Investigating the Effect of Electronic Correlation on the Physical Properties of Late 3*d* Transition-metal Based Systems using *ab-initio* Methods

A Thesis

submitted

by

Paromita Dutta

(**Enrollment No: D15033**)

for the award of the degree of

Doctor of Philosophy

School of Basic Sciences

Indian Institute of Technology Mandi

Mandi, Himachal Pradesh-175075

January, 2022

(Revised)

I would like to dedicate this thesis to my beloved baba.

Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis is the result of investigations carried out by me in the ***School of Basic Sciences***, Indian Institute of Technology Mandi, under the supervision of ***Dr. Sudhir Kumar Pandey***, and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigations.

Place: IIT Mandi
Date: 13-01-2022

Signature
Name: Paromita Dutta

Declaration by the Research Guide

I hereby certify that the entire work in this Thesis has been carried out by ***Paromita Dutta*** under my supervision in the ***School of Basic Sciences***, Indian Institute of Technology Mandi, and that no part of it has been submitted elsewhere for any Degree or Diploma.

Name of the Guide: Dr. Sudhir Kumar Pandey

Signature

Date: 13-01-2022

Acknowledgements

To my surprise the day has finally come when I have to acknowledge each and every person who walked alongside while I was trying to complete my Ph.D. I was very skeptical of completing my Ph.D when I had to restart the journey with a blank canvas after two years. As it is said, a person, who enrolls for Ph.D, comes out as a completely different person when finishes it. Perhaps, very few people will understand it better than I do because I started this journey with a group of people and am finishing it with a completely different bunch of people. During this journey, I also dealt with my fears, failures with my determination, dedication and perseverance. In this period, I also experienced some irreparable loss in my personal life. Yet, I never felt alone and always had people who encouraged me from time to time and enlightened my path with their collective wisdom. So, there are many people I am indebted to for their valuable contribution to my thesis.

First of all, I would like to express my sincere gratitude to my Research Advisor **Dr. Sudhir K. Pandey**. He has been an amazing supervisor without whose guidance and continuous support I would not be able to complete my Ph.D. He made all of us believe that we are full of capabilities and it is our job to nurture them. He also taught us how to manage work-life balance. Because of his never ending patience and positive attitude towards life, discussion sessions with him always yielded positive energy which boosted my confidence and inspired me to overcome all the hurdles. I will always cherish those days when he used to sit with me and tried to make me understand a problem innumerable number of times. He always says, *'We should be able to visualize Physics and this is the only way to understand it. Unless someone understands a concept clearly, it can not be penned down properly. One's writing is the mirror image of her understanding of a topic.'* These words have been etched on my memory. Words will fall short to properly justify his contribution on shaping me for who I am today and also on this thesis in particular.

I would also like to take this opportunity to thank my Doctoral Committee members: **Dr. Aditi Halder** (Chair), **Dr. Hari Varma**, **Dr. Pradeep Kumar** and **Dr. Vishal S. Chauhan** for their valu-

able time and suggestions/critical comments on my research work which have further improved the quality. I would like to express my gratitude towards **Dr. Aditi Halder** in particular for supporting me at my lowest ebb during this journey. She always believed in me and encouraged me to outperform myself.

I would do injustice without expressing my gratitude to my lab members cum new found family at IIT Mandi - Antik, Shastri, Shamim, Arzena, Vivek, Abhishek, Shivani and Prakash for their constant support and critical comments on my thesis. They helped me to sail through this journey of a lifetime by being there with me. Antik, Shastri and Shamim in particular took a great deal of trouble to make sure that I don't lose focus and stay on correct path. I also extend my sincere thanks to my ex-lab members Dr. Sohan Lal and Dr. Saurabh Singh for helping me during my initial days of Ph.D. Special thanks to Dr. Sohan Lal for teaching me the initial basics of my research work. I would also like to thank Dr. Rohit Pathak and Dr. Imran Ahmed for their guidance.

Without the opportunity provided by IIT Mandi to pursue Ph.D. in this esteemed institution and the financial support of HTRA, this journey could not have possibly started. Hence, I extend my sincere thanks and humble gratitude to IIT Mandi. I also thank HPC facility of IIT Mandi as handle by Dr. Prashanth Jose and Dr. Gaurav Bhutani for providing the much needed computational facility for my research work. They are always there to help us out as when needed. Special thanks to SERB-DST for granting me a financial support for an international educational trip to Germany, which I will always cherish in my life.

I also acknowledge the contribution of my friends and family members without whose continuous support this journey would have not been possible. My special thanks to my dear roommate and great friend Dr. Manushree Vishnoi (Manu) for her continuous encouragement and never shaken belief on me. I will always remember our late night talks which used to be our best time of the day. I extend my gratitude to my dear friends of IIT Mandi - Dr. Ankita Mathur, Dr. Vyoma Singh, Dr. Mona Subramanium, Dr. Manju Bisht, Prabhjot Kaur, Dr. Ashish Mishra, Dr. Yashika Arora (Yashi), N. V. Amrutha (Ammu), Arshdeep Boparai (Arsh), Sujata (Su), Rishabh, Rasheed (Rashi), Shubham, Faizan (Faizu), Nooria, Dr. Gaurav Sharma, Jaskirat, Alam, Anindita di, Pooja di, Anjali, Bhoomika, Priyamedha, Chethna, Saahil, Khurshida Nazmin bhabhi, Surbhi, Suman, Bulti, Kavita, Amarjit, Dheeraj, Manish, Portia,Varnika, Sumanta, Moumita and Ayaan (my chotu) for filling me in with unforgettable memories which I will cherish throughout my life. I would also like to thank my dear

old friends (outside IIT Mandi) Maddy, Rashmi, Manish and Payal. Sometimes, we feel great even with the presence of few people. These four people are such persons in my life for which I will always be great full. These friends stood beside me without any demands and complains which itself a best part of it.

Last but not the least, I would like to express my warmest gratitude to my parents late Bijan Dutta and Ms. Biva Rani Dutta and my little sister Praneta Dutta. At first it was my dream to do Ph.D in Physics but eventually it became the dream of my family. I started this journey with my father but unfortunately I lost his physical presence. I hope he is watching me from heaven and must be proud of me today. It was their trust, selfless love and blessings which helped me to move forward and achieve my goal. I also extend my heartfelt gratitude to my new family- Mr. Alok Chandra Pal, Mrs. Champa Pal and to my dearest husband Mr. Arnab Paul. I am indebted to my family members and Arnab for being patient and keeping faith in me and my dreams.

Abstract

The aim of the thesis is to understand how the electronic correlations are affecting various physical properties of late 3*d* transition-metal based systems like $LaCoO_3$, FeSi and CoSi. The thesis presents a consistent study of these systems by using different *ab-initio* methods such as DFT, DFT+U, G_0W_0 and DFT+DMFT with the self-consistently calculated values of U & J. Each of these *ab-initio* methods deal differently with the different levels of electronic correlation existing in a material. The thesis shows an interesting study of $LaCoO_3$ and CoSi where they have different strength of correlations while having same Co 3*d* orbital. At the same time, FeSi and CoSi exhibits same structure and just differ by one electron, but still their properties are differently affected by electronic correlation.

The present thesis is divided into seven chapters. In chapter one, we discuss the history and development of the *ab-initio* methods for studying the properties of a material in condensed matter physics. This historical aspect is followed with the introduction of on-site Coulomb interaction U & Hund's like exchange interaction J. For performing the electronic structure calculations these two parameters play an important role. After this, we reasoned out the need of these parameters and then followed by the description of *first-principles* based methods developed for calculating these parameters. After this chapter, we provide an overview of the theoretical methods such as DFT, DFT+U, GW, DFT+DMFT and semiclassical transport theory used for the investigations carried out in chapter two.

Chapter 3 provides a systematic study of the electronic structure of $LaCoO_3$ by using DFT, DFT+U and DFT+DMFT methodologies. The objective of this chapter is to see what level of electronic correlation is existing in the electronic structure of the compound. In this chapter we compared the density of states (DOS) as calculated from DFT, DFT+U and DFT+DMFT separately with photoemission (PES) and inverse photoemission spectra (IPES), respectively. The chapter brings out the difference between theoretical methods with their individual limitations in describing the experimental spectral attributes of the occupied and unoccupied states of $LaCoO_3$. For the investigation, U is calculated using cDFT method $\sim$ 6.9 eV for Co 3*d* and using this U value J is calculated as $\sim$ 1.18 eV. The study shows that DFT has failed in even creating the hard gap while the

DOS distribution seems to be similar to the experimental attributes. However, DFT+U created the gap $\sim$ 1.8 eV but eventually failed in explaining the DOS distribution with PES mainly. However, DFT+DMFT created the gap $\sim$ 1.1 eV and successfully explained the DOS distribution for both PES and IPES. This indicates that the level of correlations as treated within DFT+DMFT seems appropriate to understand the electronic states of $LaCoO_3$.

In chapter 4, we studied the effect of correlations of Fe (and Co) 3d electrons in FeSi (and CoSi) using DFT and DFT+DMFT methods. This is because FeSi has been reported to possess unusual temperature-dependent properties which are the consequences of its electron-electron interactions. At the same time, CoSi exhibits the same structure as FeSi does and just differs by one electron. So, there is an expectation of seeing the similar unusual temperature-dependent behavior in CoSi. We compared the calculated spectral functions from both DFT and DFT+DMFT methods with the available experimental x-ray PES data of both compounds. The calculated spectral functions from DFT+DMFT are found to provide fairly good representation for the experimentally observed PES for both compounds. This motivated us to carry forward the investigation by using DFT+DMFT method. From the study of the temperature-dependent (100-800 K) DOS and momentum resolved spectral functions the influence of electronic correlations on the electronic states of FeSi are found be largely affected than CoSi. From momentum resolved spectral functions, the excitations have shown enhanced broadening with temperature rise in FeSi whereas an opposite behavior is observed in CoSi.

Chapter 5 studies the effect of pressure and temperature on the role of electronic correlation Fe 3d electrons in FeSi. In this chapter, the we tried to understand the pressure-dependent experimental observations of resistivity and bandgap by using *ab-initio* methods. At first, we studied the DFT obtained partial DOS and then DFT+DMFT obtained total DOS for T = 100 K and T = 300 K. Both the calculations have revealed the widening of the bandgap with increase in pressure which is similar to other experimental observations for stoichiometric FeSi. However, they could not explain the experimental observation of insulator-to-metal transition when T $<$ 50 K with the condition P $\geq$ 14.4 GPa for nearly stoichiometric FeSi samples. As it is generally seen that the samples prepared experimentally are often found to be off-stoichiometric. Considering this fact, we then studied the electronic structure of $Fe_{1.02}Si_{0.98}$ using DFT based KKR-CPA method. KKR-CPA calculations revealed that the impurity states have been generated in the gapped region around the Fermi level and they have half-metallic behavior. With pressure increment the closure of the energy gap (in one channel) appears to be responsible for the experimental observation for the Fe excess sample. Further, KKR-CPA calculations have suggested the presence of strong Hund's coupling responsible for creation of net magnetic moment at Si site when Fe is in excess.

CoSi having the crystal structure which belongs to the B20 type with $P2_13$ spacegroup lacks the inversion center. Such a symmetry causes the emergence of unconventional fermionic quasiparticles (QPs) in CoSi which has been shown experimentally and theoretically (studies based on DFT). Since interacting picture is quite important because this picture takes account of the electronic correlations differently. Therefore, it is very important to see its effect onto these newly found fermions. In chapter 6, we studied the spectral functions of bulk and (001) surface of CoSi using DFT, DFT + DMFT (T = 100 K) and G_0W_0 methodologies with and without inclusion of spin–orbit coupling (SOC), respectively. SOC and electronic correlations appear to modify the nature of bands involved at Γ point. The existence of both coherent and incoherent features indicates the presence of QP–QP interactions which is eventually affecting the lifetime (τ) of exotic fermionic QPs. As CoSi has been reported to have exotic fermions at three nodal points in the band structure such as two at Γ (G1 & G2) and one at R (R1). Thus, if the chemical potential is kept close to the energies of these nodal points then there is a possibility of capturing the unconventional charge carriers' contribution to electronic transport of CoSi. Based on this, the chapter 6 further studies the transport coefficients at these three nodal points for the temperature 40-300 K by using first principle based DFT method.

At last in chapter 7, we summarize the thesis, with a brief overview of the significant conclusions drawn and give directions for future work.

Table of contents