

Investigation of Structural, Electronic and Magnetic Properties of Spinel by using Density Functional Theory

A Thesis

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*I would like to dedicate this thesis to my loving parents,
brothers, sister and wife.*

Declaration by the Research Guide

This is to certify that the thesis entitled “**Investigation of Structural, Electronic and Magnetic Properties of Spinel**s by using Density Functional Theory”, submitted by Mr. Sohan Lal to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Sudhir Kumar Pandey
October, 2017

Declaration by the Research Scholar

This is to certify that the thesis entitled “**Investigation of Structural, Electronic and Magnetic Properties of Spinel by using Density Functional Theory**”, submitted by me to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by me under the supervision of Dr. Sudhir Kumar Pandey. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Sohan Lal
October, 2017

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Abstract

The aim of the thesis is to study the structural, electronic and magnetic properties of spinels by using *ab initio* electronic structure calculations. In our research, we have applied density functional theory (DFT), DFT+*U* and DFT+dynamical-mean-field theory (DMFT) methods to resolve the various fundamental issues reported experimentally and theoretically in V and Cr spinels.

The present thesis is divided into seven chapters. In chapter one, we discuss the basic physics that is required to understand the materials under study, these are (i) historical aspects and structure of spinel compounds, (ii) details of strongly correlated materials including the definition of geometrical frustration and its effect on physical properties, (iii) crystal field splitting and Jahn-Teller effect in transition metal oxides, (iv) importance of orbital and spin degrees of freedom in deciding the various phenomena observed in the strongly correlated systems, (v) methods of calculating orbital ordering (OO) in these materials and describe the detailed issues of structural, electronic and magnetic properties of V and Cr spinels that are the subject of present thesis. After this chapter, we discuss a brief theoretical background of electronic structure calculations based on DFT, DFT+*U* and DFT+DMFT approaches along with the relevant computational methods in chapter two.

Chapter three explains the OO and cubic to tetragonal distortion in V and Cr spinels. In this chapter, we first study the long issue related to the OO in V spinels by using density matrices of V atoms computed in DFT+*U* method. In the absence of spin-orbit coupling (SOC), we have predicted the anti-ferro OO in the global (local octahedral) coordinate system where d_{xz} and d_{yz} ($d_{xz}+d_{yz}$ and $d_{xz}-d_{yz}$) orbitals are mainly occupied at the neighboring V sites for all the compounds. Then, we apply the spin unpolarized DFT calculations to understand a contentious issue of cubic to tetragonal distortion in V and Cr spinels and found that the main cause for such a distortion in these spinels are the effect of ionic sizes.

The role of orbital degrees of freedom in investigating the magnetic properties of geometrically frustrated V spinels are discussed in chapter four, using DFT+*U*+SOC calculations. In this chapter, we address the issue related to the inconsistency about the degree of geometrical frustration in these spinels, which arises from the two experimental results: (i) frustration indices and (ii) magnetic moments. The inclusion of the orbital and spin angular momenta

for calculating the frustration indices improve the understanding about the degree of geometrical frustration in these compounds. As compared to ZnV_2O_4 , the calculated values of the frustration indices (f_J) are the largest for MgV_2O_4 and the smallest for CdV_2O_4 for $3.3 \leq U \leq 5.3$ eV. In this range of U , we have also found the calculated values of $\Delta M_2 = M_{\text{total}} - M_{\text{exp}}$ (where, $M_{\text{total}} = M_{\text{spin}} - |M_{\text{orbital}}|$) to be the largest for MgV_2O_4 and the smallest for CdV_2O_4 . Hence, the consistency about the degree of geometrical frustration, which arises from the f_J as well as from the ΔM_2 is achieved and improves the understanding about the degree of geometrical frustration in these compounds.

In chapter five, we investigate the applicability of the DFT+ U method in understanding the electronic and magnetic properties of a geometrically frustrated V and Cr compounds, where the delicate balance of electrons, lattice, orbital and spin interactions play an important role in deciding its physical properties. Firstly, we describe the limitations of unconstrained (normal) DFT+ U method in predicting the electronic and magnetic ground state of a geometrically frustrated ZnV_2O_4 compound. Our work clearly suggests that the unconstrained DFT+ U calculations are not the correct methods for predicting the experimentally observed anti-ferromagnetic ground state of this system, while constrained DFT+ U calculations give it for wide parameter range of U . Hence, it is suggested that the constrained DFT+ U calculations should be preferred, if one wants to predict the real magnetic ground state of an unknown complex system, as small change in the magnetic moments of magnetic atoms in various spin configurations may lead to the prediction of wrong ground state of the compound. Secondly, we apply constrained DFT+ U method to understand the inconsistency reported by Yaresko in the theoretically estimated sign of nearest neighbour exchange coupling constant (i.e. Curie-Weiss temperature) and variation of its magnitude with increasing U in Cr spinels and found that such inconsistency is resolved by using this approach.

Electronic structure study of V spinels by using DFT and DFT+DMFT approaches is explained in chapter 6. In the first part of this chapter, we discuss the degree of localization of V $3d$ electrons in V spinels based on calculated values of $\frac{t}{U_{\text{eff}}}$ ratio (where t and U_{eff} are the transfer integral between neighbouring sites and on-site effective Coulomb interaction, respectively) and found that the degree of localization of these electrons is largest for CdV_2O_4 and smallest for ZnV_2O_4 as compared to MgV_2O_4 . In the second part of this chapter, we study the electronic structure of V spinels by using DFT and DMFT, where the self-consistently calculated material specific parameters, U_{eff} and Hund's coupling, J are used. Corresponding to these parameters, we have found that the main features, such as insulating band gaps, degree of itinerancy of V $3d$ electrons and position of the lower Hubbard band, are closely matched with the experiment data.

At last in chapter seven, we summarize the thesis, with a brief overview of the significant conclusions drawn and give direction for future work.

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