

Structural, Electronic and Magnetic Properties of Geometrically Frustrated Spinel CdCr_2O_4 from First-principles Based on Density Functional Theory

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Abstract

First-principles calculations are used to investigate the structural, electronic, and magnetic properties of CdCr_2O_4 with magnetic Cr cations, focusing on the changes through the magnetic phase transitions which shows relief of the geometric frustration of the ferromagnetic and antiferromagnetic orderings on the pyrochlore lattice. We computed the structural and electronic properties for the paramagnetic, ferromagnetic and antiferromagnetic orderings in cubic ($Fd\bar{3}m$) and tetragonal ($I4_1/amd$) structures of CdCr_2O_4 . We optimized the crystal structures with the PM, FM and AFM orderings using a pseudopotential plane wave (PP-PW) method within the generalized gradient approximation (GGA), and computed the electronic properties to investigate the magnetic properties in the geometrically frustrated ferromagnetic and antiferromagnetic spinel CdCr_2O_4 based on density functional theory and understanding of the principles of Quantum ESPRESSO in magnetic materials. On the other hand, the effect of magnetism were obtained and analyzed on the basis of density of states (DOS), projected density of states (PDOS), and charge density distribution.

Keywords: Spinel; Geometric frustration; Density functional theory; Phase transitions; Quantum Espresso; Electronic and magnetic properties; Ground states

Introduction

Spinel is a captivating class of materials that indicate rich complex behavior and novel ground states such as large magnetoresistance effects [1], non-collinear spin configurations [2], magnetodielectric coupling [3], and spin liquid states [4]. Spinel is the magnesium aluminum oxide member of this large group of materials with the $\text{Mg}^{2+}\text{Al}^{3+}_2\text{O}_4$ formula that gives its name to the family of compounds that are identified by two cation sites: an octahedral site and a tetrahedral site [5]. It is named as spinel to any material that have the general formula $\text{A}^{2+}[\text{B}^{3+}]_2[\text{X}^{2-}]_4$ which crystallizes in the face-centered cubic crystal system and are described by the space group $Fd\bar{3}m$ (No. 227). In this structure, the X anions are located in a cubic close packed lattice, the cations A occupy tetrahedral (1/8, 1/8, 1/8) sites, and the cations B occupy octahedral (1/2, 1/2, 1/2) sites in the lattice. Tetrahedral and octahedral cations occupy the special Wyckoff positions 8a and 16d, respectively. The anions are located at general Wyckoff 32e positions that are assigned the parameter u, which takes on different values around the optimal position $u=0.25$ for various spinels. In particular, chromium spinels ACr_2O_4 ($A=\text{Cd}, \text{Zn}$) are an interesting class of frustrated antiferromagnets that are considering as the most frustrating lattice because of the direct overlap of the t_{2g} orbitals of the neighboring $\text{Cr}^{3+}(3d^3)$ ions with the dominant antiferromagnetic nearest neighbor interactions [6,7]. It also remains paramagnetic far below temperatures corresponding to the major exchange strength, i. e. the Curie-Weiss temperature $|\Theta_{\text{CW}}|=88$ K for Cd [8-10] and $|\Theta_{\text{CW}}|=390$ K [11]. Upon further cooling, however, phase transition occurs from a cubic paramagnet to a tetragonal Néel state at $T_{\text{N}}=7.8$ K for Cd [7,8] and $T_{\text{N}}=12.5$ K for Zn [12]. At high temperatures, ACr_2O_4 spinels have a cubic ($Fd\bar{3}m$) structure in which Cr^{3+} ions are enveloped by octahedral oxygen cages and form a pyrochlore lattice, while A^{2+} ions are in tetrahedral oxygen environment and form the diamond lattice (Figure 1). The octahedral crystal field splits the Cr 3d orbitals into a lower-lying t_{2g} triplet and a higher-energy e_g doublet. Cr^{3+} has three

outer electrons that fill the majority t_{2g} states which results in a net Cr spin $S=3/2$ [13]. In some magnetic materials, magnetic order does not appear even when the system is cooled down to the temperatures far below the characteristic strength of the interactions between the spins. We are particularly interested in the case where the crystal structure is responsible for the suppression of the magnetic phase transition; this is generally called geometrical frustration. The physics of frustrated magnetism is a subject of existing interest. Spinel with Cr^{3+} ions on the B sites are good examples to study the geometrical frustration [14-17]. Spinel oxides AB_2O_4 with magnetic B cations have received special attention because they are identified by three-dimensional geometrical frustration.

In this paper, we used first-principles calculations to investigate the effects of magnetic ordering on the minimum energy structure of geometrically frustrated spinel CdCr_2O_4 . Obviously, with a nearest-neighbor antiferromagnetic (AFM) exchange interactions on threefold rings, CdCr_2O_4 is completely frustrated. CdCr_2O_4 has a Curie-Weiss temperature $|\Theta_{\text{CW}}|\approx 88$ K, while its magnetic transition occurs at a temperature as low as $T_{\text{N}}=7.8$ K. The estimated frustration factor $f\approx 31$, demonstrating a large degree of geometrical frustration. This frustration is lifted from a cubic-to-tetragonal lattice distortion ($c<a=b$) that occurs with the magnetic transition, simultaneously. We begin by examining the crystal structure of spinel CdCr_2O_4 and then, analyzing the electronic and magnetic properties that are important in magnetic spinel oxides.

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Received March 27, 2016; Accepted April 22, 2016; Published May 02, 2016

Citation: Bolandhemat N, Rahmana M, Shuaibua A (2016) Structural, Electronic and Magnetic Properties of Geometrically Frustrated Spinel CdCr_2O_4 from First-principles Based on Density Functional Theory. J Material Sci Eng 5: 250. doi:10.4172/2169-0022.1000250

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Materials and Methods

Crystal structure

CdCr₂O₄ is a magnetic compound that crystallizes into a cubic spinel structure, and the magnetic properties stem from the Cr³⁺ magnetic ions, that are a three-dimensional network of corner-sharing tetrahedral. The crystal structure is consisting of Cd-centered tetrahedral and Cr-centered octahedral, in which Cd is tetrahedrally coordinated by oxygen and Cr is octahedrally coordinated by Oxygen. The cations occupy either the tetrahedral 8a site (Cd atoms) or the octahedral 16d site (Cr atoms). Figure 2 shows the primitive cell and the conventional lattice cell of the cubic spinel CdCr₂O₄.

We optimized the crystal structures with paramagnetic, ferromagnetic and antiferromagnetic orderings. The crystal structure of CdCr₂O₄ for the paramagnetic, ferromagnetic ordering are cubic ($a=b=c=8.667$ Å) with the space group $Fd\bar{3}m$ (No. 227), whereas for the antiferromagnetic ordering it is tetragonal ($a=b=8.634$ Å and $c=8.694$ Å) (Figure 3). In order to visualize this system, we used XCrySDen graphic software which is a crystalline and molecular structure visualization program [18].

Calculation methods

We performed density functional theory calculations using a plane-wave basis set method with generalized gradient approximation (GGA) parameterized by Perdew-Burkew-Enzerhof (PBE) exchange correlation methods [19] as implemented in the QUANTUM ESPRESSO simulation package [20]. Ultrasoft pseudopotentials were used for both cubic and tetragonal structures. The pseudopotentials that we used are including twelve valence electrons for Cd ($4d^{10}, 5s^2$), fourteen for Cr ($3s^2, 3p^6, 3d^5, 4s^1$), and six for O ($3s^2, 2p^4$). We obtained all pseudopotentials from the plane-wave self-consistent field (PWSCF) pseudopotentials online references [21].

In order to find the actual energy cut-off and k-point mesh, the scf convergence test was performed for all parameters and considered to be achieved with the minimum consecutive iterative steps with energy difference less than 1 meV (Figure 4). We applied the kinetic energy cut-off of 40 Ry for expanding the plain wave functions and a $8 \times 8 \times 8$ k-point mesh for the Brillouin zone (BZ) integration. All calculations are performed for collinear spins without spin-orbit coupling. The optimization of atomic positions was carried through the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm where the forces and energy minimization process are considered during structural relaxation.

Results

Spinel CdCr₂O₄ with the Cd non-magnetic and the Cr magnetic ions span a huge range of magnetic exchange strengths and different magnetic ground states. In this section, we discuss about the computational results on LSDA (or spin-polarized-GGA) calculations for both cubic and tetragonal structures of geometrically frustrated spinel CdCr₂O₄ in different magnetic configurations.

The Figure 5 shows the total density of states (DOS) for three different magnetic orderings of the spinel CdCr₂O₄. By looking at the charge density plot, we can find that in the paramagnetic configuration the two spin contributions are exactly the same due to its ground state is non-magnetic. In other word the valence bands (corresponding to bonding states) are all doubly occupied and the total magnetization is zero. Also, we presented the same density of states calculation

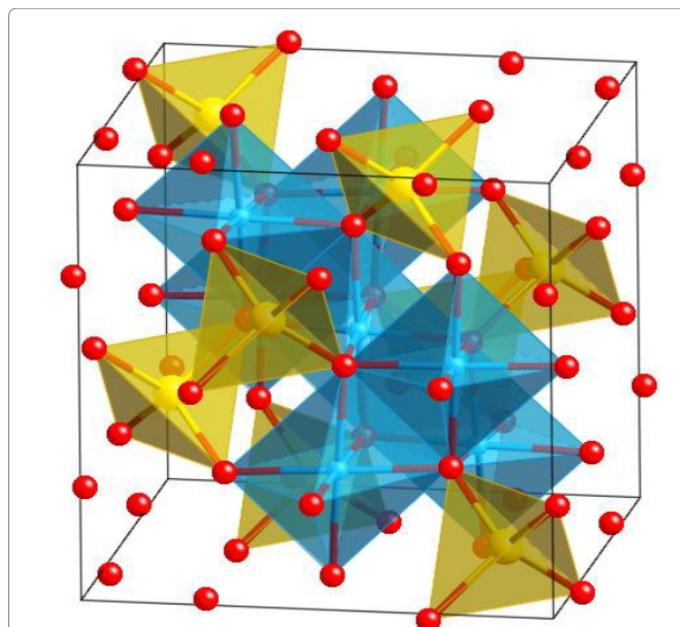


Figure 1: The cubic spinel structure of the chromium spinel ACr₂O₄: A²⁺ cations (yellow) are tetrahedrally coordinated and Cr³⁺ cations (blue) are octahedrally coordinated. Oxygen atoms are in red.

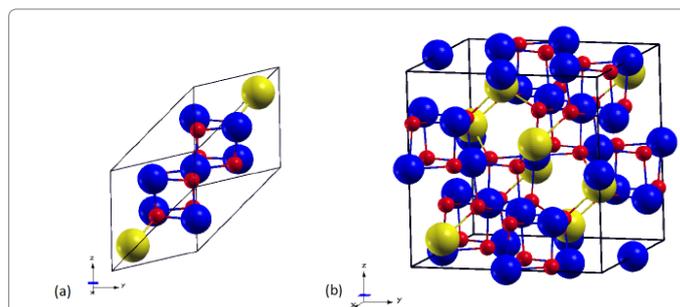


Figure 2: Crystal structures of cubic spinel CdCr₂O₄, (a) primitive cell, and (b) conventional lattice cell. The Cr is shown in blue, Cd in yellow and O in red.

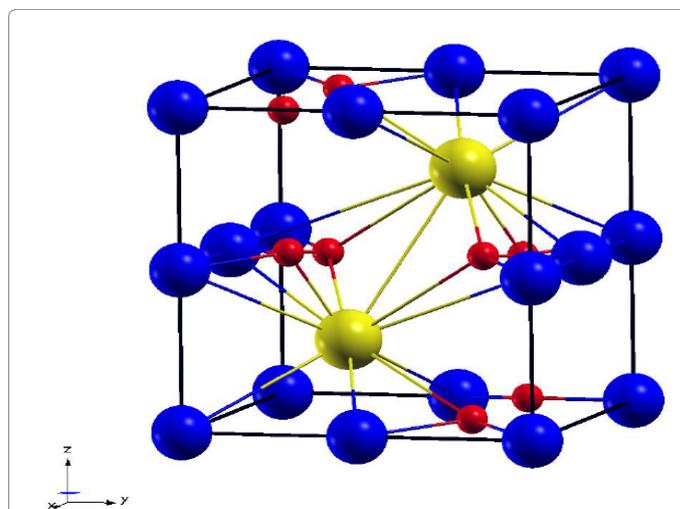


Figure 3: Tetragonal crystal structure of CdCr₂O₄ spinel for AFM ordering. Cr is shown in blue, Cd in yellow and O in red.

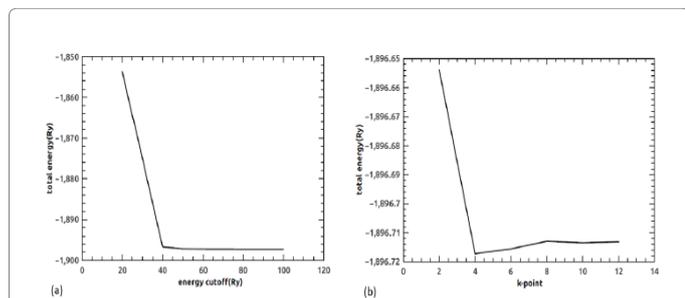


Figure 4: Convergence test with respect to (a) the energy cutoff, and (b) k-point.

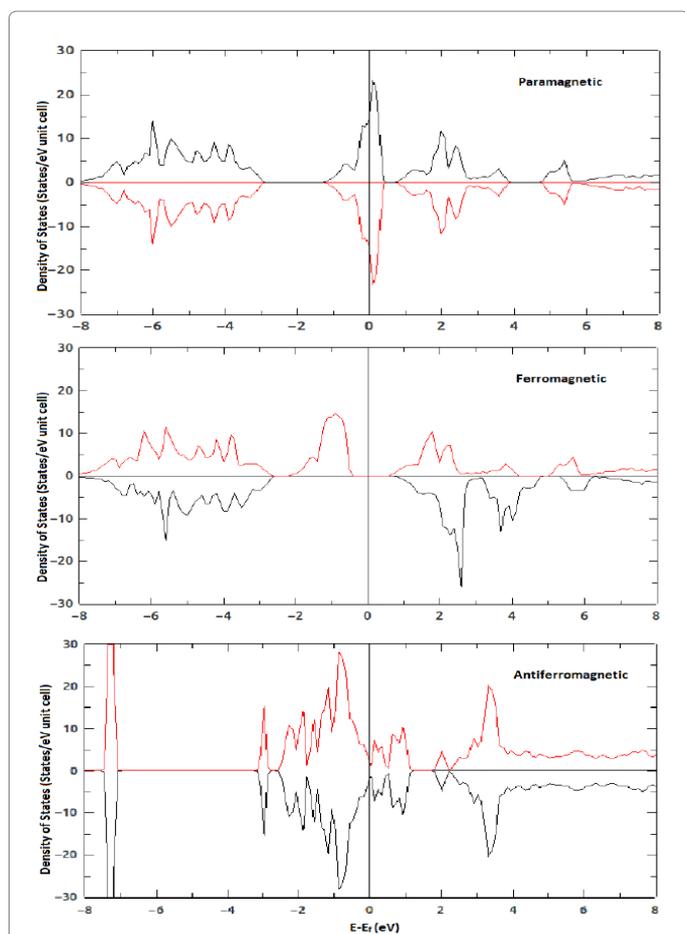


Figure 5: Density of states for CdCr₂O₄ in different magnetic configurations. The Fermi level E_f is indicated by vertical line.

for different magnetic configurations: ferromagnetic (FM) and antiferromagnetic (AFM) by applying the initial magnetization for Cr³⁺(3d³) magnetic atoms. In the FM configuration, we can observe that the density of states of the two spin are not aligned anymore and one spin population is larger than the other. Whereas, in the AFM configuration the two spin contributions are the same due to the total magnetization is zero as half of the atoms have a magnetization that is opposite to the magnetization of the other half.

In addition, the projected density of states (PDOS) is plotted for three different magnetic configurations, in order to observe the effect of magnetization by comparing the densities of Cd d, Cr d, and O p

states obtained from PDOS calculation for CdCr₂O₄ (Figure 6). As it is shown in Figure 6, in the PM and FM orderings of cubic CdCr₂O₄ the density of states of Cd and O atoms are remaining the same for both configurations, and only the density of Cr d states is changing from PM to FM. However, it is clear that by moving from cubic to tetragonal structure the density of states of the three elements have been changed, but the difference in densities is mainly for Cr atoms.

In order to understand the distribution of the total electronic charge density of CdCr₂O₄ compound, we calculated the electronic charge density in the (110) crystallographic plane for both cubic and tetragonal structures (Figure 7). From Figure 7, we can conclude that in PM and FM orderings which both are in cubic structure the Cr-O makes the covalent bonding due to sharing of charge between Cr and O atoms while Cd and O atoms shows the ionic bonding. It is clear that in cubic structure, Cd atom shows a very weak charge density but as we move to tetragonal structure, there is the stronger charge density, and also the Cd-O makes partial covalent bonding. As clear from the color charge density scale that the purple color (+1.0000) corresponds to the maximum charge accumulating site, so the chromium atoms have the greater charge density than the other atoms. By comparing the color of charge density scales in both structures, it is evident that the total electronic charge density in the tetragonal is stronger than in the cubic structure.

Summary

In the present work, we reported a comprehensive investigation of

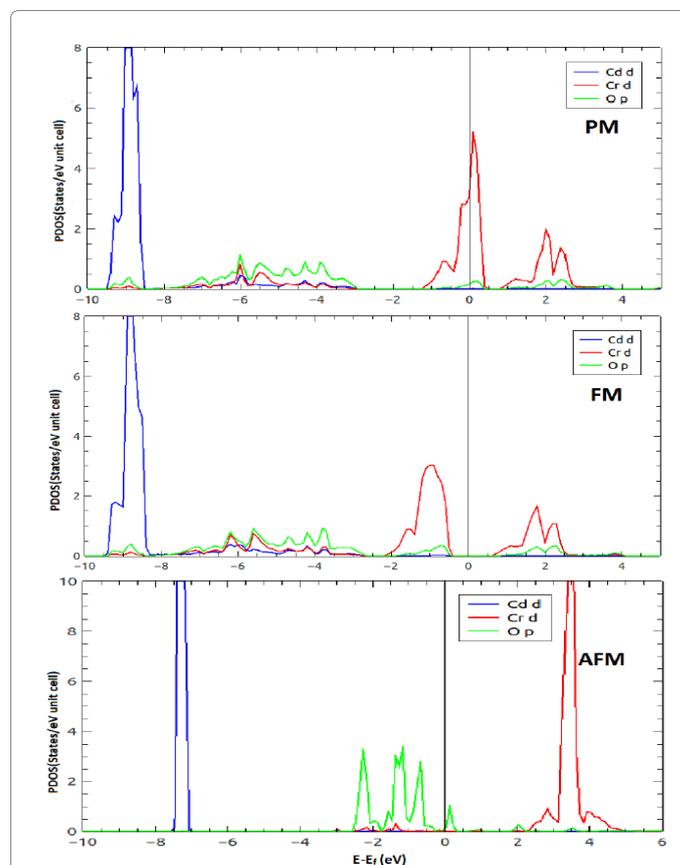
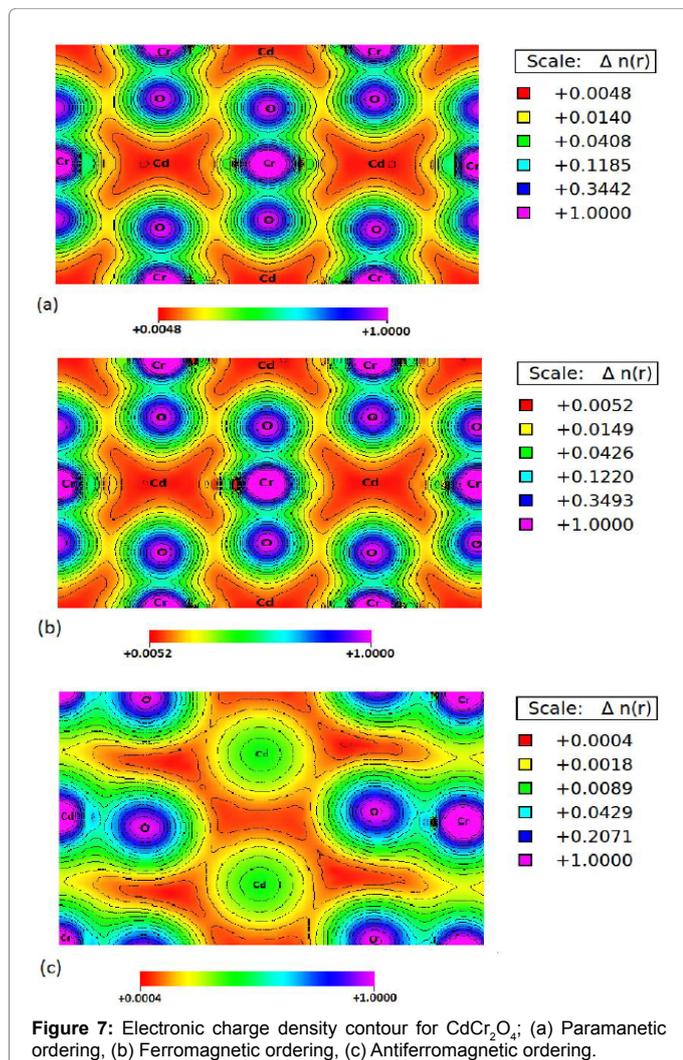


Figure 6: Projected density of states for cubic and tetragonal structure of CdCr₂O₄ in different magnetic configurations. The Fermi level E_f is indicated by vertical line.



the electronic structures, magnetic properties and chemical bonding properties of geometrically frustrated Spinel CdCr₂O₄ using the plane-wave Ultrasoft pseudopotential technique within generalized gradient approximation (GGA) parameterized by Perdew-Burkew-Enzerhof (PBE) exchange correlation calculation. Density functional calculations are performed to observe the effects of magnetic ordering on the electronic and magnetic properties of CdCr₂O₄ with non-magnetic Cd cations and magnetic Cr cations from a pyrochlore lattice.

Acknowledgments

This work is supported by University Putra Malaysia and Ministry of Higher Education (MOHE) Malaysia, through Fundamental Research Grant Scheme (FRGS) (Project Code: FRGS/1/11/ST/UPM/02/11). Figures showing electronic configurations, charge density and charge density contour are generated using the XCRYSDEN program.

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