UNIVERSITI PUTRA MALAYSIA

DENSITY FUNCTIONAL STUDY FOR STRUCTURAL, ELECTRONIC, MAGNETIC AND CHEMICAL BONDING PROPERTIES OF GEOMETRICALLY-FRUSTRATED CdCr2O4

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By

NAJMEH BOLANDHEMAT

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

This thesis is dedicated to God Almighty as well as to my precious parents,
Amir Bolandhemat and Zeinab Saber.

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

DENSITY FUNCTIONAL STUDY FOR STRUCTURAL, ELECTRONIC, MAGNETIC AND CHEMICAL BONDING PROPERTIES OF GEOMETRICALLY-FRUSTRATED $CdCr_2O_4$

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Chairman : Md. Mahmudur Rahman, PhD
Faculty : Science

Spinels are an attracting class of materials that demonstrate rich complex behaviors at ground states. Among spinel materials, chromium spinels span an enormous range of magnetic exchange strengths and different magnetic ground states. Spinel oxides AB_2O_4 with magnetic B cations have received special attention due to their identification by three-dimensional geometrical frustration. The physics of frustrated magnetism is a subject of existing interest. Spinel oxides with Cr^{3+} ions on the B sites are good examples to study the frustration.

Geometrically frustrated spinel $CdCr_2O_4$ has been chosen as a model system to study because it has a well-defined magnetic order with a single ordering wave vector. Spinel $CdCr_2O_4$ is a magnetic compound that crystallizes into a cubic spinel structure, and the magnetic properties stem from the Cr^{3+} magnetic ions, that are a three-dimensional network of corner-sharing tetrahedral.

In the present work, density functional calculations are performed to investigate the effects of magnetic ordering on the electronic structure and bonding properties of $CdCr_2O_4$ with non-magnetic Cd cations and magnetic Cr cations from a pyrochlore lattice, by examining the crystal structure of spinel $CdCr_2O_4$ and followed by analyzing the electronic and magnetic properties that are important in magnetic spinel oxides. The structural, electronic, and chemical bonding properties of geometrically frustrated spinel $CdCr_2O_4$ with cubic $(F\bar{d}3m)$ and tetragonal $(I4_1/amd)$ structures have been calculated using density functional method combined with the spin-polarized theory, and compared the results in both cubic and tetragonal structures for different magnetic orderings. Density functional theory applied with the ground-state theory recovered in the zero temperature limit.

In order to optimize the crystal structures of spinel $CdCr_2O_4$, the plane-wave Ultrasoft pseudopotential technique is used within the generalized gradient approximation. XCrySDen graphic software is applied as a crystalline and molecular structure visualization program to visualize this system. In order to calculate the total energy, the exchange and correlation functional is described within the generalized gradient approximation based on exchange-correlation energy optimization. The optimization of atomic positions and cell parameters is approved through the minimization of energy using Hellman-Feynman forces acting on atoms with the Broyden-Flecher-Goldfarb-Shanno scheme and to get the actual relaxed atomic positions and cell parameters for each element the PWscf (VC-relax) input code is applied.

To search for the most stable structure of spinel $CdCr_2O_4$ in term of magnetic ordering, the lowest energy in each structure with different magnetic ordering is calculated. What is important for this work is to converge the parameters by applying the scf convergence test, in order to find the actual kinetic energy cutoff and k-point in different crystal structures and also to determine the structural properties of spinel $CdCr_2O_4$, in term of lattice parameters, symmetry properties and charge density distributions in different magnetic configurations. Fallowing that, the effect of magnetism is obtained and analyzed on the basis of total density of states, projected density of states, and charge density distribution within paramagnetic, ferromagnetic and antiferromagnetic orderings using density functional calculations and understanding of the principles of Quantum ESPRESSO in magnetic materials. In continue, to complete the findings of the electronic density of states for spinel $CdCr_2O_4$, the density of states for each atom is calculated, in order to analyze the band gap in each state, separately. Finally, the electronic charge density distribution in the (1 1 0) crystallographic planes are obtained, for both cubic and tetragonal structures, to explain and compare the bonding properties of spinel $CdCr_2O_4$ in paramagnetic, ferromagnetic and antiferromagnetic orderings.

Abstrak tesis yang dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGIRAAN FUNGSIAN DIKAJI UNTUK CIRI-CIRI STRUKTUR, ELEKTRONIK, MAGNET DAN IKATAN KIMIA $CdCr_2O_4$ BERFRUSTRASI-GEOMETRI

Oleh

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Spinel adalah satu kelas bahan menarik yang menunjukkan sifat kompleks yang kaya pada keadaan dasar. Antara bahan spinel, spinel kromium merentangi renj kekuatan tukar ganti magnet yang besar dan mempunyai pelbagai keadaan dasar magnet. Oksida spinel AB_2O_4 denagan kation magnet B telah menerima perhatian khas kerana bahan ini dapat dicam dengan frustrasi geometri tiga dimensi. Fizik kemagnetan frustrasi adalah satu subjek yang menarik kini. Oksida spinel dengan ion Cr^{3+} pada tapak B adalah contoh yang baik untuk dikaji frustrasi.

Spinel $CdCr_2O_4$ berfrustrasi geometri dipilih sebagai sistem model untuk dikaji kerana ia mempunyai tertib magnet yang tertakrif rapi dengan vektor gelombang bertertib tunggal. Spinel $CdCr_2O_4$ adalah sebatian magnet yang terhablur kepada struktur spinel kubus dengan sifat magnetnya datang daripada ion bermagnet Cr^{3+}, yang berbentuk rangkaian tetrahedron berbucu sepunya.

Dalam kajian ini, pengiraan fungsian ketumpatan dibuat untuk mengkaji kesan tertiban magnet ke atas struktur elektronik dan ciri ikatan $CdCr_2O_4$ dengan kation Cd yang tak bemagnet dengan kation Cr bermagnet daripada kekisi piroklor, dengan pemeriksaan struktur hablur spinel $CdCr_2O_4$ dan diikuti dengan analisis ciri-ciri elektronik dan magnet yang penting dalam oksida spinel bermagnet. Struktur elektronik, ciri magnet dan ciri ikatan kimia bagi spinel $CdCr_2O_4$ berfrustrasi geometri dengan struktur kubus ($F\bar{d}3m$) dan tetragon ($I4_1/amd$) telah dikira menggunakan kaedah fungsian ketumpatan digabung dengan teori pengutuban spin, dan keputusan dibandingkan bagi kedua-dua struktur kubus dan tetragon untuk tertib bermagnet berbeza. Teori fungsian ketumpatan diaplikasi bersama teori keadaan dasar dipulih semula dalam had suhu sifar. Bagi

mengoptimumkan struktur hablur $CdCr_2O_4$, teknik gelombang satah Pseudo-Keupayaan Ulltralembut (USP) diguna dalam penghampiran kecerunan teritlak (GGA). Perisian grafik XCrySDen diguna sebagai program visualisasi struktur hablur dan molekul bagi mengvisualisasi sistem ini. Bagi tujuan mengira jumlah tenaga, fungsian tukarganti dan korelasi diperihal dalam penghampiran kecerunan teritlak berdasarkan pengoptimuman tenaga tukarganti-korelasi. Pengoptimuman kedudukan atom dan parameter sel disahkan melalui meminimumkan tenaga dengan daya Hellman-Feynman bertindak ke atas atom dengan skema Broyden-Flecher-Goldfarb-Shanno dan bagi mendapatkan kedudukan atom santaian dan parameter sel bagi setiap unsur, kod input PWscf (VC-relax) diaplikasikan.

Bagi mencari struktur spinal $CdCr_2O_4$ yang paling stabil berasaskan tertib bermagnet, tenaga paling rendah bagi setiap struktur dengan tertib bermagnet berbeza dikirakan. Apa yang penting bagi kajian ini adalah penumpuan parameter dengan aplikasi ujian penumpuan scf, bagi mencari penggalan tenaga kinetic sebenar dan titik-k dalam struktur hablur berbeza dan juga bagi menentukan ciri struktur spinel $CdCr_2O_4$, dalam sebutan parameter kekisi, ciri simetri dan taburan ketumpatan cas dalam konfigurasi bermagnet yang berbeza. Seterusnya, kesan kemagnetan diperolehi dan dianalisis berasaskan jumlah ketumpatan keadaan, ketumpatan keadaan yang diunjurkan, dan taburan ketumpatan cas bagi tertib paramagnet, feromagnet dan antiferomagnet menggunakan pengiraan fungsian ketumpatan dan kefahaman prinsip Quantum ESPRESSO dalam bahan bermagnet. Seterusnya, bagi melengkapkan penemuan ketumpatan keadaan elektronik bagi spinel $CdCr_2O_4$, ketumpatan keadaan bagi setiap atom dikira untuk tujuan analisis jurang jalur bagi setiap keadaan secara berasingan. Akhir sekali taburan ketumpatan cas electron dalam satah kristalografi (1 1 0) diperolehi bagi kedua-dua struktur kubus dan tetragon, untuk penjelasan dan perbandingan ciri-ciri spinel $CdCr_2O_4$ dalam tertib paramagnet, feromagnet dan antiferomagnet.

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I certify that a Thesis Examination Committee has met on 19 January 2017 to conduct the final examination of Najmeh Bolandhemat on her thesis entitled "Density Functional Study for Structural, Electronic, Magnetic and Chemical Bonding Properties of Geometrically-Frustrated $CdCr_2O_4$" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the supervisory committee were as follows:

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LIST OF ABBREVIATIONS

AFM	Antiferromagnetic
BFGS	Broyden Fletcher Goldfarb Shanno
BOA	Born-Oppenheimer approximation
BZ	Brillouin Zone
CF	Crystal Field
CW	Curie-Weiss
DFPT	Density Functional Perturbation Theory
DFT	Density Functional Theory
DOS	Density of States
E_{cut}	Cut-off Energy
ECUTRHO	Kinetic Energy Cut-off of Charge Densities
ECUTWFC	Kinetic Energy Cut-off of Wave Functions
E_F	Energy or Fermi energy
FCC	Face Centered Cubic
FFT	Fast Fourier Transforms
FM	Ferromagnetic
GGA	Generalized Gradient Approximation
HS	High Spin
HSC	Hamann-Schlüter-Chiang
IBZ	Irreducible Brillouin Zone
JT	Jahn Teller
KS	Kohn and Sham
LDA	Local Density Approximation
LMTO	Linear Muffin-Tin Orbital
LS	Low Spin
LSDA	Local Spin-Density Approximation
PBE	Perdew, Burke, and Ernzerhof
PDOS	Projected Density of States
PM	Paramagnetic
PP	Pseudo Potentials
PW	Plane-Waves
PWscf	Plane-Wave Self-Consistent Field
QE	Quantum ESPRESSO
SCF	Self-Consistent Field
TM	Transition-Metal
T_N	Néel Temperature
UEG	Uniform Electron Gas
USP	Ultrasoft Pseudo-Potentials
VASP	Vienna Ab Initio Simulation Package
WFT	Wave Function Theory
ΔCF	Crystal Field Splitting

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

For over two decades, one of the major research concerns in both theoretical and experimental condensed matter physics has been predicting a novel material, or rather producing a simple method that can explain some of the known physical properties of these novel materials. Spinels are a captivating class of materials that indicate rich complex behavior and novel ground states such as large magnetoresistance effects (Ramirez et al., 1997), non-collinear spin configurations (Yafet, & Kittel, 1952), magnetodielectric coupling (Lawes et al., 2006), and spin liquid states (Kemei et al., 2013). Spinel is the magnesium aluminum oxide member of this large group of materials with the following formula, $Mg^{2+}Al^{3+}{}_2O^{2-}{}_4$. It gives its name to the family of compounds that are identified by two cation sites: an octahedral site and a tetrahedral site (Finger et al., 1986). Any material that have the general formula of $A^{2+}[B^{3+}]_2[X^{2-}]_4$ which crystallizes in the face-centered cubic crystal system and are described by the space group $F\bar{d}3m$ (No. 227) are labeled as a spinel.

Spinel-type compounds with the general formula of AB_2X_4 (A, B=transition-metal, X=oxides, chalcogenides) have attracted extensive interest not only due to their diverse properties but also wide applications in electronics, catalysis, magnetism and electrochemical technologies, these including i.e. batteries, fuel cells and electrolysers (Yamasaki et al., 2006; Hemberger et al., 2005; Xie et al., 2009; Thackeray, 1997). Spinels are traditionally synthesized through solid-state methods involving grinding and firing the mixtures of the corresponding metal oxides, nitrates or carbonates (Armijo, 1969; Lu et al., 2014), which require elevated temperature and prolonged time in order to overcome the reaction energy barriers (Stein et al., 1993). The prepared spinels often show irregular shape, large particle size and low surface area, all these factors seriously affecting their physicochemical properties.

Chromium spinel compounds with the general formula ACr_2X_4 (where A = Cd, Zn, Hg, Ga, Cu; X = S, Se, O) have been analyzed during the last decades due to their interesting structural, electronic, and magnetic properties (Krok-Kowalski et al., 2004; Parker et al., 2004; Warczewski et al., 2003) . The spinels are perfect materials for many current technological applications such as magnetic sensors used as the read-write heads in the computer hard discs or as the temperature sensors.

Since many of the spinels are common minerals, they also have great geological and geophysical interest; especially chromium spinel is regarded as important petrogenetic indicator in ultramafic to mafic rocks (Fan et al., 2008). It is also known fact that some chromium spinels, e.g. $HgCr_2S_4$ and $CdCr_2S_4$ exhibit multiferroic behavior. Chromium spinels with a specific formula ACr_2X_4, where A= Zn, Cd, or Hg is a divalent nonmagnetic cation and X = O, S, or Se is a divalent anion are investigated. The Cr^{3+} ion is in the $3d^3$ configuration, its three 3d electrons occupy the t_{2g} levels with total spin S=3/2. The Cr-sublattice is designed by corner sharing tetrahedral named as pyrochlore lattice which displays a highly frustrated geometry of antiferromagnetically coupled spins. Although charge and orbital degrees of freedom in the ACr_2X_4 spinels are frozen out because electrons are localized by a strong Coulomb repulsion, and only spin degrees of freedom remain in the ground and lowest excited states, these compounds show a wide variety of magnetic properties ranging from those of a strongly frustrated antiferromagnet to a Heisenberg ferromagnet. In the ACr_2O_4 spinels, antiferromagnetic nearest-neighbor interactions between Cr spins residing on a pyrochlore lattice are geometrically frustrated. The magnetic ground state of a frustrated antiferromagnet is highly degenerate which leads to infrequent low-temperature properties.

Electron correlation in condensed matter always seems to throw up a plethora of novel, exotic, and complex phenomena that routinely destabilizes every attempt to formulate or formalize understanding. In the last few decades several challenges are posed by the high temperature superconductors, colossal magneto resistance materials, spin glasses, and frustrated systems, just to name few. Experimental and theoretical tools have been stretched to their limits to comprehend the complexities, but the horizon of convergence appears to recede further and further. Amongst the complex, correlated condensed matter systems, 'frustrated systems' are a class in itself and they exhibit novel ground states like spin liquids, spin ice, and valence bond solids. The spinel compounds amongst these are unique in exhibiting such unconventional ground states. Ordering of the charge degree of freedom in a spinel system is a rare and contested phenomenon. Very few spinel compounds have shown coupling of the charge degree of freedom with the lattice as against a number of those that have shown frustration and ordering of spin degrees of freedom.

Investigations of electronic structures of different functional materials using quantum mechanical simulation has become a practically optional tool in present day science. This understanding is a key feature behind the tailoring of new materials for specific applications such as spin based electronics, energy applications, drug designs, and catalysis being just few worth mentioning. Besides the physical and life science contributions in this field it is valuable to remark the existing advancement of computer hardware and software which also acts as a motivation to the magnificent growth in this field. To deal with a larger molecular system one needs to make a compromise between the computational cost and the accuracy of results. In this respect, density functional theory has become the preferred method for electronic structure theory, as its cost scales favorably

with system size in comparison to the cost of other expensive quantum mechanical method that is based on wave function theory. In addition to reasonable computational cost, it also competes well in terms of accuracy.

A breakthrough in these computational efforts was recognized in 1964 when Walter Kohn et al. developed the density functional theory; a theory based on electron density, which is a function of only three spatial coordinates (Hohenberg, & Kohn, 1964; Kohn, & Sham, 1965). The Kohn–Sham equations of density functional theory cast the intractable complexity of the electron–electron interactions into an effective single-particle potential determined by the exchange-correlation functional. This exchange-correlation functional (i.e. a function whose argument is another function) explains the complex kinetic and energetic interactions of an electron with other electrons.

In the present work, it is mainly focused on frustrated magnetism, which is formed by the simple and unique geometry of the spinel structure. The spinel structure with the chemical formula AB_2X_4 (X=O, S, Se), is one of the most frequently stabilized amongst the wide variety of structural categories in complex transition-metal oxides and chalcogenides. Due to the existence of many antiferromagnetic spinels preferring the oxide state rather than chalcogenides state, the major considerations is restrict basically to oxides. Materials with the spinel structure have provided physicists with a surprisingly rich variation of phenomena, few of these being ferromagnetism, ferrimagnetism, and Jahn-Teller transitions (Kugel, & Khomskii, 1982; Feiner et al., 1997). More recently, the spinels have attracted increasing interest as a playground for the physics of frustration.

Study on spinel materials such as $ZnCr_2O_4$ and $CdCr_2O_4$ with frustrated crystal structures are among the best options when it comes to energy source as this is a clean and non-polluted way of energy generation (Chung et al., 2005; Lee et al., 2004). With the help of theoretical study based on density functional calculations, the detailed properties of such novels energy based materials are provided for more experimental research. For the present study purpose, $CdCr_2O_4$ has been chosen as a model system. While its frustration factor is smaller than that of $ZnCr_2O_4$, $CdCr_2O_4$ is preferred as it has a well-defined magnetic order with a single ordering wave vector. In the case of $CdCr_2O_4$, the first-principles calculation for these systems can provide valuable information about structural, electronic structure, and magnetic properties of $CdCr_2O_4$ by using density fuctional calculatation method.

1.2 Problem Statement of the Research

Within the past 20 years, there has been an explosion of attention in the magnetic behavior of pyrochlore oxides of the type AB_2O_4 in which A is a rare-earth ion and B is generally a transition metal. Both A and B sites produce a network of corner

sharing tetrahedral, which is the quintessential framework for a geometrically frustrated magnet. In these systems, the expected tendency to form long-range ordered ground states in accord with the third law of thermodynamics at absolute zero temperature is frustrated, resulting in some original short-range ordered alternatives such as spin ices, spin glasses, and spin liquids. This research aims to analyze and evaluate some of the properties found in pyrochlore oxides, essentially from a materials perspective with an applicable theoretical context.

In the search for complex oxide materials incorporating technologically functional properties, one of the most studied structural families is spinels. In fact, the earliest discovery of magnetism itself can be attributed to the discovery of the mineral lodestone, which contains naturally polarized magnetite: a spinel with the composition Fe_3O_4. Investigation into spinels, whose general formula is AB_2X_4, began in 1915 when Bragg and Nishikawa published the first descriptions of the structure via X-ray diffraction (Bragg, 1915; Nishikawa, 1915). Barth and Posnjak presented a more detailed description of the cation distribution between the sites and introduced the idea of the inverse spinel in 1932 (Barth, & Posnjak, 1932). Early work on potential technological applications for spinels such as in ferrite cores was led by Lotgering, Jonker, and Blasse at the Philips Research Lab in Eindhoven throughout much of the 1950's and 60's. The list of related physical phenomenon that have been discovered since then has grown to include magnetoresistance ($LiMn_2O_4$ (Basu et al., 2000), $FeCr_2S_4$ (Lang et al., 2000; Ramirez et al., 1997)), superconductivity ($CuRh_2S_4$ (Bitoh et al., 1992; Dawes, & Grimes, 1975), $LiTi_2O_4$ (Johnston et al., 1973)), spin driven Jahn-Teller distortions (MCr_2O_4, M = Zn (Lee et al., 2000; Lee et al., 2007), Cd (Matsuda et al., 2007)) and metal-insulator transitions (Fe_3O_4 (Verwey, & Haayman, 1941; Verwey et al., 1947)).

It has been known for over 40 years that chromium spinels (ACr_2X_4) span an enormous range of magnetic exchange strengths and different magnetic ground states (Baltzer et al., 1966). As a function of lattice constant, or equivalently as a function of Cr-Cr separation, these compounds are categorized by Curie-Weiss temperatures from -400 K to 200 K and, at low temperatures, expose both complex antiferromagnetism and ferromagnetism with different crystal structures. The chromium oxide-spinels undergo antiferromagnetic ordering with the transition of order 10 K, in spite of the fact that the exchange interactions, as deduced from the paramagnetic Curie-Weiss temperatures, are one order of magnitude larger. This can be clarified by the fact that the Cr spins reside on a pyrochlore lattice revealing strong geometrical frustration.

Meanwhile, $CdCr_2O_4$ is a magnetic compound that crystallizes into what is recognized as a cubic spinel structure, and the magnetic properties stem from the Cr^{3+} ions that create a network of corner-sharing tetrahedral (Lee et al., 2000; Tchernyshyov et al., 2002). Despite the presence of relatively strong antiferromagnetic, nearest-neighbor interactions between these ions, the peculiar

spatial arrangement of the Cr atoms within the spinel structure serves to suppress magnetic order. Actually, true long-range, elastic magnetic order is set up just after cooling to the Néel temperature (T_N = 7.8 K), which is one order of magnitude smaller than the Curie-Weiss temperature ($|\theta_{CW}|$ = 88 K), the temperature at which magnetic order is predicted. Moreover, a structural transition, where the dimensions of the cubic unit cell distort tetragonally such that c > a = b, occurs at the same temperature as the onset of long-range magnetic order at T_N . Below T_N, $CdCr_2O_4$ displays standard spin wave excitations, which are inelastic features characteristic of ordered magnetic phases (Chung et al., 2005).

Furthermore, the modeling of materials has become a very useful tool to make reliable predictions of the electronic, structural, and magnetic properties of novel hard materials. Several approaches are used in the computational modeling of materials. In addition, the density of states and charge density investigations play a significant role to establish crystalline and electronic structures of several compounds. There are many publications concerning the magnetic crystals (spinels), especially with respect of their potential for industrial applications. For example, the electronic companies, such as IBM, undertake major research efforts in order to understand in more detail such effects as e.g. magnetoresistance.

The goal of this research is to investigate and explain the magnetic effects in the crystal structure and electronic properties of spinel $CdCr_2O_4$, using first-principle density functional calculations. The magnetism and related properties is considered for spinel $CdCr_2O_4$ that have magnetic transition metal cations exclusively on B-sites. Therefore, possible effects of magnetism on the electronic properties of a geometrically frustrated spinel are broadly investigated. As a conclusion of this study, the following hypothetical research questions have risen with the demand of seeking appropriate answers:

1. Does the change of crystal structures from cubic to tetragonal show different magnetic orderings?

2. What are the effect(s) of magnetization on the ground state energy and what are the effect(s) of magnetization on electronic properties of spinels?

3. Do different magnetic configurations affect on the type of chemical bonding in spinels?

1.3 The Objective of the Study

Following the above questions, this research has been done based on the following objectives:

1) To identify the most stable structure of spinel $CdCr_2O_4$ with different magnetic orderings through geometry optimization procedure.

2) To determine the structural properties of spinel $CdCr_2O_4$, in term of lattice parameters, symmetry properties and charge density distributions in different magnetic configurations.

3) To analyze the electronic properties (i.e. density of states, projected density of states, and chemical bonding properties of spinel $CdCr_2O_4$ with different magnetic orderings.

4) To investigate the magnetic properties in the geometrically frustrated spinel $CdCr_2O_4$ using density functional theory and understanding the principles of Quantum ESPRESSO in magnetic materials.

1.4 The Significances of the Study

Just recently, it has been predicted that many spinel-type compounds of transition metal materials can be used for a different number of technological applications. For example, chromium spinels have been theoretically predicted and proved to be of a fundamental significance for analysis of a numeral theory of condensed matter physics as well as chemistry. This compound may perhaps be used in different technological application.

Motivation for selecting materials with spinel structure (AB_2X_4) stems from its ability to accept many d-series ions, allowing many different oxidation states, and its manifestation of strong geometrical frustration (Lacroix et al., 2011). These characteristics of materials within the spinel family of structures give rise to a rich and diverse catalogue of low temperature magnetic states. Chemically, the spinel structure is rather accommodating, with many different combinations of available transition metal ions. The variation is further enhanced due to O, Se, and S allowed for the ligand X. Oxides tend to be insulating while sulphides generally have better conductive properties due to better overlap of the p and d orbitals between the ligand and metal ion.

In addition, transition-metal compounds (mainly oxides) are the most studied compounds in condensed matter physics due to their motivating physical phenomena, such as a high-T_c superconductivity, Mott insulating state, charge ordering, ferromagnetism, antiferromagnetism, ferroelectricity, antiferroelectricity etc. The major role in these phenomena is played by the d-orbital valence electrons of the transition metal ions. The strong electronic-correlations due to the spatial confinement in narrow d-orbitals play an essential role in the properties of these materials. The internal degrees of freedom of d-electrons, i.e. charge, spin, and orbital angular momentum and the lattice degrees of freedom make a refined balance and hence d-electron systems are highly susceptible to any external impact such as temperature, pressure, magnetic field, or doping, which can shift materials to the new phases. Besides, the orbital degeneracy in d-electron system is a main and obligatory foundation of their complex behavior. Also, lots of compounds of

the AB_2X_4 category, specifically oxides (X = O), crystallize at ambient conditions in the spinel structure.

There are several groups of magnetic materials in spite of the conventional magnets such as ferromagnets, antiferromagnets, and ferrimagnets, which occupy various three dimensions, ranges, and signs of interactions and reveal the anisotropy of the magnetic spin. The different ground states of the magnetic system are characterized with the evaluation of frustration and disorder in the lattice. Geometrical frustration is an important feature in magnetism, where it stems from the topological arrangement of spins. The term frustration, in the microscopic sense, characterizes a system with competing interactions that cannot be simultaneously satisfied (Lacroix et al., 2011). Much interest has been generated in frustrated materials as they have been shown to have a variety of unique ground states such as spin glasses (Binder, & Young, 1986; Fischer, & Hertz, 1993; Mydosh, 2015), and spin ices (Harris et al., 1997).

Chromium spinels are one of the most widely investigated materials among spinels classes of materials. They belong to the frustrated magnetic family (geometrical and bond frustrated) and at low temperatures, they show ferromagnetic and antiferromagnetic orders. The investigated Cr-spinels compounds with formula ACr_2X_4, have *A*-site nonmagnetic divalent cation (Zn, Cd, or Hg) and *B*-site (Cr^{3+}) magnetic trivalent cation. The Cr^{3+} ions are octahedraly coordinated with various elements of group VI (i.e., O, S, and Se). As mentiond before, our focus is only on oxides. Oxides with spinel structure are geometrically frustrated, and their frustration causes extensive degeneracy in the ground state of the system, frequently and avoid any ordering down to low temperatures, e.g. $CdCr_2O_4$ endures the antiferromagnetic ordering only at 7.8 K.

1.5 Research Hypothesis

From the above listed significances, it is clearly seen that predicting similar material such as $CdCr_2O_4$ along with exploring some of the properties (e.g. magnetism and frustration) will not be only a key importance of the technological applications, but also to the fundamental understanding of some numerous theories in condensed matter physics and materials science.

In the field of predicting a better material for technological use and also understanding some of the physical laws, quantum mechanical simulation within a density functional theory have been the most reliable method for over a decade. Therefore, this study will not be significant to the predicting a spinel material, but to show how density functional calculation as well as spin-polarized theory play a role in understanding many properties of these spinel compounds as an excellent transition metal materials. The fallowing research hypothesis is proposed in this research work:

1. Considering the spin-lattice coupling for small deformations which is favorable for tetragonal phase of geometrically frustrated structure, the tetragonal structure of spinel $CdCr_2O_4$ with antiferromagnetic ordering would be more stable after geometry optimization.
2. The most stable tetragonal phase of $CdCr_2O_4$ would have the symmetry of $I4_1/amd$ with experimentally comparable lattice constant since Cr-site and Cd-site cations in the geometrically frustrated network formed tetraheral and diamond like lattice, which are all situated at the center of oxygen tetrahedral. They would equally have mixed bonding nature with ionic and covalent behavior.

3. Depending on the favorable magnetic ordering, the structures would have electronic ground state ranging from metallic to semiconductor electronic character.
4. Due to coupling between Cr-site and Cd-site in different charge states and high-spin configuration in Cr-site as compared to Cd-site, the antiferromagnetic ordering with reasonable magnetic moment would be favorable in tetragonal stable phase of $CdCr_2O_4$.

1.6 Scope of the Research Work

This research work is limited to employing a theoretical framework (i.e. no experimental methods), to formulate and implement density functional theory for spin-polarized systems (this approach goes under the name of Local Spin-Density Approximation, or LSDA), and to investigate the ground state properties of geometrically frustrated spinel $CdCr_2O_4$ compound at zero temorature. Also it is limited to predict the effect of magnetization and magnetic fluctuations on the electronic properties as well as chemical bonding properties of this compound based on the density functional calculation.The structural parameters used in this study have been obtained using the crystal parameters reported in the literature (Chung, & Matsuda, 2005; Kumar et al., 2012; Kemei et al., 2013). Moreover, the study attempts to examine the properties that arise during the formations of these compounds.

However, as it is well-known, the density functional theory method have limited accuracy for predicting an accurate van der Waals forces and strong body correlations (Neumann, & Perrin, 2005; Bucko et al., 2010). Also, in order to apply density functional theory for spin-polarized systems, the exact exchange-correlation functional should be able to predict the magnetic ground states and the corresponding charge densities. Knowing this, the effect of temperature on this compound is not investigated in this study.

1.7 Outline of the thesis

This thesis is organized as follows: in the first chapter, a general introduction which provides a description of the origin of spinel material, its properties and brief area of the technological applications, as well as short outline of the proposed method is presented. Fallowing that, the main aims and objectives, the problem statement, the significance of the study, the hypothesis and the limitations of this research work are arranged in the chapter.

In the second chapter, a general review of the relevant literature on spinel materials as well as transition metal compounds with the geometrically frustrated magnetic structure has been presented and discussed, including the reported experimental and theoretical results in the electrical and magnetic property investigations. Emphasis is mainly on chromium spinels structural characteristics. To continue, a review of density functional theory applications to transition metal compounds is highlighted.

The third chapter reflects on the theoretical foundations of the research. Electronic structure methods, solving many body problems by using density functional theory and Kohn-Sham method is presented and discussed. Particularly, the local density approximation and the generalized gradient approximation are outlined for the exchange and correlation functionals and the treatment of the plane wave basis set and the pseudopotential approximation. The explanation of spin-polarized system within density functional theory is highlighted. . Fallowing that, the description of magnetism, crystal field and spin fluctuations in spinels is discussed.

In the fourth chapter, the computational model applied in our research is presented in details, followed by the given description of the Quantum ESPRESSO method and its capabilities for density functional calculations.

The fifth chapter is devoted to the discussion of the results of the calculations, as well as the new findings relevant to the data obtain. The stability of crystal structure, convergence test calculation, magnetic and electronic properties as well as chemical bonding properties are given in this chapter.

In the sixth chapter, the conclusions drawn from this work are given along with explanations, and finally, several ways to expand this work in future are stated together with some recommendations is presented.

REFERENCES

Andersen, O. K. (1975). Linear methods in band theory. *Physical Review B*, 12, 3060.

Anderson, P. W. (1956). Ordering and antiferromagnetism in ferrites. *Physical Review*, 102:1008–1013.

Aprà, E., Bylaska, E. J., Dean, D. J., Fortunelli, A., Gao, F., Krstic, P. S., Wells, J. C., Windus, T. L. (2003). NWChem for Materials Science. *Computational Materials Science*, 28, 209–221.

Armijo, J. S. (1969). The kinetics and mechanism of solid-state spinel formation—A review and critique. *Oxidation of Metals*, 1, 171–198.

Bachelet, G. B., Hamann, D. R., & Schlüter, M. (1982). Pseudopotentials that work: From H to Pu. *Physical Review B*, 25, 2103.

Bacorisen, D., Smith, R., Ball, J. A., Grimes, R. W., Uberuaga, B. P., Sickafus, K. E., Rankin, W. T. (2006). Molecular dynamics modelling of radiation damage in normal, partly inverse and inverse spinels. *Nuclear Instruments and Methods in Physics Research B*, 250, (1–2).

Balents, L. (2010). Spin Liquids in frustrated Magnets , *Nature* 464, 199.

Baltzer, P. K., Wojtowicz, P. J., Robbins, M., & Lopatin, E. (1966). Exchange Interactions in Ferromagnetic Chromium Chalcogenide Spinels. *Physical Review*,151:367–77.

Barth, T. F. W., & Posnjak, E. (1932). Spinel structures with and without variate atom equipoints. *Zeitschrift für Kristallographie*, 82:325–341.

Bartolotti, L . J ., & Flurchick, K. (1996). An introduction to density functional theory. *Reviews in Computational Chemistry*, 7, 187.

Basu, R., Felser, C., Maignan, A., & Seshadri, R. (2000). Magnetization and magnetoresistive response of $LiMn_2O_4$ near the charge ordering transition. *Journal of Materials Chemistry*, 10:1921–1924.

Becke, D., Savin, A., & Stoll, H. (1995). Extension of the local-spin-density exchange-correlation approximation to multiplet states. *Theoretical Chemistry Accounts*, 91, 147.

Bergman, D., Alicea, J., Gull, W., Trebst, S., & Balents, L. (2007). Order-by-disorder and spiral spin-liquid in frustrated diamond-lattice antiferromagnets. *Nature Physics*, 3:487–491.

Bertaut, E. F., Vanqui, V., Pauthenet, R., & Murasik, A. (1964). Structure magnetique et proprietes magnetiques de GeNi2O4. *Journal of Physics*, 25:516–521.

Binder, K., & Young, A. P. (1986). Spin Glasses: Experimental Facts, Theoretical Concepts, and Open Questions. *Reviews of Modern Physics*, 58:801–976.

Bitoh, T., Hagino, T., Seki, Y., Chikazawa, S., & Nagata, S. (1992). Superconductivity in thiospinel $CuRh_2S_4$. *Journal of the Physical Society of Japan*, 61:3011–3012.

Blaha, P., Schwarz, K., Sorantin, P., & Trickey, S. B. (1990). Full-potential, linearized augmented plane wave programs for crystalline systems. *Computer Physics Communications*, 59, 399.

Blasse, G. (1963). New type of superexchange in the spinel structure. *Philips research reports*, 18:383–392.

Bragg, W. H. (1915). The structure of magnetite and the spinels. *Nature*, 95:561.

Bramwell, S.T., & Gingras, M. J. P. (2001). Spin ice state in frustrated magnetic pyrochlore materials. *Science*, 294, 1495.

Bucko,T., Hafner, J., Lebegue, S., & Angyan, J. G. (2010). Improved description of the structure of molecular and layered crystals: ab initio DFT calculations with van der Waals corrections. *The Journal of Physical Chemistry*, A 114 (43), 11814-11824.

Büttgen, N., Hemberger, J., Fritsch, V., Krimmel, A., Mücksch, M., Krug von Nidda, P., Lunkenheimer, H. A., Fichtl, R., Tsurkan, V., & Loidl, A. (2004). Orbital physics in sulfur spinels: ordered, liquid and glassy ground states. *New Journal of Physics*,6:191.

Calder, S. (2010). *Investigation of geometric frustration in magnetic oxides*. PhD thesis, University of London.

Ching, W. Y., Shang-Di, M., Tanaka, I., & Yoshiya, M. (2001). Prediction of spinel structure and properties of single and double nitrides. *Physical Review B*, 63, 064102.

Chung, J. H., Matsuda, M., Lee, S. H., Kakurai, K., Ueda, H., Sato, T. J., Takagi, H., Hong, K. P., & Park, S. (2005). Statics and Dynamics of Incommensurate Spin Order in a Geometrically Frustrated Antiferromagnet $CdCr_2O_4$. *Physical Review Letters*, 95, 247204.

Chung, J. H., Kang, H. J., Ratcli, R., & Gehring, P. (2007). *The Magnetic Phase Transition and Spin Fluctuations in the Geometrically Frustrated Antiferromagnetic Spinel CdCr2O4: An Experiment Using the SPINS Triple-Axis Spectrometer*. Summer School on Methods and Applications of Neutron Spectroscopy NIST Center for Neutron Research, June 25-29.

Cramer, C. J., & Truhlar, D. G. (2009). Density functional theory for transition metals and transition metal chemistry. *Physical Chemistry Chemical Physics*, 11 (46), 10757-10816.

Cuevas, J. C. (2011). *Introduction to Density Functional Theory.* Institut für Theoretische Festkörperphysik, Universität Karlsruhe, Germany.

Dawes, P. P, & Grimes. N.W. (1975). Superconductivity among compounds with spinel structure and the strong coupling mechanism. *Solid State Communications*, 16:139–141.

Fan, D., Zhou, W., Liu, C., Liu, Y., Jiang, X., Wan, F., Liu, J., Li, X., & Xie, H. (2008). Thermal equation of state of natural chromium spinel up to 26.8 GPa and 628 K. *Journal of Materials Science*, 43, 16, 5546–5550.

Feiner, L. F., Oles, A. M., & Zaanen, J. (1997). Quantum melting of magnetic order due to orbital fluctuations. *Physical Review Letters*, 78 2799.

Fennie C. J., & Rabe, K. M. (2006). Magnetic and electric phase control in epitaxial $EuTiO_3$ from first principles. *Physical Review Letters*, 97:267602.

Figgis, B. N., & Hitchman, M. A. (1999). *Ligand Field Theory and its Applications*. Wiley-VCH, New York.

Finger, L.W., Hazen, R. M., Hofmeister, A.M. (1986). High-pressure crystal-chemistry of spinel ($MgAl_2O_4$) and Magnetite (Fe_3O_4) - Comparisons with silicate spinels. *Physics and Chemistry of Minerals*, 13:215–220.

Fischer, K.H., & Hertz, J. A. (1993). *Spin Glasses. Cambridge Studies in Magnetism.* Cambridge University Press.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Vreven, T., Kudin, K. N., Burant, J. C. et al. (2004). Gaussian 03, Revision D.01; Gaussian, Inc., Wallingford, CT.

Fritsch, V., Hemberger, J., Büttgen, N., Scheidt, E.W., Krug von Nidda, H.A., Loidl, A., & Tsurkan, V.(2004). Spin and orbital frustration in $MnSc_2S_4$ and $FeSc_2S_4$. *Physical Review Letters*, 92:116401.

Fu, Z. (2012). *Spin Correlations and Excitations in Spin-frustrated Molecular and Molecule-based Magnets*. PhD thesis, RWTH Aachen University.

Futschek, M. T. (2005). *Structural, electronic and magnetic properties of transition metal clusters.* PhD thesis, Center for Computational Materials Science, Universität Wein.

Gaertner, H. R. (1930). Die Kristallstrukturen von Loparit und Pyrochlor. *Neues Jahrb. Mineral. Abh*, 61, 1-30.

Gardner, J. S., Gingras, M. J. P., Greedan, Greedan, J. E. (2009). Magnetic pyrochlore oxides. *Condensed Matter, eprint arXiv*, 0906.3661.

Gaulin, B. D. (2004). The texture of frustrated magnets. *Nature Materials*, 4, 269.

Giannozzi, P. (2010). *Magnetism and magnetic systems.* African School on Electronic Structure Methods, AIM.

Giannozzi, P., Baroni, S., Bonini N., Matteo C., Roberto C., Cavazzoni C., Davide C. (2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39), 395502.

Greedan, J. E. (2001). Geometrically frustrated magnetic materials. *Journal of Materials Chemistry*, 11, 37.

Greedan, J. E. (2006). Frustrated rare earth magnetism: spin glasses, spin liquids and spin ices in pyrochlore oxides, *Journal of Alloys and Compounds*, 408-412, 444.

Guerra, C. F., Snijders, J. G., te Velde, G., & Baerends, E. J. (1998). Towards an order-N DFT method. *Theoretical Chemistry Accounts*, 99, 391.

Hafner, J. (2008). Ab-initio simulations of materials using VASP: Density-functional theory and beyond. *Journal of Computational Chemistry*, 29, 2044.

Harris, M. J., Bramwell, S. T., McMorrow, D. F., Zeiske, T., & Godfrey, K. W. (1997). Geometrical Frustration in the Ferromagnetic Pyrochlore $Ho_2Ti_2O_7$. *Physical Review Letters*, 79:2554–2557.

Hemberger, J., Lunkenheimer, P., Fishtl, R., & Loidi, A. (2005). Relaxor ferroelectricity and colossal magnetocapacitive coupling in ferromagnetic $CdCr_2S_4$. *Nature*, 434, 364–367.

Hemmida, M. (2011). *Electron Spin Resonance in Frustrated Two- and Three-Dimensional Chromium Magnets*. PhD thesis, Universität Augsburg.

Henley, C. L. (2001). Effective Hamiltonians and Dilution Effects in Kagom´e and Related Anti-ferromagnets. *Canadian Journal of Physics*, 79(11-12):1307–1321.

Hohenberg, P., & Kohn, W. (1964). Inhomogeneous Electron Gas. *Physical ReviewB*, 136, 864 ,8.

Houtappel, R. M. F. (1950). Order-disorder in hexagonal lattices. *Physica*, 16, 425.

Imada, M., Fujimori, A., & Tokura, Y. (1998). Metal-insulator transitions. *Reviews of Modern Physics*, 70, 1039.

Jacobs, P. (2005). *Group Theory with Applications in Chemical Physics*. Cambridge University Press.

Jahn H. A., Teller, E. (1937). Stability of polyatomic molecules in degenerate electronic states. I. orbital degeneracy. *Proceedings of the Royal Society*, A161:220.

Johnston, D. C., Prakash, H., Zachariasen, W. H., & Viswanathan, R. (1973). High temperature superconductivity in the lithium-titanium-oxygen ternary system. *Materials Research Bulletin*, 8:777–84.

Jones, R. O., & Gunnarsson, O. (1989). The density functional formalism, its applications and prospects. *Reviews of Modern Physics*, 61, 689.

Joubert, D. (1998). *Density functionals: theory and applications*. Lecture Notes in Physics, Berlin Springer Verlag 500.

Kant, C., Deisenhofer, J., Rudolf, T., Mayer, F., Schrettle, F., & Loidl, A. (2009). Optical phonons, spin orrelations, and spin-phonon oupling in the frustrated pyro hlore magnets $CdCr_2O_4$ and $ZnCr_2O_4$. *Condensed Matter. ArXiv*, 0906.3639v1, 1.

Kaplan, T. A., Dwight, K., Lyons, D., & Menyuk, N. (1961). Classical theory of the ground spin state in spinels. *Journal of Applied Physics*, 32:S13–S20.

Kemei, M. C., (2014). *Magnetostructural and magnetodielectric coupling in spinel oxides.* PhD thesis, University of California.

Kemei, M. C., Barton, B.T., Moffitt, S.L., Gaultois, M.W., Kurzman, J.A., et al. (2013). Crystal structures of spinJahn-Teller-ordered $MgCr_2O_4$ and $ZnCr_2O_4$. *Journal of Physics: Condensed Matter*, 25(32), 326001.

Kendall, R. A., Apra, E., Bernholdt, D. E., Bylaska, E. J., Dupuis, M., Fann, G. I., Harrison, R. J., Ju, J., Nichols, J. A., Nieplocha, J., Straatsma, T. P., Windus, T. L., & Wong, A. T. (2000). High Performance Computational Chemistry: An Overview of NWChem a Distributed Parallel Application. *Computer Physics Communications*, 128(1 - 2):260 - 283.

Kino, Y., & LÜthi, B. (1971). Magnetic and elastic properties of zinc-chromite. *Solid State Communications*, 9, 805–8.

Kleinman, L., & Bylander, D. (1982). Efficacious Form for Model Pseudopotentials. *Physical Review Letters*, 48, 1425.

Kohn, W., Becke, A. D., & Parr, R. G. (1996). Density Functional Theory of Electronic Structure. *journal of physical chemistry*, 100, 12974.

Kohn, W., & Sham, L. J. (1965). Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review*, 140, 1133.

Korobanik, J. T. (2016). *The Effects of Magnetic Dilution and Applied Pressure on Several Frustrated Spinels.* PhD thesis, Brock University.

Kresse, G., & Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, 54, 11169.

Krok-Kowalski, J., Warczewski, J., Koroleva, L.I., Krajewski, K., Gusin, P., Duda, H., Zajdel, P., Pacyna, A., Mydlarz, T., Matyjasik, S., Demin R.V. (2004). On the influence of Sb concentration onto the magnetization and magnetoresistivity in the spinel compounds $CuCr_2$-x$SbxS_4$ (where x = 0.3, 0.4, 0.5). *Journal of Alloys and Compounds*, 377(1-2), 53-58.

Kugel, K. I., & Khomskii, D. I. (1982). The Jahn-Teller effect and magnetism: transition metal compounds. *Soviet Physics Uspekhi*, 25, 231.

Kumar, A., Fennie, C. J., & Rabe, K. M. (2012). Spin-lattice coupling and phonon dispersion of CdCr2O4 from first principles. *Physical Review B*, 86, 184429.

Lacroix, C., Mendels, P., & Mila, F. (2011). Introduction to Frustrated Magnetism: Materials, Experiments, Theory. *Springer Series in Solid-State Sciences.*

Lang, O., Felser, C., Seshadri, R., Renz, F., Kiat, J. M., Ensling, J., Gütlich, P., & Tremel, W. (2000). Magnetic and electronic structure of the CMR chalcospinel Fe0:5Cu0:5Cr_2S_4. *Advanced Materials*, 12:65–69.

Lawes, G., Melot, B. C., Page, K., Ederer, C., Hayward, M.A.,et al. (2006). Dielectric anomalies and spiral magnetic ordering in CoCr2O4. *Physical Review B*, 74, 024413:1-6.

Lechermann, F., Georges, A., Poteryaev, A., Biermann, S., Posternak, M., Yamasaki, A., & Andersen, O. K. (2006). Dynamical mean-field theory using Wannier functions: A flexible route to electronic structure calculations of strongly correlated material. *Physical Review B*, 74, 125120.

Lee, S. H, Takagi, H., Louca, D., Matsuda, M., Ji, S., Ueda, H., Ueda, Y., Katsufuji, T., Chung, J. H., Park, S., Cheong, S. W., & Broholm, C. (2010). Frustrated magnetism and cooperative phase transitions in spinels. *Journal of the Physical Society of Japan*, 79:011004.

Lee, S. H., Broholm, C., Aeppli, G., Perring, T. G., Hessen, B., &Taylor, A. (1996). Isolated Spin Pairs and Two-Dimensional Magnetism in $SrCr_9pGa_{12-9}pO_{19}$. *Physical Review Letters*, 76:4424–4427.

Lee, S. H., Broholm, C., Kim, T. H., Ratcliff, W., Cheong, S. W. (2000). Local Spin Resonance and Spin-Peierls-like Phase Transition in a Geometrically Frustrated Antiferromagnet. *Physical Review Letters*, 84, 3718.

Lee, S. H., Gasparovic, G., Broholm, C., Matsuda, M., Chung, J. H., et al. (2007). Crystal distortions in geometrically frustrated ACr_2O_4 (A = Zn, Cd). *Journal of Physics: Condensed Matter*, 19, 145259.

Lee, S. H., Broholm, C., Ratcliff, W., Gasparovic, G., Huang, Q., et al. (2002). Emergent excitations in a geometrically frustrated magnet. *Nature* 418: 856-858.

Lee, S.H., Louca, D., Ueda, H., Park, S., Sato, T. J., Isobe, M., Ueda, Y., Rosenkranz, S., Zschack, P., Íñiguez, J., Qiu, Y., Osborn, R. (2004). Orbital and Spin Chains in ZnV_2O_4 . *Physical Review Letters*, 93, 156407.

Levi, B. G. (2007). New candidate emerges for a quantum spin liquid. *Physics Today*, 60:16.

Liehr, A. D. (1963). The Three Electron (or Hole) Cubic Ligand Field Spectrum. *Journal of Physical Chemistry*, 67, 1314.

Lowther, J.E., Schwarz, M., Kroke, E., & Riedel, R. (2003). Electronic Structure Calculation of Cohesive Properties of Some Si6-zAlzOzN8-z Spinels. *Journal of Solid State Chemistry*, 176, 549-555.

Lu, J., Zhan, C.,Wu, T., Wen, T., Lei, Y., Kropf, A. J., Wu, H., Miller, D. J., Elam, J. W., Sun, Y. K., Qiu, X., & Amine, K. (2014). Effectively suppressing dissolution of manganese from spinel lithium manganate via a nanoscale surface-doping approach. *Nature Communications*, 5, 5693.

Martin, R. M. (2004). *Electronic structure: basic theory and practical methods*. Cambridge university press.

Mathew, T. (2002). *Synthesis and characterization of mixed oxides containing cobalt, copper and iron and study of their catalytic activity*. PhD thesis, University of Pune.

Matsuda, M., Takeda, M., Nakamura, M., Kakurai, K., Oosawa, A., Leli`evre-Berna, E., Chung, J. H., Ueda, H., Takagi, H., & Lee, S. H. (2007). Spiral spin structure in the Heisenberg pyrochlore magnet $CdCr_2O_4$. *Physical Review B*, 75:104415.

Melot, B. C., Drewes, J. E., Seshadri, R., Stoudenmire, E. M. & Ramirez, A. P. (2009). Magnetic phase evolution in the spinel compounds $Zn_{1-x}Co_xCr_2O_4$. *Journal of Physics: Condensed Matter,* 21:216007.

Melot, B. C (2010). *Competing Magnetic Interactions in Complex Oxides*. PhD Thesis, University of California.

Menyuk, N., Dwight, K., Arnott, R. J., Wold, A. (1966). Ferromagnetism in $CdCr_2Se_4$ and $CdCr_2S_4$. *Journal of Applied Physics*, 37, 1387.

Moessner, R, & Ramirez, A. P.(2006). Geometrical frustration. *Physics Today*, 59:24.

Monkhorst, H.J. & Pack, J. D. (1976). Special points for Brillouin-zone integrations *Physical Review B*, 13, 5188.

Neumann, M. A., Perrin, M. A. (2005). Energy Ranking of Molecular Crystals Using Density Functional Theory Calculations and an Empirical van der Waals Correction. *Journal of Physical Chemistry B*, 109:15531–15541.

Nishikawa, S. (1915). Structure of some crystals of the spinel group. *Proceedings of the Tokyo Mathematico-Physical Society*, 8:199–209.

Parker, D. R., Green, M. A., Bramwell, S.T., Wills, A. S., Gardner, J.S., Neumann, D.A. (2004). Crossover from positive to negative magnetoresistance in a spinel. *Chemical Society*,126, 2710.

Payne, M. C., Teter, M. P., Allan, D. C., Arias, T. A., & Joannopoulos, J. D. (1992). Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. *Reviews of Modern Physics*, 64, 1045.

Perdew, J. P., Tao, J., & Kümmel, S. (2007). Uniform Density Limit of Exchange-Correlation Energy Functionals. *ACS Symposium Series*, 958, 13.

Pfrommer, B.G., Cote, M., Louie, S.G., & Cohen, M.L. (1997). Relaxation of Crystals with the Quasi-Newton Method. *Journal of Computational Physics*, 131, 233, 228.

Polo, V., Kraka, E., Cremer, D. (2002). Electron correlation and the self-interaction error of density functional theory. *Molecular Physics*, 100 (11), 1771-1790.

Rabia, K. (2012). *Structural and optical properties of transition-metal compounds under pressure.* PhD Thesis, University of Augsburg.

Radaelli, P. G. (2005). Orbital ordering in transition metal spinels. *New Journal of Physics*, 7, 53.

Ramirez, A. P. (1994). Strongly geometrically frustrated magnets. *Annual Review of Materials Research*, 24, P:453–480.

Ramirez, A. P., Cava, R. J., Krajewski, J. (1997). Collossal magnetoresistance in Cr-based chalcogenide spinels. *Nature*, 386:156.

Recio, J. M., Franco, R., Pendas, M., Blanco, M. A., & Pueyo, L. (2001). Theoretical explanation of the uniform compressibility behavior observed in oxide spinels. *Physical Review B*, 63, 184101.

Romeijn, F. C. (1953). *Physical and Crystallographical Properties of Some*. Eindhoven Press.

Roy, B., Pandey, A., Zhang, Q, Heitmann,T., Vaknin, D., Johnston,D., & Furukawa, Y. (2013). Experimental Evidence of a Collinear Antiferromagnetic Ordering in the Frustrated $CoAl_2O_4$ Spinel. *Physical Review B*, 88:174415.

Rudolf, T., Kant, C., Mayr, F., Schmidt, M., Tsurkan, V., Deisenhofer, J., & Loidl, A. (2009). Optical properties of $ZnCr_2Se_4$. *European Physical Journal B*, 68, 153.

Santos, E. J., Ayuela, A., and S´anchez-Porta D. (2010). First-principles study of substitutional metal impurities in graphene: structural, electronic and magnetic properties. *New Journal of Physics*, 12(5), 053012.

Scandolo, S., Giannozzi, P., Cavazzoni, C., Gironcoli, S., Pasquarello, A., & Baroni, S. (2005). First-principles codes for computational crystallography in the Quantum-ESPRESSO package. *Zeitschrift für Kristallographie*, 220, 574.

Schiffer, P. (2002). Magnetic frustration squeezed out. *Nature*, 420, 35.

Schwarz, K., & Blaha, P. (2003). Solid state calculations using WIEN2k. *Computational Materials Science*, v, 259.

Shull, C. G. and J. S. Smart, J. S. (1949). Detection of antiferromagnetism by neutron diffraction. *Physical Review*, 76:1256.

Sickafus, K. E., Wills, J. M., & Grimes, N. W. (1999). Structure of Spinel. *Journal of the American Ceramic Society*, 82, 3279.

Stein, A., Keller, S. W., & Mallouk T. E. (1993). Turning down the heat: design and mechanism in solid-state synthesis. *Science*, 259, 1558–1564.

Stevens, R., Woodfield, B. F., Goates, J. B., & Crawford, M. K.(2004). Heat Capacities, Third-law Entropies and Thermodynamic Functions of the Geometrically Frustrated Antiferromagnetic Spinels $GeCo_2O_4$ and $GeNi_2O_4$ from T= (0 to 400) K. *The Journal of Chemical Thermodynamics*, 36(5):359–375.

Tchernyshyov, O., Moessner, R., Sondhi, S. L. (2002). Order by distortion and string modes in pyrochlore antiferromagnet. *Physical Review Letters*, 88, 067203.

Thackeray, M. M. (1997). Manganese oxides for lithium batteries. *Progress in Solid State Chemistry*, 25, 1–71.

Toulouse, G., & Vannimenus, J. (1977). Theory of the frustration effect. II. Ising spins on a square lattice. *Journal of Physics C: Solid State Physics*, 10 (18).

Troullier, N., Martins, J. L. (1991). Efficient pseudopotentials for plane-wave calculations. *Physical Review B*, 43, 1993.

Truhlar, D. G. (2007). The two faces of static correlation. *Journal of Chemical Physics*, 28, 73.

Tsurkan, V., Hemberger, J., Krimmel., A., Krug von Nidda, H. A., Lunkenheimer, P., Weber, S., Zestrea, V., & Loidl, A. (2006). Experimental evidence for competition of antiferromagnetic and ferromagnetic correlations in $HgCr_2S_4$. *Physical Review B*, 73 224442.

Ueda, H., Katori, H. A., Mitamura, H., Goto, T., Takagi, H. (2005). Magnetic-Field Induced Transition to the 1/2 Magnetization Plateau State in the Geometrically Frustrated Magnet $CdCr_2O_4$. *Physical Review Letters*, 94, 047202:1-4.

Vanderbilt, D. (1990). Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B*, 41, 7892.

VandeVondele, J., Krack, M., Mohamed, F., Parrinello, M., Chassaing, T., & Hutter, J. (2005). Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Computer Physics Communications*, 167 (2), 103-128.

Verwey, E. J. W., & Haayman, P. W. (1941). Electronic conductivity and transition point of magnetite (Fe_3O_4). *Physica*, 8:979–987.

Verwey, E. J. W., & Heilmann, E. L. (1947). Physical properties and cation arrangement of oxides with spinel structures I. Cation arrangement in spinels. *The Journal of Chemical Physics*, 15:174–180.

Verwey, E. J. W., Boer, F. D., & Santen, J. H. V. (1948). Cation Arrangement in Spinels. *Journal of Chemical Physics*, 16, 1091.

Wannier, G. H. (1950). Antiferromagnetism. The Triangular Ising Net. *Physical Review* 79, 357.

Warczewski, J., Krok-Kowalski, J., Gusin, P., Duda, H., Fijak, J., Kozerska, K., Nikiforov, K.G., Pacyna, A. (2003). On the mechanisms of obtaining the spin-glass state in the spinels with chromium. *Nonlinear Optics & Quantum Optics*, Vol. 30 (3-4), 301-320.

Weber, S., Lunkenheimer, P., Fichtl, R., Hemberger, J., Tsurkan, V., & Loidl, A. (2006). Colossal Magnetocapacitance and Colossal Magnetoresistance in $HgCr_2S_4$. *Physical Review Letters*, 96 157202.

Wessner, W. (2006). *Mesh Refinement Techniques for TCAD Tools*. PhD thesis, technical university Vienna.

Xie, X., Li, Y., Liu, Z. Q., Haruta, M., & Shen, W. (2009). Low-temperature oxidation of CO catalysed by Co_3O_4 nanorods. *Nature*, 458 (7239), 746–749.

Yafet, Y., & Kittel, C. (1952). Antiferromagnetic arrangements in ferrites. *Physical Review*, 87, 2: 290.

Yamasaki, Y. (2006). Magnetic reversal of the ferroelectric polarization in a multiferroic spinel oxide. *Physical Review Letters*, 96, 207204.

Yamashita, Y., & Ueda, K. (2000). Spin-Driven Jahn-Teller Distortion in a Pyrochlore System. *Physical Review Letters*, 85, 4960.

Yanbing, L. (2011). *Elastic properties of complex transition metal oxides studied by Resonant Ultrasound Spectroscopy.* PhD thesis, University of Tennessee.

Yaresko, A. N. (2008). Electronic band structure and exchange coupling constants in ACr2X4 spinels. *Physical Review B, 77, 115106.*

Yoshimura, E. M., & Yukihira, E. G. (2006). Optically stimulated luminescence of magnesium aluminate ($MgAl_2O_4$) spinel. *Radiation Measurement*, 41(2), 125-246.

Zeller, R. (2006). Spin-Polarized DFT Calculations and Magnetism. *Computational Nanoscience*, 31, 3-00-017350-1, 419-445,