High-throughput study of the structural stability and thermoelectric properties of transition metal silicides

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Abstract. The phase stability, electronic structure and transport properties of binary 3d, 4d and 5d transition metal silicides are investigated using high-throughput density functional calculations. An overall good agreement is found between the calculated 0K phase diagrams and experiment. We introduce descriptors for the phase-stability and thermoelectric properties and hereby identify several candidates with potential for thermoelectric applications. This includes known thermoelectrics like Mn$_4$Si$_7$, β-FeSi$_2$, Ru$_2$Si$_3$ and CrSi$_2$ as well as new potentially meta-stable materials like Rh$_3$Si$_5$, Fe$_2$Si$_3$ and an orthorhombic CrSi$_2$ phase. Analysis of the electronic structure shows that the gap formation in most of the semiconducting transition metal silicides can be understood with simple hybridization models. The transport properties of the Mn$_4$Si$_7$, Ru$_2$Ge$_3$ and Ir$_3$Si$_5$ structure types and the orthorhombic CrSi$_2$ phase are discussed. The calculated transport properties are in good agreement with available experimental data. It is shown that a better thermoelectric performance may be achieved upon optimal doping. Finally, the high-throughput data are analysed and rationalized using a simple tight-binding model.

S Online supplementary data available from stacks.iop.org/NJP/15/105010/mmedia

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1. Introduction

Waste heat is one of the main sources for energy loss. Thermoelectrics may be used for an efficient conversion of this waste heat, provided suitable materials are available. For practical use materials with a dimensionless figure of merit $zT = S^2\sigma T/\kappa > 1$ at the working temperature of the device are required. Here $S$ is the Seebeck coefficient, $\sigma$ and $\kappa$ are the electrical and thermal conductivity and $T$ is the temperature. While several materials with a high value of $zT$ are available [1], their practical use is often limited by cost or toxicity. One of the interesting material classes for the search of new thermoelectric materials are transition metal (TM) silicides, which benefit from the abundance and non-toxicity of Si [2, 3]. Among these phases MnSi$_{1.73}$ with a reported $zT$ up to 0.7–0.8 [4, 5], ReSi$_{1.75}$ with $zT = 0.8$ [6] and FeSi$_2$ with $zT$ up to 0.4 [7, 8] have received attention for their thermoelectric properties.

High-throughput computations [9] have become an important tool in the search for materials with tailored properties. One of the conceptionally simplest approaches for such high-throughput computations is to calculate a given property for a set of known structures [10]. Scanning entire composition ranges for new materials is computationally feasible by systematic substitution of elements for a list of candidate structures [11, 12]. Clearly phase stability is one the basic pre-requisites for a functional material and a suitable search strategy is thus to first identify stable structures by systematic substitution and then to proceed with the calculation of the desired properties [12].

A byproduct in such high-throughput calculations is a large amount of data for the energetics of alloys in various structures. These data may be used to analyse trends in the structural stability and electronic structure for given alloy systems. There are several strategies to understand these trends. This can be datamining based on stochastic methods [13] or simplified chemical based descriptors such as electro-negativity differences [14]. In principle tight-binding (TB) models [15] also belong to the chemically based models, where structural stability can be rationalized in terms of valence orbitals and differences in atomic size, electronegativity and chemical hardness. When searching for stable phases several highly unstable structures will be considered. Especially in view of multi-component systems like ternary or higher alloys, the fact that there are numerous possible structures is a major obstacle.

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for the computational design of new materials. This makes TB models especially attractive, as they are a total energy method. One can therefore imagine a pre-screening step in the high-throughput search, so that the fairly expensive density functional theory (DFT) structure optimizations is limited reasonably close to the convex hull.

In this paper we use our recently developed high-throughput environment [12] to explore the 0 K DFT phase diagrams of binary TM silicides. We introduce descriptors for the phase-stability and thermoelectric properties and hereby identify several candidates with potential for thermoelectric applications. We calculate the electronic transport properties of the semiconductor alloys and discuss their prospects for thermoelectrics. For the frequently observed alloy compositions TM$_2$Si, TMSi and TMSi$_2$ we discuss in detail the trends observed in the structural stability.

2. Computational details

The phase stability of the binary TM silicides TM–Si was evaluated following a similar procedure as described in [12]. For each TM element TM a set of at least $^2$ 63 trial structures was optimized and the respective formation energy calculated. Trial structures were created by suitable substitution from known binary TM–Si alloys recorded in Pearson’s database [16]. In addition, some of the most frequently observed structure types were included. The structure prototypes are listed in the supplementary material (available from stacks.iop.org/NJP/15/105010/mmedia). In total, about 2000 trial structures were used for the construction of the phase diagrams of the TM silicide series. In case of the magnetic 3d elements (TM=Cr, Mn, Fe, Co and Ni) spinpolarized calculations were used, assuming initially a ferromagnetic alignment of the magnetic moments. Thus, a possible gain in energy through antiferromagnetic alignment of the spins which is expected for instance for some Mn compounds is neglected.

For the structure optimizations and the calculation of formation energies we employed the VASP code [17–19] using the projector augmented wave method with a cut-off energy of 350 eV and a k-space density corresponding to about 13 × 13 × 13 points in the full Brillouin zone of Si. Some of the data points were additionally cross checked with the all electron full potential local orbital (FPLO 9.01-35) method [20], which was also used for the calculation of band structures and the density of states (DOS). For the evaluation of band structure dependent transport properties we used the BolzTraP code [21] together with the VASP code. Convergence with respect to the number of k-points was checked with a sequence of meshes with increasing k-space density. The transport data shown were obtained with 47 × 47 × 47 (CrSi$_2$), 30 × 30 × 10 (Mn$_4$Si$_7$), 15 × 18 × 29 (Ru$_2$Si$_3$) and 21 × 9 × 12 (Ir$_3$Si$_5$) k-points in the full Brillouin zone. The general gradient approximation in the parameterization of Perdew et al [22] was used for all calculations. Relativistic effects were treated in a scalar relativistic approach. For W–Si, a possible influence of spin–orbit coupling on the energetics of the low lying structures was checked with the relativistic version [23] of the FPLO code [20], but found to be insignificant for the present discussion.

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$^2$ The HTE database contains for some TM silicides additional data points, which are however not relevant for the present discussion.
3. Phase stability and semiconducting phases

In the following we discuss the phase stability and electronic structure of stable or almost stable binary TM silicides with a finite band gap. The entire set of convex hulls for the group 3–12 silicides is given in the supplementary material (available from stacks.iop.org/NJP/15/105010/mmedia). In what follows, we use the notation TMSi(NaCl) for a TMSi alloy crystallizing in the NaCl structure, etc.

While the 0 K DFT energy can only be an approximation of the true temperature dependent phase stability, one would still expect the experimental possible structures to be closely related to the calculated phase stability [24]. In figure 1 we show the distance from the convex hull for TM–Si alloys found in the Pearson’s database. About 80% of the alloys lie within a distance $\Delta E_h < 50$ meV atom$^{-1}$ from the calculated convex hull, confirming the good agreement between calculated stability and experimentally observed structures. In the following we will use the criteria $\Delta E_h < 50$ meV atom$^{-1}$ as a descriptor for the identification of potentially stable or meta-stable structures. Four data points show exceptionally large deviations $\Delta E_h > 250$ meV atom$^{-1}$, but their stability is questionable.

All stable structures with a calculated band gap are found among the group six to nine TM silicides and the calculated convex hulls for these compounds are shown in figure 2. The structures within a distance of 50 meV atom$^{-1}$ from the convex hull are marked with a square. Furthermore, materials with a calculated band gap are highlighted (filled squares), which illustrates that semiconducting phases are only observed on the Si rich side of the phase diagram, while all phases with less than 50 at% Si content are metallic. The lowest formation energies $E_f$ among the group six to nine TM silicides are observed for the 4d elements. This is a consequence of the magnetism in the 3d series, where especially the bulk elements and the

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The proposed hexagonal IrSi$_3$ structure [25] ($\Delta E_h = 0.49$ eV atom$^{-1}$) has not been confirmed in more recent experiments [26]. URe$_2$-type AgSi$_2$ (400 meV atom$^{-1}$) and CsCl-type RhSi (290 meV atom$^{-1}$) are kinetically stabilized meta-stable structures [27, 28]. In addition there is a computed CaF$_2$ structure of the recently discovered RuSi$_2$ (290 meV) which was discarded by the authors after comparison with experiment [29].

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Figure 2. Calculated formation energy $E_f$ of ordered group 6–9 TM silicides (from left to right) for the 3d, 4d and 5d elements (from top to bottom). Shown are only data points of alloys which are stable with respect to decomposition into the elements ($E_f < 0$). Alloys within 50 meV atom$^{-1}$ from the convex hull are highlighted with blue squares (open squares: metals, filled squares: semiconductors). The calculated convex hull, which connects the stable ground state structures, is shown as blue line.

TM rich phases are stabilized through spin polarization, while the Si rich phases are typically nonmagnetic. Without spin-polarization, the lowest $E_f$ among Fe/Ru/Os silicides would be observed for the iron silicides. However, there is no unique trend observable for the whole TM silicide series, see calculated convex hulls in the supplementary material (available from stacks.iop.org/NJP/15/105010/mmedia).

There is an excellent agreement between the calculated stable structures with a band gap and the known semiconducting compounds. A review of semiconducting silicides [30] lists: CrSi$_2$, MnSi$_{1.73}$, $\beta$-FeSi$_2$, Ru$_2$Si$_3$, ReSi$_{1.75}$, OsSi, OsSi$_2$, Os$_2$Si$_3$ and Ir$_3$Si$_5$. Furthermore, FeSi [32, 33] and RuSi [31, 34] are known to be semiconductors. Recently, also the RuSi$_2$ phase was shown to form [35]. Finally, there is some mentioning of meta-stable semiconducting TM phases like MoSi$_2$ and WSi$_2$ in CrSi$_2$ structure [36, 37]. Except for WSi$_2$, all these known semiconducting silicides are found within this 50 meV atom$^{-1}$ range of the convex hulls (see figure 2 and table 1). Additionally, we find previously unknown semiconducting alloy phases, Tc$_4$Si$_7$ (Mn$_4$Si$_7$), TcSi$_2$ (OsGe$_2$), Fe$_2$Si$_3$ (in the Ru$_2$Ge$_3$ and Ru$_2$Sn$_3$ structures) and Rh$_3$Si$_5$ (Ir$_3$Si$_5$), within the 50 meV range of the convex hulls, table 1. The Tc$_4$Si$_7$ structure is known experimentally [38] and the lack of knowledge of its electronic structure is probably due to the obvious lack of interest in Tc chemistry. Also listed in table 1 is a so far unknown CrSi$_2$(TiSi$_2$) phase, which is weakly metallic but included due to its interesting electronic and transport properties (see section 5).
Table 1. Binary TM silicides with a finite band gap and a distance $\Delta E_h$ of less than 50 meV atom$^{-1}$ from the convex hull. The formation energy $E_f$, the calculated band gap $E_{g0}^\text{calc}$ and the experimental band gap $E_g^\text{exp}$ (no data available) are also listed. Estimated values for the figure of merit $zT$ at 300 and 600 K for n- and p-type doping at optimal carrier concentration are given as a descriptor for the comparison of the alloys. The estimated $zT$'s are given using $\kappa_f/\tau = 10^{14}$ W K$^{-1}$ms$^{-1}$ (see section 5 for discussion).

| at% | Si | alloy (structure type) | $E_f$ (eV at$^{-1}$) | $\Delta E_h$ (eV at$^{-1}$) | $E_{g0}^\text{calc}$ (eV) | $E_g^\text{exp}$ (eV) | ‘$zT$$_{300K}$’ n/p | ‘$zT$$_{600K}$’ n/p |
|-----|----|------------------------|----------------------|--------------------------|----------------------|----------------------|------------------|------------------|
| 66.7 | Cr$_3$Si$_{16}$ (CrSi$_2$) | 0.359 | 0.011 | 0.34 | 0.27–0.67$^a$ | 0.25/0.30 | 0.98/1.01 |
| 66.7 | Cr$_3$Si$_2$ (TiSi$_2$) | 0.323 | 0.047 | 0.00$^b$ | – | 0.16/0.24 | 0.45/0.73 |
| 66.7 | Mo$_5$Si$_6$ (CrSi$_2$) | 0.478 | 0.027 | 0.10 | 0.37–0.30 | 1.18/0.84 |
| 63.6 | Mn$_{16}$Si$_{28}$ (Mn$_2$Si$_7$) | 0.433 | 0.000 | 0.77 | 0.4–0.83$^a$ | 0.37/0.30 | 1.12/0.69 |
| 63.6 | Si$_3$Ti$_6$ (Mn$_2$Si$_7$) | 0.574 | 0.000 | 1.04 | 0.51/0.19 | 0.38/1.12 |
| 66.7 | Si$_2$C$_6$ (OsGe$_2$) | 0.487 | 0.038 | 0.12 | 0.13/0.39 | 0.83/0.41 |
| 63.6 | Re$_6$Si$_{32}$ (Mn$_2$Si$_7$) | 0.352 | 0.000 | 0.51 | 0.12–0.2$^a$ | 0.08/0.11 | 0.78/0.69 |
| 50.0 | Fe$_2$Si$_4$ (FeSi) | 0.512 | 0.000 | 0.16 | 0.05–0.1$^c$ | 0.98/0.77 | 0.84/0.35 |
| 60.0 | Fe$_2$Si$_{12}$ (Ru$_5$Sn$_3$) | 0.425 | 0.046 | 0.24 | – | 0.24/0.10 | 0.84/0.28 |
| 60.0 | Fe$_16$Si$_{12}$ (Ru$_2$Ge$_3$) | 0.442 | 0.029 | 0.44 | – | 0.22/0.07 | 0.84/0.28 |
| 66.7 | Fe$_2$Si$_{16}$ (FeSi) | 0.444 | 0.000 | 0.56 | 0.77–0.79$^a$ | 0.42/0.16 | 1.12/0.70 |
| 50.0 | Ru$_2$Si$_4$ (FeSi) | 0.639 | 0.000 | 0.02 | 0.24$^d$ | 1.17/0.56 | 1.44/0.93 |
| 60.0 | Ru$_4$Si$_{12}$ (Ru$_5$Sn$_3$) | 0.603 | 0.023 | 0.38 | 0.44$^a$ | 0.17/0.08 | 0.73/0.35 |
| 60.0 | Ru$_4$Si$_{12}$ (Ru$_2$Ge$_3$) | 0.625 | 0.000 | 0.55 | 0.7–1.09$^a$ | 0.19/0.07 | 0.67/0.30 |
| 66.7 | Ru$_2$Si$_6$ (FeSi) | 0.535 | 0.000 | 0.27 | – | 0.10/0.13 | 0.54/0.39 |
| 50.0 | Os$_4$Si$_4$ (FeSi) | 0.354 | 0.015 | 0.55 | 0.34$^a$ | 0.91/0.47 | 1.86/1.33 |
| 60.0 | Os$_3$Si$_2$ (Ru$_5$Sn$_3$) | 0.412 | 0.031 | 0.75 | – | 0.33/0.20 | 1.00/0.59 |
| 60.0 | Os$_3$Si$_2$ (Ru$_2$Ge$_3$) | 0.443 | 0.000 | 0.88 | 2.3$^a$ | 0.15/0.24 | 0.57/0.84 |
| 66.7 | Os$_3$Si$_2$ (FeSi) | 0.442 | 0.000 | 0.67 | 1.4–1.8$^a$ | 0.08/0.18 | 0.42/0.78 |
| 62.5 | Rh$_2$Si$_4$ (Ir$_3$Si$_5$) | 0.600 | 0.025 | 0.46 | – | 0.19/0.21 | 0.60/0.68 |
| 62.5 | Ir$_2$Si$_4$ (Ir$_3$Si$_5$) | 0.621 | 0.000 | 0.94 | 1.2–1.57$^a$ | 0.22/0.28 | 0.55/0.68 |

$^a$ Experimental value from [30].

$^b$ Experimental value from [31].

$^c$ Experimental value from [32].

$^d$ See text for discussion.

A closer look at table 1 shows that stable semiconducting structures are often observed throughout an isovalent 3d, 4d and 5d TM–Si series, as is expected due to their chemical similarity. This is the case for instance for the FeSi- and FeSi$_2$-structures. The relative stability of the structures depends however also on the size of the TM atom. In case of the hexagonal CrSi$_2$ structure the distance from the convex hull $\Delta E_h$ increases with increasing size of the TM atom. For CrSi$_2$, the hexagonal experimental ground state is found to be slightly higher in energy compared to the tetragonal CrSi$_2$(MoSi$_2$), in agreement with earlier reports [39]. For the metastable WSi$_2$(CrSi$_2$) we find $\Delta E_h = 67$ meV atom$^{-1}$, showing that the 50 meV range should only be taken as a rule of thumb. The relative stability of the monoclinic Ir$_3$Si$_5$ structure decreases with decreasing size of the TM and becomes more than 50 meV atom$^{-1}$ for the (experimentally not observed) Co$_3$Si$_5$. 

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Figure 3. Calculated DOS (black solid lines) of (a) Tc$_4$Si$_7$, MoSi$_2$ and Ru$_2$Si$_3$ and (b) RuSi, RuSi$_2$ and Rh$_3$Si$_5$. Also shown is the DOS integrated over the energy window shown (IDOS, black dotted lines) and the partial contributions of Si (blue) and the respective TM atom (red). The insets show the total DOS in the vicinity of the Fermi energy.

The calculated and experimental band gaps $E_g$ are also listed in table 1. For CrSi$_2$(CrSi$_2$) we find a band gap of 0.34 eV, while the band gaps of MoSi$_2$(CrSi$_2$) and WSi$_2$(CrSi$_2$) are nearly vanishing. This is in good agreement with earlier reports [36, 40] and available experimental data. Mn$_4$Si$_7$, Tc$_4$Si$_7$ and Re$_4$Si$_7$ in the tetragonal Mn$_4$Si$_7$ structure are found to have intermediate band gaps between 0.51 and 1.04 eV in our calculations, with the largest band gap for the 4d silicide Tc$_4$Si$_7$. The cubic FeSi-type alloys are found to be small band gap semiconductors in the range of 0.16–0.55 eV. In agreement with experiment an increase of the band gap from FeSi(FeSi) to OsSi(FeSi) is observed. A similar trend is also observed for Fe$_2$Si$_3$, Ru$_2$Si$_3$ and Os$_2$Si$_3$, but with larger values of $E_g$. For the orthorhombic FeSi$_2$ structure, the smallest band gap is found for RuSi$_2$ (0.27 eV), while FeSi$_2$ and OsSi$_2$ are found to have intermediate band gaps of 0.56 and 0.67 eV. The calculated band gap of the so far unknown meta-stable Rh$_3$Si$_5$ is about 0.46 eV. For the stable Ir$_3$Si$_5$ we find a band gap of about 0.94 eV in good agreement with earlier band structure calculations [41].

4. Density of states and formation of band gap

Figure 3(a) shows the calculated DOS of the 4d silicides MoSi$_2$, Tc$_4$Si$_7$ and Ru$_2$Si$_3$. These compounds all have a valence electron count of 14 electrons per TM atom, where the formation
of a band gap has been attributed to the formation of different bonding/nonbonding pd blocks [42]. Figure 3(a) illustrates the similar bonding features of these compounds. The DOS in the low energy region of the energy window shown is dominated by hybridized Si 3s and 3p states due to Si–Si bonding, followed by a region with strong hybridization between TM d states and Si 3p states. The upper valence bands close to the Fermi energy are dominated by TM d states with some admixture of Si 3p, while the conduction bands are formed by strongly hybridized Si 3p and TM d states. Similar features in the electronic structure are also observed for the isovalent 3d and 5d compounds (not shown).

Figure 3(b) shows the calculated DOS of the 4d silicides RuSi, RuSi₂ and Rh₃Si₅. The two Ru alloys have an even valence electron count with 12 (RuSi) and 16 (RuSi₂) valence electrons per TM atom. Similar to the case of the 14 electron rule, regions with Si s and p states and a bonding Si/TM complex can be distinguished in the low energy part of the DOS shown. In case of RuSi and the isovalent FeSi and OsSi compounds, the upper valence and lower conduction bands have almost entirely TM d character with only small admixture of Si 3p, while RuSi₂ and the isovalent FeSi₂ and OsSi₂ show a strong hybridization of Si p and TM d states in the vicinity of the Fermi level. The electronic structure of FeSi and FeSi₂ type alloys was already discussed in earlier publications and the reader is referred for further details to the literature [35, 39, 43–45].

In case of Rh₃Si₅ and the isovalent Ir₃Si₅ with a non-integer valence electron count per TM atom the formation of a band gap cannot be explained by a simple hybridization scheme, but must take into account details of the crystal structure. The unit cell of the monoclinic Ir₃Si₅ structure has 64 atoms with 16 non-equivalent positions. While the overall features of the DOS are similar to the other silicides shown in figure 3(b), a closer look at the electronic structure reveals that the occupation of different Si sites differ by about 0.15 electrons.

5. Transport properties

In the following we discuss the transport properties of TM silicides listed in table 1, where we focus mainly on alloys which haven’t received much theoretical attention up to now. An overview about the expected thermoelectric performance on the basis of our calculations is given in table 1, where estimates of zT at 300 and 600 K are given for optimal n- and p-doping, respectively. Based on the calculated carrier dependent properties, S and σ/τ, the estimates are obtained using the Wiedemann–Franz law for the electronic contribution to thermal conductivity and rewriting

\[ zT = \frac{S^2\sigma/\tau}{LT\sigma/\tau + \kappa_l/\tau} T, \]  

which introduces \( \kappa_l/\tau \) as a parameter. We will use \( \kappa_l/\tau = 10^{14} \text{W K}^{-1}\text{ms}^{-1} \). This accounts for the fact that for many of the alloys listed in table 1 more detailed data is not available and we have discussed the validity of this approach earlier [10, 46]. It is clear that the \( \kappa_l \) and \( \tau \) depend on the alloy and can be influenced independently by e.g. nanostructuring. However, the estimated \( zT \) can be thought of as a descriptor to give a fair comparison of the electronic contribution to the thermoelectric performance, which is in the focus of our high-throughput study. For instance the known thermoelectrics β-FeSi₂ and Mn₄Si₇ can be identified as promising materials on the basis of the estimates in table 1. An exception are the FeSi-type alloys, where experimentally only small values of \( zT \) around 0.1 are found in contrast to the estimated values close to 1.
This failure is probably due to the strongly correlated nature of these alloys, in addition to the uncertainty in $\kappa / \tau$. A further uncertainty is that even if a material can be predicted to have favourable thermoelectric properties at a given carrier concentration, the realization can be limited by the lack of control of the carrier concentration [10, 47, 48]. While in principle $\kappa$, $\tau$ and accessible doping level can be calculated, this goes beyond the scope of our present study.

CrSi$_2$(CrSi$_2$) has received some experimental attention as a potential thermoelectric without finding $zT$ values higher than 0.2 at 600 K [37, 49, 50]. Also the band structure dependent transport for both CrSi$_2$(CrSi$_2$) [40] and MoSi$_2$(CrSi$_2$) [36] have been investigated in detail and we will not examine it further here. We have found CrSi$_2$ in the TiSi$_2$ structure to be only 47 meV above the Cr–Si convex hull. The structure has an interesting band structure which is metallic, but with a pseudo gap of more than 0.6 eV along most of the high symmetry directions (figure 4). Along $\Gamma$-(010) (short orthorhombic axis), a steep p-type valence band and a pd derived conduction band are crossing the Fermi level giving rise to a weakly metallic behaviour. Despite this metallic character a Seebeck coefficient as high as 160 $\mu$V K$^{-1}$ at 500 K can be reached upon optimal hole doping. An estimated $zT \approx 0.2$ at room temperature and 0.7 at 600 K for optimally p-doped CrSi$_2$(TiSi$_2$) is found which is comparable to several known potential thermoelectrics, table 1.

The Mn/Tc/Re-silicides form a set of highly complex structures around the composition $1 : 1.75$ [51]. In the present study we have considered only the simplest structure type, Mn$_4$Si$_7$. Several studies have shown these structures to have interesting thermoelectric properties. For Mn$_4$Si$_7$ a $zT = 0.62$ with a $S = 210 \mu$V K$^{-1}$ at 450 $^\circ$C has recently been reported [4, 52]. Also for a mixed Ru$_2$Si$_3$–Mn$_4$Si$_7$ system and for Re$_4$Si$_7$, $zT \approx 0.8$ at around 900 K have been found [5, 6]. In figure 5 we show the calculated transport properties. At the experimental carrier concentration, a good agreement is found between the calculated 600 K Seebeck coefficient and experiment. A similar agreement is found for the 300 K Seebeck coefficient (not shown), confirming the general good agreement found between our approach and experiment [46]. The calculated Seebeck coefficient is only weakly anisotropic. In agreement with the measurements of [53] we find a slightly higher magnitude of $S$ parallel to the $c$-axis compared to the $a$-axis at
the experimental carrier concentration. Comparing our calculated $\sigma/\tau$ with the experimentally measured $\rho$ yields $\tau \approx 7.5 \times 10^{-15}$ s. Furthermore, using Wiedemann–Franz’ law and the measured $\kappa$ and $\rho$ we estimate an experimental $\kappa_l$ of 1.2 W m$^{-1}$ K (see text). The calculated power factor and figure of merit are in a good agreement with the experimental data of [4] (figure 5). The power factor $S^2\sigma$ and the figure of merit $zT$ show a pronounced anisotropy especially in the n-doped regime due to a strong anisotropy in the conductivity. It is interesting that, assuming the same $\tau$ and $\kappa_l$, we find a $zT$ almost a factor two higher for optimally n-doped Mn$_4$Si$_7$ along the $a$-axis and an about 50% higher value for the isotropic $zT$. An interesting point is furthermore that both positive and negative Seebeck coefficients of large magnitude have been

Figure 5. Transport properties of Mn$_4$Si$_7$(Mn$_4$Si$_7$) (red) and Re$_4$Si$_7$(Mn$_4$Si$_7$) (blue) at $T = 600$ K. Shown are the magnitude of the Seebeck coefficient $S$ (bottom), and estimates for the power factor $S^2\sigma$ (middle) and the figure of merit $zT$ using $\tau = 7.5 \times 10^{-15}$ s and $\kappa_l = 1.2$ W m$^{-1}$ K (see text). The corresponding direction dependent transport data are shown as dotted lines ($a$-axis) and dashed lines ($c$-axis). The experimental points are taken from [4].
measured for these compounds [5, 6] which indicates that it could be possible to dope the structures for both as n and p-type conductors.

The transport properties of Ru$_2$Si$_3$(Ru$_2$Ge$_3$) have been discussed in some detail earlier [12, 35, 54]. A strong anisotropy in the transport was measured [54] and calculated [12]. Both n- and p-doped samples can be prepared [30]. For Mn-doped (p-type) Ru$_2$Si$_3$ samples, a Seebeck coefficient $S$ of about $300 \mu$V K$^{-1}$ was measured at room temperature [55]. The S shaped temperature dependence of the Seebeck coefficient $S$ with a change of sign at about 540 K observed in Ru$_2$Si$_3$ [55], can be due to strong correlation effects, phonon drag or impurity states in the gap, but can not be simply explained by the present approach. Interestingly, we find that p-doped Os$_2$Si$_3$ shows a better thermoelectric performance compared to Ru$_2$Si$_3$, while for n-doping it is vice versa (figure 6), which may be of benefit in a thermoelectric device. The calculated transport properties of Fe$_2$Si$_3$(Ru$_2$Ge$_3$) are almost identical to those of Ru$_2$Si$_3$ in the p-doped regime and slightly enhanced for n-doping (figure 6). Here, $zT$ was estimated using the same parameters as for CrSi$_2$(TiSi$_2$).

Another group of well studied systems are the FeSi-type and FeSi$_2$-type systems [7, 35, 56], which have been of interest for their thermoelectric properties for a long time [31]. FeSi shows unusual transport properties, which have been interpreted in both a strong correlation [32, 57] and strong electron–phonon coupling scheme [58]. Very recently the theoretical thermoelectric properties have been discussed in detail from a strong correlation point of view [59] and we will not discuss it further. $\beta$-FeSi$_2$ is also a promising thermoelectric, which has the advantage
Figure 7. Transport properties of Ir$_3$Si$_5$ (Ir$_3$Si$_5$) (red) and Rh$_3$Si$_5$ (Ir$_3$Si$_5$) (blue) at 800 K. The magnitude of the Seebeck coefficient $S$ (bottom) and the estimated figure of merit $zT$ (top) are shown as a function of the logarithm of the carrier concentration $n_c$ for hole doping (left) and electron doping (right). The estimated $zT$’s are calculated using $\kappa_l/\tau = 10^{14}$ W K$^{-1}$ ms$^{-1}$, equation (1).

that it allows for n- and p-type doping. n-doped FeSi$_2$ ($zT = 0.4$) has a higher efficiency compared to p-doped FeSi$_2$ ($zT = 0.2$), [30] in agreement with our calculations. The electronic and transport properties of $\beta$-FeSi$_2$ have received much attention and the reader is referred for further discussion to the literature.

Fe-doped Ir$_3$Si$_5$ was reported to show favourable transport properties with high values of $zT$ at elevated temperatures [60]. Figure 7 shows a comparison of our calculated transport properties between Ir$_3$Si$_5$ and Rh$_3$Si$_5$ at 800 K. Indeed we find maximum values of the estimated $zT$ close to unity for both alloys independent of the type of doping. Rh$_3$Si$_5$ shows a smaller Seebeck coefficient with a maximum around 300 $\mu$V K$^{-1}$ compared to Ir$_3$Si$_5$ (500 $\mu$V K$^{-1}$), but has a higher conductivity owing to the smaller band gap. This results in comparable values of the power factor and the figure of merit.

6. Trends in the structural stability

The trends in structural stability for 2 : 1, 1 : 1 and 1 : 2 stoichiometries for substitutional TMs belonging to the 4d period are shown in figure 8. At the early TMs the tetragonal CuAl$_2$ dominates the 2 : 1 stoichiometries. The CuAl$_2$ structure can be described as a system of
Figure 8. DFT energies for relevant 2 : 1 (a), 1 : 1 (b) and 1 : 2 (c) stoichiometric structures with respect to the number of d electrons. The structures are labelled by their prototype. The energies are reported in dimensionless units, chosen by scaling the local extrema to an absolute value of 1.

interpenetrating graphite-like nets which create channels occupied by infinite chains of Si atoms [61]. For the later TMs the orthorhombic Co$_2$Si (TiNiSi) and monoclinic Re$_2$Si structure types dominate. The Co$_2$Si can be described in terms of four-connected networks of Co and Si atoms with other Co sitting in large channels [62]. The Re$_2$Si structure is based on a distorted hexagonal close packed arrangement of TM and Si atoms [63]. For the 1 : 1 the early TM structures are dominated by the structurally similar TlI/FeB structures [64]. These are followed by the FeSi structure, which can be viewed as a distorted rocksalt structure [39], and the FeAs structure type, which can be described as a distorted NiAs structure with reduced interlayer Si–Si distances [65]. Finally, for the 1 : 2 structures, the stable structure type changes from the ZrSi$_2$, over the three related Cr/Mo/Ti–Si$_2$ structures [66] to the FeSi$_2$ structure. The FeSi$_2$ structure can be viewed as a distorted CaF$_2$ structure [44] which corresponds well with the fact that the Rh and Pd compounds relax to the CaF$_2$ structure.

To analyse the relative stability of the TM–Si structures, we will apply the structural energy difference theorem [67], which states that to first order the relative stability of two structures is determined by the difference in bond energy at the scaled volumes where the structures have the same repulsive energy. In principle, the theorem could also be applied to DFT calculations. However, the computational effort in searching for the desired volumes would be prohibitive. Furthermore, the aim is to explain the relative stabilities of the structures using
Figure 9. TB energies for relevant 2:1 (a), 1:1 (b) and 1:2 (c) stoichiometric structures with respect to the number of d electrons. The structures are labelled by their prototype. The energies are reported in scaled units. On the x-axis the filling of the TM d-states is shown, since we assume three valence p-electrons per silicon atom.

It is clear that the pd-model is mainly valid for the central d-band elements and when the silicon bonding is dominated by p-states, which is not the case for the semiconducting Si rich phases in figure 3. A quantitative agreement, as would be needed for a pre-screening of the DFT calculations, would demand more transferrable TB models, for example, environmental TB models [68]. However, the general agreement between the TB model and the calculated stabilities confirms that the overall stability ranges of the TM–silicides can be accounted for by a simple TB-model.

$dd(\sigma, \pi, \delta) = (-6, 4, -1)(r_d/R)^3$ $pp(\sigma, \pi) = (2, -1)(r_p/R)^3$ $pd(\sigma, \pi) = (3, \sqrt{3})\sqrt{r_p^3 r_d R^{-4}}$ with $r_p = 3a_0$ and $r_d = 4a_0$. 

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Figure 10. (a) Trigonal prisms of TM atoms (in blue) centred by zig-zag chains of Si atoms (in red). (b) ZrSi$_2$ (c) TII and (d) FeB structures. The unit cells are shown in black.

Figure 11. Difference between the integrated p-DOS with TII as a reference.

A further interesting point is that the infinite chains of Si bonding are a general feature of the FeP$_2$, CuAl$_2$, TII, FeB structures which are stable at low electron count. This highlights the early stability of the ZrSi$_2$ structure, which is often considered related to the TiSi$_2$ structure [69, 70]. However, the ZrSi$_2$ structure can also be described in terms of zig-zag chains of silicon atoms running through infinite rows of trigonal prisms of TM atoms sharing a rectangular face, figure 10(a). Figure 10(b–d) shows how the ZrSi$_2$ structure contains the same basic building block of infinite rows of trigonal prisms as the TII and FeB crystal structures. It can therefore be
constructed from TII by inserting layers of fourfold coordinated silicon atoms separating every series of rows of prisms.

The importance of the Si–Si bonding along the infinite chain is illustrated in figure 11. The projected DOS for FeB, TII, FeSi, FeAs and RhSi (qualitatively similar plots were obtained for the 2 : 1 and 1 : 2 structures) is shown. It is clear that the bonding p-states lead to an increase of the bonding Si–p contribution at the bottom of the bands, explaining the relative stability at low band fillings. The FeAs structure, which also contains infinite zig-zag chains of short Si contacts but does not show increased p-bonding nor stability at low electron counts, would challenge this interpretation. The local coordination is however different where the Si in FeAs are octahedrally coordinated, whereas the Si in e.g. the TII/FeB coordinate to seven TM atoms.

7. Conclusions

In summary, we have shown that a high-throughput screening within DFT provides a useful guideline for the search of thermoelectric materials. We find an overall good agreement between the calculated 0K phase stability of binary 3d, 4d and 5d TM silicides and experiment. Using phase stability as a basic criterion we identify several candidates with potential for thermoelectric applications. This includes known thermoelectrics like Mn$_4$Si$_7$ (Mn$_4$Si$_7$), FeSi$_2$ (FeSi$_2$), CrSi$_2$ (CrSi$_2$) or Ru$_2$Si$_3$ (Ru$_2$Ge$_3$), as well as new potentially meta-stable materials like CrSi$_2$ (TiSi$_2$), Fe$_2$Si$_3$ (Ru$_2$Ge$_3$) and Rh$_3$Si$_5$ (Ir$_3$Si$_5$). For the identification of potentially stable or meta-stable structures a descriptor $\Delta E_h < 50$ meV atom$^{-1}$ was introduced based on a statistical analysis of known structures, where $\Delta E_h$ is the distance from the convex hull in the 0K DFT calculations.

Analysis of the high-throughput data shows that semiconducting phases are exclusively found on the silicon rich side of the group 6–9 TM silicides. Further analysis of the electronic structure shows that the formation of a band gap in MoSi$_2$, Tc$_4$Si$_7$, Ru$_2$Si$_3$, RuSi, RuSi$_2$ and their 3d and 5d analogues can be understood with simple hybridization models. Moreover, we observe distinct trends in the structural stability. The lowest formation energies are observed among the 4d silicides. With increasing valence electron count for a given stoichiometry, a distinct structural sequence is observed, which is similar for 3d, 4d and 5d TMs. Our TB calculations show that this structural sequence can be reproduced with a simple pd TB model apart from the Si rich phases, where the agreement with DFT becomes poorer due to increasing importance of Si s states to the bonding.

Our calculated transport properties are in good agreement with available experimental data at the respective carrier concentration. For Mn$_4$Si$_7$ we show that about 50% higher values of $zT$ may be achieved, provided n-doped material can be prepared, whereas the thermoelectric performance of p-doped samples is close to the calculated optimum. Interesting transport properties are also found for the so far unknown Rh$_3$Si$_5$ (Ir$_3$Si$_5$) and CrSi$_2$ (TiSi$_2$). For Rh$_3$Si$_5$ a similar performance as for the known high temperature thermoelectric Ir$_3$Si$_5$ is expected on the basis of our calculations. CrSi$_2$ (TiSi$_2$) has a very interesting electronic structure with a pseudo gap of about 0.6 eV and a high Seebeck coefficient despite a weakly metallic behaviour.

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