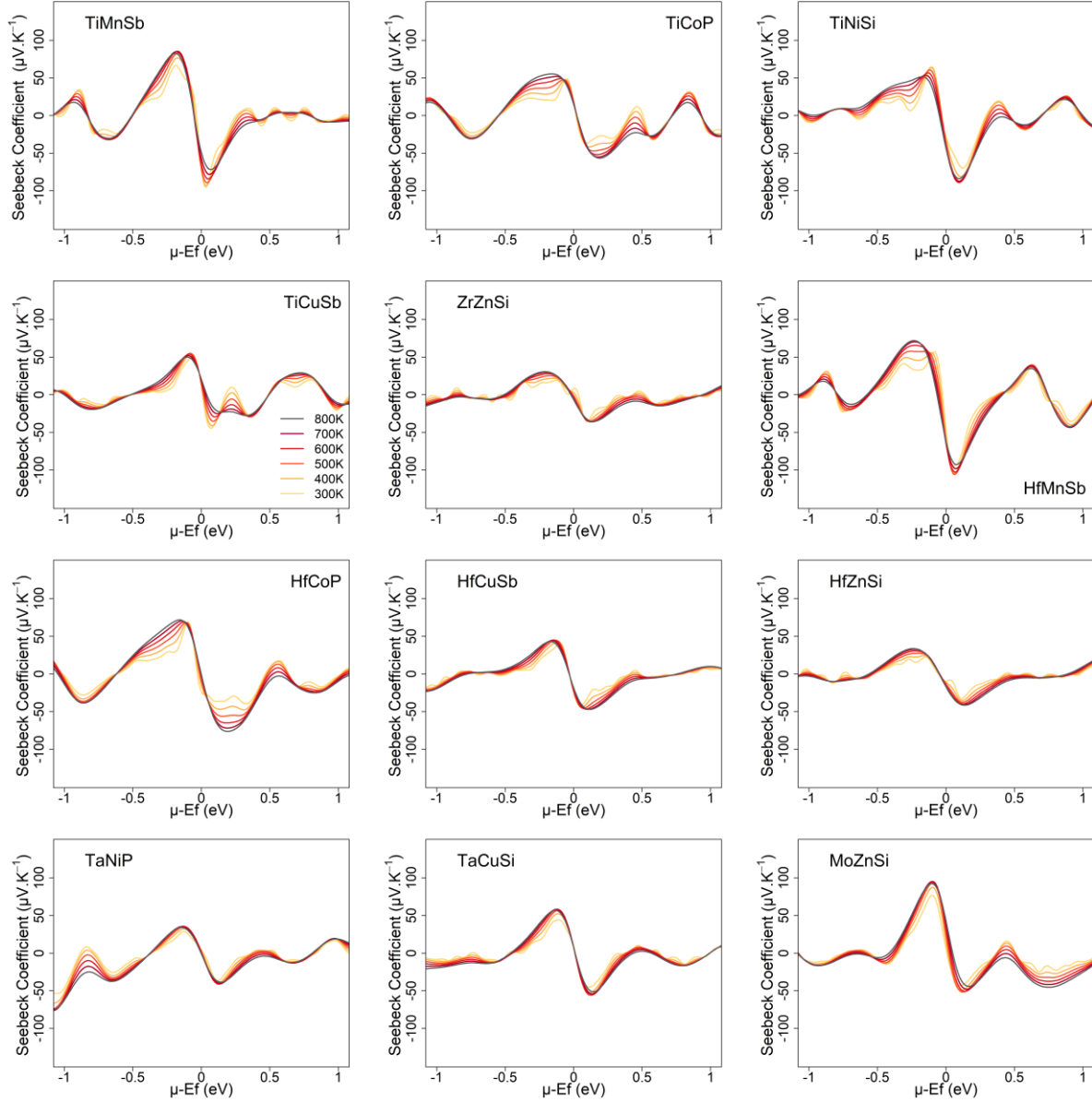
179 Seven compounds among the 12 have not been reported in crystal structure databases. However,  
180 a careful study of phase diagrams may provide additional information. For the Ti-Cu-Sb, Zr-  
181 Zn-Si, Hf-Cu-Sb, and Ta-Cu-Si systems, no equimolar compound has been reported in the  
182 ternary phase diagram<sup>41-45</sup>. It is therefore unlikely that an equimolar compound is stable in the  
183 ternary orthorhombic structure, but it cannot be formally discarded. For the 3 other unreported  
184 compounds, HfMnSb, MoZnSi, and HfZnSi, no phase diagram is available for the  
185 corresponding systems, it is therefore difficult to conclude on their existence.

186 Among the 5 reported compounds, TiMnSb has been reported in the literature to crystallize in  
187 the BeZrSi structure type<sup>46</sup> in contrast with our calculations of a stable TiNiSi prototype.  
188 However, as discussed in our previous work<sup>1</sup>, this discrepancy can be explained by the  
189 experimental conditions for the synthesis. Indeed, Noda *et al.*<sup>46</sup> have obtained TiMnSb under  
190 extreme conditions (high pressure and high temperature) possibly giving rise to a non-  
191 equilibrium phase.

192 Finally, four compounds are reported in the crystallographic databases in the orthorhombic  
193 TiNiSi structure. In the cases of TiCoP and TaNiP, the literature only deals with their crystal  
194 structure and there is no investigation of their electronic properties <sup>47-48</sup>. More information is  
195 provided for the other two compounds: TiNiSi and HfCoP. Recently, Huang *et al.* <sup>49</sup>  
196 investigated the thermoelectric properties of TiNiSi-based solid solutions. Theoretical results,  
197 based on DFT calculations with PBE-GGA, confirmed the presence of a pseudo-gap in the  
198 electronic band structure of TiNiSi. Measurements of the electric conductivity versus the  
199 temperature confirmed that TiNiSi is a semi-metal while thermoelectric properties were  
200 improved by the substitution of Ti by V <sup>49</sup>. These results confirm a previous report by Kong *et*  
201 *al.* <sup>50</sup> who have also highlighted the semi-metallic ground state of TiNiSi, thanks to their  
202 calculations. HfCoP, based on an extended Hückel calculation by Kleinke *et al.* <sup>51</sup>, was  
203 considered as a metal. However, neither the electronic density of states nor the electrical  
204 resistivity was reported in this reference. The ground state of HfCoP is hence currently  
205 unknown.

## 206 **Seebeck coefficient and lattice thermal conductivity at finite temperature**

207 The Seebeck coefficient was calculated at finite temperatures within the semi-classical  
208 Boltzmann transport theory with the BoltzTrap package, assuming a constant relaxation time.  
209 The possibility of calculating the electronic thermal conductivity and electrical conductivity  
210 offered by the package was not implemented because these quantities depend on the electronic  
211 relaxation time, which then plays the role of an adjustable parameter. This is not the case for  
212 the Seebeck coefficient, which is independent on the relaxation time when it is assumed to be  
213 constant.



214

215 **Figure 3.** Calculated Seebeck coefficient as a function of the chemical potential for each  
 216 compound. Each curve corresponds to a temperature varying by steps of 100K in the range 300  
 217 K (yellow) to 800 K (black).

218 The Seebeck coefficient has been plotted as a function of the chemical potential ( $\mu$ ) for each  
 219 selected compound in the energy window  $[-1; +1$  eV], which systematically covers the charge  
 220 carrier concentration range  $[-10^{22} - 10^{22}$  cm $^{-3}$ ], well beyond the experimental doping  
 221 concentrations conventionally achieved. Figure 3 presents for each compound the variations of  
 222  $S$  for several temperatures varying by steps of 100 K in the range 300 K and 800 K. For the  
 223 positive values of the Seebeck coefficient, increase with the temperature rise is generally  
 224 observed. Only, TiNiSi and TiCuSb exhibit a different behaviour with Seebeck coefficient at

225 300 K higher than at 800 K. Even though this trend is maintained for the negative Seebeck  
 226 coefficient, with the absolute value at 800 K higher than at 300 K, four compounds exhibit an  
 227 opposite behaviour, TiMnSb, TiCuSb, MoZnSi and HfMnSb.

228 Several compounds like ZrZnSi or HfZnSi do not show values of the Seebeck coefficient larger  
 229 than  $\pm 50 \mu\text{V K}^{-1}$  and therefore do not seem to be very promising in contrast with TiMnSb or  
 230 MoZnSi for example. First extremum of the calculated Seebeck coefficient close to the Fermi  
 231 level are listed in Table 2. In this table, values at 700 K are reported, to compare the compounds  
 232 in the same way as it will be done for the lattice thermal conductivity (values at 300 K are  
 233 reported in table S2). We choose to focus on the maximal values of the Seebeck coefficient  
 234 when  $\mu$  is near the Fermi level for an easy comparison.

235 **Table 2.** Values of the first extremum of the calculated Seebeck coefficient close to the  
 236 Fermi level and Slack's lattice thermal conductivity at 700 K for the TiNiSi compounds.

<i>TMX</i> compounds	$S_{\max} (\mu\text{V K}^{-1}) > 0$ (700K)	$S_{\max} (\mu\text{V K}^{-1}) < 0$ (700K)	Slack's lattice Thermal conductivity at 700K ( $\text{W m}^{-1}$ $\text{K}^{-1}$ )
TiMnSb	85	-78	5.4
TiCoP	52	-55	15.7
TiNiSi	54	-87	13.7
TiCuSb	52	-28	3.9
ZrZnSi	30	-36	9.9
HfMnSb	70	-98	6.1
HfCoP	71	-72	11.6
HfCuSb	44	-47	3.7
HfZnSi	33	-41	7.4
TaNiP	41	-76	7.6
TaCuSi	58	-54	9.7
MoZnSi	95	-48	6.5

237  
 238 As mentioned before, ZrNiSi, HfZnSi, HfCuSb, and TaCuSi present quite low Seebeck  
 239 coefficient near the Fermi energy, regardless their conduction type. Considering both positive  
 240 and negative values, TiMnSb and HfMnSb can be considered as the best compounds when other  
 241 compounds could be promising at most in one of the two conduction types. For example, TiNiSi  
 242 has a negative Seebeck coefficient twice as large as its positive counterpart whereas it is the

243 opposite for MoZnSi. These results are comparable at other temperatures where similar trend  
244 can be noticed (table S2). No clear tendencies can be noticed in the evolution of the Seebeck  
245 coefficient regarding the nature of each  $T$ ,  $M$  or  $X$  element in these compounds.

246 Lattice thermal conductivity, which is essential for the determination of  $ZT$ , can be estimated  
247 by the Slack's equation <sup>11-12</sup> by assuming that heat is conducted only by acoustic phonons <sup>52-53</sup>,  
248 through the equation 2:

$$249 \quad K_L = 3.1 \times 10^{-6} \frac{M \theta_D^3 \delta}{\gamma^2 n^3 T} \quad (2)$$

250 where  $\theta_D$  is the Debye temperature in K,  $\delta^3$  is the volume per atom in  $\text{\AA}^3$ ,  $n$  is the number of  
251 atoms in the primitive unit cell,  $M_{av}$  is the average atomic mass in the atomic unit and  $\gamma$  is the  
252 average Grüneisen parameter. The Debye temperature and the Grüneisen parameter are  
253 evaluated from the transverse and longitudinal sound velocity, which are obtained from the  
254 calculated elastic modulus. The calculated elastic properties (table S3) have been obtained from  
255 the phonon calculations for each compound (see figure S2). Slack's model neglects the transport  
256 of heat by optical phonons and this could lead to underestimated values of lattice thermal  
257 conductivity. However, it also assumes that the acoustic phonons are scattered only by acoustic  
258 phonons, neglecting all the other scattering mechanisms (isotopes, impurities, vacancies, charge  
259 carriers, dislocations, grain boundaries, crystal boundaries, etc.) This last approximation has the  
260 strongest impact on Slack's values <sup>12</sup>, which are systematically overestimated (up to an order  
261 of magnitude) as soon as the relative atomic mass difference of the constituting elements is  
262 larger than roughly  $\sim 100\%$  <sup>12</sup>: this condition is indeed fulfilled for the 12 screened compounds.  
263 Despite these drawbacks, Slack's model provides reliable trends at temperatures larger than the  
264 Debye temperature, when phonon – phonon scattering dominates over the other scattering  
265 processes. To fulfil this condition for all the compounds, the values presented in Table 2 were  
266 calculated at 700 K.

267 The range of lattice thermal conductivity values is quite broad with estimated values between  
268 3 and  $15 \text{ W m}^{-1} \text{ K}^{-1}$  which cannot be compared to experimental values due to lack of data. These  
269 values are quite large compared to the best thermoelectric materials such as  $\text{Bi}_2\text{Te}_3$  or  $\text{Sb}_2\text{Te}_3$   
270 which exhibit low thermal lattice thermal conductivity ( $\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$ )<sup>54</sup>. They are, nonetheless,  
271 still promising because they were calculated for a perfect crystal and thus as above discussed,  
272 overestimated. Moreover, it is known that defects or impurities can strongly decrease the lattice  
273 thermal conductivity. For instance, the half-Heusler  $\text{HfNiSn}$  displays a thermal conductivity of  
274  $10 \text{ W m}^{-1} \text{ K}^{-1}$  at 300 K<sup>55</sup> while the solid solution  $\text{Hf}_{0.75}\text{Zr}_{0.25}\text{NiSn}_{0.99}\text{Sb}_{0.02}$  displays a thermal  
275 conductivity of  $5 \text{ W m}^{-1} \text{ K}^{-1}$  at 300 K and  $ZT = 0.9$  at 800 K<sup>56</sup>.

276 Keeping the  $X$ -element constant and considering the  $T$  element, as expected, the lattice thermal  
277 conductivity is, in general, lower for “heavier”  $T$  in the same columns of the periodic table as  
278 for  $\text{TCuSb}$  or  $\text{TCoP}$ . In the case of  $\text{TMnSb}$ , the trend is reversed as  $\kappa_{\text{L}}(\text{TiMnSb})$  is lower than  
279  $\kappa_{\text{L}}(\text{HfMnSb})$ . Keeping the  $T$  element constant and considering the  $X$  element, we noticed-that  
280 the antimonides present the lowest thermal conductivity compared to the silicides or the  
281 phosphides, in accordance with the larger atomic mass of antimony.

## 282 DISCUSSION

283 Keeping in mind that the values presented here are from calculations based on DFT-PBE and  
284 constant relaxation time approximation implemented in a perfect crystal, our study offers the  
285 possibility to identify the most promising compounds among the 12 selected  $\text{TiNiSi}$ -type  
286 compounds from our screening of 570 possible compositions. For example according to Table  
287 2, even though, lattice thermal conductivity is quite low for the two  $\text{TCuSb}$  compounds, their  
288 Seebeck coefficients are also systematically low.  $\text{ZrNiSi}$  and  $\text{TaCuSi}$  exhibit also low Seebeck  
289 coefficient, which are for these compounds accompanied by high lattice thermal conductivity  
290 values. Thus, if one adds to these low values the fact that, according to the reported ternary



291 phase diagram, these four compounds are not stable, it is probably not worth trying their  
292 synthesis.

293 On the other hand, HfMnSb and MoZnSi combine large Seebeck coefficients and a small lattice  
294 thermal conductivity that could lead to interesting properties. Nonetheless, their existence is not  
295 established.

296 Regarding the four compounds which have already been reported in the literature, a ranking is  
297 also possible. The highest value of the Seebeck coefficient is reached in TiNiSi, which has  
298 already been reported as interesting for its thermoelectric properties in the solid solution  
299  $\text{Ti}_{1-x}\text{V}_x\text{NiSi}$ <sup>49</sup>. The presently calculated values of the Seebeck coefficient seem to confirm the  
300 calculated values calculated by Huang *et al.*<sup>49</sup>, with  $S \approx \pm 65 \mu\text{V} \cdot \text{K}^{-1}$  at 300 K for both type of  
301 charge carrier whereas our calculation gives  $S = 64 \mu\text{V} \cdot \text{K}^{-1}$  and  $S = -69 \mu\text{V} \cdot \text{K}^{-1}$  at 300 K.  
302 However, the measured values ( $-16 \mu\text{V} \cdot \text{K}^{-1}$  at 300K) in Ref.<sup>49</sup> differ from the calculated one,  
303 but this difference can be explained by the charge carrier concentration of the pristine TiNiSi,  
304 which is around  $2 \times 10^{21} \text{ cm}^{-3}$ . This relatively large value indicates the presence of intrinsic  
305 defects in the sample. Finally, HfCoP seems to be more interesting than TiCoP as its Seebeck  
306 coefficient is larger and associated with a lower lattice thermal conductivity. TaNiP exhibits  
307 the lowest lattice thermal conductivity of the four reported compounds and negative Seebeck  
308 coefficient of the same order of magnitude as in HfCoP.

## 309 CONCLUSION

310 After determining the stability of thousands of *TMX* compositions in 4 structure types, a more  
311 focused investigation has been undertaken on the compounds which crystallize in the TiNiSi  
312 structure type. In a second stage, the electronic band structure has been examined and an  
313 effective criterion of the DOS at the Fermi level has been established by comparing calculated  
314 DOS of known semiconducting elements and compounds. Then, this empirical criterion of 0.1

315 state  $eV^{-1}$  by atom has been applied to the *TMX* compounds, stable in the orthorhombic  
316 structure. It has led to the selection of 12 non-metallic compounds among the 317 possible  
317 compounds while it was commonly admitted that all the TiNiSi are metallic <sup>57</sup>. Additional  
318 phonon and BoltzTrap calculations allowed to rank the 12 selected compounds to identify those  
319 which are the most interesting to be synthesized from the point of view of their anticipated  
320 thermoelectric properties. Although MoZnSi could be an interesting compound as it presents  
321 the highest Seebeck coefficient associated with a small lattice thermal conductivity, there is no  
322 information about its possible stability. So, it seems more relevant to focus on HfCoP and  
323 TaNiP as starting points. Both compounds are already reported in the literature as crystallizing  
324 in the TiNiSi structure type <sup>48, 51</sup> and present the best compromise between high Seebeck  
325 coefficient and a low lattice thermal conductivity.

## 326 ACKNOWLEDGEMENTS

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329 acknowledged (ANR-18-CE05-0010-01).

## 330 SUPPORTING INFORMATION AVAILABLE

331 **Table S1:** Elemental, binaries and ternaries compounds information's

332 **Figure S1:** Electronic density of states for the twelve *TMX* compounds calculated by DFT  
333 using GGA-PBE approximation. The Fermi level is chosen as the origin of energies. The  
334 discrimination criterion is represented by the red dotted line.

335 **Figure S2:** Phonon curves dispersion of the twelve *TMX* compounds calculated using the  
336 Phonopy code.

337 **Figure S3:** Electronic density of states for the four (half-metals) *TMX* compounds calculated  
338 by DFT using GGA-PBE approximation. The Fermi level is chosen as the origin of energies.  
339 Both spin directions are presented.

340 **Figure S4:** Phonon curves dispersion of the four (half-metals) *TMX* compounds calculated  
341 using the Phonopy code.

342 **Table S2:** Values of the first extremum of the calculated Seebeck coefficient close to the Fermi  
343 level at 300 K for the TiNiSi compounds.

344 **Table S3:** The bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson ratio  
345 ( $\nu$ ) of the screened *TMX* compounds.

## 346 REFERENCES

- 347 1. Barreteau, C.; Crivello, J.-C.; Joubert, J.-M.; Alleno, E., Looking for new thermoelectric materials  
348 among *TMX* intermetallics using high-throughput calculations. *Comput. Mater. Sci* **2019**, *156*, 96-103.
- 349 2. Villars, P.; Cenzual, K., Pearson's Crystal Data: Crystal structure database for inorganic  
350 compounds. International, A., Ed. Materials Park: Ohio, USA, 2017/2018.
- 351 3. Belsky, A.; Hellenbrandt, M.; Karen, V. L.; Luksch, P., New developments in the Inorganic Crystal  
352 Structure Database (ICSD): accessibility in support materials research and design. *Acta Crystallogr. B*  
353 **2002**, *58*, 364-369.
- 354 4. Feng, Z.; Fu, Y.; Putatunda, A.; Zhang, Y.; Singh, D. J., Electronic structure as a guide in screening  
355 for potential thermoelectrics: demonstration for half-Heusler compounds. *Phys. Rev. B* **2019**, *100*,  
356 085202.
- 357 5. Guo, S.; Jia, T.-T.; Zhang, Y., Electrical properties dominated promising half-Heusler  
358 thermoelectrics through high-throughput materials computations. *J. Phys. Chem. C* **2019**, *123*, 18824-  
359 18833.
- 360 6. Legrain, F.; Carrete, J.; van Roekeghem, A.; Madsen, G. K. H.; Mingo, N., Materials screening  
361 for the discovery of new half-Heuslers: Machine learning versus *ab initio* methods. *J. Phys. Chem. B*  
362 **2017**, *122*, 625-632.
- 363 7. Ma, J.; Hegde, V. I.; Munira, K.; Xie, Y.; Keshavarz, S.; Mildebrath, D. T.; Wolverton, C.; Ghosh,  
364 A. W.; Butler, W. H., Computational investigation of half-Heusler compounds for spintronics  
365 applications. *Phys. Rev. B* **2017**, *95*, 024411.
- 366 8. Zeeshan, M.; Singh, H. K.; van den Brink, J.; Kandpal, H. C., *Ab initio* design of new cobalt-based  
367 half-Heusler materials for thermoelectric applications. *Phys. Rev. Mater.* **2017**, *1*, 075407.
- 368 9. Madsen, G. K. H.; Singh, A. K., BoltzTrap. A code for calculating band-structure dependent  
369 quantities. *Comput. Phys. Comm.* **2006**, *175*, 67-71.
- 370 10. Madsen, G. K. H.; Carrete, J.; Verstraete, M. J., BoltzTrap2, a program for interpolating band  
371 structures and calculating semi-classical transport coefficients. *Comput. Phys. Comm.* **2018**, *231*, 140-  
372 145.

- 373 11. Slack, G. A., Nonmetallic crystals with high thermal conductivity. *J. Phys. Chem. Solids* **1973**, *34*,  
374 321-335.
- 375 12. Slack, G. A., The thermal conductivity of nonmetallic crystals. *Solid State Physics* **1979**, *34*, 1-  
376 71.
- 377 13. Kresse, G.; Hafner, J., *Ab-initio* molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*,  
378 558(R).
- 379 14. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave  
380 method. *Phys. Rev. B* **1999**, *59* (3), 1758-1775.
- 381 15. Kresse, G.; Furthmüller, J., Efficient iterative schemes for an *ab-initio* total-energy calculations  
382 using plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169-11186.
- 383 16. Hafner, J.; Kresse, G.; Vogtenhuber, D.; Marsman, M. The Vienne *Ab-Initio* Simulation Package  
384 (VASP).
- 385 17. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Phys.*  
386 *Rev. Lett.* **1996**, *77*, 3865-3868.
- 387 18. Blöchl, P. E.; Jepsen, O.; Andersen, O. K., Improved tetrahedron method for Brillouin-zone  
388 integrations. *Phys. Rev. B* **1994**, *49* (23), 16223-16233.
- 389 19. Parlinski, K.; Li, Z. Q.; Kawazoe, Y., First-principles determination of the soft mode in cubic ZrO<sub>2</sub>.  
390 *Phys. Rev. Lett.* **1997**, *78*, 4063-4066.
- 391 20. Togo, A.; Tanaka, I., First-principles phonon calculations in materials science. *Scr. Mater.* **2015**,  
392 *108*, 1-5.
- 393 21. Togo, A.; Oba, F.; Tanaka, I., First-principles calculations of the ferroelastic transition between  
394 rutile-type and CaCl<sub>2</sub>-type SiO<sub>2</sub> at high pressures *Phys. Rev. B* **2008**, *78*, 134106.
- 395 22. Ashcroft, N. W.; Mermin, N. D., *Solid State Physics*. Saunders College Publishing: Orlando, 1976.
- 396 23. Tran, F.; Blaha, P., Importance of the kinetic energy density for band gap calculations in solids  
397 with density functional theory. *J. Phys. Chem. A* **2017**, *121*, 3318-3325.
- 398 24. Yakovkin, I. N.; Dowben, P. A., The problem of the band gap in LDA calculations. *Surface Review*  
399 *and Letters* **2007**, *14* (3), 481-487.
- 400 25. Greiner, E. S.; Gutowski, J. A., Electrical Resistivity of Boron. *J. Appl. Phys.* **1957**, *28*, 1364-1365.
- 401 26. Yu, C.; Liu, J.; Lu, H.; Chen, J., *Ab initio* calculation of the properties and pressure induced  
402 transition of Sn. *Sol. State. Commun.* **2006**, *140*, 538-543.
- 403 27. Busch, G. A.; Kern, R., Semiconducting properties of gray tin. *Sol. Stat. Phys.* **1960**, *11*, 1-40.
- 404 28. Goodman, N. B.; Ley, L.; Bullett, D. W., Valence-band structures of phosphorus allotropes. *Phys.*  
405 *Rev. B* **1983**, *27*, 7440-7450.
- 406 29. Reitz, J. R., Electronic band structure of Selenium and Tellurium. *Phys. Rev.* **1957**, *105*, 1233-  
407 1240.
- 408 30. Gaspar, R., Electronic structure of semi-conducting selenium and tellurium. *Acta Physica* **1957**,  
409 *7*, 289-311.
- 410 31. Loucks, T. L.; Cutler, P. H., Band structure and Fermi surface of Beryllium. *Phys. Rev.* **1964**, *133*,  
411 A819-A829.
- 412 32. Mitchell, M. A., Electrical resistivity of beryllium. *J. Appl. Phys.* **1975**, *46*, 4742-4746.
- 413 33. Chou, M. Y.; Lam, P. K.; Cohen, M. L., *Ab initio* study of structural and electronic properties of  
414 beryllium. *Phys. Rev. B* **1983**, *28*, 4179-4185.
- 415 34. Papaconstantopoulo, D. A., *Handbook of the band structure of elemental solids*. Springer US:  
416 2015; Vol. 3, p 655.
- 417 35. Gillessen, M.; Dronskowski, R., A combinatorial study of full Heusler alloys by first-principles  
418 computational methods. *J. Comput. Chem.* **2009**, *30*, 1290-1299.
- 419 36. Li, S.; Zhu, H.; Mao, J.; Feng, Z.; Li, X.; Chen, C.; Cao, F.; Liu, X. J.; Singh, D. J.; Ren, Z.; Zhang, Q.,  
420 n-type TaCoSn-based half-Heusler as promising thermoelectric materials. *Appl. Mater. Interfaces* **2019**,  
421 *11*, 41321-41329.
- 422 37. Maier, S.; Denis, S.; Adam, S.; Crivello, J.-C.; Joubert, J. M.; Alleno, E., Order-disorder transitions  
423 in the Fe<sub>2</sub>VAl Heusler alloy. *Acta Materialia* **2016**, *121*, 126-136.

- 424 38. Kuentzler, R.; Clad, R.; Schmerber, G.; Dossmann, Y., Gap at the Fermi level and magnetism in  
425 RMSn ternary compounds (R= Ti, Zr, Hf and M= Fe, Co, Ni). *J. Magn. Magn. Mater.* **1992**, *104-107*,  
426 1976-1978.
- 427 39. Hu, T.; Yang, D.; Su, X.; Yan, Y.; You, Y.; Liu, W.; Uher, C.; Tang, X. F., Interpreting the combustion  
428 process for high-performance ZrNiSn thermoelectric materials. *ACS Appl. Mater. Interfaces* **2018**, *10*,  
429 864-872.
- 430 40. de Groot, R. A.; Mueller, F. M.; van Engen, P. G.; Buschow, K. H. J., New class of materials: half-  
431 metallic ferromagnets. *Phys. Rev. Lett.* **1983**, *50*, 2024-2027.
- 432 41. Dolotko, O. V.; Dmytriv, G. S.; Pavlyuk, V. V., Interaction of Components in the Zr-Zn-Si System  
433 at 600 °C. *Pol. J. Chem.* **2001**, *75*, 453-455.
- 434 42. Koblyuk, N. A.; Romaka, L. P.; Bodak, O. I., Interaction between the components in the Ti-Cu-  
435 Sb system at 770 K. *J. Alloys Compd.* **2000**, *309*, 176-178.
- 436 43. Melnychenko-Koblyuk, N.; Romaka, L.; Akselrud, L. G.; Romaka, V. V.; Stadnyk, Y., Interaction  
437 between components in Hf-Cu-Sb ternary system at 770K. *J. Alloys Compd.* **2008**, *461*, 147-149.
- 438 44. Savitskii, E. M.; Efimov, Y. V.; Frolova, T. M., Copper effect on structure and superconductive  
439 properties of transition metal silicides [V(Nb, Ta, Cr, Mo, W)-Si-Cu alloy systems]. *Izv. Akad. Nauk SSSR*,  
440 *Neorg. Mater.* **1979**, *15*, 654-657.
- 441 45. Reid, J. S.; Kolawa, E.; Nicolet, M.-A., Thermodynamics of (Cr, Mo, Nb, Ta, V or W)-Si-Cu ternary  
442 systems. *J. Mater. Res.* **1992**, *7* (9), 2424-2428.
- 443 46. Noda, Y.; Shimada, M.; Koizumi, M., High-pressure synthesis and magnetic properties of  
444 MMnSb (M= Ti, V, Cr) with Ni<sub>2</sub>In type structures. *Inorg. Chem.* **1984**, *23*, 628-630.
- 445 47. Rundqvist, S.; Nawapong, P. C., The Crystal Structure of ZrFeP and Related Compounds. *Acta*  
446 *Chem. Scand.* **1966**, *20*, 2250-2254.
- 447 48. Lomnytska, Y. F.; Agatinskaya, L. P.; Kuz'ma, Y. B., Component interaction in the system  
448 titanium-cobalt-phosphorus. *Sov. Prog. Chem.* **1981**, *47*, 29-32.
- 449 49. Huang, Y.; Nagai, H.; Hayashi, K.; Miyazaki, Y., Preparation and thermoelectric properties of  
450 pseudogap intermetallic (Ti<sub>1-x</sub>V<sub>x</sub>)NiSi solid solutions. *J. Alloys Compd.* **2019**, *771*, 111-116.
- 451 50. Kong, B.; Chen, X.-R.; Cai, L.-C.; Zhu, J., Structural and elastic properties of typical equiatomic  
452 ternary intermetallic compound TiNiSi under pressure. *Physica B: Condensed Matter* **2010**, *405* (6),  
453 1591-1595.
- 454 51. Kleinke, H.; Franzen, H. F., Synthesis Crystal Structure and Properties of HfM<sup>1</sup>P (M<sup>1</sup>= Fe, Co, Ni)  
455 in Comparison to ZrNiP. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1893-1900
- 456 52. Hou, Z.; Takagiwa, Y.; Shinohara, Y.; Xu, Y.; Tsuda, K., Machine-Learning-assisted development  
457 and theoretical consideration for the Al<sub>2</sub>Fe<sub>3</sub>Si<sub>3</sub> thermoelectric material. *Appl. Mater. Interfaces* **2019**,  
458 *11*, 11545-11554.
- 459 53. Shiota, Y.; Muta, H.; Yamamoto, K.; Ohishi, Y.; Kurosaki, K.; Yamanaka, S., A new semiconductor  
460 Al<sub>2</sub>Fe<sub>3</sub>Si<sub>3</sub> with complex crystal structure. *Intermetallics* **2017**, *89*, 51-56.
- 461 54. Elsheikh, M. H.; Shnawah, D. A.; Sabri, M. F. M.; Said, S. B. M.; Hassan, M. H.; Bashir, M. B. A.;  
462 M., M., A review on thermoelectric renewable energy: Principle parameters that affect their  
463 performance. *Renewable and Sustainable Energy Reviews* **2014**, *30*, 331-355.
- 464 55. Uher, C.; Yang, J.; Hu, S.; Morelli, D. T.; Meisner, G. P., Transport properties of pure and doped  
465 MNiSn (M=Zr, Hf). *Phys. Rev. B* **1999**, *59*, 8615.
- 466 56. Yan, X.; Joshi, G.; Liu, W.; Lan, Y.; Wang, H.; Lee, S.; Simonson, J. W.; Poon, S. J.; Tritt, T. M.;  
467 Chen, G.; Ren, Z. F., Enhanced Thermoelectric Figure of Merit of p-Type Half-Heuslers. *Nano Letters*  
468 **2011**, *11*, 556.
- 469 57. Landrum, G. A.; Hoffmann, R. D.; Evers, J.; Boysen, H., The TiNiSi Family of Compounds:  
470 Structure and Bonding. *Inorg. Chem.* **1998**, *37*, 5754-5763.

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473 TABLE OF CONTENTS

474

475 **Figure 1.** Density of states (DOS) at  $E_F$  for a selection of pure elements and binary compounds;  
476 reported semiconductors and semi-metals are in yellow and metals are in blue.

477 **Figure 2 :** Density of states (DOS) at  $E_F$  for a selection of half-Heusler and Heusler  
478 compounds; reported semiconductors and semi-metals are in yellow and metals are in blue.

479 **Figure 3.** Calculated Seebeck coefficient as a function of the chemical potential for each  
480 compound. Each curve corresponds to a temperature varying by steps of 100K in the range  
481 300 K (yellow) to 800 K (black).

482 **Table 1** Non-metallic compounds in the TiNiSi structure type.

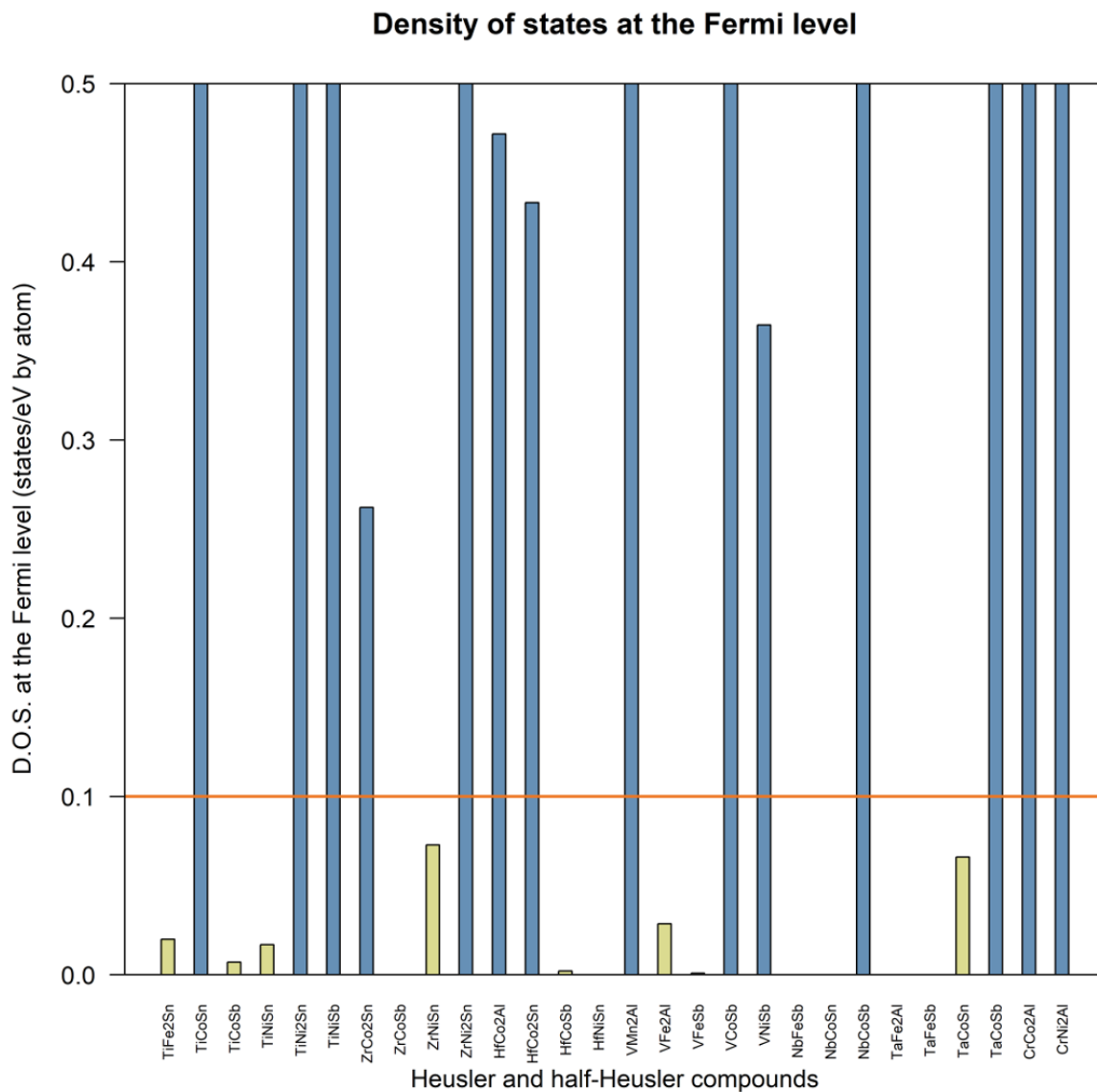
483 **Table 2.** Values of the first extremum of the calculated Seebeck coefficient close to the  
484 Fermi level and Slack's lattice thermal conductivity at 700 K for the TiNiSi compounds.

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Figure 2



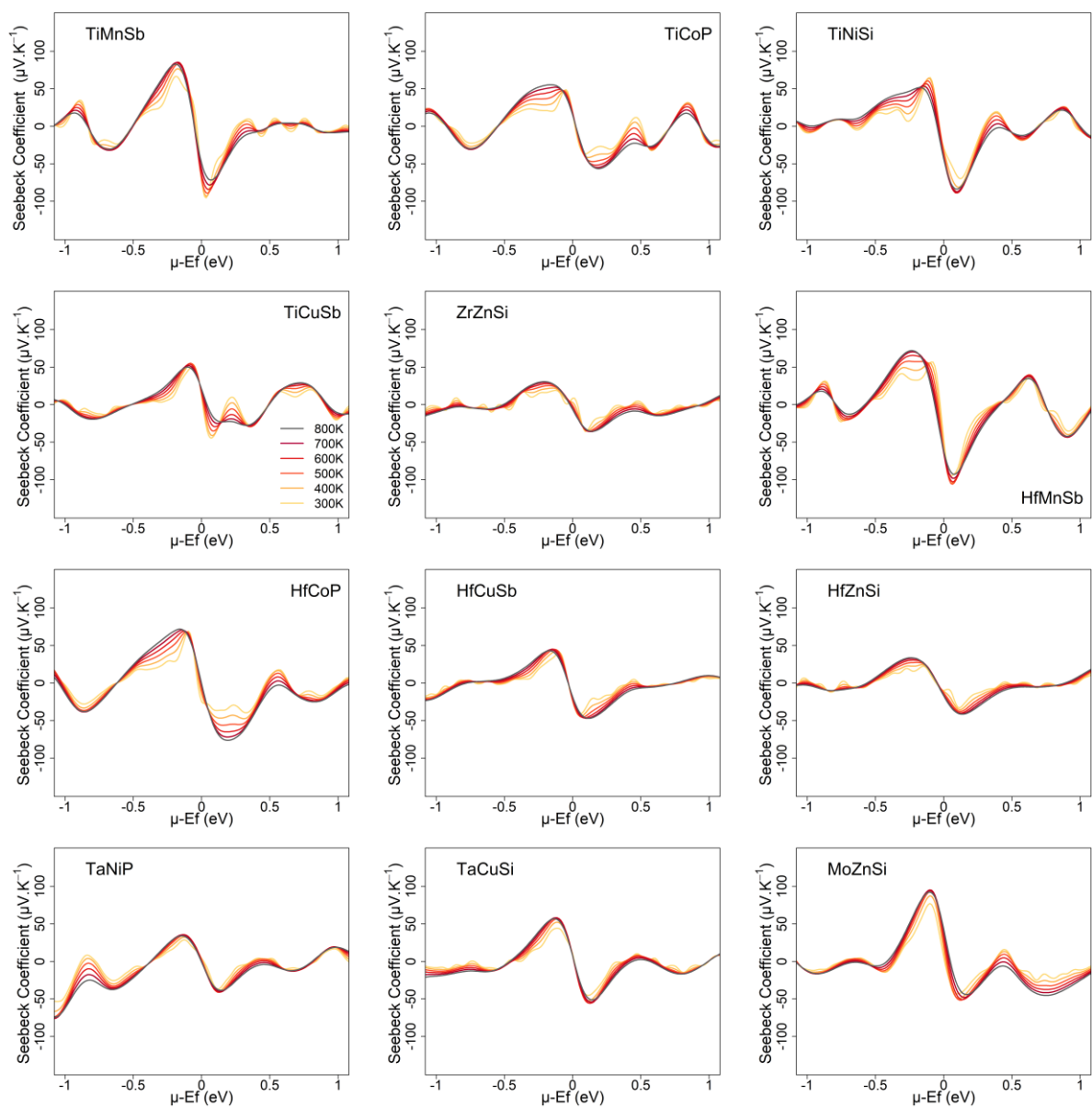


Figure 3

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Table 1

<b><i>TMX</i> Compounds</b>	<b>Crystal databases</b>	<b>Enthalpy of formation (kJ mol<sup>-1</sup>)</b>	<b>DOS at the Fermi level (state. eV<sup>-1</sup> by atom)</b>
<b>TiCuSb</b>	Unreported	-20.90	0.092
<b>ZrZnSi</b>	Unreported	-62.22	0.098
<b>HfMnSb</b>	Unreported	-26.15	0.098
<b>HfCuSb</b>	Unreported	-27.12	0.015
<b>HfZnSi</b>	Unreported	-52.84	0.098
<b>TaCuSi</b>	Unreported	-44.15	0.043
<b>MoZnSi</b>	Unreported	-15.53	0.062
<b>TiMnSb</b>	BeZrSi	-23.06	0.071
<b>TiCoP</b>	TiNiSi	-109.95	0.068
<b>TiNiSi</b>	TiNiSi	-88.47	0.061
<b>HfCoP</b>	TiNiSi	-109.99	0.032
<b>TaNiP</b>	TiNiSi	-73.48	0.062

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Table 2

<b><i>TMX</i> compounds</b>	<b><math>S_{\max}</math> (<math>\mu\text{V K}^{-1}</math>) &gt; 0 (700K)</b>	<b><math>S_{\max}</math> (<math>\mu\text{V K}^{-1}</math>) &lt; 0 (700K)</b>	<b>Slack's lattice Thermal conductivity at 700K (<math>\text{W m}^{-1}\text{K}^{-1}</math>)</b>
TiMnSb	85	-78	5.4
TiCoP	52	-55	15.7
TiNiSi	54	-87	13.7
TiCuSb	52	-28	3.9
ZrZnSi	30	-36	9.9
HfMnSb	70	-98	6.1
HfCoP	71	-72	11.6
HfCuSb	44	-47	3.7
HfZnSi	33	-41	7.4
TaNiP	41	-76	7.6
TaCuSi	58	-54	9.7
MoZnSi	95	-48	6.5

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