Structural, electronic, optical, and mechanical properties of $Al_{1-x}Z_xNi$ $(Z = Cr, V, Mn, Fe, Co \quad and \quad x = 0.25)$:First principle investigations

Md. Rokonuzzaman

Roll Id:161304
session:2016-2017
Depertment Of Physics

January 9, 2022

Abstract

We report structural, electronic, optical, and mechanical properties of cubic $Al_{1-x}Z_xNi$ ($Z = Cr, V, Mn, Fe, Co and x = 0.25$) are calculated using the full-potential linearized augmented plane wave method in the density functional theory as implemented in WIEN2k code is successfully predicting. The exchange-correlation potential is evaluated using generalized gradient approximation. The calculations of electronic band structure, the density of states show that both compounds have no bandgap. The density of states also revealed the metallic nature of these compounds. We have derived the bulk modulus for. We have found that the elastic constant C11 and C12 are in good correlation with the bonding properties. Bulk modulus B was determined based on the computed values of independent elastic constants C11 and C12. According to our result, both compounds have a metallic appearance. These perovskite compounds are excellent metallic conductors and photovoltaic application is not possible.

Contents

Chapter 1

Introduction

DFT has been actually happening for computations in solid-state physics since the 1970s. Still, DFT wasn't regarded as accurate enough for computations in quantum chemistry until the 1990s, when the approximations applied in the proposition were greatly enhanced to better model the exchange and correlation relations. Computational expenses are fairly low when compared to traditional approaches, similar to exchange only Hartree–Fock approaches and its descendants that contain electron correlation. Since, DFT has become a consequential tool for approaches of Mössbauer spectroscopy similar to nuclear spectroscopy or perturbed angular correlation, in order to derive the origin of specific electric field gradients in crystals.

Currently, computers have become an essential part of the world of modern science, particularly when it comes to calculatory challenges. For challenges that can not be answered analytically, computers and numerical approaches are of pivotal significance. The field of computational chemistry deals with cases with the calculatory determination of powers, charge allocation, di-and multipoles as well as spectroscopic amounts of molecules. Its thing is to get sapience into molecular procedures observed in trials as well as in order to prognosticate them. The determination of molecular and infinitesimal parcels is of analogous significance in the fields of solid-state physics and molecular physics.

The first way to deal with the complex and analytically not popular multiple-body Schrödinger equation was attained by Hartree and Fock, who deduced a set of tone-harmonious, wave-function- grounded equations that allowed an iterative computation of energies and other desired parameters. Up to anymore, the Hartree-Fock system is intensely . applied in atomic and nuclei physics as well as theoretical chemistry. The system has its excrescencies, even so, which will be argued in this report. One of the most consequential ones are the high expense of calculation time when large systems are researched, which .arises, among different effects, from the reliance of the multiple-body wave-function on .3N spatial variables.

A method to lessen the computational expense of molecular computations can thus be the application of a less complicated base variable. The establishment for such an approach has been delivered by Hohenberg and Kohn in 1964 when they proved that the electron density, a variable only depending on 3 spatial variables, in principle contains all data about the ground state properties of a system. This also labeled the birth of density functional theory (DFT) to which the main allowance of this report is adoring. Kohn got the Nobel prize in chemistry for his development of the density-functional theory in 1998.

In 1965 Kohn and Sham deduced a set of self-harmonious, iteratively soluble equations . which eventually allowed applying the up to that point only theoretical notion of Hohenberg and Kohn also ineffective computer simulations. And due to the fact that the electron density is a broadly less complex amount than the wave-function, the calculation times of DFT computations are chiefly lesser.

At the current day, DFT is successfully applied to a broad variety of amount mechanical. problems, similar to the list energies of molecules in chemistry or the computation of band. structures of solids in physics. The adding significance of DFT has been reported by Holthausen and Koch by a comparison of successes for the expressions DFT or density-functional in objectification from about 100 in 1990 to 2500 in 1999.

In 1965 Kohn and Sham derived a set of tone-harmonious, A major element in DFT is alike the option of the correct approximation for the . exchange-correlation functional which arises from the Kohn-Sham approach. A detailed the argument of achievable approximation exceeds the content of this bachelorette thesis, the . the interesting compilation is applied to the book of Holthausen and Koch7 and the papers by Capelle6 as well as Perdew and Kurth.

Chapter 2

Basic Quantum Mechanics

2.1 Schrödingers groundbreaking equation

Erwin Schrödinger's attempt to delineate the so-called matter waves in 1926, where he applied de Broglie's relations to render hypothetical plane waves, which directed to the most the general form of the renowned equation named after him, the time-dependent Schrödinger . equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \hat{H}\Psi(\vec{r},t) \tag{2.1}$$

It's frequently inoperable to use a complete relativistic expression of the formula; thus Schrödinger himself supposed anon-relativistic approximation which is currently frequently used, especially in quantum chemistry.

For a single particle using the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar}{2m}\vec{\nabla}^2 + V(\vec{r},t) \tag{2.2}$$

provides to the (non-relativistic) time-dependent single-particle Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \left[-\frac{\hbar}{2m}\vec{\nabla}^2 + V(\vec{r},t)\right]\Psi(\vec{r},t) \tag{2.3}$$

In this report, only the non-relativistic cases are considered from now.
In three dimensions for N particles , the Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N}\frac{\hat{p_i}^2}{2m_i} + V(\vec{r_1},\vec{r_2},\ldots,\vec{r_N},t) = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i} + V(\vec{r_1},\vec{r_2},\ldots,\vec{r_N},t) \tag{2.4}$$

The corresponding Schrödinger equation becomes

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r_1},\vec{r_2},\ldots,\vec{r_N},t) = \left[-\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i{}^2 + V(\vec{r_1},\vec{r_2},\ldots,\vec{r_N},t)\right]\Psi(\vec{r_1},\vec{r_2},\ldots,\vec{r_N},t) \tag{2.5}$$

2.2 Time independent equation

Special cases are the results of the time-independent Schrödinger equation, where the. Hamiltonian itself has no time- dependence (which implies a time-independent potential $V(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$, and the results, thus, depict standing waves which are called stationary states or orbitals). The time-independent Schrödinger equation isn't only easier to handle, but the knowledge of its results also provides pivotal sapience to manage the alike time-dependent equation.

The time-independent equation is attained by the approach of separation of variables, i.e. the spatial part of the wave function is disassociated from the temporal part via

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\tau(t) = \psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\cdot e^{-i\omega t} \tag{2.6}$$

Hence, the l.h.s. of the equation eradicates to the energy eigenvalue of the Hamiltonian multiplied by the wave function, leading to the general eigenvalue equation

$$E\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = \hat{H}\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) \tag{2.7}$$

Again, using the many-body Hamiltonian, the Schrödinger equation becomes

$$E\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = \left[-\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i{}^2 + V(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)\right]\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t) \tag{2.8}$$

2.3 The wave function

In the last section, the term wave function was constantly used. Thus, and for a . a better understanding of the following a near look at the wave function is taken.

The first and most consequential postulate is that the state of a particle is fully delineated by its (time-dependent) wave function, i.e. the wave function contains all information about the particle's state.

For the sake of plainness, the argument is confined to the time-independent wave function. A question always arising with physical measures is about possible explanations as well as compliances. The Born probability interpretation of the wave function, which ,is a major principle of the Copenhagen interpretation of quantum mechanics, provides a . physical illustration for the square of the wave function as a probability density

$$|\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_2 \ldots d\vec{r}_N \tag{2.9}$$

Equation (2.9) describes the probability that particles $1,2,\ldots,N$ are located coincidentally in the corresponding volume element $d\vec{r}_1 d\vec{r}_2 \ldots d\vec{r}_N$ 7 What happens if the positions of two particles are exchanged, must be accounted as well. Following simply logical logic, the common probability density can not depend on such an exchange, i.e.

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \hat{H}\Psi(\vec{r},t) \tag{2.10}$$

2.4 Atoms and molecules

The charged particles deal with all atomic and molecular systems. For single electron Schrödinger equation where the electron moves in a Coulomb potential,

$$i\hbar\frac{\partial}{\partial t}\Psi\vec{r} = \left[-\frac{\hbar^2}{2m}\vec{\nabla}_i^{\,2} - \frac{e^2}{4\pi\varepsilon_o}.\frac{1}{|\vec{r}|}\right]\psi(\vec{r}) \tag{2.11}$$

For the sake of simplicity, the so- called atomic units are acquainted at this point for posterior operation. That means the electron mass m_e, the fundamental charge e, the reduced Planck constant (Dirac constant) $\hbar$ as well as the vacuum permittivity factor $4\pi\varepsilon_o$ are each set to unity

For the single electron simplifes to the Schrödinger equation

$$E\psi(\vec{r}) = \left[-\frac{1}{2}\vec{\nabla}_i^{\,2} - \frac{1}{|\vec{r}|}\right]\psi(\vec{r}) \tag{2.12}$$

This configuration of the Schrödinger equation is analytically soluble. Although for the depiction of matter, indeed atoms, the Schrödinger equation surpass analytical obtainability soon. Usage of (2.8) allows a structure of a generalized many- body Schrödinger equation for a system composed of N electrons and M nuclei, where external magnetic and electric fields are neglected.

$$E_i\psi_i(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N) = \hat{H}\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N) \tag{2.13}$$

Equation (2.13) doesn't seem overly complicated on the first look, but an examination of the corresponding molecular Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{k=1}^{M}\nabla_k^2 - \sum_{i=1}^{N}\sum_{k=1}^{M}\frac{Z_k}{r_{ik}} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{1}{r_{ij}} + \sum_{k=1}^{M}\sum_{l>k}^{M}\frac{Z_k Z_l}{R_{kl}} \tag{2.14}$$

reveals the real complexity of the equation.

In equation (2.14), M_k represents the nuclear mass in atomic units (i.e. in units of the electron mass), Z_k and Z_l represent the atomic numbers, and $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$, $\vec{r}_{ik} = |\vec{r}_i - \vec{R}_k|$ and $\vec{R}_{kl} = |\vec{R}_k - \vec{R}_l|$ describe the distances between the particles (electron-electron,electron- nucleus and nucleus- nucleus).

A term-by- term exposition of the right- hand side in (2.14) reveals that the first two terms correspond to the kinetic energies of the electrons and nuclei. The ultimate three terms denote the potential part of the Hamiltonian in terms of electrostatic particle- particle interactions. This is rejected by the corresponding signs, where the negative sign denotes an attractive potential between electrons and nuclei, whereas the positive signs denote repulsive potentials between electrons and electrons as well as the nuclei among themselves.

Taking advantage of the fact, that the mass of a proton is approximately 1800 times larger than the mass of an electron, which is the minimum mass ratio of electron to the nucleus (hydrogen atom) and becomes even advanced for massive atoms, another simplification can be introduced. The so- called Born-Oppenheimer approximation states that due to the mass difference the nucleus can be, in comparison to the electrons, regarded nonmoving, i.e. spatially fixed. One can say that the core movement can be neglected on the timescale of electronic transitions which means the core movement has no influence on them

As a result, we have so-called electronic Hamiltonian instead of the general Hamiltonian.

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{k=1}^{M}\frac{Z_k}{r_{ik}} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{1}{r_{ij}}, \tag{2.15}$$

or in terms of operator,

$$\hat{H}_{el} = \hat{T} + \hat{U} + \hat{V} = \hat{T} + \hat{V}_{tot} \tag{2.16}$$

Especially for problems of molecular physics and quantum chemistry, the electronic Schrödinger's equation is of major interest. But despite all simplifications a simple look at equations (2.13) to (2.16) indicates that there are quiet a many further pivotal points left to deal with until a applicable result can be attained.

Examination of equations (2.15) and (2.16) shows that the kinetic energy term $\hat{T}$ doesn't depend on the nuclear variable R_{kl}, or in other words, it's only a function of the electron number. Also, the electron-electron aversion $\hat{U}$ is the same for every system with only Coulomb interactions.

Thus the only part of the electronic Hamiltonian which depends on the atomic the independently molecular system is the external potential $\hat{V}$ caused by the nucleus-electron repulsion.

thereafter, this also means that $\hat{T}$ and $\hat{U}$ only need the electron number N as input and will thus be expressed as' universal', whereas $\hat{V}$ is system-dependent. The expectation value of $\hat{V}$ is also frequently expressed as the external potential $\hat{V}_e xt$, which is harmonious as long as there are no external magnetic or electrical fields.

As soon as the external potential is known, the next step is the determination of the wave functions ψ_i which hold all possible information about the system. As simple as that sounds, the accurate knowledge of the external potential isn't possible for maximum natural systems, i.e. in similarity to classical mechanics, the largest system which can be solved analytically is a 2-body-system, which corresponds to a hydrogen atom. Using all approximations introduced up to now it's possible to calculate a problem alike to H_2, a single ionized hydrogen molecule. To get results for larger systems, further approximations have to be made

2.5 The Hartree-Fock approach

In order to determine a suitable system to approximate the analytically not affordable solutions of many- body problems, a actually useful tool is variational calculus, analogous to the least-action principle of classical mechanics. By the use of variational calculus, the ground state wave function ψ_o, which corresponds to the lowest energy of the system E_o, can be approached. A practical literature source for the principles of variational calculus has been handed by T. Flieÿbach.

Therefore,the Schrödinger equation is interest for only the electronic , therefore in the following sections we use $\hat{H} \equiv \hat{H}_e l$, $E \equiv E_e l$, and so on.

The expectation values of operators are calculated from the observables in quantum mechanics . The Hamilton operator corresponding to observable energy, therefore the energy to a general Hamiltonian can be calculated as

$$E = \langle \hat{H} \rangle = \int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \hat{H} \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{2.17}$$

The actual ground state wave function is different from the main idea of the Hartree-Fock approach is that the energy obtained by any (normalized) trial wave function, is always an upper bound, i.e. higher than the actual ground state energy. If the trial function happens to be the desired ground state wave function, the energies are equal

$$E_{trial} \geq E_o, \tag{2.18}$$

which

$$E_{trial} = \int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \hat{H} \psi_{trial}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{2.19}$$

and

$$E_o = \int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \hat{H} \psi_o(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{2.20}$$

The above expressions are usually inconvenient to handle. For the sake of a compact notation, in the following the bra-ket notation of Dirac is introduced.

In that notation, equations (2.19) to (2.20) are expressed as

$$\langle \psi_t rial | \hat{H} | \psi_t rial \rangle = E_{trial} \geq E_o = \langle \psi_o | \hat{H} | \psi_o \rangle \tag{2.21}$$

The eigenfunctions ψ_i of the Hamiltonian $\hat{H}$ (each corresponding to an energy eigenvalue E_i) form a complete basis set, therefore any normalized trial wave function ψ_{trial} can be expressed as linear combination of those eigenfunctions.

$$\psi_{trial} = \sum_i \lambda_i \psi_i \tag{2.22}$$

The assumption is made that the eigenfunctions are orthogonal and normalized. Hence it is requested that the trial wave function is normalized, it follows that

$$\langle \psi_{trial}|\psi_{trial}\rangle = 1 = \langle \sum_i \lambda_i \psi_i|\hat{H}|\sum_i \lambda_j \psi_j\rangle = \sum_i \sum_j \lambda_i^* \lambda_j \langle \psi_i \psi_j\rangle = \sum_j |\lambda_j|^2 \tag{2.23}$$

On the other hand, following (2.22) and (2.23)

$$E_{trial} = \langle \psi_{trial}|\hat{H}|\psi_{trial}\rangle = \langle \sum_i \lambda_i \psi_i|\hat{H}|\sum_i \lambda_j \psi_j\rangle = \sum_j E_j |\lambda_j|^2 \tag{2.24}$$

Together with the fact that the ground state energy E_o is per definition the lowest possible energy, and therefore has the smallest eigenvalue ($E_o \leqslant E_i$), it is found that

$$E_{trial} = \sum_j E_j |\lambda_j|^2 \leqslant E_o \sum_j |\lambda_j|^2 \tag{2.25}$$

what resembles equation (2.21)

The mathematical framework used above, i.e. rules which assign numerical values to functions, so called functionals, is also one of the main concepts in density functional theory. A function gets a numerical input and generates a numerical output whereas a functional gets a function as input and generates a numerical output.

2.6 Limitations and failings of the Hartree-Fock approach

Atoms as well as molecules can have an even or odd number of electrons. If the number of electrons is even and all of them are located in double occupied spatial orbitalsψ_i , the . compound is in a singlet state. Such systems are called closed- shell systems. Composites with an odd number of electrons as well as composites with single occupied orbitals, i.e. species with triplet or higher ground state, are called open- shell systems respectively. These two types of systems correspond to two different ways of the Hartree-Fock system. In the confined HF system (RHF), all electrons are considered to be paired .in orbitals whereas in the unrestricted HF (UHF)- system this limitation is lifted completely. It's also possible to describe open- shell systems with an RHF approach where only the single occupied orbitals are excluded which is also called a confined open- shell HF (ROHF) which is an approach closer to reality but also more complex and thus less popular than UHF.7 There are also closed- shell systems that bear the unrestricted approach in order to get proper results. For case, the description of the dissociation of H_2 (i.e. the behavior at a large internuclear distance), where one electron must be located at one .hydrogen snippet, can logically not be acquired by the use of a system that places both . electrons in the same spatial orbital. Thus the choice of system is always a veritably important point in HF calculations.1

The size of the investigated system can also be a limiting factor for calculations. Kohn states a number of $M = p^5$ with $3 \leq p \leq 10$ parameters for a result with sufficient accuracy in the investigation of the H_2 system. For a system with $N = 100$ (active) electrons the number of parameters rises to

$$M = p^{3N} = p^{100} \quad to \quad 10^{300} \approx 10^{150} \quad to \quad 10^{300} \tag{2.26}$$

Equation (2.26) states, that the minimization of the energy would have to be performed in a space of at least 10^{150} dimension which exceeds the computational possibilities nowadays by far. HF-methods are therefore restricted to systems with a small number of involved electrons ($N \approx 10$). Referring to the exponential factor in (2.26) this limitation is sometimes called exponential wall. Since a many electron wave function cannot be described entirely by a single Slater determinant, the energy obtained by HF calculations is always larger than the exact ground state energy. The most accurate energy obtainable by HF-methods is called the Hartree-Fock-limit.

The difference between E_{HF} and E_{exact} is called correlation energy and can be denoted

$$E_{corr}^{HF} = E_{min} - E_{HF} \tag{2.27}$$

Despite the fact that E_{corr} is usually small against E_{min}, as in the example of a N_2 molecule where

$$E_{corr}^{HF} = 14.9eV < 0.0001.E_{min} \tag{2.28}$$

it can have a huge influence

For instance, the experimental dissociation energy of the N_2 molecule is

$$E_{diss} = 9.9eV < E_{corr} \tag{2.29}$$

which corresponds to a large contribution of the correlation energy to relative energies such as reaction energies which are of particular interest in quantum chemistry

The main contribution to the correlation energy arises from the mean field approximation used in the HF-method. That means one electron moves in the average field of the other ones, an approach which completely neglects the intrinsic correlation of the electron movements. To get a better understanding what that means, one may picture the repulsion of electrons at small distances which clearly cannot be covered by a mean-field approach like the Hartree-Fock-method

Chapter 3

Density functional theory

3.1 A new base variable - the electron density

In the section 2.3 about the wave function ψ , a general statement about the calculation of observables has been provided. A quantity calculated in a very similar way is the topic of this section. The electron density (for N electrons) as the basic variable of density functional theory is defined as

$$n(\vec{r}) = N \sum_{s_1} \int d\vec{x}_2 \ldots \int d\vec{x}_N \psi^*(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) \psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) \tag{3.1}$$

What has to be mentioned is that the notation in (3.1) considers a wave function dependent on spin and spatial coordinates. In detail, the integral in the equation gives the probability that a particular electron with arbitrary spin is found in the volume element $d\vec{r}_1$. Due to the fact that the electrons are indistinguishable, N times the integral gives the probability that any electron is found there. The other electrons represented by the wave function $\psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$ have arbitrary spin and spatial coordinates

If additionally the spin coordinates are neglected, the electron density can even be expressed as measurable observable only dependent on spatial coordinates

$$n(\vec{r}) = N \int d\vec{r}_2 \ldots \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{3.2}$$

which can e.g. be measured by X-ray diffraction

Before presenting an approach using the electron density as variable, it has to be ensured that it truly contains all necessary informations about the system. In detail that means it has to contain information about the electron number N as well as the external potential characterized by $\hat{V}$.The total number of electrons can be obtained by integration the electron density over the spatial variables

$$N = \int d\vec{r} n(\vec{r}) \tag{3.3}$$

What is left to proof is that also the external potential is characterized uniquely by the electron density, where uniquely means up to an additive constant.

3.2 The Hohenberg-Kohn theorems

The basic lemma of Hohenberg-Kohn states that not only $n(\vec{r})$ is a functional of$v(\vec{r})$ but that also $v\vec{r}$ is up to a constant determined by $n(\vec{r})$ uniquely

Since the original publication of Hohenberg and Kohn deals with an electron gas, the Hamiltonian is resembled by the electronic Hamilton operator introduced in equation (2.17), $\hat{H}_{el} = \hat{T} + \hat{V} + \hat{U}$, with the one difference that the non-universal contribution $\hat{V}$ in this case represents a general external potential (which in case of the electronic Hamilton approximated by Born-Oppenheimer contains a nuclear field contribution).

Following the original approach of Hohenberg and Kohn, accompanied by their proof via reductio ad absurdum, the discussion in this thesis is restricted to non-degenerate ground states. This restriction nevertheless doesn't affect the presented proof for the second theorem and can be lifted as well for the first theorem

The energy of the system can be denoted

$$E = \langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{T} + \hat{U} + \hat{V}|\psi\rangle = \int v(\vec{r})n(\vec{r})d\vec{r} + \langle\psi|\hat{T} + \hat{U}|\psi\rangle \tag{3.4}$$

which will be used for the proof of Hohenberg and Kohn's first theorem

Theorem The external potential $v(\vec{r})$ is a functional of the electron density$n(\vec{r})$ and, up to an unimportant constant, uniquely determined by it.

3.3 The Kohn-Sham equations

The framework by Hohenberg and Kohn is exact, yet not very useful in actual calculations. The only possibility would be the direct use of the second Hohenberg-Kohn theorem for energy minimization, a way that is possible in general but has proven itself to be impractical. The most desirable way in which quantities can be calculated for problems without an exact analytical solution is one that allows iterations

An early example of an iterative approach are the self-consistent single particle Hartreee-quations. Of course, the Hartree-equations are clearly wave-function based and not directly related to the work of Hohnberg and Kohn, yet they have been proven very useful. Hartree's approximation assumes that every electron moves in an effective single-particle potential of the form

$$v_H(\vec{r}) = -\frac{Z}{|\vec{r}|} + \int \frac{\vec{r}'}{|\vec{r} - \vec{r}'|} \tag{3.5}$$

The first term is an attractive Coulomb potential of a nucleus with atomic number Z, whereas the integral term corresponds to the potential caused by the mean electron density distribution $n(\vec{r})$.

The mean density can be denoted in terms of the single particle wave functions

$$n(\vec{r}) = \sum_{j=1}^{M} |\phi_j \vec{r}|^2 \tag{3.6}$$

It is important to mention that the sum in (3.6) runs over the M lowest eigenvalues in accordance to the Pauli principle.

Chapter 4

Result and discussion

4.1 Density of state

The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy. DOS calculations allow one to determine the general distribution of states as a function of energy and can also determine the spacing between energy bands. Also, the Density of state describes the probability of electron distribution in the energy spectrum.

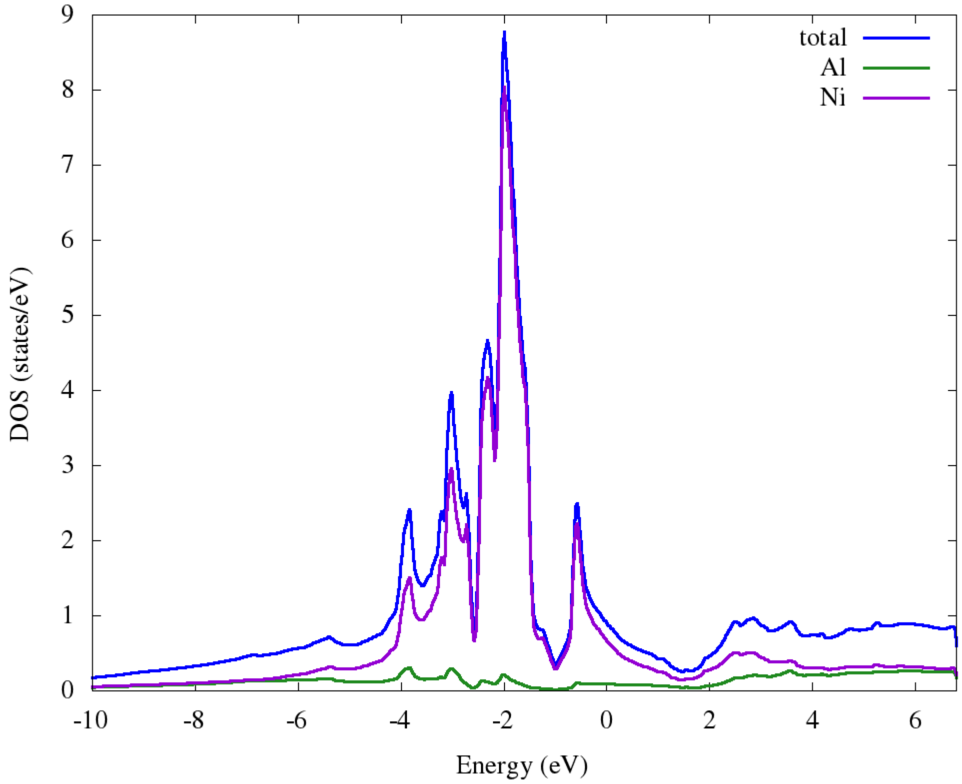

Figure 4.1: Total density of states plotted using PBE potential for AlNi

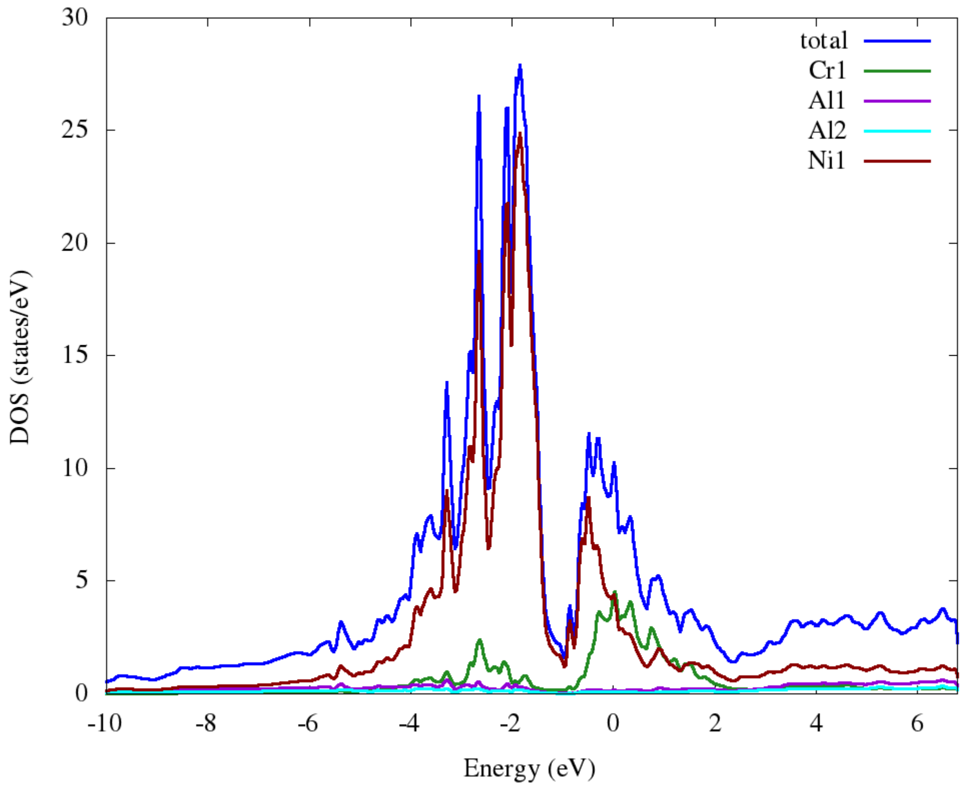

Figure 4.2: Total density of states plotted using PBE potential for AlNiCr

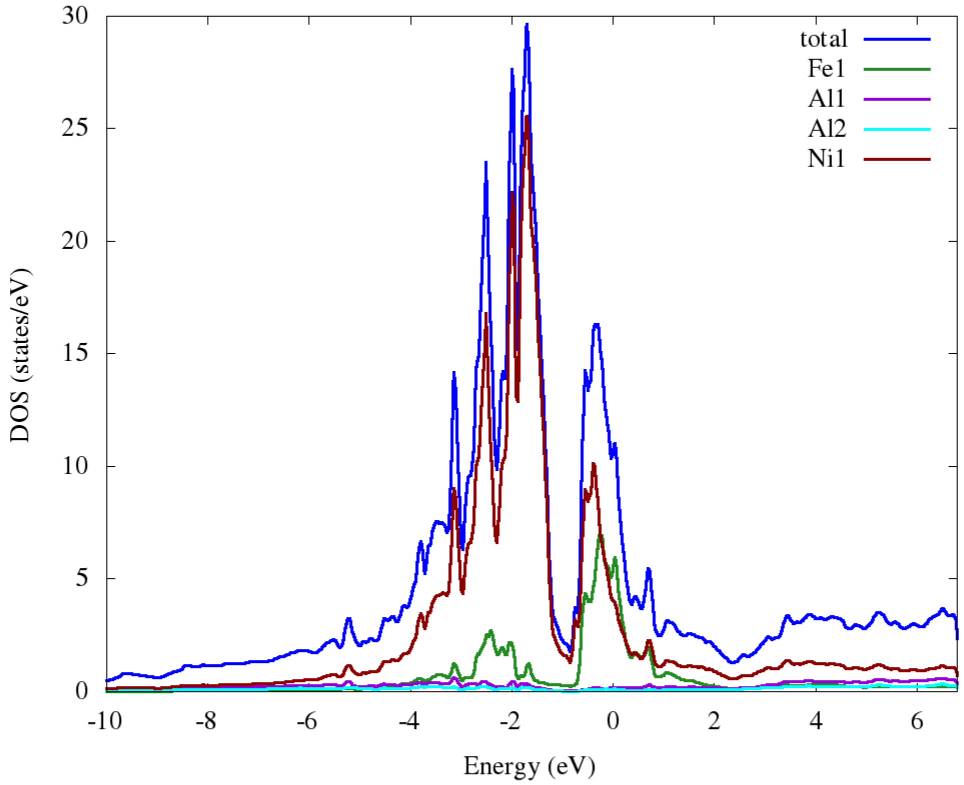

Figure 4.3: Total density of states plotted using PBE potential for AlNiFe

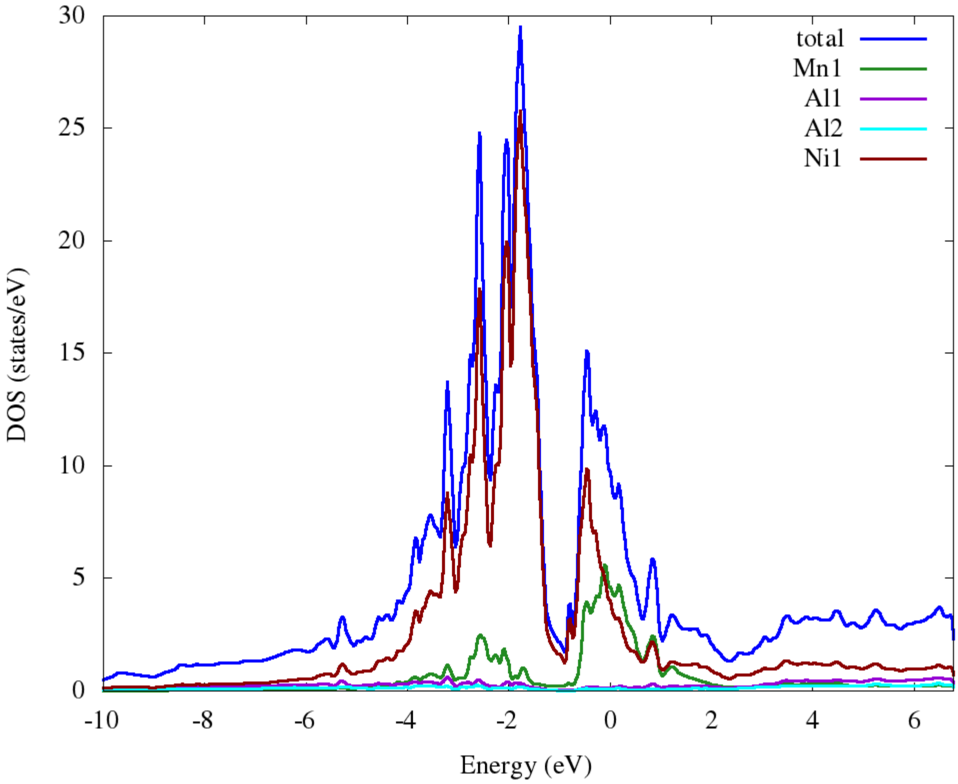

Figure 4.4: Total density of states plotted using PBE potential for AlNiMn

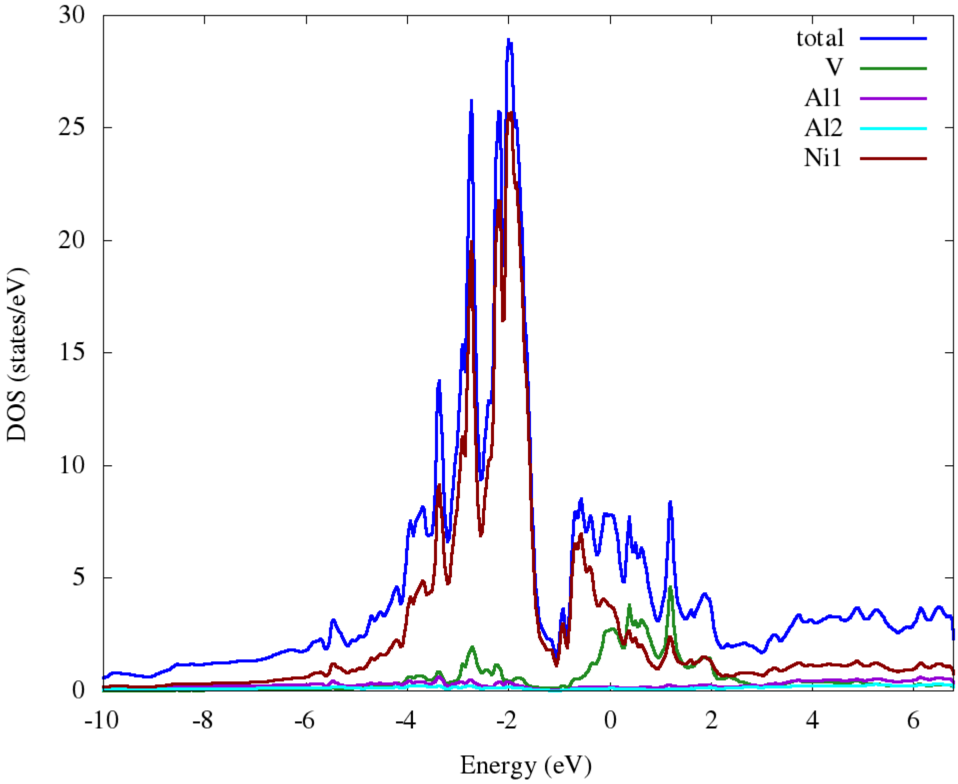

Figure 4.5: Total density of states plotted using PBE potential for AlNiV

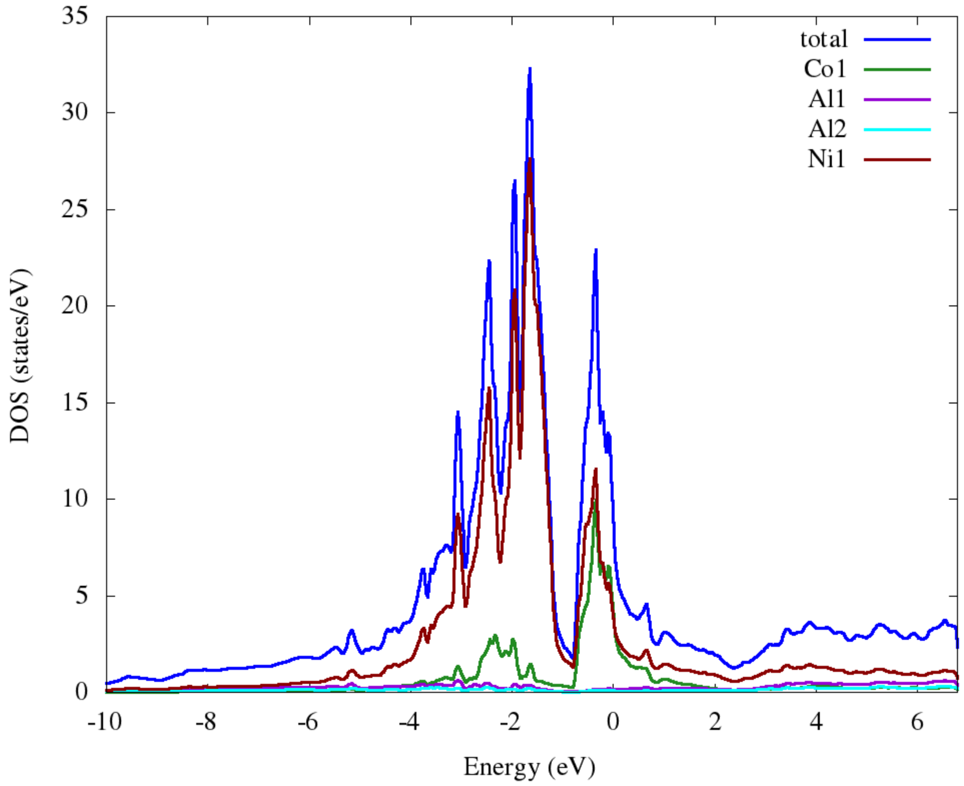

Figure 4.6: Total density of states plotted using PBE potential for AlNiCo