

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

© 2022 Author name

Thesis Title

<http://www.duo.uio.no/>

Printed: Reprosentralen, University of Oslo

Abstract

Contents

1	Introduction	1
I	Theory	3
2	Background	4
2.1	Overview of sold-state physics	4
2.2	3d Silicides	4
3	High-Entropy alloys	5
3.1	Fundamentals	5
3.2	Core effects and properties of high-entropy alloys	8
4	Special quasi-random Structures	10
4.1	The fundamentals of SQS	10
4.2	Mathematical formulation	11
4.3	Application of SQS to high-entropy alloys - Add figure	13
5	Density-Functional Theory	15
5.1	Review of Quantum Mechanics	15
5.1.1	The Shrödinger equation	15
5.1.2	Simplifications and approximations to solve the many-electron Shrödinger equation	16
5.2	Fundamentals of Density-Functional Theory	17
5.3	Limitations of DFT	18
II	Methodology and Implementation	20
6	Practical application of DFT	21
6.1	The Exchange-Correlation functional	21
6.2	Fundamental aspects of practical DFT calculations	22
6.3	Self-consistent field calculation	24
7	Computational details	26
7.1	Vienna Ab initio Simulation Package	26
7.2	Generation of SQS	28
7.3	Band-structure	28

7.4	Utility scripts	30
III	Results and Discussion	31
8	The good (CFMN fesi2)	33
8.1	CFMN Eqvimolar distribution	33
8.1.1	Introduction	33
8.1.2	The band gap	34
8.1.3	Meta-GGA and hybrid functional	39
8.2	Permutations	43
9	The bad (Other composistions)	48
10	The ugly (Other symmetry groups)	51
11	The overview	53
IV	Conclusion	55
A	Density of states	57
B	PDFs	58
C	Charge density	59

List of Figures

3.1	Formation of HEA based on δ and N . Figures adopted from [hea2016_ch2]	7
3.2	A schematic illustration of lattice distortion in high-entropy alloys. Figure from [owen_jones_2018]	9
6.1	Self consistent iteration of a DFT calculation. Figure adopted from lecture notes fys-mena4111 cite	25
7.1	48 atom SQS based on eqvimolar distribution of Cr, Fe, Mn and Ni in and $FeSi_2$ cell.	29
8.1	Density of states SQS D CFMN (fesi2) from PBE calculation .	35
8.2	Local density of states SQS D CFMN (fesi2) from PBE calculation	36
8.3	Density of states SQS B CFMN (fesi2) from PBE calculation .	37

List of Tables

8.1	Total energy per atom, final magnetic moment, band gap (GGA) and formation enthalpy of $Cr_4Fe_4Mn_4Ni_4Si_{32}$ SQSs based on $FeSi_2$	34
8.2	Band gap transition of CFMN (fesi2) SQSs with PBE functional	35
8.3	Band gap (eV) with PBE in spin up and spin down channels of CFMN (fesi2) SQSs	37
8.4	Band gap of CFMN ($FeSi_2$) SQSs with GGA (PBE), meta-GGA (SCAN) and hybrid-functionals (HSE06).	39
8.5	Mean and stadard deviation of the total energy and magnetic moment per atom, plus enthalpy of formation of the listed mean energies ($FeSi_2$).	43
8.6	Total and spin polarized band gap of 4 permutations of CFMN (fesi2) with PBE GGA calculation. The structures that are excluded from this list either failed in calculations, or does not show any band gap.	46

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

Trenger jeg denne biten? Evt hvor? In this one year long project, we have collected results of a great number of materials with various structures and compositions. The initial experimentation was based on high-entropy silicides of the Fe_2Si unit cell, created from the special quasi-random structure approach as described above. Despite the non-semiconducting character of this compound, we worked under the idea that the extraordinary properties that have been observed in high-entropy alloys through effects such as the cocktail effect, we could discover specific combinations of elements that would yield a semiconductor. In addition, the ratio between silicon atoms to metals allowed us to create nearly equimolar high-entropy alloys.

Following this attempt, we transitioned into studying high-entropy silicides based on well known semiconducting 3d silicides such as β - $FeSi_2$, $CrSi_2$ and $MnSi_{1.75}$. The main outcome of this project is that for all 4 different starting silicides, we could only produce high-entropy silicides from one unit cell, furthermore in this cell only one specific compositions of elements was semiconducting. This was $Cr_{0.25}Fe_{0.25}Mn_{0.25}Ni_{0.25}Si_2$, here-in CFMN, in the β - $FeSi_2$ crystal structure.

This section will be structured in the following manner, firstly we will investigate the CFMN (fesi2) compound and various permutations of the composition. Thereafter we will look at other possible compositions of fesi2 based high-entropy silicides, and lastly test the CFMN composition in other crystal symmetries. In final we will present an overview of the complete study and the various compounds that have been investigated in order to propose promising directions and guideline future research directions in this field. In this way, we aim to understand the unique properties of CFMN (fesi2) and why this particular compound is semiconducting compared to the other testes structures in this project. Properties we will cover is the overall stability by total energy and corresponding enthalpy of formation, the magnetic properties and which elements contribute to the magnetism. But in majority, we will look at the band gap and related properties, as this is the main motivation and distinction of the study.

Chapter 8

The good (CFMN fesi2)

$\beta - \text{FeSi}_2$ in the orthorhombic cmce crystal lattice is a well known semiconductor with an experimentally measured band gap of around 0.8 eV **cite**, the nature of the band gap is under debate, all though most ab initio studies point to an indirect gap, experimental work indicate a direct gap. From our own DFT calculations, we find an indirect band gap close to 0.65 eV with PBE. This is in good agreement with other measurements from ab initio studies **cite materials projects, other studies**.

The density of states and charge density of bulk $\beta - \text{FeSi}_2$ from PBE calculations can be seen in figure .., .. From the figures we observe a clear band gap and semiconducting character. Moreover, we note from the density of states that the gap is identical in both spin channels, indicating that this material is diamagnetic. We find this to be true from the written magnetization in VASP, this also is in agreement with relevant literature **cite**. **Find reference for stability and ΔH^0** . Finally, the enthalpy of formation of this compound is -18.6583 eV.

8.1 CFMN Eqvimolar distribution

8.1.1 Introduction

The CFMN alloys of the fesi2 unit cell alloys can be seen in figure ... The supercells consist of 48 atoms, 16 of which is evenly distributed between Cr, Fe, Mn, and Ni, the remaining 32 sites occupied by silicon atoms. Bellow in table .. we list the total energy per atom (Toten), final magnetic moment per atom (Mag), and the band gap of the five distinct SQSs corresponding to the CFMN (fesi2) compound. In addition we include the mean and standard deviation of the values, plus the enthalpy of formation. For simplicity, we denote the SQSs as A, B, C, D and E.

Structure	Toten (eV)	Mag (?)	Band gap (eV)
A	-6,6080	0.0833	0.0280
B	-6,6138	0.0833	0.0523
C	-6,6063	0.0834	0.0344
D	-6,6155	0.0833	0
E	-6,6089	0.0833	0.0495
Mean	-6.6105	4.0000	0.0328
Std	0.0039	0.0000	0.0210
ΔH_{mean}^0	-11.5000 eV	-	-

Table 8.1: Total energy per atom, final magnetic moment, band gap (GGA) and formation enthalpy of $Cr_4Fe_4Mn_4Ni_4Si_{32}$ SQSs based on $FeSi_2$

Write a section on magnetism in method From a first glance, we observe very similar properties between the SQSs regarding both the total energy and final magnetic moment. Comparing to bulk $FeSi_2$, this compound is both less stable, from the enthalpy of formation, and magnetic. For the magnetic character of the compound, we performed self-consistent total energy calculations with three different magnetic configurations, non-magnetic (ispin=1), colinear magnetism with the initial magnetic moment equal to 1 times the number of ions, and lastly two times N ions. Of the three starting positions, we found the two latter to yield near identical total energies, with the middle setting winning out in some SQSs. The consistent magnetic moment between the 5 supercells is expected seeing as all 5 structures consist of equivalent elements. The magnetic moment observed is solely attributed from 3d electrons and in particular those of chromium and manganese atoms.

8.1.2 The band gap

The most interesting property of these SQSs is in fact the band gap. We note a mean band gap of about 0.03 eV, much lower than 0.65 eV of bulk $FeSi_2$. But a band gap in this smaller range makes for excellent application in for instance thermoelectrics. The gap is seen in 4 out of 5 SQSs, but surprisingly not in the most stable arrangement (D), the largest gap observed is about 0.05 eV from structure B, which is slightly below D in terms of total energy, but still a way above the mean energy. Similar to the bulk material, also these band gaps are indirect, the transitions are listed below in table ..

Structure	Gap (D/I)	Transition
A	I	(0.500,0.333,0.500) \rightarrow (0.500,0.000,0.000)
B	I	(0.250,0.000,0.250) \rightarrow (0.000,0.000,0.000)
C	-	(0.500,0.000,0.500) \rightarrow (-0.250,0.333,0.500)
D	I	-
E	I	(0.000,0.000,0.000) \rightarrow (0.250,0.000,0.250)

Table 8.2: Band gap transition of CFMN (fesi2) SQSs with PBE functional

A very useful method to extract information regarding the band gap of a material is to plot and study the band structure, however this is not as insightful when considering large supercells consisting of several elements and a large number of energy bands. The solution to this is normally to do a band unfolding, but given the complex structure and implementation of these SQS is VASP we where not able to do either. Instead we can study the band gap by firstly observing the density of states, in figure .. we plot both the total density of states (TDOS) and the local density of states (LDOS) of SQS D.

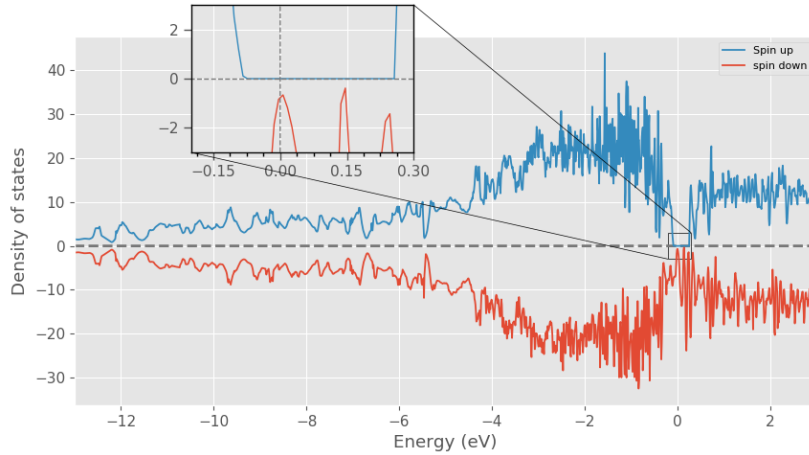


Figure 8.1: Density of states SQS D CFMN (fesi2) from PBE calculation

From TDOS we learn that D is in fact a half-metal with a sizable band gap in the spin \uparrow channel, and a metal in spin \downarrow . From the local density of states we observe that states corresponding to energies much lower than E_F is dominated by the s electrons of silicon atoms. At slightly higher energies, we see strong hybridization of Si p electrons and TM 3d electrons. In both spin channels Ni lie at the lowest energies of the 3d elements, followed by iron and then manganese and chromium very close to the fermi energi. Above the fermi energy there is more of an equal contribution from all elements, however slightly above E_f particularly iron and chromuim show a distinction in spin up and down respectfully. At higher energies, the LDOS is attributed to Si and Cr in both spin states, while elements such as Ni, Fe and Mn have a lesser role on the total DOS. One key distinction of

str D is a heavy amount of Manganese at energies right above E_f in spin down, this is not the case in the other SQSs (Appendix A). An additional distinction is that we observe higher overall peaks in the local density of states in the semiconducting SQSs B and e, compared to D.

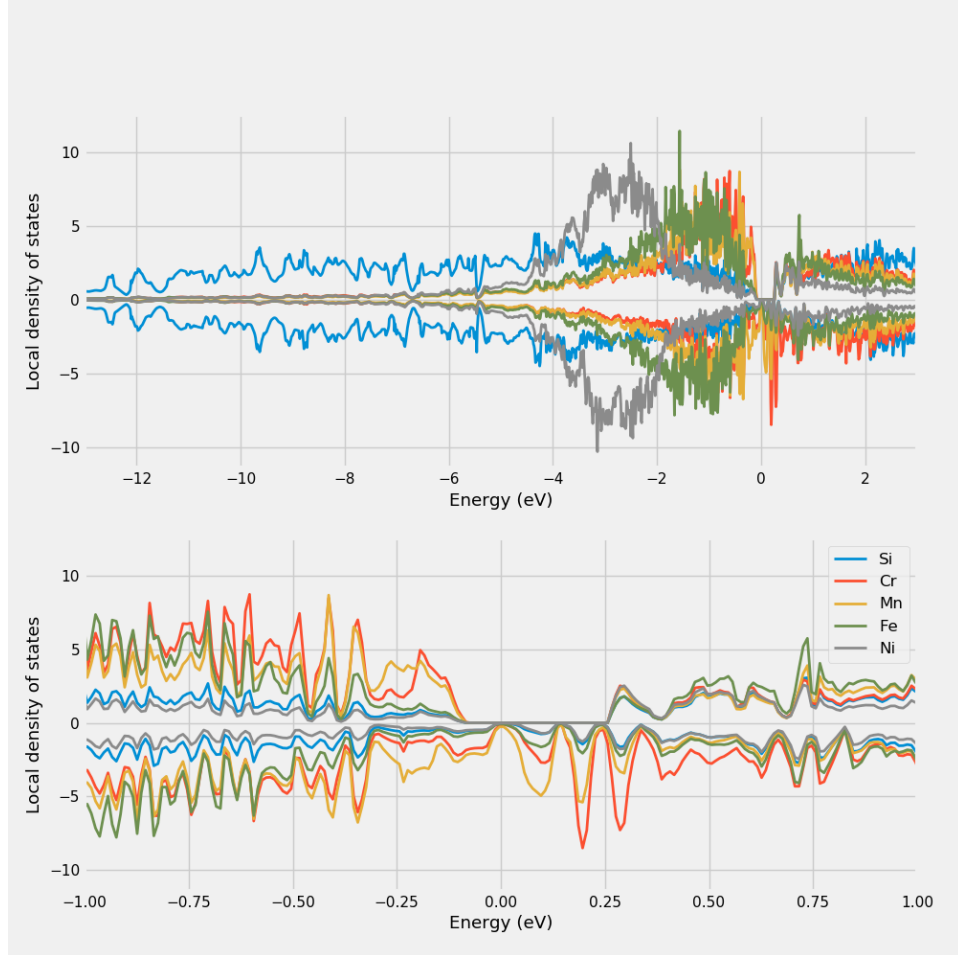


Figure 8.2: Local density of states SQS D CFMN (fesi2) from PBE calculation

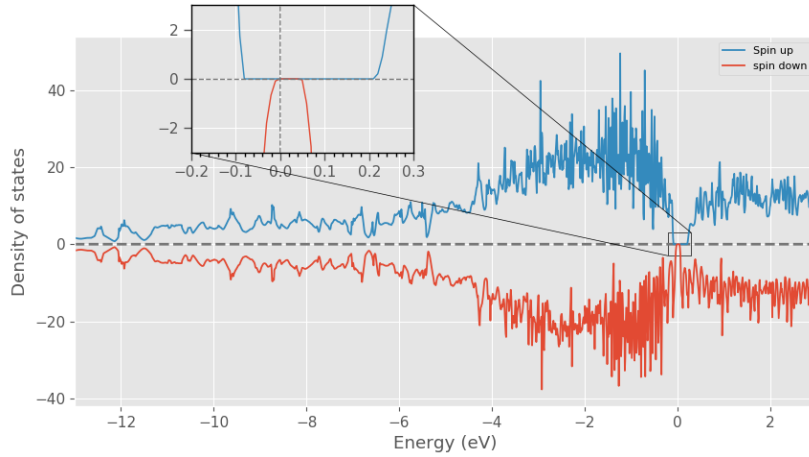


Figure 8.3: Density of states SQS B CFMN (fesi2) from PBE calculation

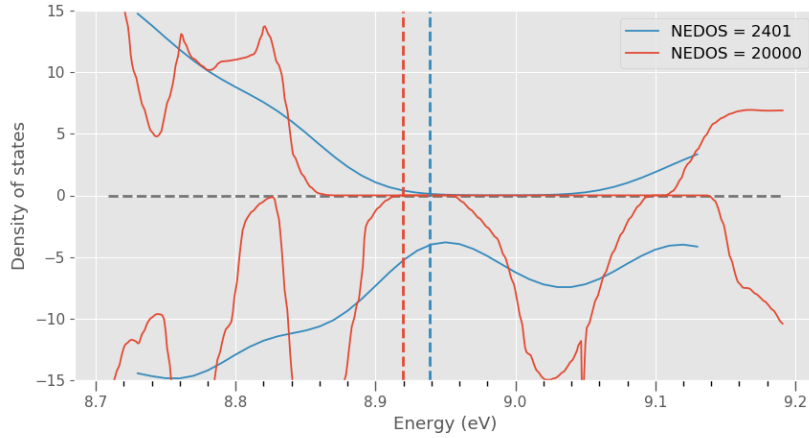
Above we have plotted the density of states of SQS B of this compound, here clearly showing a band gap in both spin channels. Similarly, also this SQS have a spin-polarized band gap, in spin up we see a band gap of around 0.3 eV, while the spin down states have a lesser band gap of 0.05 eV. This is a common trend of all SQSs excluding D of this composition. In table .. we list the band gap in both spin channels and the resulting total gap of all 5 SQSs.

Structure	Spin-up	Spin-down	Total
A	0.0814	0.0522	0.0281
B	0.2932	0.0523	0.0523
C	0.2355	0.0343	0.0343
D	0.3386	0	0
E	0.3078	0.0495	0.0495

Table 8.3: Band gap (eV) with PBE in spin up and spin down channels of CFMN (fesi2) SQSs

The density of states is a widely used and an insightful tool to learn about the character of a solid. For instance we can clearly see the magnetic character of the alloys and the magnitude of the band gap from the above plots. **What more can we say about the density of states? Find articles.** In the context of DFT and VASP however, the DOS include several factors that may contribute to inaccurate and sensitive results. As mentioned in section .., the type of numerical smearing is paramount for accurate DOS calculations. In this project we experienced large differences between calculations from gaussian and TBS smearing in relation to the band gap and DOS, this will be covered in more detail later. Moreover the DOS is very sensitive to computational factors such as the number of points in the DOS (NEDOS in VASP) and the number of k-points (to solve the DOS integral, see section ..). For example, the band gap in

structure C could only be seen in the density of states when increasing the number of points in the DOS from 2401 to 20000 points. This is shown bellow in figure blabla, where we plot the density of states around the fermi energy, denoted by the strippled red and blue lines, relative to the density of states with 2401 points and 20000 points respectfully, all other parameters remained unchanged, it should however be noted that the second calculations applied the charge density calculated by the former for quicker convergence.



Despite of the higher accuracy of the greater number of points, we continue to perform calculations with 2401 points in most calculations, mostly down to the increased workload for analyzing and producing DOS related results with such a large number of points, and the use of vaspkits tools.

A more secure method of evaluating the band gap is to consider the Kohn-Sham eigenvalues. The eigenvalues are provided for all energy bands for the given number of k-points used in the calculation, with listed energies and corresponding occupancy in both spin channels. The values listed in table (..) above was calculated from the eigenvalues. In addition to validate and provide an additional measure to the density of states, we can qualitatively differentiate SQS D. For certain k-points the occupancy does not transition from 1 to 0 directly between two bands, but rather contain one or more partially occupied bands in between (**Visualize? type fermi-dirac plot**), however only in the spin down channel. If we were to neglect these partially occupied states and only consider bands where the occupancy is above 0.99 or bellow 0.01, the band gap of structure D remain consistent in spin up, but we now observe a band gap of around 0.05 eV in the spin down channel resulting in a total band gap in the structure. Again, this would have been extremely insightful to investigate with the help of a band structure diagram.

Something on the flaws of EIGENVALUES, bloch corrections yield un-physical eigenvalues in structures without band gap. Some times we find band gap from eigenvalues but not DOS or other script. What does

the distance between up and down 1 occ and 0 occ mean?

8.1.3 Meta-GGA and hybrid functional

As expressed previously, in this work we include 3 level of depths GGA (PBE), meta-GGA (SCAN) and hybrid functionals (HSE06). In table .. bellow we show the results from these functionals.

Structure	PBE	SCAN	HSE06
A	0.0281	0.0000	0.0207
B	0.0523	0.0890	0.1808
C	0.0344	0.0690	0.0196
D	0.0000	0.0000	0.0000
E	0.0495	0.1048	0.0133

Table 8.4: Band gap of CFMN (FeSi_2) SQSs with GGA (PBE), meta-GGA (SCAN) and hybrid-functionals (HSE06).

The most obvious result of the more advanced functionals is the fact that aside from A, all 3 methods agree on the presence of the band gap. On the other hand it's clear that the actual value of the gap is debatable between methods. For this system we find generally that calculations with the SCAN functional yields the largest band gaps, and vice versa the lowest values corresponding to the HSE06 functionals. This is an surprising trend, typically a band gap found with PBE calculations widen from extending to more complex exchange-correlation functionals **Find references and point to relevant studies and relate to the XC section earlier**. However we find one exception to this trend, in structure B the band gap increase from 0.05 to 0.09 and 0.18 eV from PBE to SCAN to HSE06. The most likely reason for this abnormal large gap is a consequence of the small number of k-points we had to employ in order for the calculations to converge. Recalling that the transition in the PBE calculation was (0.250,0.000,0.250)-(0.000,0.000,0.000), comparing to HSE, the gap transition is between (0.500,0.000,0.000)-(0.000,0.000,0.000). Moreover, the point (0.250, 0.000, 0.250) in k-space is not included in the hybrid functional due to the narrow mesh (from IBZKIT file). Thus we may conclude that the large gap from HSE06 is a result of that the minimal gap is not encapsulated by the k-mesh. On the other hand, in the bulk $\beta\text{-FeSi}_2$ structure we managed to converge HSE06 calculations with the same number of k-points as in PBE and SCAN, and in this case the two latter functionals agree on a band-gap around 0.65 eV, the HSE06 calculation yields a a greatly exaterated band gap of 1.5 eV. This value exceeds by a large amount the experimentaly measured value of this compound, meanwhile PBE and SCAN slightly underestimate the gap. **Save the overall discussion on functionals and reference to litterature and studies to the overview section? Or place here?** Additionally the same point about the band transition can be said for the SCAN functional

as well, we observe that the increased band gap compared to PBE come from a different k-points (0.250,0.000,0.250)-(0.000,0.333,0.000) despite the identical k-mesh. This trend is also seen across the other 4 SQSs. **More on this**

Wait for hse06 ismear0 hse06 D to finish

In contrast to the more conflicting results discussed above, we generally find the SCAN functional to yield expected values of the band gap, ie slight increament of the PBE band gap. The only exception is for SQS A, where both PBE and HSE06 determine A to be a semiconductor with a band gap between 0.02 and 0.03 eV, while we find no apparent band gap from calculations with SCAN. Similar to structure D, this is because the eigenvalues contain so-called defect states and non-physical occupancy. Neglecting these, we find a band gap of about 0.03 eV, which is in good agreement with the PBE calculation. **Include the non-defect results, if so I need to elaborate on it?, more on the SCAN or no?.** As seen in table .., applying the HSE06 functional results in a band gap close to 0.021 eV for this SQS, from the point(0.000, 0.500, 0.500) to (0.500, 0.000, 0.000). From the eigenvalues we know that the gap is 0.7 eV in the spin up channel, and 0.02 eV in spin down **See DOSCAR maybe?.** As discussed in section .., in order for the HSE06 calculations to converge we had to first perform a self-consistent run with Gaussian smearing, then reapply the calculated charge density to perform subsequent calculations with TBC smearing. Between the two we report a large difference in the calculated band gap. The outcome of the former (Gaussian) yielded a band gap of 0.15 eV, (0.78 up and 0.15 down). However the eigenvalues contain defect states and is not observable from the density of states. **Figure?** By reducing the smearing width from 0.05 eV to 0.005 eV we find that the gap is reduced to about 0.1 eV (0.21 up and 0.1 down), additionally this band gap is both without any defect states and apparent in the density of states. **Conclude the segment on smearing, find references. Will include more examples of this later.**

Do I need to list all values of the gap: spin down, up for all functionals, smearings, SQSs etc? If so where/how?

In structure B, we have calculated the band gap with both gaussian and TBC smearing for PBE and HSE06. From PBE, both methods agree on a band gap around 0.05 eV, but the gaussian method yield eigenvalues with defect states, and a metallic density of states. Without defect states the band gap from gaussian PBE is found to 0.17 eV. In this supercell, the SCAN functional find a total band gap of 0.088 eV from 0.15 eV up and 0.088 eV down, the eigenvalues are pure and the gap is well represented in the density of states. The hybrid functional of this SQS is in pretty good agreement independent of smearing. From gaussian smearing and a consistent smearing width of 0.05 eV the band gap is calculated as 0.15 eV with significant spin polarization and defect states. Similar to the previous case, reducing the smearing width results in a more consistent and agreeable band gap. From both smaller width gaussian smearing and TBC, a band gap of around 0.18 eV.

Do we see the same spin polarization in hse, scan and pbe. Other results that agree/disagree

Structure C is similar to B with PBE, where the smearing method produce similar band gaps, but the gaussian contain defect states. Interesting of this structure is that the SCAN functional result in an opposite gap to the PBE functional. With PBE, the gap was largest in spin up and limited by the down states. From Scan, we observe that the gap is about 0.11 eV in down, and 0.07 eV in up. HSE06 agree with PBE, and find that the spin up channel have a band gap of 0.17 eV and 0.032 eV in spin down. With gaussian smearing, we find HSE06 to yield a gap around 0.1 eV in both channels and 0.065 eV in total (with defect states).

In structure D, we observe the same result. From PBE, the we find a band gap in spin up around 0.33 eV, but a metal in spin down. If we remove the defect states, the spin up gap remain constant, but we now find small gap of around 0.05 eV in down and correspondingly in total. And from the SCAN functional, the inverse is true. ie we initially find a band gap for spin down electrons, but not spin up. The results of HSE06 for this supercell is similar to structure C, in agreement with PBE and disagreement with SCAN. The band gap from HSE06 is calculated to about 0.37 eV in up and 0 in down from gasuusan smearing. We find a total gap of 0.26 eV when overlooking the defect states in the eigenvalues. **Wait for ismear-5 HSE06 to finish.**

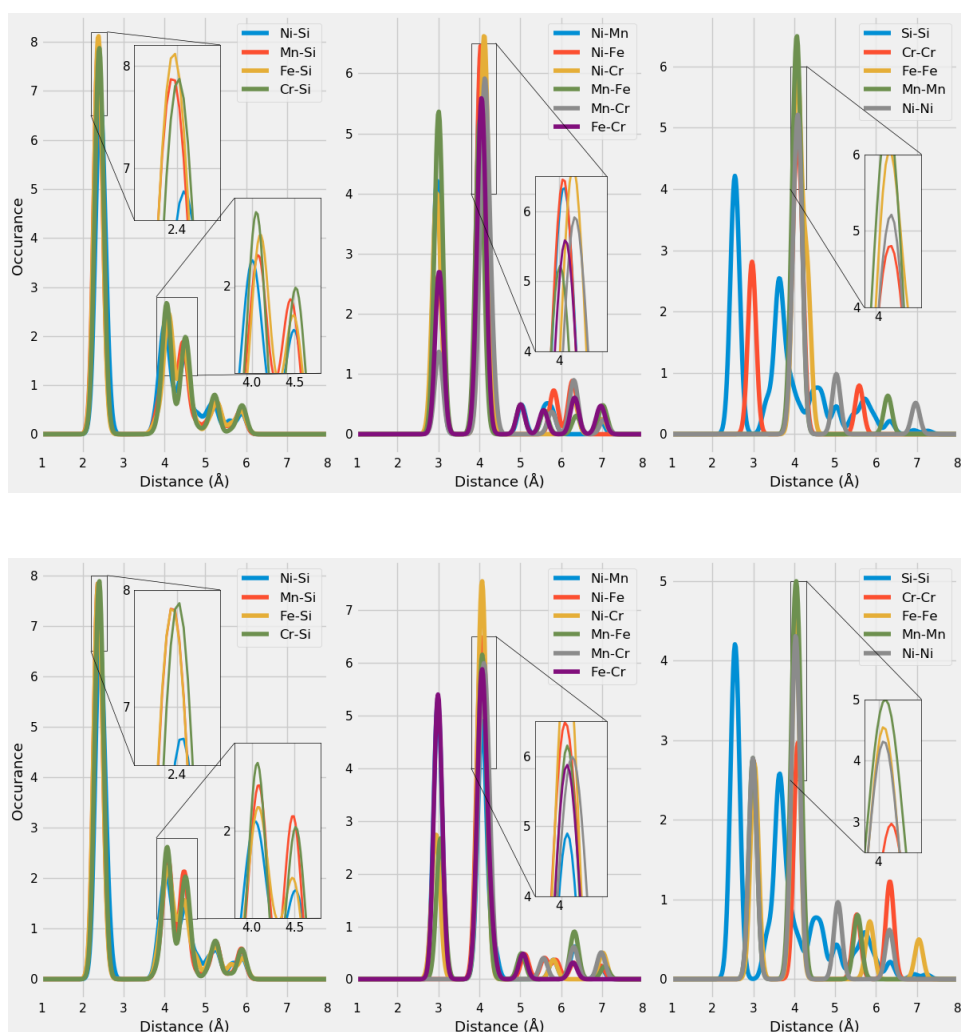
Finally, we observe the same pattern again for structure E. The PBE functional find a large gap in up and near 0 in down with TBC smearing. And the gaussian smearing find a similar gap in spin up, and the small gap in spin down is consistent, but caused by defects. Removing these defects we find a gap in down around 0.16 ev resulting in an increased total gap. Also in this case, the SCAN functional finds a different band transition than PBE, despite identical k points and parameters. The gap is calculated to 0.15 eV in spin up, 0.11 eV in down and 0.10 in eV in total. The HSE06 calculations of this structure resemble that of structure A. With TBC, the band gap is very large in spin up, about 0.55 eV, but close to 0 in down. The gaussian smearing finds similarly a large gap in up (0.66 eV) and a larger spin down gap around 0.15 eV, with defect states and 0.16 eV without. This gap is not apparent in the density of states, but we have found merit that the gap could become viable, by reducing the smearing width, as in structure A.

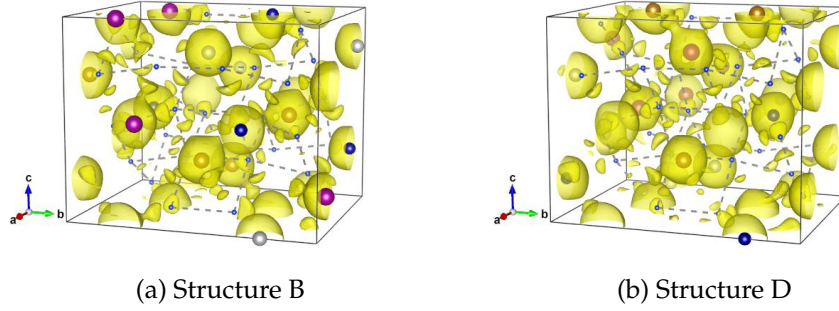
Why does only str B agree between gaussian and TBC in HSE06. And which method is more reliable, surely one would expect the gaps from HSE06 to be bigger than PBE/SCAN. But the tetraedon method is considered the most accurate?

At the risk of becoming repetitive and tedious, we still include this section where we walk though every SQS and the 3 functionals to make the reader aware of the differences and and disagreement we have observed in this study, both in relation to 5 SQSs of the same compound, but also from three highly praised exchange-correlation functionals. In conclusion, its very strange that the two smearing methods produce the same band gap in several instances, but that one of the channels is caused by defects in gaussian, but TBC find the same gap but without defects. And in addition, the large differences observed for HSE06 between the two

methods is interesting. I think I will include something like this in the summary/conclusion: Due to the disagreement between methods, SQS'sizes and etc, we may not confidently report a precise value of the band gap, but we can with some confidence conclude that we have found semiconducting high-entropy silicides.

If we now consider the probability distribution functions (PDFs), shown in figure **insert ref!**. From these figures there is a lot of useful information to investigate. With the aid of the ICSD (insert citation), we can locate the expected PDFs based on recent research and experiments from a host of different compounds. As our compound contain a total of 15 different bonds, comparing each one of these for all 5 supercells to the ICSD values would be an exhaustive process. For our purpose we are satisfied by comparing the 4 different metal-Si bonds and note ourselves of key distinctions. We find that the preferred bond-length of TM-Si is observed at two values, the most dominant being the shorter of the 2. For Fe-Si these are between 2.25-2.75 and 4-5, Mn-Si 2.25-2.75 and 3.5-5. Ni-Si lie between 2.25-2.5 and 3.85-5 and Cr-Si between 2.35-2.65 and 4-5.





At the surface, figure .. show that are supercells are in good agreement with the listed values for Tm-Si bonds, with the most occurring bond length falling at around 2.4 Å for all TMs, and some bonds at around 4.1 Å. The relative height of the peaks follow a similar trend, Fe-Si, Mn-Si, and Cr-Si all lie close to 8 for the first peak at 2.4 Å, and Ni-Si slightly below around 7. **More on the PDFs?**

Lastly we include the charge density of blabla, **something on these**.

8.2 Permutations

Up until this point we have investigated the structure CFMN (FeSi_2). Morre specifcly we have looked at the center of a quasiternary pahse diagram. In this section, we aim to exapand our search of this diagram by studying SQSs slightly away from eqvimolar distribution of 3d elements. In table (bellow) we list the mean total energy and magnetic moment per atom with corresponding standard deviation, and enthalpy of formation of 4 different permutations of the quasiternary phase diagram. Ideally we would like to only alter one element at a time, but the TDEP method insist in also reducing Nickel to stay consistent with the 48 atom supercells. The 4 permuations are listed bellow

	Toten (eV)		Enthalpy of formation	Mag	
$\text{Cr}_3\text{Fe}_3\text{Mn}_7\text{Ni}_3\text{Si}_{32}$	6.6947	0.0040	-11.9586	0.1375	0.0186
$\text{Cr}_5\text{Fe}_5\text{Mn}_3\text{Ni}_3\text{Si}_{32}$	6.6705	0.0030	-11.1991	0.1127	0.0223
$\text{Cr}_5\text{Fe}_3\text{Mn}_5\text{Ni}_3\text{Si}_{32}$	6.6852	0.0041	-10.5200	0.1375	0.0456
$\text{Cr}_3\text{Fe}_5\text{Mn}_5\text{Ni}_3\text{Si}_{32}$	6.6801	0.0036	-12.6426	0.0937	0.0209

Table 8.5: Mean and stadard deviation of the total energy and magnetic moment per atom, plus enthalpy of formation of the listed mean energies (FeSi_2).

Interestingly we find that we can increase the stability of the compound by adjusting the distribution of 3d elements. The most stable permutation is found when we increase the amount of manganese relative to the other TMs. In said permutation we find very similar properties as the equal distribution in terms of the band gap. From PBE calculations, we find

that the band gap ranges from 0.13-0.47 eV in spin up, depending on the supercell and all except for structure D have zero gaps in down, here we find a total band gap of 0.0063 eV. In contrast to equally distributed CFMN (fesi2), the SCAN functional does not find a band gap in any of the five supercells, except for small gaps less than 0.06 eV in spin up for structures D and E. Extending to the HSE06 functional, we find that structure D contain a large band gap of 0.17 eV, 0.57 eV and 0.26 eV in spin up and down respectfully. Both the gaussian and TBC smearing method are in excellent agreement of the gap. However, the result of the hybrid functional are surrounded by the same factors of uncertainty as described for CFMN (fesi2), in that also in this case we find that the transition of the indirect band gap is sensitive to the applied functional and especially the limited number of k-points used to perform HSE06 calculations.

If we now move in the opposite direction and reduce the number of manganese atoms we observe the opposite, namely the least stable permutation in terms of the total energy. One of the 5 SQSs (D) is a semiconductor, this supercell show from PBE calculations a band gap of 0.067 eV (up) and 0.041 eV (down) and 0.037 eV in total. The SCAN functional in contrast predict a half-metal with a band gap of 0.17 eV in spin down. The conflicting band gap continue with the HSE06 functional, resulting in 0.77 eV in spin up and 0.22 eV in down and total. Thus PBE and HSE06 result in a semiconductor with HSE06 pointing to a large spin polarization and PBE finding symmetric spin values. And on the other side, meta-GGA calculations predict a half-metal with semiconduction in the spin-down channel, opposite of the polarization from HSE06. As follows drawing a conclusion on the band gap is challenging, but as discussed previously we emphasize the results of GGA and hybrid functionals for the universal application and reputation they hold in self-consistent method studies of electronic structure.

The two most stable SQSs C and E, both exhibit large band gaps solely in the spin up channel. These gaps contain a few partially occupied bands that result in the gap vanishing in the density of states. This is an interesting result, as opposed to structures where many bands are partially filled, the structure is obviously a metal as apparent from both the calculated band gap and density of states. But in cases where there are only very few states with partial occupation we see a band gap from the eigenvalues and also the density of states show indication of a band gap with the DOS becoming very low near the Fermi energy, but not exactly zero as in the structures with no partial occupants. **Include DOS figure??** The spin up band gap in C and E discussed above is calculated from the eigenvalues as 0.21 and 0.36 eV respectfully. In both cases the gap vanishes with SCAN, and HSE06 calculates unfortunately proved difficult to converge for these structures, thus we were unable to obtain results with the hybrid functional. A positive conclusion of this permutation, is that if we include the possible half-metal gaps in C and E, we can report that the most stable arrangements are half-metals, then semiconducting and the least stable SQS is metallic. In conclusion we can then state that semiconducting and especially half-metallic are the preferred state over metallic in this

permutation.

$\text{Cr}_5\text{Fe}_3\text{Mn}_5\text{Ni}_3\text{Si}_{32}$ is on par with $\text{Cr}_5\text{Fe}_5\text{Mn}_7\text{Ni}_3$ in terms of both stability and magnetism. We note that the high magnetic moment is mostly attributed to the least stable SQSs, and the more stable arrangements have magnetic moment 5/48, as opposed to the first permutation in which we found high magnetism also in the stable SQSs. From PBE GGA calculations we obtain spin-polarized half-metals in structures A, B, C, and E with the spin up gap ranging between 0.21(A)-0.47(C) eV. Whereas structure D is a semiconductor with a 0.012 eV band gap (slightly larger in up than down). Additionally this is also the most stable SQS second only to A. In most cases, the use of SCAN results in very small spin up gaps, the rest 0. From the hybrid functional we find very conflicting results of structure D. With TBC smearing, HSE06 predict a metallic gap, but we see signs in the density of states that may indicate a half-metal in spin down **Figure?**. Using instead the gaussian smearing method results in a gap of 0.063 eV and 0.27 eV in spin down with some partial occupancy in both channels, but much rarer and less impactful in the spin down states (Similar DOS as TBC).

Lastly, the final permutation we did of CFMN (fesi2) was to reduce the amount of Cr. The most dominant display of this is the magnetism, out of the 4 permutations and the baseline system, this was the least magnetic system, according to our calculations with a fixed magnetic configuration. This is not a surprising result recalling that in CFMN fesi2, the magnetic moment was primarily attributed to Cr atoms in the lattice. We find 2 semiconductors (D and E) and 2 half-metals (A and C). Similar to the other systems discussed in this section, the half-metals display a sizable band gap in the spin up direction, 0.39 eV and 0.12 eV respectfully. SCAN calculations result in structure A being a semiconductor with a band gap of 0.015 eV, and B a metal. Of the two semiconductors, both PBE and SCAN agree of a band gap, PBE predict a band gap of 0.1 eV (0.25 up and 0.1 down) in D, and 0.014 eV (0.21 up and 0.08 down) with SCAN. In contrast to both, HSE06 calculations produce a semi-metal with a spin up gap of 0.53 eV. In E we find a band gap of 0.35 and 0.10 eV in the two spin directions, yielding a total gap of 0.084 eV. The SCAN calculations find several nonphysical eigenstates and thus no band gap. From HSE06, we find as before greatly exatereaded band gaps of 0.74 eV in spin up, and 0.25 eV in total. An additional positive regarding this permutation is that the two semiconducting SQSs are the most stable of the set, with D having the highest total energy, followed by E. The least stable supercell is A, it's important to note however that the total energy very similar across all SQSs as seen from the standard deviation in table ..

In this section we have seen that it's definitivly a merit for exploring the quasiternary phase diagram. We find the overall most stable composition by increasing the number of manganese atoms in the composition. Judging from the most stable supercells of the permutations, we can say that the high magnetic moment is attributed to chromium and manganese atoms as in the CFMN (fesi2) system. The same can be saif for the $\text{Cr}_5\text{Fe}_3\text{Mn}_5\text{Ni}_3\text{Si}_{32}$ alloy where we increase the proportions of the magnetic elements Cr and Mn relative to Fe and Ni. From these patterns observed

		Spin up (eV)	Spin down (eV)	Total (eV)
Cr₃Fe₃Mn₇Ni₃Si₃₂	A	0.3390	0	0
	B	0.4745	0	0
	C	0.1342	0	0
	D	0.1950	0.0063	0.0063
	E	0.4211	0	0
Cr₅Fe₅Mn₃Ni₃Si₃₂	C	0.2103	0	0
	D	0.0674	0.0413	0.0372
	E	0.3619	0	0
Cr₅Fe₃Mn₅Ni₃Si₃₂	A	0.2082	0	0
	B	0.4053	0	0
	C	0.4659	0	0
	D	0.0843	0.0121	0.0121
	E	0.3008	0	0
Cr₃Fe₅Mn₅Ni₃Si₃₂	A	0.3922	0	0
	C	0.1285	0	0
	D	0.2595	0.1004	1.004
	E	0.3591	0.1003	0.0848

Table 8.6: Total and spin polarized band gap of 4 permutations of CFMN (fesi2) with PBE GGA calculation. The structures that are excluded from this list either failed in calculations, or does not show any band gap.

in the permutations and the equal distribution of CFMN (fesi2), we can conclude that the magnetic properties of this compound is reliant on chromium and manganese. This is also seen from the magnetism in the permutations where we reduce these elements, ie low magnetic moment. **Something on why one is more stable than the other, and why they all are more stable than equal dist.**

With reference to the band gap, we see from table .. that half-metallic is the most preferred state in most permutaions. This is in line with the eqvimolar distribution, as also here we observed severe spin polarization, mainly spin up, in addition to the semiconducting character. As was the case in CFMN (fesi2), we can not report any concise relation between the stability of the supercells and band gap, except for that the semiconducting SQSs is rarely the most stable of the set, but always above the mean total energy, the exception for this obviously being the chromium reduced alloy in which the two highest energy SQSs both were semiconductors. An interesting observation of the band gap is the relation to the magnetic moment. From table .. we see that the permutations differ in magnetic moment, but internly as highlighted by the standard deviation we also note a variation in the magntic moment. And facinatingly, all reported semiconductors have the identical magnetic moment equal to 5.0000/48. The only exception is the eqvimolar system, were all structures had identical mag equal to 4.0000/48. However, this observation does not

point to any dominating direction as this value is not the minimum or maximum magnetization, so we can not report a relation between high/low magnetization and the band gap.

As a conclusion to this segment we do not find one best direction to explore of the quasiternary phasediagram, as good and promising results was unveiled to some degree in all directions. This definitively motivates the further exploration of the diagram, with the prospect of both improving the properties of the equimolar system and the ability to tune the properties by going in certain directions. In respect to the band gap, the most promising direction seems to be along manganese, as we see the most frequently large band gaps (in spin up) by increasing manganese, and the least frequent by reduction of manganese. For purely semiconducting compounds, reduction of chromium appears as a viable option seen from the 50% ratio of semiconducting to half-metallic ratio. An interesting proposition for future work would thus be to reduce chromium and increase manganese simultaneously.

Conclusion example: In this project we have found many structures that show signs of semiconducting properties, but only CFMN fesi2 produced clear indication through all 3 levels of measures, ie eigenvalues, bandgap.py and dos, 3 levels of depth; PBE, SCAN, HSE06, and 5 levels of width, ie the 5 SQSs

Skriv i introduksjonen av resultater intensjonen vår med å nevne ting som stabilitet og magnetisme, og hvor overfladisk den analysen her. En ordentlig analyse av dette ville involvert mange flere jobber med ulike magnetiske konfigurasjoner og innstillinger. En stabilitetssavhandling ville involvert grundigere relaksering og analyse av gitterparametere og celle, finite temperatur beregninger osv. Hovedvekten i denne oppgaven er på båndgapet

Chapter 9

The bad (Other compositions)

In similar fashion to the preceeding section, we here list the mean and standard deviation of a set of SQSs for different high-entropy silicides of the fesi2 unit cell. The compositions we have selected in this segment is to a degree arbitrary aside from being 3d elements we simply wish to observe the outcome of different alloys in respect to the band gap. The compositions are equimolar distributions of CrFeCoNiSi₂ and CrFeTiNi where manganese is replaced by Cobalt, then Titanium. Furthermore CrFeMnTiSi₂ where the large Ni atoms are replaced by much smaller Ti, and CoFeMnNiSi₂ where Cobalt takes the place of Chromium. Keep in mind, that these SQSs were not simply created by replacing elements in the existing supercells of CFMN (fesi2), but rather generated through TDEP and the SQS theory to form 5 new distinct supercells per composition out of the fesi2 unit cell, identical to how we tested CFMN (fesi2). Additontly, all supercells contain 48 total atoms as before.

	Toten (eV)		Enthalpy of formation	Mag	
CrFeCoNi	- 6.4655	0.0056	-12.7536	0.0083	0.0155
CoFeMnNi	- 6.4731	0.0046	-15.0836	0.0000	0.0000
CrFeTiNi	- 6.4217	0.0087	-7.5040	0.0305	0.0293
CrFeMnTi	-6.6994	0.0071	-7.3060	0.1142	0.0641

The first observation we make of table .. is that the total energy is much lower than CFMN, ie less stable ?. The magnetization follows in line with the topics discussed above, clearly the magnetization is drastically reduced by removing either manganese or chromium. **Vent på svar fra O.M om å sammenligne energier/entalpi på tvers av sammensetninger**

Of the total 20 supercells we calculated in this compositional spectrum, the overwhelming majority are metals. In the CrFeCoNi composition all SQSs were metallic, we performed additional calculations with the SCAN functional that corresponded well with the observed outcome from PBE. From the CrFeTiNi alloy we include the results of SQS A and B, where A display very small gaps in both spin channels with PBE of 0.039 eV and 0.002 eV, but no total band gap. This structure contain defect states in both channels, moreover the spin gaps are not observed in the density of

states. However this could be because of low resolution in the density of states, as we observed in structure C in the CFMN (fesi2) SQS and some of the permutations. Our last measure of calculating the band gap from the pymatgen package point to a metal. From these conflicted results we can not with certainty confirm the observed band gaps in this SQS, as we did in CFMN where all methods were in agreement. We observe a similar case in B, the eigenvalues indicate a small total band gap of 0.008 eV and spin polarized gaps around 0.01 eV, in despite of defect states. But as in A, the gap is not found from other methods of evaluation or functionals.

In the two previous examples we replaced manganese with Co and Ti and found very limited success in regards to our task of finding semiconducting high-entropy silicides. Replacing Cr with Co instead, yielded two semiconducting SQSs A and E. We note that these supercells lie around the mean total energy of the set, but the upmost stable SQSs are metals. The band gap in A is in good agreement throughout all 3 measures to a value of 0.033 eV with PBE and 0.041 with SCAN. What's more the gap transition is consistent across both functionals in contrast to the results of CFMN (fesi2). Surprisingly, the band gap vanishes with HSE06 calculations (TBC). Using gaussian smearing with smearing width 0.005 and 20000 points to calculate the DOS yields a band gap of 0.039 eV. We have found previously for CFMN (fesi2) that these calculations typically are in good agreement with TBC and reliable. On the other hand, the gap is not entirely visible in the density of states, and not found from bandgap.py, but this could be a consequence of the inaccuracy in DOS calculations both with gaussian smearing and a small number of k-points.

In E, we find a band gap of 0.0058 eV from both the eigenvalues and bandgap.py with PBE, and a lesser gap of 0.0037 eV with SCAN. The density of states is not zero at E_f as seen in figure **insert figure**, but show very small values that may indicate a band gap as we have experienced in other cases as well. On the grounds that we find complementary band gaps with both SCAN and PBE from eigenvalues and bandgap.py and no defect states in the eigenvalues, we conclude that this band gap is legitimate despite of the DOS values. We relate this result to the low resolution of 2500 points in calculating the density of states, considering that the gap is very narrow. **Wait for HSE06**

In the final composition of fesi2 based high-entropy silicides tested in this project, we replace Ni atoms with much smaller Ti. As stated in the introduction we find the highest magnetic moment of all compositions with this arrangement, due to the inclusion of both chromium and manganese in the structure. **Most stable?** Among the 5 SQSs of this particular mix, there is a significant variation in the magnetic moment between supercells, the lowest observed magnetic moment is 0.04 in E, and the highest 0.20 in B. We recognize a clear distinction between stability and magnetism in this compound, the 3 lesser magnetic SQSs have very comparable high total energy, and the two highly magnetic supercells are notably less stable.

Write in the conclusion somewhere: In this project, we have read the band gap from our own written script where we evaluate the eigenvalues

from the EIGENVAL file in vasp, used a script called bandgap.py from pymatgen, and considered the density of states. In the structures where we report a band gap, all these 3 have corresponded, additionally the SCAN functional all though most frequently alter the value, agree on the presence of a band gap. However, we have found other structures where the eigenvalues show a small band gap. But due to the fact that the eigenvalues contain defect states, and nonphysical occupancy, the validity of these results are uncertain, and we do not include them unless they are observable from the other methods mentioned above. We will however include some of these in the discussion.

Chapter 10

The ugly (Other symmetry groups)

In the discussion above we have covered in great detail the possibilities of high-entropy silicides based on the β -FeSi₂ 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 CrSi₂ (*P6₄₂₂*), both tetragonal and orthorhombic Mn₁₆Si₂₈ (*P4c2and, Pcca*), and trigonal Fe₂Si (*P3m1*) 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 total energy 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 orthorombic 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 orthorombic cell, so these results could be inaccurate.

Fe2Si 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 Fe2Si **cite** https://www.sciencedirect.com/science/article/pii/S0925838816329796?casa_token=g9DRpU9IClcAAAAA:6Gd12A4Kh9J2igUWMVwHN8OSIKzD27VACA052FNsSAWhRY6PE

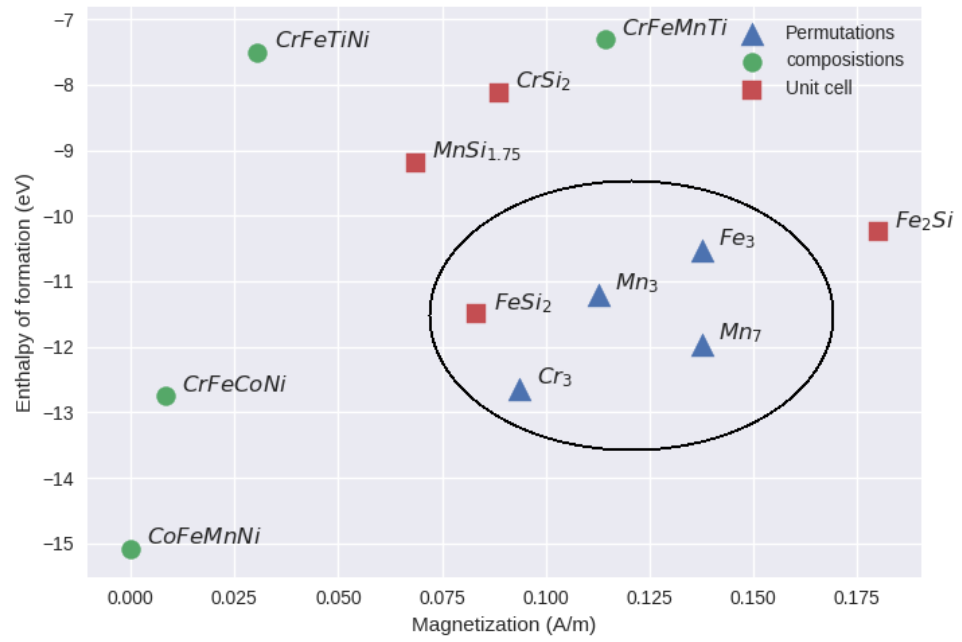
Our results are subject to errors, particularly we note that the eigenvalues used to calculate the gap contain nonphysical values in the spin down channel. However, the gap is evident in the density of states thus we include the result in this report, but acknowledge the uncertainties revolving the value.

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.

Chapter 11

The overview

Summary and discussion of all results.



Part IV

Conclusion

Write conclusion here

Appendix A

Density of states

something

Appendix B

PDFs

something

Appendix C

Charge density