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# Abstract

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# Preface

# Chapter 1

## Introduction

some introduction on the importance of discovering new materials and alloying.

**Need something on thermoelectricity related to both the band gap and high-entropy alloys.**

High-entropy alloys is a novel class of materials based on alloying multiple components, as opposed to the more traditional binary alloys. This results in an unprecedented opportunity for discovery of new materials with a superior degree of tuning for specific properties and applications. Recent research on high-entropy alloys have resulted in materials with exceedingly strong mechanical properties such as strength, corrosion and temperature resistance, etc **find references**. Meanwhile, the functional properties of high-entropy alloys is vastly unexplored. In this study, we attempt to broaden the knowledge of this field, the precise formulation of this thesis would be an exploration on the possibilities of semiconducting high-entropy alloys.

A key motivation of this thesis is the ability to perform such a broad study of complex materials in light of the advances in material informatics and computational methods. In this project, we will employ Ab initio methods backed by density functional theory on top-of the line supercomputers and software. 20 years ago, at the breaking point of these methods, this study would have been significantly narrower and less detailed firstly, but secondly would have totaled ... amount of CPU hours to complete (**Calculate this number**). In the addition to the development in computational power, is also the progress of modeling materials, specifically we will apply a method called Special Quasi-random Structures (SQS) to model high-entropy alloys or generally computationally complex structures. Together with the open landscape of high-entropy alloys described above, these factors produce a relevant study in the direction of applying modern computational methods to progress the research of a novel material class and point to promising directions for future research.

In specifics, this thesis revolve around the electrical properties of high-entropy alloys, mainly the band gap as this is the key indicator for a semiconducting material and it's applicability. Semiconductors are the building blocks in many different applications in today's world, ranging

from optical and electrical devices, to renewable energy sources such as solar and thermoelectricity. Given the economic and sustainable factors concerning silicon, in addition to its role in relevant applications such as microelectronics and solar power. Silicon emerges as a natural selection to build our alloys around. Furthermore, the development and research on both high entropy alloys and metal silicides have been heavily centered around 3d transition metals. Keeping in line with the economic and environmental factors, we will continue this direction by focusing on high entropy stabilized sustainable and economic 3d metal silicides **Not happy with this writing**. Throughout the study we will analyze a great number of permutations of 3d silicides, from different initial metal silicides such as  $CrSi_2$ ,  $FeSi_2$ ,  $MnSi_{1.75}$ ,  $Fe_2Si$ , each with distinct properties relating to the band gap, crystal structure and metal to silicon ratio. In addition, the permutations include numerous metal distributions and elements within the 3d-group of metals. Examples are Co, Cr, Fe, Mn, and Ni.

Given a background in high-entropy alloys, one could ask if this study is truly sensible. In the later sections we will cover the details of this field, and it quickly become clear that the materials investigated in this study does not fall under the precise definition of high-entropy alloys, nor do we intend to explore the properties and factors relating to high-entropy stabilized alloys such as the configurational entropy, phase stability and finite temperature studies. However this study is motivated from the discovery of these materials and promising properties, and venture into a more hypothetical space of materials, enabled by the computational methods available to study the potential properties of such materials. On the other hand, very recent studies **Mari, and other HEA silicide study** have experimentally synthesized high-entropy disilicides, thus in some way justifying the direction of this project.

We begin this project by reviewing key concepts of solid-state physics for readers lacking a background in materials science, and an introduction to the base 3d silicides of the experimental work. Later follows a theoretic walk-through of the relevant concepts of this thesis, these topics include high-entropy alloys, special quasi-random structures, and density functional theory. Next we shine light on the implementation of DFT in this project, and other computational details required to reproduce the results in this thesis, such as the use of the Vienna Ab Initio Simulation Package (VASP) and implementation of SQS. Finally we present the results of our study, these include the band gap and electronic properties of various structures and the success and challenges of the computational methods applied throughout the study.

# **Part I**

# **Theory**

## **Part II**

# **Methodology and Implementation**



**Part III**

**Results and Discussion**

## Chapter 4

# Different compositions and crystal structure

### 4.1 New compositions

In similar fashion to the previous sections, we here begin by presenting the mean and standard deviation of the total energy and magnetization of a set of SQSs corresponding to different high-entropy silicides of the  $\text{FeSi}_2$  unit cell. The compositions we have tested are deliberate combinations intended to investigate both the impact of manganese by replacing the element with Co or Ti, and concepts related to HEA theory such as the atomic size effect. Furthermore Co is a very common element in many stable HEA, as seen in section 2.2, thus we include 3 compositions with Co to study the impact on stability and the functional properties. The results of the aforementioned alloys can be seen below in table 9.1, note that all compounds contain a total of 48 atoms as before.

Composition	Toten (eV)		Mag ( $\mu_B$ )		$\Delta H$ (eV)
	mean	std	mean	std	mean
$\text{Cr}_4\text{Fe}_4\text{Co}_4\text{Ni}_4\text{Si}_{32}$	- 6.4655	0.0056	0.0083	0.0155	- 12.7536
$\text{Co}_4\text{Fe}_4\text{Mn}_4\text{Ni}_4\text{Si}_{32}$	- 6.4731	0.0046	0.0000	0.0000	- 15.0836
$\text{Cr}_4\text{Fe}_4\text{Ti}_4\text{Ni}_4\text{Si}_{32}$	- 6.4217	0.0087	0.0305	0.0293	- 7.5040
$\text{Cr}_4\text{Fe}_4\text{Mn}_4\text{Ti}_4\text{Si}_{32}$	-6.6994	0.0071	0.1142	0.0641	- 7.3060
$\text{Cr}_4\text{Fe}_4\text{Mn}_4\text{Co}_4\text{Si}_{32}$	-6.7687	0.0034	0.1331	0.0326	- 13.7796

Table 4.1: Overview new compositions

From table 9.1 we see that the stability of the relative compositions vary greatly. By introducing cobalt to the alloys, particularly at the cost of manganese result in a large positive effect on the stability, contrary replacing either manganese or nickel with titanium significantly lowers the stability. **Wait for new formation enthalpies.** In table 9.1 we have listed the mean magnetic moment of the compositions, in line with previous results

in this project the magnetization is very dependent on chromium and manganese. This is seen by the overall lowest magnetic moments in the two compositions without these elements, and reversely the highest magnetic moments is found for compositions with both Cr and Mn. Comparing the magnetic moment of  $(\text{CrFeCoNi})\text{Si}_2$  and  $(\text{CoFeMnNi})\text{Si}_2$  it seems in our study that chromium is most responsible for the magnetic moment in these alloys. Furthermore we find that substituting Ni with both Ti and Co result in more magnetic compounds. These are truly surprising results, one would expect that the magnetic moments would be larger in the ferromagnetic elements Ni, Fe and Co than Cr, Mn and Ti. This could go back to our simplistic and superficial study of the magnetic properties in this project, additionally the PBE functional as we covered in section .. have shown limitations for 3d elements and particularly Ni. Thus this could be a factor affecting our results. Another factor is that we here based our comparison on the mean values between 5 SQSs. As we have experienced throughout this project the uniqueness of the SQSs can be troublesome to handle, and our best guess is to study the most stable super-cell. Below in table 9.2 we list the magnetic moments of the most stable SQSs. Here we find several dissimilarities to the mean value such as the  $\text{Cr}_4\text{Fe}_4\text{Co}_4\text{Ni}_4\text{Si}_{32}$  being nonmagnetic in the most stable supercell. Thus based on the utmost stable configurations we can state that replacing either Cr or Mn (with Co) removes the magnetic moment in the alloy. Furthermore we find from these supercells that the magnetic moment is reduced by replacing Ni with Ti, and increased from Co. These results are in much better accordance with previous knowledge of ferromagnetic elements and their interplay in high-entropy alloys.

Composition	Magnetic moment ( $\mu_B$ )
$\text{Cr}_4\text{Fe}_4\text{Co}_4\text{Ni}_4\text{Si}_{32}$	0
$\text{Co}_4\text{Fe}_4\text{Mn}_4\text{Ni}_4\text{Si}_{32}$	0
$\text{Cr}_4\text{Fe}_4\text{Ti}_4\text{Ni}_4\text{Si}_{32}$	0,0653
$\text{Cr}_4\text{Fe}_4\text{Mn}_4\text{Ti}_4\text{Si}_{32}$	0,0785
$\text{Cr}_4\text{Fe}_4\text{Mn}_4\text{Co}_4\text{Si}_{32}$	0,1666

Table 4.2: Final magnetic moment of the most stable supercell of each composition.

In regards to the band gap of the compositions, we can report that a heavy majority are metals. We found no evidence of a band gap in both the  $\text{CrFeCoNiSi}_2$  and  $\text{CrFeMnTiSi}_2$  alloys across all supercells, as seen in the density of states in figure 9.1. Further also the most stable SQSs of the  $\text{CrFeTiNiSi}$  alloy point to a metal. Similarly the most stable SQSs of the  $\text{CoFeMnNiSi}_2$  alloy are clearly metals. Noteworthy of this composition however is that we find clear evidence of a narrow band gap in two SQSs (A and B). In terms of stability, these lie around the mean total energy of the set. The respective band gaps are 0.033 eV in A and 0.0058 eV in B.

Composition	$occ$	$E_G^{up, eigen}$ (eV)	$E_G^{dw, eigen}$ (eV)	$E_G^{tot, eigen}$ (eV)
CrFeCoNiSi <sub>2</sub>	0.5	0	0	0
	0.1	0.00095	0.0399	0.00095
	0.01	0.063	0.063	0.063
CrFeTiNiSi <sub>2</sub>	0.5	0.0067	0	0
	0.1	0.061	0.0087	0.0087
	0.01	0.061	0.037	0.037
CoFeMnNiSi <sub>2</sub>	0.5	0	0	0
	0.1	0.0037	0.0037	0.0037
	0.01	0.0268	0.0268	0.0268
CrFeMnTiSi <sub>2</sub>	0.5	0	0	0
	0.1	0.021	0.00049	0
	0.01	0.03	0.03	0.022
CrFeMnCoSi <sub>2</sub>	0.5	0.461	0	0
	0.1	0.607	0.0218	0.0218
	0.01	0.607	0.0245	0.0245

Table 4.3: Band gaps of the most stable SQS of  $\beta$ -FeSi<sub>2</sub> high-entropy silicide compositions as a function of occupancy in the eigenvalues.

skiiiiiaaaat! **To follow is details on the gaps in A and B, is it worth to include this?** In the density of states plotted in figure .., the band gap in A is clearly visible. On the other hand the very narrow gap in B is not as apparent, as the states around  $E_f$  contain very small nonzero values. This could be related to the low resolution of 2500 points in the density of states as seen before, especially considering the size of the gap. In opposite to the CFMN calculations previous we here experience excellent cohesion between PBE and SCAN simulations on the band gap. With the meta-GGA functional the band gap of SQS A and B respective is 0.04 eV and the 0.003 eV. Moreover we find the identical gap transition with both functionals, which was not the case in previous endeavors with this functional. Additionally we also find that the HSE06 functional produce dissimilar results to previous experiences. In this scenario, the HSE06 functional fails to recognize the observed band gap of PBE and SCAN in both supercells. The greater number of k-points in the GGA and meta-GGA calculations offer more accurate band gaps, however lesser k-points will not result in a smaller gap, only bigger. Thus the uncertainties of previous calculations of the HSE06 functional does not apply in this case. For this reason in addition to the reputation of hybrid functionals and the lack of other factors to negatively affect the validity of the result, we find it challenging to conclude on the band gap of these structures between functionals.

## 4.2 Crystal structures

In the discussion above we have covered in great detail the possibilities of high-entropy silicides based on the  $\beta$ -FeSi<sub>2</sub> unit cell with twice as many silicon atoms to 3d elements. The primary outcome and conclusion of this research was that particularly the combination of Cr, Fe, Mn and Ni resulted in superior properties in the light of the motivation behind this project. The next question we wish to answer is if the promising results of the CFMN system be reproduced in other symmetries. In this section we will implement the CFMN composition in crystal structures based on hexagonal CrSi<sub>2</sub> (*P*6<sub>422</sub>), both tetragonal and orthorhombic Mn<sub>16</sub>Si<sub>28</sub> (*P*4<sub>2</sub>*c* and *Pcca*), and trigonal Fe<sub>2</sub>Si (*P*3<sub>2</sub>*m*1) where we test the CFMN system to varying metal and silicon ratios, and crystal structures. As before, the total energy, enthalpy of formation and magnetic moment per atom can be found below in table ..

	Total energy per energy		Enthalpy of formation	Mag per atom	
CrSi2	-6.4837	0.0087	-8.1205	0.0887	0.0387
MnSi	-6.6658	0.0071	-9.1848	0.0687	0.0398
Fe2Si	-7.5082	0.0107	-10.2474	0.3848	0.0588

### CrSi2

From our calculations with PBE DFT we find the bulk crsi2 material to be an indirect semiconductor with a band gap of 0.33 eV, slightly below the listed value of 0.36 eV in materials project [cite](#), surprisingly we find a smaller gap of 0.32 eV from the SCAN functional. The compound is also nonmagnetic in agreement with materials project. For the bulk material we employed a 9 atom cell, with 6 silicon and 3 cr atoms, from this we generated SQSs of 72 atoms with the same ratio. **Include toten per atom for the unit cell? and figure of SQS + unit cell?** For this given composition and system we observe very similar results to that of the compositions discussed above, the eigenvalues of several SQSs report a small band gap, but its not apparent from neither the density of states or from the bandgap.py script of pymatgen. Additionally, we can not reproduce the gap with the SCAN functional, as was possible for the CFMN (fesi2) system.

### MnSi

In the tetragonal configuration, the bulk material is a nonmagnetic indirect semiconductor with a band gap of 0.76 eV according to our PBE calculations, and 0.78 eV from SCAN. Materials project find a band gap of 0.76 eV, in good agreement with our own PBE results. The unit cell consist of 44 total atoms, 16 manganese and 28 silicon. In the orthorhombic cell, with equal number of elements we find a band gap of 0.76 eV (0.77 eV SCAN) as well. In contrast, the CFMN alloy of both these cells produce metallic compounds. It should be noted that structures B and D in the tetragonal system did not fully relax, same for D in the orthorhombic cell, so these results could be inaccurate.

## Fe<sub>2</sub>Si

In this cell, we drastically alter the metal-silicon ratio, this is seen both in the band gap and magnetic properties of the material. The magnetic moment of this cell consisting of 4 iron atoms and 2 silicon atoms is 0.67, from the iron atoms. This magnetic character can also be observed from the discrepancy between the two spin channels. In spin down we find a band gap of 0.21 eV, while there is no gap in spin up. This gap can also be seen in the density of states **Include figure**. This however is an abnormal result in regard to other experimental work and literature on the Fe<sub>2</sub>Si cite [https://www.sciencedirect.com/science/article/pii/S0925838816329796?casa\\_token=g9DRpU9IClcAAAAA:6Gd12A4Kh9J2igUWMVwHN8OSIKzD27VACA052FNsSAWhRY6PE](https://www.sciencedirect.com/science/article/pii/S0925838816329796?casa_token=g9DRpU9IClcAAAAA:6Gd12A4Kh9J2igUWMVwHN8OSIKzD27VACA052FNsSAWhRY6PE)

Our results are subject to errors, particularly we note that the eigenvalues used to calculate the gap contain nonphysical values in the spin down channel. However, the gap is evident in the density of states thus we include the result in this report, but acknowledge the uncertainties revolving the value.

From this unit cell we generate 54 atom SQSs. From table .. we see that the magnetic nature remains, producing the overall highest magnetic moment of all studied supercells, which is not a surprising result considering the 3d metal to silicon ratio. **More on magnetic and total energy.** The magnetism can also be seen in the difference between the two spin channels, the bands where the occupancy transition from 1 to 0, ie occupied to not occupied is very different. In the most magnetic supercell D, we saw a distance of 22 bands between the spin down transition and spin down transition. Most supercells are metals from our PBE calculations. B and D show a very small gap of around 0.01 eV in one spin channel. In E we find a very narrow gap semiconductor with a total gap of 0.002 eV. This gap is surrounded by the same uncertainties as discussed previously.

**Part IV**

**Conclusion**

Write conclusion here