UNIVERSITI PUTRA MALAYSIA

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

NAJMEH BOLANDHEMAT

FS 2017 63
DENSITY FUNCTIONAL STUDY FOR STRUCTURAL, ELECTRONIC, MAGNETIC AND CHEMICAL BONDING PROPERTIES OF GEOMETRICALLY-FRUSTRATED CdCr$_2$O$_4$

By

NAJMEH BOLANDEHMAT

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

January 2017
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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$_2$O$_4$

By

NAJMEH BOLANDHEMAT

January 2017

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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ with non-magnetic Cd cations and magnetic Cr cations from a pyrochlore lattice, by examining the crystal structure of spinel CdCr$_2$O$_4$ 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$_2$O$_4$ with cubic (Fd$ar{3}$m) and tetragonal (I$4_1$/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$_2$O$_4$, 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$_2$O$_4$ 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$_2$O$_4$, 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$_2$O$_4$, 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$_2$O$_4$ in paramagnetic, ferromagnetic and antiferromagnetic orderings.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGIRAAN FUNGSIAN DIKAJI UNTUK CIRI-CIRI STRUKTUR, ELEKTRONIK, MAGNET DAN IKATAN KIMIA CdCr₂O₄ BERFRUSTRASI-GEOMETRI

Oleh

NAJMEH BOLANDHEMAT

Januari 2017

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Spinell adalah satu kelas bahan menarik yang menunjukkan sifat kompleks yang kaya pada keadaan dasar. Antara bahan spinel, spinel kromium merentangi rentang kekuatan tukar ganti magnet yang besar dan mempunyai pelbagai keadaan dasar magnet. Oksida spinel AB₂O₄ 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 Cr³⁺ pada tapak B adalah contoh yang baik untuk dikaji frustrasi.

Spinel CdCr₂O₄ berfrustrasi geometri dipilih sebagai sistem model untuk dikaji kerana ia mempunyai tertib magnet yang tertakrif rapi dengan vektor gelombang bertertib tunggal. Spinel CdCr₂O₄ adalah sebatian magnet yang terhablur kepada struktur spinel kubus dengan sifat magnetnya datang daripada ion bermagnet Cr³⁺, 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 CdCr₂O₄ dengan kation Cd yang tak bermagnet dengan kation Cr bermagnet daripada kekisi piroklor, dengan pemeriksaan struktur hablur spinel CdCr₂O₄ 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 CdCr₂O₄ berfrustrasi geometri dengan struktur kubus (Fd̅̅̅̅3m) dan tetragon (I4₁/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
mengoptimukan struktur hablur CdCr\textsubscript{2}O\textsubscript{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, fungsi tukarganti dan korelasi diperhal 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 sataian dan parameter sel bagi setiap unsur, kod input PWscf (VC-relax) diaplikasikan.

Bagi mencari struktur spinal CdCr\textsubscript{2}O\textsubscript{4} yang paling stabil berasaskan tertib bermagnet, tenaga paling rendah bagi setiap struktur dengan tertib bermagnet berbeza dikerahkan. 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\textsubscript{2}O\textsubscript{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 fungsi ketumpatan dan kefahaman prinsip Quantum ESPRESSO dalam bahan bermagnet. Seterusnya, bagi melengkapkan penemuan ketumpatan keadaan elektronik bagi spinel CdCr\textsubscript{2}O\textsubscript{4}, ketumpatan keadaan bagi setiap atom dikerahkan 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\textsubscript{2}O\textsubscript{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$_2$O$_4$" 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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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
$E_{\text{cut}}$  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
$\Delta CF$ Crystal Field Splitting

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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$^{3+}$O$_2$-$\delta$. 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 $Fd\bar{3}m$ (No. 227) are labeled as a spinel.

Spinel-type compounds with the general formula of AB$_2$X$_4$ (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$_2$X$_4$ (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$_2$S$_4$ and CdCr$_2$S$_4$ exhibit multiferroic behavior. Chromium spinels with a specific formula ACr$_2$X$_4$, 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$_2$X$_4$ 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$_2$O$_4$ 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 \( \text{AB}_2\text{X}_4 \) (\( \text{X}=\text{O}, \text{S}, \text{Se} \)), 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 \( \text{ZnCr}_2\text{O}_4 \) and \( \text{CdCr}_2\text{O}_4 \) 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, \( \text{CdCr}_2\text{O}_4 \) has been chosen as a model system. While its frustration factor is smaller than that of \( \text{ZnCr}_2\text{O}_4 \), \( \text{CdCr}_2\text{O}_4 \) is preferred as it has a well-defined magnetic order with a single ordering wave vector. In the case of \( \text{CdCr}_2\text{O}_4 \), the first-principles calculation for these systems can provide valuable information about structural, electronic structure, and magnetic properties of \( \text{CdCr}_2\text{O}_4 \) by using density functional calculation 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 \( \text{AB}_2\text{O}_4 \) in which \( \text{A} \) is a rare-earth ion and \( \text{B} \) is generally a transition metal. Both \( \text{A} \) and \( \text{B} \) 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 \( \text{Fe}_3\text{O}_4 \). Investigation into spinels, whose general formula is \( \text{AB}_2\text{X}_4 \), 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\(_2\)O\(_4\) (Basu et al., 2000), FeCr\(_2\)S\(_4\) (Lang et al., 2000; Ramirez et al., 1997)), superconductivity (CuRh\(_2\)S\(_4\) (Bitoh et al., 1992; Dawes, & Grimes, 1975), LiTi\(_2\)O\(_4\) (Johnston et al., 1973)), spin driven Jahn-Teller distortions (MCr\(_2\)O\(_4\), M = Zn (Lee et al., 2000; Lee et al., 2007), Cd (Matsuda et al., 2007)) and metal-insulator transitions (Fe\(_3\)O\(_4\) (Verwey, & Haayman, 1941; Verwey et al., 1947)).

It has been known for over 40 years that chromium spinels \( (\text{ACr}_2\text{X}_4) \) 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\(_2\)O\(_4\) 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 \( |\theta_{\text{CW}}| = 88 \) 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\(_2\)O\(_4\) 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\(_2\)O\(_4\), using first-principle density functional calculations. The magnetism and related properties is considered for spinel CdCr\(_2\)O\(_4\) 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\(_2\)O\(_4\) with different magnetic orderings through geometry optimization procedure.
2) To determine the structural properties of spinel CdCr$_2$O$_4$, 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$_2$O$_4$ with different magnetic orderings.

4) To investigate the magnetic properties in the geometrically frustrated spinel CdCr$_2$O$_4$ 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$_2$X$_4$) 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\(_2\)X\(_4\) 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 spinel 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 A\(\text{Cr}_2\text{X}_4\), have A-site nonmagnetic divalent cation (Zn, Cd, or Hg) and B-site (Cr\(^{3+}\)) magnetic trivalent cation. The Cr\(^{3+}\) ions are octahedrally coordinated with various elements of group VI (i.e., O, S, and Se). As mentioned 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\(_2\)O\(_4\) 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\(_2\)O\(_4\) 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 following 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$_2$O$_4$ with antiferromagnetic ordering would be more stable after geometry optimization.

2. The most stable tetragonal phase of CdCr$_2$O$_4$ 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 tetrahedral 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$_2$O$_4$.

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$_2$O$_4$ compound at zero temperature. 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. Following 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. Following 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.
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