Thesis Title

A subtitle of your thesis

Author name

Thesis submitted for the degree of
Master in Master's Program Name <change at
main.tex>
60 credits

Department Name <change at main.tex>
Faculty name <change in duoforside.tex>

UNIVERSITY OF OSLO

Spring 2022

Thesis Title

A subtitle of your thesis

Author name

Abstract

Contents

List of Figures

List of Tables

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 silcides 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 9

The bad (Other compositions of the FeSi$_2$ unit cell)

Include results for CRFeMnCo to finish! 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 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 .., thus we include two (3?) compositions with this element to study the impact on stability and the functional properties. The results of the aforementioned alloys can be seen bellow in table 9.1, note that all compounds contain a total of 48 atoms as before.

	Toten (eV)		Enthalpy of formation	Mag	
Cr$_4$Fe$_4$Co$_4$Ni$_4$Si$_{32}$	- 6.4655	0.0056	-12.7536	0.0083	0.0155
Co$_4$Fe$_4$Mn$_4$Ni$_4$Si$_{32}$	- 6.4731	0.0046	-15.0836	0.0000	0.0000
Cr$_4$Fe$_4$Ti$_4$Ni$_4$Si$_{32}$	- 6.4217	0.0087	-7.5040	0.0305	0.0293
Cr$_4$Fe$_4$Mn$_4$Ti$_4$Si$_{32}$	-6.6994	0.0071	-7.3060	0.1142	0.0641

Table 9.1: Summary of the total energy, enthalpy of formation and magnetization of several composistionally different SQS high-entropy alloys based on the $\beta-$ FeSi$_2$ unit cell.

   Maybe discuss the std of mag and relation to energy of sqs, several cases we find large differences between SQSs. 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. In terms of the magnetization, the results are in line with the observations of the CFMN composition, from table 9.1 it's clear that replacing either manganese or chromium drastically reduces the magnetization of the alloys. In addition, we find

indication of chromium being further significant to the magnetization than manganese as seen from the first and second compounds in table 9.1 respectively. In opposition to the study of the CFMN system we observe here a clear relation between magnetization and stability. However, we are not confident if the observed outcome is a direct consequence of the magnetization or simply a product of addition of cobalt and titanium respectively to the alloys. On the other hand, in both cases the least magnetic composition is also the most unstable, thus there is weight behind the magnetic relation to stability. **Wait for CrFeMnCoSi2 to finish**

Insert figures related to the band gap, stability to band gap results, which SQS of each compo is most stable

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 CrFeCoNiSi2 and CrFeMnTiSi2 alloys across all supercells, as seen in the density of states of the two most stable SQSs of the respective compounds **Add figures**. Further also the most stable SQSs of the CrFeTiNiSi alloy point to a metal. Similarly the most stable SQSs of the CoFeMnNiSi2 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. **Include DOS or other figures for these results.**

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 Ef 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 uncertainites 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.

Now interesting to look at the LDOS and PDFs, maybe also CHGCAR

Part IV

Conclusion

Write conclusion here