First-principles study of the magnetism in indium oxide-based dilute magnetic semiconductors

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FIRST-PRINCIPLES STUDY OF THE MAGNETISM IN
INDIUM OXIDE-BASED DILUTE MAGNETIC
SEMICONDUCTORS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2011

**FIRST-PRINCIPLES STUDY OF
THE MAGNETISM IN INDIUM OXIDE-BASED
DILUTE MAGNETIC SEMICONDUCTORS**

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A thesis submitted to Nanyang Technological University in partial
fulfillment of the requirement for the degree of Doctor of Philosophy

2011

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other university or institution.

Aug 04 2011

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SUMMARY

Using In_2O_3 as a host matrix, extensive calculations based on density functional theory (DFT) have been carried out to understand the electronic and magnetic properties of this system. Transition metal (TM) doping, $2p$ elements doping as well as native defects, alkali and alkaline-earth metal elements substitutions have been used to introduce the local magnetic moment, for which the role of magnetic coupling have been studied. As is well known, TM doping is the conventional approach to introduce local magnetic moment into various DMS systems. Among all TM-doped In_2O_3 , Fe-doped In_2O_3 (IFO) is the suitable prototype system for study due to its high solubility of Fe in In_2O_3 (>20%). Our DFT studies show that the ground state of pure IFO is antiferromagnetic (AFM), but the existence of O vacancy (V_O) or with Cu co-doping (IFCO) could lead to a weak ferromagnetic (FM) coupling for some special configurations. The coexistence of V_O and Cu co-doping (IFCO- V_O) can greatly enhance the stability of the ferromagnetism. The role of Cu ions is to act as super-exchange mediators causing an indirect FM coupling between Fe cations through the hybridization of the Cu $3d$ states with the O $2p$ states. In favor of the FM state, Cu ions prefer to locate adjacent to the Fe ions in order to form Fe1-O1-Cu-O2-Fe2 coupling chain.

In case of the $2p$ non-magnetic element doping, N was used to substitute the O atoms. Our investigations suggest that N dopant introduces spin-polarized hole states in the band gap generating a total magnetic moment of $1.0 \mu_B$ per N, which is mainly localized on the doped N atoms. The FM exchange interaction between N dopants is activated through holes induced by N doping via a $\text{N1}:p\text{-In}_{\text{br}}:d/p\text{-N2}:p$ coupling chain in short N-N separations, which plays the major role in forming the ferromagnetism in N- In_2O_3 system.

Our calculations show it is In vacancies (V_{In}) rather than V_{O} that introduce magnetism in undoped In_2O_3 . Furthermore, alkali doping can also lead to FM coupling which is more favored for the room temperature ferromagnetism due to the negative formation energy. The induced magnetic moments are mainly localized on the first shell of O atoms around X_{In} sites for all cases. The FM coupling is activated by intra- and inter-correlation of the $X_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complexes. A coupling chain composed of neighboring In and O atoms is recognized to mediate the long range FM coupling. However, in cases of Mg or Ca doped In_2O_3 , the ground state is nonmagnetic.

In summary, our theoretical investigations illustrate that In_2O_3 is a promising host material for potential room temperature DMSs, among which the FM coupling can be tuned up through multiple means. Especially, it can be engineered by non-magnetic elements doping, which are more attractive compared to TM doping due to the well-known problems in the latter.

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Chapter one

Introduction

1.1 Background

With the development of science and technology, a new kind of materials called spintronics materials have come into being. As the extension of the conventional electronics, spintronics materials exploit spin properties of electrons instead of or in addition to charge properties. Combined spin and charge degrees of freedom, the spintronics devices would give extensive advantages, such as non-volatility, increased data processing speed, decreased electric power consumption, and increased integration density. The prototype device already used in industry is the giant-magnetoresistive (GMR) material in a read head and a memory-storage cell.

To make the spintronics device a reality, many technical issues need to be solved. For instance, in order to reduce the resistivity mismatch on spin injection, diluted magnetic semiconductors (DMSs) have been demonstrated to be the best choice. This has inspired a great deal of experimental and theoretical work in seeking high (above room temperature) Curie temperature (T_C) DMS. Other technical essentials include the carriers transport within the host semiconductor,

and the ability to detect and control the spin transport through external means. Nitta *et al.* [5] demonstrated that a spin-orbital interaction in a semiconductor quantum well could be controlled by applying a gate voltage. A proposed technology tree of spin-based devices is illustrated in Figure 1.1.

Figure 1.1 Technology tree for spin-based devices and their potential applications (after http://spintronics.korea.ac.kr/research_map1.htm).

As is well known, for functional material design and elucidating underlying mechanisms of experimental phenomena, first-principles density functional theory (DFT) is a theoretical approach that completely independent on experimental work. It is clean and efficient than the experimental methods. Therefore, combined with experimental work, theoretical modeling and computations become more and more widely used and successfully applied to the spintronics material design and mechanism illustration.

1.2 Magnetism in solids

For an ion or atom, the magnetic properties are determined by the orientation and the number of its electron spins. The macroscopic magnetic properties of a solid are the collective effect of all the spin of the atoms. Normally, materials can exhibit a variety of magnetic properties, such as Pauli paramagnetism, diamagnetism, spin glasses, antiferromagnetism, ferrimagnetism and ferromagnetism. In $3d$ transition metal (TM) oxides, the same $3d$ electrons usually determine both the electronic and magnetic properties, whereas in $4f$ TM oxides, the $4f$ electrons determine the magnetism, and $5d/6s$ electrons determine the electronic properties. In TM oxides the individual electrons are so strongly correlated in their motion that the spin of an ion is better characterized by one total spin than the individual electron spins. The atomic spins of neighboring ions may also be strongly correlated with each other through exchange interaction effect.

Magnetic interactions are usually described by exchange interactions using Heisenberg Hamiltonian, $H = -2J \sum_{i>j} S_i \cdot S_j$. The short-range interaction couples spins and depends on the overlap of the interacting orbitals. The collective effects of magnetic magnetism includes electronic structure of oxides, magnetic interactions and charge and orbital order, which are therefore classified in details as Mott and charge-transfer insulators, hopping conduction, super-exchange interactions, Goodenough-Kanamori rules, double exchange, interatomic orbital interactions, orbital order and charge order, *etc.*

1.3 Theoretical modeling of magnetism in solids

In a ferromagnetic (FM) material, the interaction among spins is so strong that the magnetic moments are aligned parallel to each other. Such an internal

interaction is called exchange field. The macroscopic magnetism is a competition result of exchange and kinetic energy. The exchange energy is gained by parallel alignment of the electron spins, which causes a loss of kinetic energy. Spin-polarized calculation within the framework of DFT is a powerful tool to theoretically model the magnetism in solids. Using spin-polarized DFT, one can theoretically determine the spin magnetic moments in solids, and most importantly, be able to understand the basic mechanisms of magnetism in those materials. The magnetic moment of individual atom inside the solids is considered separately and the integral spin moment, M_{spin} , is simply described assuming a collinear system:

$$M_{spin} = \int m(r) dr = \int (n^+(r) - n^-(r)) dr$$

The exchange-correlation potential used will affect the accuracy of an actual calculation. In this thesis, the exchange-correlation potential has been treated by the projector augmented-wave (PAW) [6] method with Perdew-Burke-Ernzerhof (PBE) form generalized-gradient approximation (GGA), [7] which has been demonstrated to be the most efficient method for big magnetic system study without sacrificing the accuracy.

1.4 Objectives

The main objective of this thesis is to make a theoretical investigating on the mechanism of the magnetism in doped In_2O_3 , both TM and non-TM doping and the effect introduced by the doping. The detailed objectives can be split up into the following parts:

Recently, there are abundant yet controversial experimental reports on $3d$ TMs doped In_2O_3 . Numerous experimental findings as well as some previous first-

principles calculations of the electronic structure and magnetic interaction of the doped, especially TMs doped oxide-based DMS [8-14], suggest that the vacancies or some other defects induced during the sample preparation process may serve as important factors to introduce ferromagnetism in these kinds of materials. Among all TMs doped In_2O_3 , Fe doped In_2O_3 ($\text{In}_2\text{O}_3\text{:Fe}$, IFO) is a suitable prototype system for study due to the high solubility of Fe in the In_2O_3 ($> 20\%$) and a homogeneous solid solution can be realized at least up to 15% Fe doping [12-13]. Cu has been co-doped with Fe into In_2O_3 (IFCO) in order to achieve multiple oxidation states of Fe^{2+} and Fe^{3+} , which has been reported to be essential for exhibiting FM coupling [12-15]. Part of this thesis has been devoted to theoretically study the origin of ferromagnetism in TMs doped In_2O_3 , especially TMs co-doped In_2O_3 .

On the other hand, the magnetic elements doping suffers from the problems related to precipitates or secondary phase formation. These extrinsic magnetic behaviors are undesirable for practical applications. This promotes searching for other dopants, which do not contain ions with partially filled d or f bands. Recently, it is reported that p electron doping is an alternative way to provide free carriers that can be introduced simultaneously and can be spin polarized by the local moments induced by the defects. As shown in Figure 1.2, this has been demonstrated to be due to the narrow $2p$ wavefunction of N and O, which is comparable to that of Mn $3d$. In this thesis, we choose N to investigate the effect of $2p$ electron doping in In_2O_3 to explore the possibility of using nitrogen as a dopant to produce oxides-based DMSs. Other than $2p$ element doping, the effects of intrinsic defects and alkali metals doping, i.e. s electron doping, at In site has also been studied.

Figure 1.2. A plot of radial charge distribution for N $2p$, along with O $2p$, S $3p$ and Mn $3d$ -states for comparison. After Ref. [1].

1.5 Major contributions of the thesis

The major contributions achieved in this thesis are summarized as follows:

(1) The electronic structures and the ferromagnetic (FM) stability in $\text{In}_2\text{O}_3\text{:Fe}$ (IFO) with additional Cu and oxygen vacancy (V_{O}) doping have been investigated using first-principles calculations within the framework of density functional theory. It is found that pure IFO has an antiferromagnetic (AFM) ground state, but the existence of V_{O} or with Cu co-doping could lead to a weak FM coupling in IFO system for some special configurations. The stability of the ferromagnetism is greatly enhanced by the coexistence of V_{O} and Cu co-doping in IFO system (IFCO- V_{O}). We demonstrate that the role of Cu ions is to act as superexchange mediators causing an indirect FM coupling between Fe cations through the hybridization of the Cu $3d$ states with the O $2p$ states. The delocalized

hybridization consisted of Fe $3d$, O $2p$, and Cu $3d$ is found to be very efficient to mediate the FM exchange interaction. In favor of the FM state, Cu ions prefer to locate adjacent to the Fe ions in order to form Fe1-O1-Cu-O2-Fe2 coupling chain. The results of our calculations suggest the possibility of fabricating In_2O_3 based transparent spintronics by (Fe, Cu) co-doping in a reduced growth ambient.

(2) In nitrogen doped In_2O_3 (N- In_2O_3), our calculations predict a total magnetic moment of $1.0 \mu_B$ per N, which is mainly localized on the doped N atoms. FM coupling is possible to be activated between adjacent N dopants. Examination of spin density distribution and density of state (DOS) spectra reveals that the direct coupling between N dopants serves as the major role for FM coupling between them. In addition to the direct coupling, the spin-polarized O $2p$ holes states coupled with the N $2p$ localized spins by a like p - p interaction can mediate the spin alignment of the N dopants indirectly.

(3) Using In_2O_3 as a host matrix, extensive calculations based on DFT have been carried out to understand the electronic and magnetic properties of native defects, alkali and alkaline-earth metal elements substitutions as disputed in recent theoretical and experimental studies. Our calculations show that the magnetism in undoped In_2O_3 is originated from In vacancies (V_{In}) instead of O vacancies. The ferromagnetic (FM) coupling between the moments introduced by two V_{In} is found to be strong enough to achieve room temperature ferromagnetism. Moreover, FM coupling is also strongly favored for alkali doping with negative formation energy. For all X_{In} ($X = V_{\text{In}}$, Li, Na and K) doped In_2O_3 , the induced magnetic moments are mainly localized on the first shell of O atoms around X_{In} sites. The FM coupling between the moments induced by X_{In} defects is activated by intra- and inter-correlation of the $X_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complexes. A $X_{\text{In}}\text{-O}_{\text{NN}}\text{-In}_{\text{NN}}\text{-O}_{\text{NN}}\text{-}X_{\text{In}}$ chain is required

to mediate the long range FM coupling. However, in cases of Mg or Ca doped In_2O_3 , the ground state is nonmagnetic.

1.6 Organization of the thesis

This thesis consists of seven Chapters. Chapter 1 gives a background introduction to the studies involved in this thesis. The objectives of this thesis, the major contributions as well as the organization of the thesis are also presented in this Chapter.

Chapter 2 briefly describes the theoretical framework, ranging from many-body quantum mechanics to DFT theory. The description of the most popular approximations of exchange correlation energy used in DFT calculation have also been covered

Chapter 3 provides an introduction of DMS materials, which is the material system studied in this thesis. The magnetic coupling mechanism models as proposed for DMS system have also been detailed in this chapter.

The study of the roles of TM doping in In_2O_3 is devoted in Chapter 4. In this chapter, the role of Cu co-doping and oxygen vacancies on ferromagnetism in $\text{In}_2\text{O}_3\text{:Fe}$ has been investigated.

In Chapter 5, we performed the first-principles study on non-TM $2p$ element doped In_2O_3 . A possible room temperature ferromagnetism of N doped In_2O_3 has been predicted and the origin of the magnetic coupling in this system is elaborated.

Chapter 6 studies nonconventional magnetism in pristine and alkali doped In_2O_3 , which is another non-TM doping case, i.e., s electron doping.

In Chapter 7, a summary of this thesis as well as the future work have been given.

Chapter two

Theoretical framework

2.1 Introduction

In this chapter, we introduce the many-body problem and some earlier approximations and theories that built up the density functional theory (DFT). We should also keep in mind of the limitations of DFT in describing some material properties, such as the weakness of treating strongly correlated systems and underestimating the band gap in semiconductors. It is still a hot research topic to further improve the DFT theory to overcome these problems, by developing the exchange and correlation potentials or by the inclusion of additive terms.

2.2 Many-body quantum mechanics

Most of the physical properties are predictable based on the quantum mechanics laws that are widely perceived as leading to first-principles approaches to understand condensed matter materials properties. First-principles studies mean to obtain material properties without any adjustable parameters. In principle, all physical properties of the system being studied can be obtained from the wavefunctions of electrons, which are the solutions to the Schrödinger equation of

the complete N -electrons system. The full Hamiltonian of a system consisting of N -electrons and K -nuclei reads:

$$\begin{aligned}
 H = & -\sum_i^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_n^K \frac{\hbar^2}{2M_n} \nabla_n^2 + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \\
 & - \frac{1}{4\pi\epsilon_0} \sum_i^N \sum_n^K \frac{Z_n e^2}{|\vec{R}_n - \vec{r}_i|} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n \neq l} \frac{Z_n Z_l e^2}{|\vec{R}_n - \vec{R}_l|} \\
 = & T_e + T_{ion} + V_{ee} + V_{e-ion} + V_{ion-ion}
 \end{aligned} \tag{2.1}$$

The index i refers to the electrons and n to the nuclei, m_e and M_n are the masses of electrons and nuclei. The first two terms on the right side of Eq. (2.1) represent the kinetic energies of electrons and ions, respectively; the next three terms are the Coulomb repulsion between the electrons, the Coulomb attraction between electrons and nuclei and the Coulomb repulsion between the nuclei, respectively. In principle, the eigenfunctions and eigenvalues for this quantum mechanics problem can be obtained by solving the time-independent Schrödinger equation:

$$\hat{H}\psi(\vec{r}_i, \vec{R}_n) = E\psi(\vec{r}_i, \vec{R}_n) \tag{2.2}$$

where $\psi(\vec{r}_i, \vec{R}_n)$ is the many-body eigenfunction of $\hat{H}$ which depends on both the positions $\vec{r}_i$ and $\vec{R}_n$ of the electrons and nuclei, E is the eigenvalue of $\hat{H}$.

However, such N -body Schrödinger equation is too complex to be handled directly. It turns out that if the number of electrons and nuclei is not extremely small (typically smaller than four), it is impossible to solve such N -body Schrödinger equation directly on even the most speedy supercomputer available. Important approximations must be made to simplify this Hamiltonian in order to proceed any further.

2.3 The Born-Oppenheimer approximation

Due to the fact that the massive nuclei move much slower than the electrons, Born and Oppenheimer made the approximation [16] that the motion of electrons and the nuclei in molecules can be separated so that the electrons can be considered as moving in the field of fixed nuclei to simplify an interacting many-body system. Therefore, the wavefunction of the system can be decoupled in real systems and written as,

$$\psi(\vec{r}_i, \vec{R}_n) = \psi_R(\vec{r}_i) \Phi(\vec{R}_n) \quad (2.3)$$

where $\Phi(\vec{R}_n)$ is the wavefunction of the nuclei and $\psi_R(\vec{r}_i)$ is the many-electron wavefunction that depends on the ionic configuration $\vec{R}_n$ parametrically. This approximation involves the following: (1) the electron wavefunction depends upon the nuclei positions but not upon their velocities; (2) the nuclei motion (e.g., rotation, vibration) sees a smeared out potential from the speedy electrons.

Furthermore, T_{ion} can be neglected since it is much smaller than T_e by a factor of $\sim 10^3$ - 10^5 . Thus for a fixed nuclei configuration, we have the full Hamiltonian of the many-body system as,

$$\begin{aligned} H_{BO} = & - \sum_i^N \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \\ & - \frac{1}{4\pi\epsilon_0} \sum_i^N \sum_n^K \frac{Z_n e^2}{|\vec{R}_n - \vec{r}_i|} + \frac{1}{8\pi\epsilon_0} \sum_{n \neq l} \frac{Z_n Z_l e^2}{|\vec{R}_n - \vec{R}_l|} \\ = & T_e + V_{ee} + V_{e-ion} + V_{ion-ion} \end{aligned} \quad (2.4)$$

The term $V_{ion-ion}$ is negligible in the above equation, since it is just a constant and shifts the eigenvalues by some constant amount. Leaving $V_{ion-ion}$ out, the Schrödinger equation is simplified as,

$$(T_e + V_{ee} + V_{e-ion})\psi_R(\vec{r}_i) = \epsilon(\vec{R}_n)\psi_R(\vec{r}_i)$$

$$\text{or } H_e \psi_R(\vec{r}_i) = \epsilon(\vec{R}_n) \psi_R(\vec{r}_i) \quad (2.5)$$

Although greatly simplified, further approximations are needed to solve the equations describing N -interacting-electrons ($N \sim 10^{23}$) in a solid. One of the earlier attempts to tackle this problem was the Hartree-Fock approximation, which was first proposed by D. R. Hartree (1928), and further improved by V. A. Fock (1930).

2.4 Hartree and Hartree-Fock approximations

2.4.1 Hartree approximation

Hartree approximation starts from the one-electron equations. In order to apply the variational principle, it assumes the trial wavefunction, $\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N)$, for the many-electron as the product of one-electron wavefunctions φ_i , i.e.

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N) = \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \cdots \varphi_N(\vec{r}_N) \quad (2.6)$$

and each of the functions is normalized to unity and satisfies the orthonormality condition. To pick $\{\varphi_i\}$ such that $\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle = E$ is a minimum of the many-electron Hamiltonian [see Eq. (2.5)], the variational principle is applied and we have

$$\frac{\delta}{\delta \varphi_i^*} [\langle \psi | \hat{H} | \psi \rangle - \varepsilon_i \langle \varphi_i | \varphi_i \rangle] = 0 \quad (2.7)$$

where ε_i is the Lagrange multipliers which is used to make sure the normalized condition of the one-electron wave functions. Eq. (2.7) leads to a set of single particle equations,

$$\varepsilon_i \varphi_i(\vec{r}) = \left[-\frac{1}{2} \nabla^2 + V_{e-ion} + \sum_{j \neq i} \int d^3 \vec{r}' \frac{|\varphi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} \right] \varphi_i(\vec{r})$$

$$\text{or, } (T_e + V_{e-ion} + V_H) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}) \quad (2.8)$$

$$\text{where, } V_H = \int d^3\vec{r}' \frac{\sum_{j \neq i} |\varphi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|}$$

For the sake of convenience, the reduced units have been applied by setting $e = m_e = \hbar = 1$ in the above equations. The third term, V_H , on the left-hand side of the Eq. (2.8) is called the Coulomb or Hartree potential.

The Hartree approximation reduces the interaction of many-electron system to that of the independent particles, i.e., each electron moving in the averaged Coulomb potential due to the rest of the others. Therefore, the Lagrange multipliers ε_i can be treated as the single particle orbital energies. The Hartree equation is a nonlinear equation and is solved self consistently by iteration and in the older literatures, it is, therefore, often called the self-consistent field (SCF) method.

2.4.2 Hartree-Fock approximation

However, the Hartree equations fail to give the right physical picture for fermion system. The Hartree-Fock approximation is an extension of the above Hartree approximation by including the permutation symmetry of the wavefunction which leads to the exchange interaction due to the Pauli's exclusion principle. Therefore, the total wavefunction for the system must be antisymmetric under particle exchange. This means that when two arguments are swapped the wavefunction changes sign,

$$\psi(\xi_1, \xi_2, \dots, \xi_i, \dots, \xi_j, \dots, \xi_N) = -\psi(\xi_1, \xi_2, \dots, \xi_j, \dots, \xi_i, \dots, \xi_N) \quad (2.9)$$

where ξ_i includes both spin and position coordinates. The exact N -electron wavefunction of the system has been approximated by a single Slater determinant (in the case where the particles are fermions) or by a single permanent (in the case

of bosons) of N -spin-orbitals. This approximation to the many-electron wavefunction was proposed by V. Fock in 1930, resulting in the Hartree-Fock (HF) approach,

$$\psi(\xi_1, \xi_2, \dots, \xi_i, \dots, \xi_j, \dots, \xi_N) = \begin{vmatrix} \varphi_1(\xi_1) & \varphi_1(\xi_2) & \cdots & \varphi_1(\xi_N) \\ \varphi_2(\xi_1) & \varphi_2(\xi_2) & \cdots & \varphi_2(\xi_N) \\ \vdots & \vdots & \cdots & \vdots \\ \varphi_i(\xi_1) & \varphi_i(\xi_2) & \cdots & \varphi_i(\xi_N) \\ \vdots & \vdots & \cdots & \vdots \\ \varphi_j(\xi_1) & \varphi_j(\xi_2) & \cdots & \varphi_j(\xi_N) \\ \vdots & \vdots & \cdots & \vdots \\ \varphi_N(\xi_1) & \varphi_N(\xi_2) & \cdots & \varphi_N(\xi_N) \end{vmatrix} \quad (2.10)$$

To work out the Schrödinger equation with the wavefunction given above for the same-spin electrons, one reaches the following set of one-electron equations, the HF equations, using the same method as was used in the derivation of the Hartree equations to minimize the expectation system energy with respect to the one-electron wavefunctions,

$$\varepsilon_i \varphi_i = \left[\left(-\frac{1}{2} \nabla^2 + V_{e-ion} \right) + \int d^3 \vec{r}' \frac{\sum_{j \neq i} |\varphi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} \right] \varphi_i - \sum_j \delta_{s_i; s_j} \int d^3 \vec{r}' \frac{\varphi_j^*(\vec{r}') \varphi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} \varphi_j \quad (2.11)$$

$$\text{or } \varepsilon_i \varphi_i = (T_e + V_{e-ion} + V_H) \varphi_i + \int V_{ex}(\vec{r}, \vec{r}') \varphi_i(\vec{r}') d^3 \vec{r}' \quad (2.12)$$

where $T_e = -\frac{1}{2} \nabla^2$, and

$$V_{ex}(\vec{r}, \vec{r}') = V_{Fock} = - \sum_j \delta_{s_i; s_j} \int \frac{\varphi_j^*(\vec{r}') \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (2.13)$$

The fourth term in the HF Eq. (2.12) is called the exchange interaction potential (or the Fock potential). As shown in Eq. (2.13), the exchange interaction

potential $V_{ex}(\vec{r}, \vec{r}')$ is a non-local operator, and is non-zero only for the electrons of the same spin. Like the Hartree equations, the HF equation requires SCF methods for seeking their solutions.

The big development made in HF theory is the exact cancellation of the self-interaction terms coming from Coulomb and exchange interaction potentials, which makes the HF theory free of self-interaction. However, the HF theory totally neglects the correlation effects of the many-electrons system, which is due to the screening of the Coulomb interaction between the charges. Therefore, the HF method is applied successfully to atoms and molecules, but fails to describe the correct properties of the extended systems, like metals. The failure of the HF approach is improved greatly by density functional theory (DFT), which will be introduced below.

2.5 Density Functional Theory (DFT)

2.5.1 Introduction to DFT

In an interacting many-body system, wavefunction $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N)$ with its dependence on about $3N$ ($N \sim 10^{23}$) parameters is too complicated to be used as the fundamental variable in the variational approach. As the name suggests, the DFT approach developed by Kohn and Sham [17] showed that one can treat the ground state electron charge density $\rho_0(\vec{r})$ as the fundamental variable that itself is a function of three spatial variables only rather than using the wavefunction, $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N)$. It gives a great conceptual simplification of the many-body problem, as the ground state density is a scalar function of three variables only. In

principle it is an exact ground state theory. Kohn and Sham [18] further developed this theory by mapping the complicated system of N interacting electrons onto an auxiliary system of non-interacting particles with the same charge density as that of the original system. Till this point, DFT is formally an exact theory and it significantly reduces the computational cost of the first-principles approach, at the expense of some approximations.

Those approximations include exchange-correlation potential (V_{xc}), such as the local density approximation (LDA) and generalized-gradient approximation (GGA). Along with a good approximation for V_{xc} , the use of Bloch's theorem, plane-wave basis set and the pseudopotential or projector augmented-wave (PAW) approach lead to quite satisfactory results when compared to experimental data. It has been generalized to deal with many different situations, like spin polarized systems, multi-component systems, superconductors, and time-dependent phenomena, *etc.* Due to this great success, DFT is the most promising approach in computing the electronic structure of matter with wide applicability ranging from atoms, molecules and solids to nuclei and quantum and classical fluids.

Below section states the proof of two remarkably powerful theorems, *uniqueness and the variational principle*, which are the foundations of DFT, formulated and proved by Hohenberg and Kohn in 1964.

2.5.2 Hohenberg-Kohn theorems

I. The density $\rho_0(\vec{r})$ as the basic variable (*uniqueness*)

The basic lemma of HK. For any system of interaction particles in an external potential V_{ext} , (here, $V_{ext} \equiv V_{e-ion}$) the potential, V_{ext} , is determined uniquely, except for a constant by the ground state density.

Proof: The proof of the first theorem is remarkably simple and proceeds by *reductio ad absurdum*. Assuming two external potentials, $V_{ext}^{(1)}(\vec{r})$ and $V_{ext}^{(2)}(\vec{r})$, differed by more than a constant can give rise to the same ground state density $\rho_0(\vec{r})$. The associated Hamiltonians $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ will therefore have two distinct ground state wavefunctions $\psi_0^{(1)}$ and $\psi_0^{(2)}$ that yield the same ground state density $\rho_0(\vec{r})$. Based on the assumption, $\psi_0^{(2)}$ is not the ground state wavefunction of $\hat{H}^{(1)}$, therefore,

$$E_0^{(1)} < \langle \psi_0^{(2)} | \hat{H}^{(1)} | \psi_0^{(2)} \rangle \quad (2.14)$$

$$\begin{aligned} \text{Since, } \langle \psi_0^{(2)} | \hat{H}^{(1)} | \psi_0^{(2)} \rangle &= \langle \psi_0^{(2)} | \hat{H}^{(2)} | \psi_0^{(2)} \rangle + \langle \psi_0^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \psi_0^{(2)} \rangle \\ &= E_0^{(2)} + \int [V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r})] \rho_0(\vec{r}) d^3 r \end{aligned} \quad (2.15)$$

where, $E_0^{(1)}$ and $E_0^{(2)}$ are the ground state energies of $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, respectively.

Combining Eqs. (2.14) and (2.15), one gets,

$$E_0^{(1)} < E_0^{(2)} + \int [V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r})] \rho_0(\vec{r}) d^3 r \quad (2.16)$$

An equivalent expression for (2.16) holds when the subscripts are interchanged, which is,

$$\begin{aligned} E_0^{(2)} &< E_0^{(1)} + \int [V_{ext}^{(2)}(\vec{r}) - V_{ext}^{(1)}(\vec{r})] \rho_0(\vec{r}) d^3 r \\ &= E_0^{(1)} - \int [V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r})] \rho_0(\vec{r}) d^3 r \end{aligned} \quad (2.17)$$

Adding the interchanged inequality Eqs. (2.16) and (2.17) leads to the logical contradiction, $E_0^{(1)} + E_0^{(2)} < E_0^{(1)} + E_0^{(2)}$. Therefore, the initial assumption must be wrong and only one external potential (within an additive constant) exists, starting from the given charge density.

II. The Hohenberg-Kohn variational principle

For any external potential V_{ext} , a functional for energy $E[\rho]$ in terms of the density can be defined, where $E[\rho]$ is such that the global minimum of $E[\rho]$ equals the ground state energy of the system and the density at this minimum equals the ground state density of the system.

Proof: The proof of the second theorem is also straightforward. As just shown, the Hohenberg-Kohn theorem-I allows $\rho(\vec{r})$ to determine its own potential V_{ext} . All properties of the system can therefore be uniquely determined once the density $\rho(\vec{r})$ is specified. Hence, the total energy of the system reads,

$$\begin{aligned} E_{HK}[\rho(\vec{r})] &= T[\rho(\vec{r})] + E_{ee}[\rho(\vec{r})] + \int V_{ext}(\vec{r})\rho(\vec{r})d^3 r \\ &= F_{HK}[\rho(\vec{r})] + \int V_{ext}(\vec{r})\rho(\vec{r})d^3 r \end{aligned} \quad (2.18)$$

The functional $F_{HK}[\rho(\vec{r})]$ includes all internal energies of the system while the second term on the right side represents the electron-ion interaction energy. If $\rho_0(\vec{r})$ is the ground state density, the ground state energy is determined by,

$$E^{(0)} = E_{HK}[\rho_0(\vec{r})] = \langle \psi^0 | \hat{H}^{(0)} | \psi^0 \rangle \quad (2.19)$$

where ψ^0 is the ground state wavefunction. Any other different density $\rho'(\vec{r})$ corresponding to a different eigenfunction ψ' will yield energy higher than the ground state energy,

$$E' = \langle \psi' | \hat{H}^{(0)} | \psi' \rangle > E^{(0)} \quad (2.20)$$

The two HK theorems show that by using the electron charge density $\rho(\vec{r})$ as fundamental variable, one can determine a unique energy functional $E[\rho]$ with the exact ground state energy being the global minimum.

The HK theorems state the existence of an energy functional $E[\rho]$ and if $E[\rho]$ were known the ground state electron density could be easily found.

Unfortunately, they do not provide a way of finding the ground state density. Until 1965, Kohn and Sham further replaced the original many-body problem with an auxiliary system with independent particles having the same ground state density as the original problem. This conception led DFT into a practical level that has been widely used today to perform electronic structure calculations.

2.5. 3 The Kohn-Sham equation

In 1965, Kohn and Sham reformulated the problem by calculating the Schrödinger equations of a fictitious system of non-interacting particles (typically electrons) that generate the same charge density as the given system of interacting particles. Now in this non-interacting case, the HK variational principle takes the form,

$$E_0[\rho(\vec{r})] = T_0[\rho(\vec{r})] + \int d^3 r V_{ext}(\vec{r})\rho(\vec{r}) \quad (2.21)$$

where $T_0[\rho(\vec{r})]$ is the kinetic energy of the ground state of non-interacting electrons with density distribution $\rho(\vec{r})$. Varying equation (2.21) with respect to the density, we obtain,

$$\lambda\rho(\vec{r}) = \frac{\delta T_0[\rho(\vec{r})]}{\delta\rho(\vec{r})} + V_{ext}(\vec{r}) \quad (2.22)$$

where $\rho(\vec{r})$ is the exact ground-state charge density for $V_{ext}(\vec{r})$. Here λ is a Lagrange multiplier to assure particle conservation. Now in this soluble, non-interacting case, the ground state energy and density can be obtained by calculating the eigenfunctions $\psi_i(\vec{r})$ and eigenvalues ε_i of the non-interacting, single-particle equations,

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \quad (2.23)$$

yielding

$$E = \sum_i^N \varepsilon_i \quad (2.24)$$

then the ground-state charge density of the non-interacting system is given by,

$$\rho(\vec{r}) = \sum_i^N |\psi_i(\vec{r})|^2 \quad (2.25)$$

where the sum runs over the all the single particle states.

In Kohn–Sham approach, the energy functional of the interacting electrons, with electronic interactions deliberately included, can be written in the form,

$$\begin{aligned} E_{KS}[\rho] = T_0[\rho(\vec{r})] + \frac{1}{2} \int d^3 r d^3 r' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d^3 r V_{ext}(\vec{r}) \rho(\vec{r}) \\ + E_{xc}[\rho(\vec{r})] \end{aligned} \quad (2.26)$$

where the last term is the exchange-correlation energy which includes, by definition, all many-body effects that are not taken into account by the first three terms which represent the non-interacting particle kinetic energy functional, the Hartree and the external energy respectively. Varying equation (2.26) with respect to the density, we obtain,

$$\frac{\delta T_0[\rho(\vec{r})]}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})} + V_{ext}(\vec{r}) + \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} = \lambda \rho(\vec{r}) \quad (2.27)$$

We rewrite Eq. (2.27) into,

$$\lambda \rho(\vec{r}) = \frac{\delta T_0[\rho(\vec{r})]}{\delta \rho(\vec{r})} + V_{eff}(\vec{r})$$

where

$$V_{eff}(\vec{r}) = V_{ext}(\vec{r}) + \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}(\vec{r}) \quad (2.28)$$

and the local exchange-correlation potential

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \quad (2.29)$$

Now the form of Eq. (2.28) is identical to that of Eq. (2.22), the only difference is the potential $V_{ext}(\vec{r})$ being replaced by a more complicated effective external potential $V_{eff}(\vec{r})$. The analogue of Eq. (2.23) now becomes,

$$\left[-\frac{1}{2} \nabla^2 + V_{eff}(\vec{r}) \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \quad (2.30)$$

By solving the single-particle equation, the ground state charge density is given as,

$$\rho(\vec{r}) = \sum_i^N |\psi_i(\vec{r})|^2 \quad (2.31)$$

The ground-state energy is given by,

$$\begin{aligned} E_{KS}[\rho] = & \sum_i^N \varepsilon_i - \frac{1}{2} \int d^3 r d^3 r' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho(\vec{r})] \\ & - \int d^3 r V_{xc}(\vec{r}) \rho(\vec{r}) \end{aligned} \quad (2.32)$$

Now the difficult problem for a system with interacting electrons has been mapped onto a system of non-interacting electrons moving in an effective potential given by Eq. (2.28). Therefore, the many-body problem would be exactly solved if the form of the exchange-correlation functional was known. Equations (2.28), (2.30), (2.31) and (2.32) are the well known Hohn-Sham equations, which are first derived by Hohn and Sham in 1965. In principle, all the many-body effects are included in the KS theory with the exact E_{xc} and V_{xc} which makes the KS theory as the exact theory for the many-body system. However, the practical usefulness of ground-state DFT depends entirely on whether sufficiently simple and sufficiently accurate approximations for the functional $E_{xc}[\rho(\vec{r})]$ could be found. In the following

section, we briefly introduce the development and current status of such approximations.

2.6 Approximations on exchange-correlation functional (E_{xc})

All exchange-correlation functionals can be written in the following general form,

$$E_{xc}[\rho(\vec{r})] = \int \epsilon_{xc}(\vec{r}) \rho(\vec{r}) d^3r \quad (2.33)$$

where $\epsilon_{xc}(\vec{r})$ is the exchange-correlation energy per particle at position $\vec{r}$. Functionals can be characterized by the way in which the density $\rho(\vec{r})$ surrounding each electron is sampled in order to construct $\epsilon_{xc}(\vec{r})$. Some principal types of functional that have been adopted in this thesis are now elucidated below.

2.6.1 Local Density Approximation (LDA)

LDA is the simplest and at the same time remarkably serviceable approximation for the exchange-correlation (xc) energy functional term in DFT, which was first proposed by Kohn and Sham in 1965. It states that for regions of a material where the charge density is slowly varying, the exchange-correlation energy at that point can be considered as the same as that for a locally homogeneous electron gas of the same charge density and the xc-energy can be written as,

$$E_{xc}^{LDA}[\rho(\vec{r})] = \int \epsilon_{xc}^{hom}(\rho(\vec{r})) \rho(\vec{r}) d^3r \quad (2.34)$$

where $\epsilon_{xc}^{hom}(\rho(\vec{r}))$ is the exchange-correlation energy per electron of a homogeneous electron gas of density ρ . And $\epsilon_{xc}^{hom}(\rho(\vec{r}))$ can be decomposed into exchange and correlation terms linearly. In this case, the xc-potential, V_{xc} , defined as the functional derivative of E_{xc} is,

$$V_{xc} = \frac{\delta E_{xc}^{LDA}}{\delta \rho(\vec{r})} = \left(\epsilon_{xc}^{hom} + \rho \frac{\partial \epsilon_{xc}^{hom}}{\partial \rho} \right) |_{\rho=\rho(\vec{r})} = \epsilon_{xc}^{hom} + \frac{\partial \rho \epsilon_{xc}^{hom}}{\partial \rho} \quad (2.35)$$

The exchange energy density, ϵ_x , of the homogeneous electron gas (HEG) is analytically known as,

$$\epsilon_x^{hom}(\rho(\vec{r})) = -\frac{3}{4} \left[\frac{3}{\pi} \rho(\vec{r}) \right]^{1/3} \quad (2.36)$$

Within LDA, the exchange energy E_x^{LDA} of the inhomogeneous system is found by the point-wise application of the HEG resulting in,

$$E_x^{LDA}[\rho(\vec{r})] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d^3 r \rho^{4/3}(\vec{r}) \quad (2.37)$$

The exchange potential V_x then can be obtained from Eq. (2.35) using the expression of $\epsilon_x^{hom}(\rho(\vec{r}))$,

$$V_x = \frac{4}{3} \epsilon_x^{hom}(\rho(\vec{r})) \quad (2.38)$$

However, even in the case of HEG, there is no analytical expression for the correlation energy density ϵ_c . The correlation-energy density was first estimated by E. P. Wigner in 1938 [19],

$$\epsilon_c(\rho(\vec{r})) \approx -\frac{0.44}{r_s + 7.8} \quad (2.36)$$

Later in 1980, Ceperley and Alder give a more accurate calculation on it by using Quantum Monte Carlo (QMC) methods [20]. A commonly used correlation formula is the sets of analytical expressions by Perdew and Zunger [21] which was obtained by fixing the QMC calculations of HEG by Ceperley and Alder.

One would expect LDA is only valid when inhomogeneity of $\rho(\vec{r})$ is small, however, it is valid even if the inhomogeneity is large such as in the atoms, where the density continuously goes to zero outside the atom, as well as the covalently bonded materials. The reason is that the effects of inter-electronic repulsion due to

the Coulomb interaction and Pauli's principle obey all the sum rules exactly; the integral of the exchange-correlation hole density over all space yields an exact charge of $|e|$ [22]. However, LDA fails for describing highly localized d -states of transition metals that are pushed up in energy and it typically overestimates bonding energies while underestimates the lattice parameters.

2.6.2 Generalized-Gradient Approximation (GGA)

A successful improvement of LDA is the Generalized-Gradient Approximation (GGA), which is currently the most popular exchange-correlation functional in condensed matter physics. Within GGA, an improvement over LDA is made by expressing the functional in density as well as its local gradients, then E_{xc}^{GGA} can be symbolically written as,

$$E_{xc}^{GGA}[\rho_{\uparrow}, \rho_{\downarrow}] = \int d^3r f(\rho_{\uparrow}(\vec{r}), \rho_{\downarrow}(\vec{r}), |\nabla\rho_{\uparrow}(r)|, |\nabla\rho_{\downarrow}(r)|) \quad (2.39)$$

As in LDA, E_{xc}^{GGA} is usually split into the exchange and correlation parts. The exchange part E_x^{GGA} is first proposed by Becke [23] as,

$$E_x^{GGA} = E_x^{LDA} - \beta \sum_{\sigma} \int \frac{x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma}} n_{\sigma}^{4/3}(r) dr \quad (2.40)$$

Where σ denotes either “up” or “down” electron spin, β is a constant and x_{σ} is a dimensionless ratio, $x_{\sigma}(r) = |\nabla n_{\sigma}(r)|/\rho_{\sigma}^{4/3}(r)$. The mathematics correlation terms are complicated by the scaling relations and the different interactions that occur between like and unlike spin components. The spin-compensated correlation-energy can be written as,

$$E_c^{GGA} = \int dr n[\epsilon_c^{hom}(r_s, \zeta) + H(r_s, \zeta, t)], \quad (2.41)$$

where $\zeta = (\rho_{\uparrow} - \rho_{\downarrow})/n$ is the relative spin polarization and $t = \nabla n / 2\phi k_s n$ is a dimensionless density gradient. Here, $\phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]/2$ is a spin-scaling factor, and $k_s = \sqrt{4k_F/\pi a_0}$ is the Thomas-Fermi screening wave number. The gradient contribution H is constructed as,

$$H(r_s, \zeta, t) = \frac{\gamma \phi^3}{a_0} \ln \left[1 + \frac{\beta t^2}{\gamma} \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right] \quad (2.42)$$

where β and γ are constants, and

$$A = \frac{\beta}{\gamma} \left[\exp \left(\frac{-\epsilon_c^{hom}}{\gamma \phi^3 / a_0} - 1 \right) \right]^{-1} \quad (2.43)$$

Using GGA, some of the problems within LDA are resolved [7; 23-24]. There are several forms for gradient approximations like the Perdew-Wang 1991 (PW91) [24] and the Perdew-Burke-Ernzerhof (PBE) [7]. In this work, GGA in form of PBE is applied for all the calculations.

2.7 The Projector Augmented Wave (PAW) method and plane-wave expansion

This section briefly describes the projector augmented plane-wave methods (PAW) [6] widely used in Kohn-Sham DFT-based *ab-initio* calculations performed in this thesis.

2.7.1 Bloch's theorem and plane-wave expansion

In a perfect crystal, the ions are arranged in a regular periodic array (at $T = 0$ K). Thus the external potential felt by the electrons has the same periodicity of the underlying Bravais lattice, i.e.

$$V(\vec{r} + \vec{R}) = V(\vec{r}) \quad (2.44)$$

According to the Bloch's theorem [25], the single-electron wavefunction $\psi_{n\vec{k}}(\vec{r})$ within a periodic potential can be written as the product of a wavelike part $e^{i\vec{k}\cdot\vec{r}}$ and a lattice periodic part $u_{n\vec{k}}(\vec{r})$,

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) \quad (2.45)$$

with

$$u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r} + \vec{R}), \quad \forall \vec{R} \in \{\text{Bravais Lattice Vectors}\} \quad (2.46)$$

where n denotes the band index and $\vec{k}$ is a continuous wavevector that is confined to the first Brillouin zone of the reciprocal lattice. Since $u_{n\vec{k}}(\vec{r})$ has the same periodicity as the lattice, it can be expressed in the plane-wave basis set with wavevectors $\vec{G}$ that are reciprocal lattice vectors of the crystal, i.e.

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n,\vec{k}+\vec{G}} e^{i\vec{G}\cdot\vec{r}} \quad (2.47)$$

where $\vec{G} \cdot \vec{R} = 2\pi m$, m is an integer, $\vec{R}$ is the direct lattice vector and $c_{n,\vec{k}+\vec{G}}$ are the plane-wave coefficients. The above discussions show that the single-electron wavefunction can be expanded in terms of a linear combination of plane-waves,

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n,\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \quad (2.48)$$

Plane-waves method is a simple way to represent electron wavefunctions. It offers a complete basis set that is independent of the type of crystal and treats all areas of space equally. Substituting plane-wave solutions given by Eq. (2.48) into Eq. (2.30) leads to an especially simple form of the Kohn-Sham equations in reciprocal-space representation,

$$\sum_{\vec{G}'} H_{\vec{G}\vec{G}'}(\vec{k}) c_{n,\vec{k}+\vec{G}'}(\vec{k}) = \varepsilon_n(\vec{k}) c_{n,\vec{k}+\vec{G}}(\vec{k}) \quad (2.49)$$

where

$$H_{\vec{G}\vec{G}'} = \langle \vec{k} + \vec{G} | \hat{H} | \vec{k} + \vec{G}' \rangle = \frac{1}{2} |\vec{k} + \vec{G}|^2 \delta_{\vec{G}\vec{G}'} + V_{eff}(\vec{G} - \vec{G}', \vec{k}) \quad (2.50)$$

Equation (2.50) shows that in the momentum space, the kinetic energy is diagonal and the effective potential is written in terms of its Fourier components. The matrix diagonalization yields the band structure and the electronic wavefunctions of the system.

For an exact calculation, the dimension of the plane-wave basis set should be infinite. So to get a practical solution of Eq. (2.49), one can restrict the number of G -components in a calculation by defining a kinetic cutoff energy E_{cut} ,

$$\frac{1}{2} |\vec{k} + \vec{G}|^2 \leq E_{cut} \quad (2.51)$$

Therefore, another advantage of the plane-wave basis set is that, in principle, the accuracy of the results can be systematically improved by increasing wavefunction E_{cut} .

Since the plane-wave basis set treats all space equally, therefore, the Pulay correction terms [26] are exactly zero and one only needs to calculate the Hellmann-Feynman term to get the forces. The main drawback of plane-waves basis set is that it requires an extraordinary huge number of plane-waves to accurately describe wavefunctions with large curvature such as in the core regions of atoms. This problem can be overcome with the Projector Augmented Wave (PAW) method which is described in the followed section.

2.7.2 The PAW method

The Projector Augmented-Wave (PAW) method was developed by Peter Blöchl in 1994 [6]. PAW method combines both the formal simplicity of

pseudopotential method and the versatility of linear augmented-plane-wave (LAPW) method to accurately and efficiently calculate the electronic structure of materials within the framework of DFT. It can treat first-row and transition-metals (TMs) elements with affordable effort and provides access to the full wavefunction.

PAW formalism introduces the smooth auxiliary wavefunctions $\tilde{\psi}_{nk}(r)$ that is mapped from Bloch wavefunctions by using three types of functions: the all-electron (AE) basis functions $\Phi_i^a(\mathbf{r})$, the pseudo (PS) wavefunctions, $\tilde{\Phi}_i^a(\mathbf{r})$, and the projector functions, $\tilde{p}_i^a(\mathbf{r})$. The AE and the PS functions are chosen such that,

$$\tilde{\Phi}_i^a(\mathbf{r}) = \Phi_i^a(\mathbf{r}) \quad \text{for } r \geq r_c^a, \quad (2.52)$$

where r_c^a is the radius of a nonoverlapping sphere about the atomic site a . The projector functions vanish for $r > r_c^a$ and satisfy the orthogonality conditions,

$$\langle \tilde{p}_i^a(\mathbf{r}) | \tilde{p}_j^a(\mathbf{r}) \rangle = \delta_{ij} \quad (2.53)$$

The full Bloch wavefunction and the smooth auxiliary wavefunction are related by,

$$\psi_{nk}(r) = \tilde{\psi}_{nk}(r) + \sum_{a,i} [\Phi_i^a(r) - \tilde{\Phi}_i^a(r)] \langle \tilde{p}_i^a | \tilde{\psi}_{nk} \rangle \quad (2.54)$$

The expressions for the valence charge density and the energy follow the above definition,

$$\rho(\mathbf{r}) = \tilde{\rho}(\mathbf{r}) + \rho^1(\mathbf{r}) - \tilde{\rho}^1(\mathbf{r}) \quad (2.55)$$

where the first term on the right-hand side is the pseudo density while the last two terms are designed such that they are corrected for the proper normal behavior in the vicinity of each atom while canceled out outside the atomic spheres.

There are many advantages of PAW, such as, (1) it is as accurate as an AE method; (2) the plane wave cutoff equivalent to ultrasoft pseudopotentials and thus

have similar efficiency. In our computational studies, we use the PAW method as implemented in Vienna *ab initio* Simulation Package (VASP) [27-29].

Chapter three

Spintronics and Dilute Magnetic Semiconductors (DMSs)

3.1 Introduction

The searching for materials that combine both ferromagnetism and semiconducting properties has been a long-standing goal but elusive one for material scientists. Ferromagnetism and semiconducting properties are known to coexist in some magnetic semiconductors [schematically shown in Figure 3.1(a)], such as Eu chalcogenides [30] and ferromagnetic semiconducting spinels [31-32], which have a periodic array of magnetic elements. However, the magnetic semiconductors fail in practical sense due to the low Curie temperatures (T_C s) (typically well below 100 K), the difficulty in growth, and the incompatibility with traditional semiconductor materials like Si or GaAs used in semiconductor industry today. An alternative strategy is to alloy magnetic elements into the well-known nonmagnetic semiconductors, shown in Figure 3.1(b), to introduce magnetic local moments. The resulting new materials are called dilute magnetic semiconductors [DMSs, see Figure 3.1(c)]. DMSs are relatively easier to prepare and more desirable for integration with traditional electronics. Transition metals

(TMs) with partially filled d states and rare earth elements having partially filled f states, which contain unpaired electrons, have been used as candidates to introduce magnetic properties in DMS. Addition to traditional electronics based on nonmagnetic semiconductor relying on charge carriers only, DMS-based devices exploit electron spin as an additional degree of freedom along with the electron charge in semiconductors. However, making such materials has been problematic because the low solubility of magnetic elements in the hosts, the segregation of the magnetic dopants, and the formation of the secondary impurity phase.

Figure 3.1. Three types of semiconductors: (a) a magnetic semiconductor; (b) a nonmagnetic semiconductor; and (c) a diluted magnetic semiconductor. In the style of Ref. [33].

The magnetic properties of DMS material come from the exchange splitting that displaces the spin-up and spin-down electrons in energy with respect to one another when the temperature is below T_C . The band structure diagram for nonmagnetic semiconductors and ferromagnetic semiconductors are schematically shown in Figure. 3.2. The different numbers of spin-up and spin-down electrons

result in the observed spontaneous magnetic moment. For practical applications in functional devices, it would be desirable to have a T_C well above room temperature.

Figure. 3.2. A schematic diagram of the density of electronic states in a normal semiconductor and in a ferromagnetic semiconductor whose majority spin states in the valence band are completely filled. E is the electron energy, E_F is the Fermi level, and $N(E)$ is the density of states. In style of Ref. [2].

Following the well-know Moore's law, the density of the transistors has been doubled approximately every two years. As shown in Figure 3.3, since 1970, the area density of hard disk drives (HDD) and dynamic random access memory (DRAM) increases rapidly. As chips became smaller, they also became faster in about the same proportion. When electronic devices continue to shrink in size to the nanoscale stage, the problems of power dissipation and thermal management of circuits arise. Therefore, the future advancements to microchips would require a different approach for transmitting the sequences of ones and zeros that make up digital information. This comes to the requirement of spintronics.

Figure 3.3. The increase of areal density of HDD and DRAM in the past 40 years. (After <https://www1.hitachigst.com/hdd/technolo/overview/chart06.html>)

The emerging research area known as spintronics seeks to extend the properties and applications of established electronic devices by making use of the spin of electrons in addition to their charge. Therefore, it offers great possibilities for future improvements in data storage, transfer, and retrieval. These devices have the advantages of much smaller size, faster data processing, operation at much less power consumption, and being more effective for certain kinds of computations than today's electron charge based devices. In addition to its potential utility, the study of spin-polarized transport is revealing new and fascinating fundamental physics. By combining both the spin and charge information of the electrons, DMS materials are the promising material for spintronic devices.

3.2 DMS materials for spintronics

3.2.1 Non-oxide based DMS

The pioneer work on the DMS materials has been focused on II-VI semiconductors [34], like CdTe, ZnSe, CdSe, CdS, *etc*, with transition metal ions, e.g. Mn, Fe or Co substituting their original cations. This is because magnetic ions in III-V semiconductors have much lower solubility as well as its poor stability compared to II-VI semiconductors. On the other hand, rare earth elements (e.g. Eu, Gd, Er) are also used as magnetic atoms in DMS. A breakthrough was made by Munekata *et al.*, who prepared III-V material (In, Mn)As using molecular beam epitaxy (MBE) and the ferromagnetism was observed in *p*-type (In, Mn)As [35-36]. The success of this relies on the MBE technique which can grow thin-film in non-equilibrium conditions. Following this, Ohno *et al.* reported the first *p*-type Mn doped GaAs DMS in 1996 [37] with T_C above 60 K. About two years later, Ohno *et al.* improved the T_C of *p*-type (Ga, Mn)As to as high as 110 K [38]. These materials can serve as the host for the applications of infra-red LED. Due to its remarkable properties, a lot of attentions have been paid on (Ga, Mn)As DMSs, as well as other III-V semiconductors, like GaN and InAs systems. Some promising success has been achieved such as the long spin lifetimes and coherence times in GaAs [39] and the ability to obtain spin transfer at hetero-structure interface [35; 40-48]. However, so far, the highest T_C reported for (Ga, Mn)As is approximately 170 K [39], which sets T_C higher than room temperature as the major challenge for GaAs-based DMS.

Figure 3.4. Predicted Curie temperatures (T_C) as a function of the band gap. Computed values of the T_C for various p -type semiconductors containing 5% Mn and 3.5×10^{20} holes per cm^3 . From Ref. [3].

In 2000, Dietl [3] explained the magnetic properties in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ using Zener model and theoretically predicted T_C for various p -type semiconductors with 5% Mn doping and hole concentration of $3.5 \times 10^{20} \text{ cm}^{-3}$. The theory required charge carriers to mediate the magnetic coupling of Mn. Therefore, the hole concentration needs to be sufficiently high ($> \sim 10^{20} \text{ cm}^{-3}$) in order to get higher T_C . As shown in Figure 3.4, he predicted the existence of room temperature T_C for GaN and ZnO based DMSs. This is in part due to the strong p - d hybridization involving the valence band in the host and this prediction was experimentally verified by [49-50]. This set off a flurry of another research activity on GaN and ZnO based DMSs.

Besides the Mn-doped GaN, room temperature ferromagnetism have been reported on the doping with other TMs ions in III-nitride materials, such as Cr, Co, Fe, V or Gd-doped GaN, as well as Mn or Cr doped AlN [51-53]. Most of the reports discussed observation of ferromagnetism or ferromagnetic-like behavior with T_C near or above room temperature. In terms of the mechanism for the above room temperature ferromagnetic behavior in Mn doped GaN, some studies suggested it to be spin-charge double exchange interaction, while some others attributed the reason to possible presence of secondary phases such as ferromagnetic Ga-Mn and ferromagnetic Mn-N alloys due to the low solubility of magnetic ions in GaN. Depending on the various preparations, these precipitates might in fact be the major contributors to the total magnetic moment of the samples investigated. In contrast to Dietl's theory, Sato *et al.* reported the possibility of high T_C ferromagnetic materials could be realized in *n*-type ZnO as well if Fe, Co, or Ni is used as a dopant [54].

The above-mentioned systems are mainly ternary DMS systems. In these systems, the lattice constant and band gap can be easily tuned by varying the composition within the materials. Also, the magnetic properties of the material can be altered by changing the concentration of the magnetic ions. However codoping, the growth of quaternary compounds can be achieved, which have extended the possibilities for the band gap engineering.

3.2.2 Oxide based DMS (ODMS)

ZnO based ODMS has drawn a lot of attention at beginning partly due to the high solubility of TM elements in ZnO, such as Mn and Co can reach up to 35% into ZnO. However, contradiction exists in the early studies. For example,

although the predictions that only *p*-type Mn doped ZnO can lead to ferromagnetism [3], ferromagnetism is also observed experimentally for insulating and *n*-type Mn-ZnO [55-57]. Above room temperature ferromagnetism was observed in thin film form of Co and Fe codoped ZnO [58], while the bulk Co-ZnO has been found to be antiferromagnetic [59]. This antiferromagnetic behavior is likely to be associated with the clustering of Co, together with the existence of interstitial Co atoms instead of substitutional Co on Zn sites. This clustering effect as well as secondary phase formation for the TM doped ZnO are the major problems of the early studies.

Aside the ZnO based DMS, Matsumoto *et al.* reported the discovery of RT ferromagnetism in Co-doped TiO₂ in 2000 [60]. Following that, various 3*d* TM have been used to dope TiO₂, such as Co-TiO₂ [60-62], Cr-TiO₂ [63-64], and Fe-TiO₂ [65], in order to achieve the room temperature DMSs. Many studied ODMS systems have been predicted to exhibit large magnetic moments with T_C well above RT, for instance, ZnO doped with Co or Mn [4; 66], In₂O₃ with Cr [67-68], Fe [69], or Fe and Cu co-doping [70], TiO₂ (anatase) with Co [4; 71], SnO₂ with Co [4; 72], *etc.* Since then, oxide based DMSs (ODMS) become a new hot research topic in seeking for room temperature DMS, starting from the TM doping cases. Furthermore, the advantages that oxide based DMS possess, such as: wide bandgap, transparency, high *n*-type carrier concentration, capability to be grown at low temps, ecological safety and durability, low cost, and large electro-negativity of O atoms, make them even more attractive.

Other than the TM metal doping to substitute the cation sites, attempts have been made by using non-magnetic element, such as C and N to replace the O atom and non-magnetic metal elements to replace the In atom in the system. These two

methods are relatively new approaches and provide new insights on the d^0 magnetism. This has been found practicable for the systems like ZnO-N [73], ZnO-C [74], In₂O₃-N [75], TiO₂-N [76], TiO₂-C [77] and SnO₂-N [78]. With the development of d^0 based DMS, the problems of transition metal cluster effect, secondary phase formation, and the low solubility of transition metal in host can be eliminated. Therefore, intrinsic magnetic properties are expected for these new systems with possible different magnetic exchange mechanisms. Numerous experimental findings as well as some previous first-principles calculations of the electronic structure and magnetic interaction of the doped, especially TMs doped ODMS [8-14] suggest that the vacancies or some other defects induced during the sample preparation process may serve as important factors to introduce ferromagnetism in these kinds of materials. More interestingly, there are many reports showing that the magnetic moment introduced by intrinsic defects can be stable at RT and lead to ferromagnetism in undoped oxide systems, such as HfO₂ [79], In₂O₃ [79-82], ZnO [81], TiO₂ [79], SnO₂ [81; 83], CeO₂ [81] and Al₂O₃ [81] in forms of bulk, film or nanoparticle. It is believed that the native defects introduced during sample preparation play very important roles. However, debate still exists regarding to whether cation vacancies or anion vacancies produce the magnetic moments. Although some experimentalists attributed it to the oxygen vacancies, more and more theoretical studies tend to favor the role of the cation vacancies. Furthermore, recently, RT ferromagnetism is observed in alkali doped ZnO nanorods [84] and nanotubes [85]. This is consistent with the theoretical reports for systems of cubic ZrO₂-K [86-87], rutile TiO₂-K [86], and SnO₂-Mg [88].

Another important but relatively less studied oxide system is In_2O_3 based DMS, which would be the focus of this thesis. It is a technologically important transparent semiconductor with a direct band gap of 3.75 eV [89]. In form of thin films, In_2O_3 is superior to other transparent conductors because of the high mobility ($10 - 75 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) with a carrier density of $\sim 10^{19} - 10^{20} \text{ electrons}\cdot\text{cm}^{-3}$ [90]. These prominent capabilities make the study of In_2O_3 based DMS more technologically important, as it can integrate optical, electronic and magnetic properties into one single material. Previous studies have shown that RT ferromagnetism can be achieved by doping or co-doping of $3d$ TM impurities into In_2O_3 [12; 14; 67-68; 70]. However, the reports are somehow controversial. As it was reported that In_2O_3 doped with V [91], Cr [8; 68], Fe [12; 14], Co [92], and Ni [93-94] exhibit strong RT ferromagnetism. On the contrary, Mn, V, Fe, or Cu doped In_2O_3 have been found to show no evidence of ferromagnetism [95-97]. This suggests the complexity of the magnetic states of $3d$ TMs doped In_2O_3 , which are determined by several factors such as the synthesis methods, the existence of oxygen vacancies (V_O) or co-doping. Co-doping has attracted attention primarily due to the possibility to tailor the position and occupancy of the Fermi level (E_F) of the doped DMS [98-102].

3.3 Magnetic exchange models in DMSs

3.3.1 Introduction

Decades of research and development in semiconductor physics improved our understanding of mechanism on ferromagnetism in DMS. These magnetic phenomena cannot be explained without exchange interactions and the mechanisms considered so far are direct exchange, Ruderman-Kittel-Kasuya-

Yosida (RKKY), super-exchange, double exchange, mean-field Zener exchange, bound magnetic polaron (BMP), and *etc.* In solids, the macroscopic magnetic ordering usually results from two or more exchange mechanisms that compete and interplay with each other. Therefore, consensus must be realized that several mechanisms will coexist within the disordered TM compounds.

The mechanisms of ferromagnetism can be divided into direct exchange and indirect exchange. Among the indirect exchange models, RKKY, super-exchange, double exchange, and BMP are the well accepted models. Depending on whether there is electron transfer, the mechanisms of ferromagnetism can also be distinguished as kinetic exchange mechanism and exchange potential mechanism. In kinetic exchange mechanism, the atomic orbitals of the local magnetic moments are non-orthogonal, i.e. covalent bonding, to facilitate the electron transfer, such as direct exchange, double exchange, and carrier mediated exchange. On the other hand, in the exchange potential mechanism, the atomic orbitals are orthogonal, i.e. no bonding. The coupling between different moments relies on the potential in super-exchange and orthogonal orbitals in direct exchange.

However, the mechanism of ferromagnetism is a complex question. A lot of studies have been done to understand the magnetic properties of solids and as yet there exists no closed theory which can describe the totality of all the phenomena in a unified manner. The current mechanisms are, in general, relevant only for particular special features of magnetism. Some, such as the double exchange interaction, exclusively promote ferromagnetism, whereas most can result in either FM or AFM interactions, depending on the details of the chemical bonding, geometry, defect structure, and *etc.* Therefore, it is still active and open in

term of the mechanisms of ferromagnetism in DMS. In the following, we will review the different mechanisms in details.

3.3.2 Direct Exchange

The direct exchange is a first-order perturbation effect. The local moment formation and collective magnetization result from the electron-electron interaction. The direct exchange interaction couples the spins of localized electrons in insulators that can be described by the Heisenberg Hamiltonian,

$$H_{ex} = - \sum_{ij} J_{ij} s_i \cdot s_j \quad (3.1)$$

The direct exchange can be further divided into two parts: (1) direct exchange between orthogonal orbitals, and (2) direct exchange between the non-orthogonal orbitals. The former case could correspond to two electrons in the $3d$ shell of an atom, where FM alignment of spins is favored; the latter one could correspond to the case of two electrons in a hydrogen molecule, where the AFM alignment of spins is the lower energy state.

The use of antisymmetrized wave functions is the origin of the exchange energy in the electrons system, as initially discovered simultaneously and independently by Dirac and Heisenberg in 1926 [103-104]. Under some approximations, an effective interaction Hamiltonian can be used to describe the exchange interaction in the system and specify the origin of the exchange. For example, the direct Coulomb exchange always leads to an FM Kondo Hamiltonian for the s -like conduction bands and for TM ions with the open d shell.

3.3.3 Indirect Exchange

3.3.3.1 Ruderman-Kittel-Kasuya-Yoshida (RKKY) mechanism

The basic idea of RKKY is indirect interaction between localized electrons over relatively large distances due to the Coulomb exchange described by the s - d Kondo Hamiltonian [105]. This type of exchange was first proposed by Ruderman and Kittel [106] and later extended by Kasuya and Yosida to give the theory now generally known as the RKKY interaction. It was originally introduced to explain the ferromagnetism in various Mn-based III-V semiconductor epitaxial layers, where the Mn magnetic ions themselves act as acceptors. It should be mentioned that s and d wave functions are orthogonal and would not lead to any interaction in perfect one-electron system. As the d -orbitals are much localized, their direct overlap with each other is negligible; therefore, the localized moments couple to each other indirectly through their interactions with the conduction electrons. The RKKY interaction is a second-order effect, which very sensitively depends on the electron density of the non-magnetic matrix. In bulk crystals with the higher p-type doping, ($c_a > 2 \times 10^{19} \text{ cm}^{-3}$), one can expect that the RKKY interaction, mediated by the p - d exchange, may dominate over the AFM super-exchange and render an FM system. The exchange interaction, J , oscillates with the distance from the localized moment, R , and with the density of electrons in the free electron gas,

$$J = \frac{m^* k_F^4}{\hbar^2} F(2k_F R) \quad (3.2)$$

The oscillating function is: $F(x) = \frac{x \cos x - \sin x}{x^4}$, which has been shown in Figure 3.5.

Therefore, depending upon the separation between a pair of ions their magnetic coupling can be FM or AFM.

Figure 3.5. The function $F(x)$, which determines the oscillatory behavior of the (indirect) RKKY exchange integrals. x is proportional to the product of the Fermi wavevector and the distance from the localized moment.

3.3.3.2 Super-exchange

The super-exchange is a process in which the spins of two next-to-nearest neighbor TM cations are correlated due to the spin-dependent exchange interaction mediated by the intermediate anions. It has been shown that the super-exchange is by far the dominant spin–spin interaction responsible for the observed isotropic and anisotropic exchange constants for II–VI DMS resulting from the sp – d hybridization. The super-exchange can also be described by a Heisenberg Hamiltonian, in which the sign of J_{ij} is determined by the metal–oxygen–metal bond angle and the d electron configuration in the TM, which can be described by the semi-empirical Goodenough-Kanamori-Anderson rules. The rules state that super-exchange interactions are AFM where the virtual electron transfer is between overlapping orbitals that are each half-filled, but they are FM where the virtual electron transfer is from a half-filled to an empty orbital or from a filled to a

half-filled orbital. Empirical tight-binding model is usually applied to describe the unperturbed valence band states, which have to be summed up over the entire Brillouin zone.

If the magnetic ions are separated by non-magnetic ions (i.e. with all filled shells), the direct exchange becomes less important, while super-exchange may become the dominant interaction between the magnetic moments. In this case, the electrons in the bridging non-magnetic ion mediate the magnetic interaction between the localized spins. A schematic illustration can be found in Figure 3.6.

Figure 3.6. The Mn^{2+} cation spins are aligned antiferromagnetically as a result of super-exchange mediated by the O^{2-} $2p$ electrons.

As one can see from Figure 3.6, two cation orbitals overlap the same p orbital of a shared anion with a 180° cation-anion-cation bridge. The virtual electron transfer from the shared anion to the interacting cations is artificially introduced as the covalent component of the cation orbital. In this manner, the cation wavefunction is overlapped through the covalent component extending over the anions for the super-exchange electron transfer.

3.3.3.3 Double exchange

The double exchange mechanism was developed nearly 60 years ago by Zener [107]. In this model, magnetic ions in different charge states couple with

each other by virtual hopping of the ‘extra’ electron from one ion to the other. System with magnetic ions in FM alignment saves the energy because the hopping can give a lower kinetic energy. It has been successfully used to explain the experimentally observed ferromagnetism in the doped perovskite structure manganites.

The double exchange is typical for systems in which the magnetic ion can exist in two different valence states, like Mn^{3+} and Mn^{4+} in Mn doped systems. The kinetic energy of the system is lowered if the magnetic moments align parallel, since parallel alignment allows electron transfer from Mn^{3+} to Mn^{4+} . This electron motion leads to an indirect coupling of the Mn spins mediated by the oxygen atoms between neighboring Mn^{3+} and Mn^{4+} ions, but is distinguished from super-exchange by involving carriers. Figure 3.7 schematically shows this magnetic coupling mechanism. This can be virtually viewed in two equivalent transfer processes. First, one electron (donated as 1 in Figure 3.7) in fully occupied anion p -state is transferred to the d -orbital of Mn^{4+} cation, keeping its spin orientation. Simultaneously, another electron (donated as 2 in Figure 3.7) with the same spin jumps from the d -orbital of Mn^{3+} cation to the anion p -orbital, to restore the p -orbital configuration. The moments on the two Mn cations need to be ferromagnetically aligned to conform to the Pauli's exclusion principle.

Figure 3.7. Ferromagnetic alignment of spins on the Mn cations is favored as a result of double-exchange.

3.3.3.4 Mean-field Zener model

In 2001, Dietl *et al.* [108] proposed the mean-field Zener model to explain the a hole mediated FM interaction between localized spins in magnetic semiconductors. Based on the original model of Zener and the RKKY interaction, the mean-field Zener model reveals the important effect of the spin-orbit coupling in the valence band. It has been successfully used in explaining the T_C observed for Mn doped GaAs and ZnTe. In order to induce the long ranged ferromagnetism, the hole density has been taken into accounted. In the same time, the anisotropy of the carrier-mediated exchange interaction related to the spin orbital coupling in the host material is also considered by applying certain experimentally determined parameters.

In the Zener model, the direct interaction between TM cations (super-exchange) leads to an AFM configuration and the indirect coupling of spins through the conduction electrons tends to align the spins in a FM manner, as shown in Figure 3.8. It is only when this dominates over the super-exchange coupling between adjacent d shells that ferromagnetism is possible. The mean-field approach assumes that ferromagnetism occurs through interactions between the local moments of the dopant atoms mediated by free holes in the material. The spin-spin coupling is also assumed to be a long-range interaction, allowing the use of a mean-field approximation.

Figure 3.8. Schematic diagram of carrier mediated FM interaction between localized spins in magnetic semiconductors, the long black and short red arrows represent the spin moments of the localized magnetic ions and carriers (holes here), respectively.

3.3.3.5 Bound magnetic polaron (BMP) model

The concept of BMP was first introduced by Coey *et al.* [4] to explain the low temperature metal-insulator transition in oxygen deficient EuO [109]. In this model, the donor electrons close to the conduction band play a critical role in mediating the long ranged ferromagnetism. Oxygen vacancies donate electron, however, also trap electrons and maintain the system insulating behavior. The bound magnetic polarons are formed by the alignment of the spins of many TM ions with that of much lower number of weakly bound carriers such as excitons within a polaron radius. The localized carriers of the polarons act on the TM impurities surrounding them, and align the moments on host lattice ferromagnetically within its orbitals. This model is schematically shown in Figure 3.9. Neighboring magnetic polarons overlap and interact via magnetic impurities

forming correlated clusters of polarons. This model is inherently attractive for low carrier density systems such as many of the electronic oxides and can be applied on both p - and n -type host materials [110].

Figure 3.9. Representation of magnetic polarons. A donor electron in its hydrogenic orbit couples with its spin antiparallel to impurities with a $3d$ shell that is half-full or more than half-full. Cation sites are represented by small circles. Oxygen is not shown; the unoccupied oxygen sites are represented by squares. After Ref. [4].

Since BMP model is also carrier-mediated model, the high T_C requires a strong hybridization and charge transfer from the donor-derived impurity band to unoccupied $3d$ states at the Fermi level. The electronic structure of system need to satisfy the criteria that the empty minority-spin or majority-spin d states lie at the

Fermi level in the impurity band. Under the right conditions, such as certain polaron-polaron distances and combinations of electron-electron and electron-local moment exchange constants, the polarons may couple in a FM fashion [111-112]. The critical distance above which the exchange between two BMPs becomes FM is typically of the order of a few Bohr radii [112]. The amplitude of the exchange interaction then drops off rapidly with distance.

Chapter four

The role of Cu co-doping and oxygen vacancies on ferromagnetism in In_2O_3 -Fe

4.1 Introduction

In_2O_3 being one of the candidate hosts is a technologically important transparent semiconductor with a direct band gap of 3.75 eV [89]. RT ferromagnetism can be achieved [12; 14; 67-68; 70] by doping or co-doping of 3d transition metal (TM) impurities into In_2O_3 , which is attractive due to its integration of optical, electronic and magnetic properties into one single material. Co-doping has attracted attention primarily due to the possibility to tailor the position and occupancy of the Fermi level (E_F) of the doped DMS [98-102]. The magnetic states of 3d TMs doped In_2O_3 are determined by several factors such as the synthesis methods, the existence of oxygen vacancies (V_O) or co-doping. As it was reported that In_2O_3 doped with V [91], Cr [8; 68], Fe [12; 14], Co [92], and Ni [93-94] exhibit strong RT ferromagnetism. On the contrary, Mn, V, Fe, or Cu

doped In_2O_3 have been found to show no evidence of ferromagnetism [95-97]. Numerous experimental findings as well as some previous first-principles calculations of the electronic structure and magnetic interaction of the doped, especially TMs doped oxide-based DMS [8-14] suggest that the vacancies or some other defects induced during the sample preparation process may serve as important factors to introduce ferromagnetism in these kinds of materials.

Among all TMs doped In_2O_3 , Fe doped In_2O_3 ($\text{In}_2\text{O}_3\text{:Fe}$, IFO) is a suitable prototype system for study due to the high solubility of Fe in the In_2O_3 ($> 20\%$) and a homogeneous solid solution can be realized at least up to 15% Fe doping [12-13]. Cu has been co-doped with Fe into In_2O_3 (IFCO) in order to achieve multiple oxidation states of Fe^{2+} and Fe^{3+} , which has been reported to be essential for exhibiting FM coupling [12-15]. To the best of our knowledge, up to now, there are very few theoretical studies on the origin of ferromagnetism in TMs doped In_2O_3 , especially TMs co-doped In_2O_3 . All these make theoretical investigation highly desirable for solving the puzzle and exploring the origin of the ferromagnetism in TMs doped In_2O_3 .

In this chapter, we performed a systematical study for the evolution of the ferromagnetism in IFO system while involving Cu co-doping as well as V_{O} into the system. We report the results of detail first-principles calculations on the electronic structure and magnetic properties of the IFCO system and demonstrate the key roles of the Cu co-doping and V_{O} in the developing of ferromagnetism in this system.

4.2 Theoretical calculation details

Our calculations are carried out with a periodic supercell model within the framework of density functional theory (DFT), using the full potential projector augmented plane wave (PAW) [6] method with a plane-wave basis set, as implemented in the Vienna *ab initio* Simulation Package (VASP) [27-29]. The energy cutoff is set to 500 eV for the plane wave basis, and the exchange-correlation functional is treated by Perdew-Burke-Ernzerhof form generalized gradient approximation (GGA-PBE) [7]. The Gaussian smearing method with a smearing parameter of 0.1 eV is used for all calculations due to the weak metallicity induced by doping. For all doping configurations, both the spin polarized and non-spin-polarized calculations were performed, and the symmetry unrestricted structure optimizations are carried out using a conjugate gradient algorithm with a force convergence criterion of 2×10^{-2} eV/Å. The Brillouin zone was sampled by $3 \times 3 \times 3$ Monkhorst-Pack k -point grids for geometry optimizations, and then sampled by the finer $4 \times 4 \times 4$ grids for the self-consistent energy calculations. For density of states (DOS) spectrum calculations, self-consistent field (SCF) energy is converged to 10^{-6} eV.

Figure 4.1. Crystal structure of In_2O_3 . Grey and cyan spheres are In and O atoms. For IFO systems we examined, one of the two Fe atoms is fixed at the position labeled Fe1, and the other one (Fe2) locates at the positions labeled with *a*, *b*, *c*, *d*, *f*, and *g* in different configurations. For IFCO- V_O systems, the positions of the Cu dopant are labeled with Cu1, Cu1', and Cu1'' for different configurations. The position of oxygen vacancy is labeled with V_O for all IFO- V_O configurations.

The selected supercell is composed of 80 atoms, corresponding to 16 f.u. In_2O_3 . The supercell size is large enough to allow us to investigate various configurations of Fe doping and Fe, Cu co-doping, as well as to isolate the interaction between impurities in some configurations. According to the Wyckoff's notation, there are 8 In(1) atoms occupied the b sites, 24 In(2) atoms occupied the d sites, and 48 oxygen atoms occupied the e sites in such a supercell. In our calculations, firstly, two In atoms were substituted by two Fe dopants. We fixed one dopant Fe atom (denoted by Fe1) at In(1) position because it was reported to be the favorable position for dopant [113]. In the present work, we vary the

possible positions of the second dopant Fe atom (denoted by Fe2) within the fourth nearest-neighbor (NN) to Fe1, face-diagonal position and body-diagonal position with respect to Fe1 in the sub-lattice of the cubic In(1). These configurations are defined as a , b , c , d , f , and g , for first NN, second NN, third NN, fourth NN, face-diagonal and body-diagonal positions, respectively, as shown in Figure 4.1. Each configuration is further doped with an additional Cu atom. The variation of Cu position is also considered as a function of the separation distance to the two Fe atoms. In the present work, the studied positions of this additional Cu atom are labeled as Cu1, Cu1', and Cu1'' in Figure 4.1, respectively. In the following, we use i , ii , and iii as short-hand notation to represent Cu1, Cu1', and Cu1'', respectively. Moreover an oxygen vacancy (V_O) is introduced by removing one oxygen atom adjacent to Fe or Cu or neither, the configurations with V_O in vicinity of Fe1 is denoted as V_O in Figure 4.1. All these dopant configurations are represented by a label, such as b -IFCO- V_O - i , where b represents the configurations of the two Fe atoms, and the IFCO means the system is Fe and Cu co-doped In_2O_3 system, V_O indicates the existence of oxygen vacancy, and i represents the Cu1 position for the doped Cu atom. For all dopant configurations, the FM stabilization energy: $\Delta E_{\text{FM}}(R) = E_{\text{FM}}(R) - E_{\text{AFM}}(R)$ are calculated, where $E_{\text{FM}}(R)$ and $E_{\text{AFM}}(R)$ are the total energies of the supercell with FM and AFM aligned Fe pairs, respectively, with the Fe-Fe separation distance of R . The difference in the two energies yields the J coupling, indicating relative stability of the AFM and FM states.

4.3 Results and discussions

4.3.1 Oxygen vacancy (V_O) effect

4.3.1.1 V_O effect on FM stabilization energies

Figure 4.2. The evolution of ferromagnetic stabilization energy (ΔE_{FM}) as a function of the Fe - Fe separation distance in IFO and IFO- V_O system. The letters next to the data indicate the configurations (see text).

At first, we discuss the role that V_O plays in the Fe-doped In_2O_3 (IFO) system. Figure 2 presents the variation of FM stabilization energies (ΔE_{FM}) as a function of Fe-Fe separation distance both with and without V_O . In the absence of V_O , AFM spin ordering predominates over the exchange interaction for all studied configurations. Decrease in the magnitude of ΔE_{FM} as Fe-Fe distance increases suggests that AFM superexchange between the dopants is intermediated via the bridging oxygen (O_{br}) ions [9]. It turns to saturate and approaches zero when the separation of Fe-Fe reaches around 7.5 Å. The fade-out of AFM coupling may due to the screening by the free carriers in the system [113]. Our results are consistent

with the work done on V doped In_2O_3 [91], where the FM and AFM states are degenerate when the doped V pairs are separated by $8.76 \text{ \AA}$.

As shown in Figure 4.2, after introducing V_{O} into the IFO system, the AFM spin ordering still prevails but the coupling is softened with the presence of V_{O} . The dramatic change of the favorable magnetic ordering in $b\text{-IFO-}V_{\text{O}}$ is very surprising, where the ΔE_{FM} is a negative value, implying an energetic FM favorable ground state.

Figure 4.3. Spatial spin density distribution of $b\text{-IFO}$ (left) configuration in AFM ordering and $b\text{-IFO-}V_{\text{O}}$ (right) in FM ordering. Red and blue isosurfaces correspond to spin-up and spin-down region.

In $b\text{-IFO-}V_{\text{O}}$ configuration, the only existing O_{br} between the Fe1 and Fe2 has been removed by the way we introduce the V_{O} as stated in the preceding section. These results provide strong evidence that the role of O_{br} is to mediate the superexchange interaction for AFM coupling. The dual spin density distribution

around the O_{br} , as shown in Figure 4.3, confirms the nature of O_{br} serving as a bridge for the AFM interactions between dopant Fe atoms.

4.3.1.2 V_O effect on DOS spectra

Figure 4.4. The total DOS (TDOS) of *b*-IFO (a), *b*-IFO- V_O (b), and Fe 3d projected DOS (PDOS) of *b*-IFO (c), *b*-IFO- V_O (d) in FM ordering. The vertical line drawn indicates the E_F position. The spin-up and spin-down DOS is shown above and below the abscissa axis.

Figure 4 gives the DOS spectra of *b*-IFO and *b*-IFO- V_O in FM ordering. The Fe *d* states are more sensitive to the surrounding oxygen than the spherically symmetric *s* states of In atoms. As shown in Figure 4.4(c), for IFO system, Fe 3d electrons are mainly distributed in the valence band due to the hybridization with the O 2*p* states, leaving the unoccupied minority states in the conduction band. Since the electron configuration of Fe is $4s^23d^6$, and as shown in Figure 4.4(c), the

majority spin states of $3d$ electrons are fully occupied, the minority spin states are fully unoccupied, which indicates a $3+$ valence state of Fe in IFO. However, the Fermi level (E_F) is located in the impurity states rather than the conduction band. After introducing V_O , as shown in Figure 4.4(b), the position of E_F is slightly raised to the conduction band minimum. The Fe $3d$ minority states, as displayed in Figure 4.4(d), is partially occupied leading to the mixed valance of Fe^{2+} and Fe^{3+} , which can drive ferromagnetism [67]. The electronic states in the gap are due to the hybridization between d states of Fe and p bands of oxygen, which mediates the magnetic interactions [114]. As demonstrated above, the major role that V_O plays is to introduce electrons that cause the partially filled minority spin states of Fe $3d$ states.

The main calculation results of IFO and IFO- V_O systems are tabulated in Table 4.1.

Table 4.1. The calculation results of Fe-doped In_2O_3 (IFO) system with and without oxygen vacancy (V_{O}). The FM stabilization energies (ΔE_{FM}), the total (M_{total}) and the projected magnetic moments for Fe (M_{Fe}) in both FM and AFM ordering are summarized.

Notation	ΔE_{FM} (meV)	$M_{\text{total}}(\mu_{\text{B}})$		$M_{\text{Fe}}(\mu_{\text{B}})$			
		FM	AFM	FM		AFM	
				Fe1	Fe2	Fe1	Fe2
Only Fe impurities							
<i>a</i> -IFO	122.7	9.94	0.00	3.95	3.94	3.91	-3.89
<i>b</i> -IFO	84.8	9.82	0.03	3.97	3.91	3.95	-3.90
<i>c</i> -IFO	48.7	9.98	0.00	3.99	3.97	3.98	-3.96
<i>d</i> -IFO	17.8	9.93	0.04	3.99	3.94	3.97	-3.93
<i>f</i> -IFO	5.4	9.96	0.00	3.98	3.98	3.98	-3.98
<i>g</i> -IFO	0.03	9.96	0.00	3.98	3.98	3.98	-3.98
With oxygen vacancy							
<i>a</i> -IFO- V_{O}	65.3	9.03	0.13	3.79	3.77	3.75	-3.69
<i>b</i> -IFO- V_{O}	-12.5	9.13	0.02	3.77	3.77	3.76	-3.77
<i>c</i> -IFO- V_{O}	37.0	9.41	-0.01	3.81	3.90	3.80	-3.88
<i>d</i> -IFO- V_{O}	3.5	9.41	-0.32	3.76	3.94	3.76	-3.95
<i>f</i> -IFO- V_{O}	1.1	9.43	0.23	3.95	3.79	3.95	-3.79
<i>g</i> -IFO- V_{O}	2.4	9.45	-0.29	3.78	3.96	3.78	-3.96

Electrons induced by introducing V_O results in mixed valence of Fe^{2+} and Fe^{3+} ions, as supported by the reduced projected magnetic moments of Fe, which are $3.95 \mu_B/Fe$ and $3.77 \mu_B/Fe$ in b -IFO and b -IFO- V_O system, respectively, as shown in Table 4.1. This corroborates the previous findings of the connection between the presence of Fe^{2+} and FM coupling [70], which sustains that the FM coupling is mediated by delocalized carriers. Nevertheless, even for b -IFO- V_O configuration, the FM coupling is weak ($\Delta E_{FM} = -12.5$ meV).

The total energy minimum calculations for all the dopants configurations indicate that the b -IFO and b -IFO- V_O are the most energetically favorable structures. In favor of b configuration, the doped Fe atoms are intended to accumulate together with a short Fe-Fe distance of ~ 3.9 Å. Generally speaking, the shorter Fe-Fe distance implies a larger doping concentration. This interpretation has been supported by our recent experimental finding [13] as well as some other reports [12; 14] that the FM coupling appears only when the Fe concentration is higher than a critical value (10% in Ref 16), while paramagnetic (PM) state is more stable with lower Fe dose.

4.3.2 Cu codoping effect

In this section, we discuss the Cu co-doping effect for the IFO system. The additional doping of Cu into b -IFO renders the system, b -IFCO- i , a weak FM ground state with ΔE_{FM} of -7.3 meV. This result accords with the prediction that Cu doping was found not to be directly responsible for the RT ferromagnetism of IFCO system [12; 70]. After introducing Fe and Cu ions into In_2O_3 , significant local structure distortions occur at the Fe- and Cu- substitution sites. The optimized

Fe-O bond lengths are about ~14% smaller in comparison with that of In-O in the optimized pure In_2O_3 . The shorter Fe-O distance may be due to the reduction of oxygen-oxygen repulsion forces [70] and coincides with the fact that the radii of both Fe^{3+} and Fe^{2+} are smaller than that of In^{3+} . The change of the six Cu-O bond lengths, which form the Cu-O octahedral, is rather complicated. Two of them are shortened by ~7%, the other two are increased by ~7%, while the last two remain the same length as compared with that of In-O in the optimized pure In_2O_3 . The local distortions change the lattice structure to one with a lower symmetry, resulting in a nearly complete splitting of the $3d$ orbitals.

4.3.2.1 Cu doping effect on DOS spectra

In Figure 4.5(a), the E_F crosses the majority-spin of impurity levels. One main feature indicated in the DOS spectra is the d hole states located at the top of the impurity band in the gap. As shown in Figures 4.5(b)-(d), there are strong d - p - d hybridization between Cu, O_{br} and Fe, which induces localized distributed holes in Fe $3d$ states. The localized d holes are also present in those configurations with V_{O} where FM ordering is stable (such as b -IFCO- V_{O} - i) but disappear in configurations where AFM ordering is stable (like b -IFCO- V_{O} - ii). (We will discuss this further in next section). All these findings strongly suggest that the localized spatial distributed d holes of Fe atoms induced by additional Cu doping play a vital role for the indirect FM exchange interaction between Fe1 and Fe2 atoms via Cu mediator. The existence of the hole states agrees with the lower oxidation state of Cu than Fe and In, which can be deduced from the projected magnetic moment ($\sim -0.4 \mu_{\text{B}}$).

Figure 4.5. The total DOS (TDOS), projected DOS (PDOS) of Cu 3d, Fe 3d, and $O_{br} 2p$ for *b*-IFCO-*i*, (a)-(d), and *b*-IFCO- V_O -*i*, (e)-(h) in FM ordering, respectively. The vertical line drawn indicates the E_F position. The spin-up and spin-down DOS is shown above and below the abscissa axis.

4.3.2.2 Short range weak indirect FM coupling mediator

The role of Cu is found to enhance the stability of ferromagnetism between the dopant Fe atoms, analogical to that in Cu and Co co-doped ZnO [102]. The spin density distributions, as shown in Figure 4.6, corroborate the existence of the Cu mediated FM interaction in IFCO system. The Cu ion being spin polarized by the presence of the magnetic impurities shown in Figure 4.6, mediating an indirect magnetic interaction among them [102]. However, the Cu mediated interaction is

highly anisotropic as evidenced by the spin density shown in Figure 4.6. This can be attributed to the band filling of the d orbitals of Cu and their directionality. Furthermore, a coupling chain of Fe1-O1-Cu-O2-Fe2 can be easily recognized in Figure 4.6.

Figure 4.6. Spatial spin density distribution of b -IFCO- i configuration in FM ordering. Red and blue isosurfaces correspond to spin-up and spin-down region.

4.3.3 Cu and V_O codoping effect

As discussed above, V_O or Cu doping alone in IFO system can improve the FM coupling but neither of them is sufficient enough to achieve stable RT ferromagnetism. We thus consider a system involving both V_O and Cu co-doping. This is also motivated by the experiment finding that the IFCO system shows ferromagnetism when the samples are prepared under low oxygen pressure [14]. Our main calculation results of IFCO and IFCO- V_O are summarized in Table 4.2

involving the ferromagnetic stabilization energy and magnetic moments of Fe and Cu for each configuration studied. As can be seen in Table 4.2, by introducing of V_O into b -IFCO- i system, (b configuration has been demonstrated to be more energetically stable), a pronounced enhancement of the stability of the FM state was found ($\Delta E_{FM} = -90.4$ meV).

Table 4.2. FM stabilization energies (ΔE_{FM}) of IFCO and IFCO- V_O systems. The total (M_{total}), the projected magnetic moments for Fe (M_{Fe}) and Cu (M_{Cu}) in both FM and AFM ordering are also summarized.

Notation	ΔE_{FM} (meV)	$M_{\text{total}}(\mu_{\text{B}})$		$M_{\text{Fe}}(\mu_{\text{B}})$				$M_{\text{Cu}}(\mu_{\text{B}})$	
		FM	AFM	FM		AFM		FM	AFM
				Fe1	Fe2	Fe1	Fe2		
Only Fe and Cu impurities									
b -IFCO- i	-7.3	7.97	0.02	3.55	3.52	3.34	-3.55	-0.37	-0.21
c -IFCO- i	-9.4	7.97	0.00	3.53	3.53	3.51	-3.51	-0.37	0.00
With oxygen vacancy									
b -IFCO- $V_{\text{O}}-i$	-90.4	8.66	-0.12	3.71	3.73	3.70	-3.71	-0.37	-0.06
b -IFCO- $V_{\text{O}}-ii$	7.1	9.00	-0.70	3.85	3.86	3.85	-3.85	-0.48	-0.48
b -IFCO- $V_{\text{O}}-iii$	-45.6	8.97	0.16	3.84	3.74	3.84	-3.66	-0.41	-0.06
c -IFCO- $V_{\text{O}}-i$	-110.5	8.24	0.60	3.72	3.69	3.57	-3.34	-0.38	0.01
f -IFCO- $V_{\text{O}}-i$	-35.6	8.95	-0.67	3.83	3.77	3.81	-3.84	-0.33	-0.33

4.3.3.1 The DOS spectra of Cu and V_O codoping

To investigate the mechanism of the FM coupling, we first inspect the electronic structure of b -IFCO- V_O - i . Figures 4.5(e)-(h) present the DOS spectra of b -IFCO- V_O - i in FM ordering. (The spatial spin-density in FM ordering is shown in Figure 4.7, which also clearly show the Fe1-O_{br}-Cu-O_{br}-Fe2 coupling chain feature). As displayed in Figures 4.5(f)-(h), Fe 3d, Cu 3d and 2p states of O_{br} all span the same energy space, *i.e.* from the bottom of the valance band to E_F , which indicates that there exists a strong hybridization between d orbital of TMs (Fe and Cu) and p orbital of intermediate oxygen atoms inside the host lattice. The hybridization between the TMs and their surrounding oxygen atoms also induced significant net magnetic moments on these oxygen atoms. Therefore, the total magnetic moments are mainly derived from the complex consisting of the dopants and the neighboring O anions in these systems. Moreover, the introduction of V_O results in more electrons compensating the holes in the majority spin states in Fe d bands induced by Cu doping. However, there still presents a small amount d holes in the conduction band of the majority spin states. For b -IFCO- V_O - ii configuration, which is stable in AFM ordering, the d holes in the majority spin states are totally compensated. Combining the d hole feature and the magnetic ordering state of these two configurations, it is obvious that the holes in the Fe d bands generated by the Cu co-doping play an important role in the FM exchange coupling in IFCO- V_O system. The increased FM coupling for V_O doped IFCO confirms the essential role of the electrons induced by V_O , together with holes induced by Cu co-doping, in mediating the FM interaction.

Figure 4.7. Spatial spin density distribution of (a) *b*-IFCO- V_{O-i} , (b) *c*-IFCO- V_{O-i} , (c) *f*-IFCO- V_{O-i} configuration in FM ordering. Red and blue isosurfaces correspond to spin-up and spin-down region.

4.3.3.2 The effect of Fe-Fe configuration

The strong AFM interaction between the d orbitals of both the two Fe atoms and Cu is mediated by p orbital of the O_{br} atoms, which brings on a strong indirect FM coupling between Fe1 and Fe2 atoms. The indirect FM coupling is very strong with the ΔE_{FM} in the magnitude of -90.4 meV (for *b*-IFCO- V_{O-i} configurations), which agrees with the reports by Lathiotakis *et al.* [102] and Ye *et al.* [115] To further investigate the correlation between the FM coupling and the strength of Fe1-O1-Cu-O2-Fe2 coupling chains, we vary the Fe2 position by remaining the Fe1, Cu, and V_O locations. The Fe2 is moved from Fe1's second NN

to the third and the sixth NN, corresponding to c -IFCO- V_O - i and f -IFCO- V_O - i configurations, respectively. In all these cases, the Fe1-O1-Cu-O2-Fe2 chains still exist. The ΔE_{FM} are found to be -110.5 meV and -35.6 meV for c - and f -IFCO- V_O - i configuration, respectively. The strongest FM coupling shown in c -IFCO- V_O - i configuration is due to the highest symmetry of this configuration compared to the other ones [102]. The dramatic reduction of ΔE_{FM} in f -IFCO- V_O - i configuration suggests a strong correlation between the FM coupling and the Fe-Fe distance in the Fe1-O1-Cu-O2-Fe2 coupling chains.

4.3.3.3 The coupling strength of Cu codoping

The effect of Cu positions with respect to Fe pairs is also studied in the present work. When the Cu is placed in one In(1) position (denoted as Cu1' in Figure 4.1), which is the third and the fourth NN to Fe1 and Fe2, respectively, corresponding to b -IFCO- V_O - ii configuration, it is found that the strong AFM coupling between Cu and Fe is vanished due to the absence of the O_{br} atoms between Cu and Fe. Figure 4.8 shows the PDOS of Fe and Cu 3d in FM ordering for b -IFCO- V_O - ii configuration. It is clear that the coupling between Fe-3d and Cu-3d states is very weak, which is attributed to the fact that the Cu atom is isolated from Fe pairs in this configuration. The weak coupling between Fe and Cu atoms is also evidenced by the special spin density distribution (not shown here). In contrary, as seen in Figures 4.5 (f)-(h), the Fe and Cu 3d states as well as the 2p states of O_{br} are strong hybridized, which indicates a strong indirect FM coupling between Fe1 and Fe2 atoms. This also confirms the short range effect of Cu doping. Moreover, when the Cu is positioned in the third and the first NN to Fe1 and Fe2, respectively, (b -IFCO- V_O - iii), there are two O_{br} atoms between Fe2 and Cu, but

none between Fe1 and Cu. Strong AFM coupling exists between Fe2 and Cu while no coupling between Fe1 and Cu is found. As a consequence, the *b*-IFCO- V_O -*iii* system is a relatively weaker FM coupled system ($\Delta E_{\text{FM}} = -45.6$ meV) compared to *b*-IFCO- V_O -*i* configuration. These results, again, strongly support the importance of participation of co-doped Cu in the hybridization of the Fe1:3d-O1:2p-Cu:3d-O2:2p-Fe2:3d orbital chain, which dominates the *e-e* correlations in IFCO- V_O system. Therefore, a long range FM ordering needs large TMs dopants concentration to form the continuous Fe1-O1-Cu-O2-Fe2 paths under the existence of V_O . This interpretation are tally with the previous findings that Fe and Cu co-doped $\text{In}_2\text{O}_{3-\delta}$ shows RT ferromagnetism with the Fe doping concentration larger than 10% [12].

Figure 4.8. The projected DOS (PDOS) of Fe 3d (black solid) and Cu 3d (red dash) for *b*-IFCO- V_O -*ii* configurations in FM ordering. The vertical line drawn indicates the E_F position. The spin-up and spin-down DOS is shown above and below the abscissa axis.

From the energy point of view, b -IFCO- V_O - ii is favored over b -IFCO- V_O - i by 0.08 eV. This, however, can be easily conquered in conventional sample preparation process. For example, at $T = 1000$ °C, which is the common temperature for sample synthesis, the difference in stability, $\Delta E \sim 0.08$ eV, between b -IFCO- V_O - ii and b -IFCO- V_O - i configurations corresponds to a relative probability of the presence of b -IFCO- V_O - i being as high as 48%. On the other hand, although the b -IFCO- V_O - ii is energetically stable, its ΔE_{FM} is only 7.1 meV, as shown in Table 4.2. Therefore, at RT, the AFM ordering in b -IFCO- V_O - ii configuration will be easily broken by the thermal energy, which makes the contribution of the ferromagnetic b -IFCO- V_O - i configuration dominated in the sample.

Figure 4.9. The Cu 3d PDOS for *b*-IFCO- V_O -*i* (a), *b*-IFCO- V_O -*ii* (b) configurations in both FM (red dash) and AFM (black solid) ordering. The vertical line drawn indicates the E_F position. The spin-up and spin-down DOS is shown above and below the abscissa axis.

Figure 4.9 shows the PDOS of Cu 3d states of *b*-IFCO- V_O -*i* and *b*-IFCO- V_O -*ii* both in FM and AFM ordering. It is found that, for *b*-IFCO- V_O -*i* configuration, the strong coupling between Cu and Fe mediated by O_{br} causes a downward shifting of the Cu *d* bands to the valence band, resulting in more delocalized Cu *d* states in FM ordering compared with AFM ordering, which render the system FM ground state. On the other hand, in case of *b*-IFCO- V_O -*ii* configuration where the AFM is a more stable state, the splitting of Cu *d* orbital is almost identical for FM and AFM ordering. The identical splitting of Cu *d* orbital is also consistent with the isolated feature of the Cu atom in this configuration (*b*-IFCO- V_O -*ii*).

4.3.3.4 The distance effect of V_O

Further considerations have also been made on varying the position of V_O . Take *b*-IFCO-*i* for example, we investigated three configurations that the V_O is at the first NN to Fe but far away from Cu, and at the first NN to Cu but far away from Fe pairs, as well as the position out of the range of the second NN to both Cu and Fe. Regardless of V_O positions, FM prevails with ΔE_{FM} of -90.4 meV, -29.3 meV and -41.8 meV, respectively. Similar results were obtained for *c*-IFCO-*i* system. Our calculations demonstrate a long range effect of V_O on the ferromagnetism in IFCO system. The long range effect of V_O is also evidenced in our previous experimental results [13] that the FM coupling can be switched on even with low carrier concentration of 10^{18} electrons·cm⁻³. Further experimental supports can be found from the work of Yu *et al.* [70], where they found that the FM coupling in IFCO- V_O system is mediated by delocalized carriers.

4.3.4 The mechanisms of room temperature ferromagnetism

There are two possible mechanisms proposed for FM semiconductor: carrier mediated and super-exchange. The key difference between these two mechanisms is that the magnetic coupling is mediated by mobile carriers in the former but by localized anions in the latter. In our case, the AFM super-exchange interaction between Fe and Cu atoms follows a path through the intermediate O anion which results in an indirect FM coupling between Fe atoms. The main mechanism is the hybridization of the Fe *d* states with the O *p* and subsequently with the Cu *d* states. In the structures with pronounced ferromagnetism, the hybridization of the Cu *d* states with the O *p* is particularly enhanced. That effect is

assisted by the downwards shift of the Cu $3d_{xy}$ and $3d_{yz}$ spin majority band which overlaps (in energy scale) more with the O p band. This mechanism was more evident for the structures b -IFCO- V_O - i and c -IFCO- V_O - i , which are found to have strong FM ground state. The p - d hybridization induces a remote electron delocalization which mediates the Fe-Fe interaction. On the contrary, the long range carrier mediated mechanism is switched on by delocalized electrons introduced by V_O , which mediate the different Fe1-O1-Cu-O2-Fe2 chains.

4.4 Conclusions

In summary, we systematically studied the effect of Cu co-doping and V_O on the ferromagnetism in Fe-doped In_2O_3 by detailed first-principles calculations. It has been demonstrated that IFO are in AFM ground state for all configurations investigated. With the existence of V_O , IFO can be weakly FM ground state when the O_{br} between Fe1 and Fe2 is leaking, which acts to mediate the superexchange interaction leading to AFM coupling between Fe1 and Fe2. By additional Cu doping, strong ferromagnetism appears in the IFCO- V_O system. Examination of spin density distribution and DOS spectra reveals that the coupling between Cu and Fe are AFM for both Fe1 and Fe2 mediated by the O_{br} atoms. Thus, the strong indirect FM interaction among Fe cations is formed via the Fe1-O1-Cu-O2-Fe2 coupling chains. The role of the Cu^{2+} ions in IFCO is to act as superexchange mediators by causing an indirect FM coupling between Fe cations through the hybridization of the O $2p$ states with $3d$ states of Cu and Fe, thereby enhancing the ferromagnetism.

Our calculations suggest that the ferromagnetism in IFCO system can be achieved with a large doping concentration of Fe with coexistence of V_O . The large Fe doping concentrations would result in an average smaller Fe-Cu separation distance, which increases the chance to form the Fe1-O1-Cu-O2-Fe2 coupling chains. The concentration of V_O , however, is not critical due to its long-range coupling effect.

Chapter five

First-principles study on the magnetism in nitrogen doped In_2O_3

5.1 Introduction

By doping $3d$ TM into transparent conducting oxide (TCO) In_2O_3 , RT ferromagnetism can be achieved [12; 14; 67-68; 70]. However, no convincing evidence can verify that the observed ferromagnetism is intrinsic. Generally, the magnetic elements doping suffers from the problems related to precipitates or secondary phase formation [61]. These extrinsic magnetic behaviors are undesirable for practical applications and promote searching for other dopants, which do not contain ions with partially filled d or f bands. Following this idea, RT ferromagnetism has been found in Cu-doped TiO_2 [116], and ZnO [117] films. Promising demonstrations of RT ferromagnetism in C and N doped DMSs [1; 73-74; 77; 118-120] provides a new opportunity to understand the origin of ferromagnetism and to search new spintronic materials. For instance, both C and N doped ZnO were found experimentally and theoretically to be RT DMSs [73-74].

To improve the physical properties and to enhance the magnetic interactions in these materials, it is essential to understand the mechanism of such phenomena. The basic mechanism responsible for the RT ferromagnetism in these materials has yet to be established. Up to now, few works have been focused on the magnetism of N-doped In_2O_3 (N- In_2O_3). Therefore, it is interesting to investigate the effect of N doping in In_2O_3 to explore the possibility of using N as a dopant to produce oxide-based DMSs.

In this chapter, we report the results of detailed first-principles calculations on the electronic structures and magnetic properties of the N- In_2O_3 system for a number of distinct N doping configurations. We demonstrate that a promising RT ferromagnetism could be induced by $2p$ elements (N) doping in this system and predict that the hole-mediated double exchange mechanism is responsible for the ferromagnetism.

5.2. Theoretical calculation details

Various configurations of N- In_2O_3 with N atoms at O sites are constructed using the 80-atom supercell (Figure 5.1). For convenience of discussion, we label nine O sites with letters $a \sim i$ as shown in Figure 5.1. We use (i, j) to denote a N-N pair, in which two O atoms are replaced by N at the i and j sites in Figure 5.1. The Gaussian smearing method with a smearing parameter of 0.1 eV is used for all. Other calculation details can be referred to chapter 4.

Figure 5.1. Crystal structure of In_2O_3 employed to define various configurations of 2N doped In_2O_3 . Grey (big) and cyan (small) spheres are In and O atoms. The positions of O substituted by N are denoted by $a - i$.

5.3 Results and discussions

5.3.1 Single N doping effect

To study the magnetic properties in N- In_2O_3 system, we first consider a single N substitution by replacing an O atom with an N atom (N_O). Based on the total energy calculations, the spin-polarized state favors over the non-spin-polarized state by 267 meV. Figures 5.2(a)-5.2(e) present the calculated total density of states (TDOS) and partial DOSs (PDOSs) for the N dopant and its nearest-neighboring (NN) In and second NN (2NN) O atoms. These figures show that the N $2p$ states significantly overlap with the O $2p$ and In $5p$ and $4d$ states around the Fermi level (E_F). The main feature indicated in the spectra is the hole states located around 0.37 eV above E_F , which are mostly from the N $2p$ and O $2p$

orbitals. The existence of these deep hole acceptor levels suggests that magnetic coupling in N-In₂O₃ is mediated by the holes induced by N doping [1]. By investigating DOS spectra, the coupling between the N dopant and the host atoms is found to be limited within the range of 2NN. The hybridization between N dopant and its neighboring host atoms results in the splitting of the energy levels near the E_F , which shifts the majority spin states downward and minority spin states upward to lower the total energy of the system [73-74]. Since the spin-up bands are fully occupied while the spin-down bands are partially filled, the number of holes in the system is equal to the magnetic moment, which is 1.00 μ_B total magnetic moment per supercell. The magnetic moments are mainly contributed by the N 2*p* orbital ($\sim 0.48 \mu_B$ from N itself, $\sim 0.2 \mu_B$ from its 2NN O atoms). The examination of the spin density distribution also verified this and indicated that the holes induced by N doping are localized on 2*p* states of N and its NN O. This is consistent with the results of N doped ZnO [73] and C doped ZnO [74], CdS [120], and TiO₂ [77].

5.3.2 Two N doping: magnetic coupling

In order to investigate the magnetic coupling between N atoms in N-In₂O₃, several distinct supercell structures with two N substitutions placed at several possible sites around In1 and In2 atoms (see Figure 5.1) are examined. The structures we considered here correspond to a doping concentration of 4.17 at. %. The magnetization energy, $\Delta E_{FM} = E_{FM} - E_{AFM}$, (E_{FM} and E_{AFM} are the total energies for FM and AFM ordering, respectively) is used to indicate the relative stability of the FM and AFM states. Calculation results are tabulated in Table 5.1 according to the N-N separation. It is found that the FM state is the ground state

when the N-N separation is no more than 3.5 Å. The magnitude of ΔE_{FM} becomes larger when two N_O get closer to each other and the magnetic moment per N in the ground state of each configuration is increased. When the N-N distance is greater than 4.5 Å, the FM and AFM states become degenerate, *i.e.*, the corresponding exchange interactions in these configurations are small. Among all configurations, the (a, c) has the lowest total energy and the largest magnitude of ΔE_{FM} (84 meV). This is larger than that of Cu-doped ZnO (43 meV) which is known to be FM at RT [115; 117] and some other systems, such as C-ZnO [74] and N-ZnO [73]. The large ΔE_{FM} implies the RT ferromagnetism for N-In₂O₃ is expected.

Figure 5.2. (Left) DOS for single N substituted supercell: total DOS (TDOS) (a), N 2p partial DOS (PDOS) (b), a second nearest neighboring (2NN) O 2p PDOS (c), and a nearest neighboring In 5p (d) and 4d (e). (Right) DOSs for 2N doped In₂O₃ in FM ordered (a, c) configuration: TDOS (f), N1 2p PDOS (g), N2 2p PDOS (h), a 2NN O 2p PDOS (i), In_{br} 5p (j) and In_{br} 4d (k) PDOSs. The vertical line drawn indicates the E_{F} position and the up/down-spin DOS is shown above/below the abscissa axis.

TDOS and PDOSs for the N dopant and its neighboring In and O atoms in FM ordered (a, c) configuration are depicted in Figures 5.2(f)-5.2(k). Similar to the single N doping case, hole states arising from the hybridizations between N and its neighboring atoms are also limited to 2NN atoms. The main difference compared to that of single N doping case is that there are more hole states in N $2p$ orbitals and obvious hole states in bridging In (In_{br}) $5p$ and $4d$ orbitals due to the significant hybridization between the N dopants and In_{br} atoms. The hole states in the In_{br} p/d orbitals indicate the existence of N1- In_{br} -N2 chains which has later on been evidenced to dominate the FM coupling in N- In_2O_3 system. The hybridization between the N $2p$ and In (In_{br}) $5p$ and $4d$ orbitals leads to a formation of N1: p - $\text{In}_{\text{br}}:d/p$ -N2: p chain, which facilitates an indirect FM coupling between N dopants mediated by the holes introduced. The existence of N1: p - $\text{In}_{\text{br}}:d/p$ -N2: p coupling chain is originated from the delocalized nature of N p orbitals compared to the d orbitals of TMs.

Figure 5.3. $2p$ -PDOS of N1 in (a, c) (a) and (i, a) (b) configurations in FM (black solid) and AFM (red dashed) ordering. The vertical line drawn indicates the E_F position and the up/down-spin DOS is shown above/below the abscissa axis. Spatial spin-density distribution of (a, c) configuration in FM and AFM ordering are shown in (c) and (d), respectively. The yellow iso-surface (in c) presents the total net spin density in FM ordering, and the red/blue iso-surfaces (in d) correspond to up/down-spin densities.

5.3.3 The role to magnetic coupling

The $2p$ -PDOS of N1 in (a, c) configuration, shown in Figure 5.3(a), clearly reveals that the strong indirect FM coupling between N1 and N2 via the N1: p -In_{br}: d/p -N2: p chain results in stronger spin-exchange splitting of the N $2p$ orbitals in FM ordering than that in the AFM ordering. On the other hand, for (i, a) configuration, which is in the weak FM ground state, the spin-exchange splitting of

N $2p$ orbitals are nearly identical in FM and AFM ordering, as shown in Figure 5.3(b). Moreover, the comparison made between the PDOSs of N $2p$ for (a, c) and (i, a) configurations (not shown) suggests that the increased spin-exchange splitting is achieved mainly by the overly upward shifted p_x minority orbital. Our results are consistent with the previous reports for the Cu d band splitting in Cu co-doped $\text{In}_2\text{O}_3\text{:Fe}$ [121] and Cu co-doped ZnO:Co systems [102].

The strong indirect FM interaction between N dopants in (a, c) configuration driven by $\text{N1:}p\text{-In}_{\text{br}}\text{:}d/p\text{-N2:}p$ coupling chain is also confirmed by its spin-density distribution, as shown in Figure 5.3(c) and 5.3(d), respectively. This notion can be easily recognized by the dual feature of spin density around each N dopant in AFM state, where the up-spin (down-spin) density distribution of both N1 and N2 are pointing to $\text{In}_{\text{br}1}$ ($\text{In}_{\text{br}2}$). This feature strongly suggests that the spin-up (down) electron in N1 and N2 are indirectly coupled to each other through the mediator of $\text{In}_{\text{br}1}$ ($\text{In}_{\text{br}2}$). This dual spin density distribution feature is not observed in configurations with larger N-N separations, which are in weak FM ground states, such as (i, a) configuration. The spatial coexistence of up- and down-spin density in AFM ordered configurations also explains the smaller net magnetic moment per N with respect to their corresponding FM phase (see Table 5.1).

Table 5.1. Values of the N-N distance of the ground state ordering after relaxation, the relative stable energies (ΔE), the magnetization energy (ΔE_{FM}), and the magnetic moment (m) per N atom calculated for all doped configurations in FM/AFM ordering. The relative stable energy is referred to the (a, c) configuration and the most stable state (either FM or AFM) is used for each configuration.

Configurations	[N-N]	ΔE	ΔE_{FM}	$m (\mu_B/\text{N})$
(i, j)	(Å)	(meV)	(meV)	(FM/AFM)
(a, c)	2.840	0	-84	0.56 / 0.30
(i, h)	2.896	158	-67	0.53 / 0.34
(i, g)	3.406	253	-30	0.50 / 0.44
(a, e)	3.613	349	-2	0.47 / 0.47
(b, c)	4.206	320	4	0.47 / 0.47
(a, d)	4.191	251	-9	0.48 / 0.47
(b, e)	4.446	300	-15	0.46 / 0.45
(i, a)	4.461	290	-6	0.48 / 0.47
(h, e)	6.081	313	-5	0.47 / 0.47

By examining the DOS spectra and spatial spin density distributions of various N-In₂O₃ configurations, we find that the strong FM coupling between N dopants and the magnetization energy decrease significantly when the N-N separation increases. This indicates that the N1: p -In_{br}: d/p -N2: p hybridization is short-ranged and strongly correlated to the magnetization energy. Therefore, we propose that the localized holes induced by N doping mediate the FM interaction

in N-In₂O₃ system, which is strengthened by a N1:*p*-In_{br}:*d*/*p*-N2:*p* coupling chain. Similar to the *p*-*d* interactions in the TMs-doped semiconductors, such as in Cu-doped ZnO [122], this N1:*p*-In_{br}:*d*/*p*-N2:*p* interaction is the key to stabilize the ferromagnetism in the N-In₂O₃ system.

5.4 Conclusions

In summary, we have demonstrated that N-In₂O₃ system is in FM ground state with no obvious clustering effect and calculated magnetization energy of N-In₂O₃ is found to be larger than some of the known RT DMS which implies the RT ferromagnetism for N-In₂O₃ can be expected. The FM exchange interaction between N dopants is activated through holes induced by N doping via a N1:*p*-In_{br}:*d*/*p*-N2:*p* coupling chain in short N-N separations, which plays the major role in forming the ferromagnetism in N-In₂O₃ system.

Chapter six

Nonconventional magnetism in pristine and alkali doped In_2O_3

6.1 Introduction

Besides the anion site doping, another approach to achieve d^0 magnetism in the system is to introduce cation defects or doping with non-magnetic element. This approach has been motivated by the fact that RT ferromagnetism has been evidenced in undoped oxides systems such as: HfO_2 [79], In_2O_3 [79-82], ZnO [81], TiO_2 [79], SnO_2 [81; 83], CeO_2 [81], and Al_2O_3 [81] in forms of bulk, film or nanoparticle. Although the ferromagnetism obtained in undoped oxides mentioned above is conformably attributed to the existence of native defects, contradicting arguments still exist. While early experimental groups proposed that the magnetism arises from O vacancies [79; 81; 83; 123], all theoretical work suggest that it is the cation vacancies that contribute to the magnetism observed [124-127]. The latter has also been supported by recent experiments [80; 82; 128-129].

As the discussion in the Chapter 5, the holes play very important roles in

terms of generating magnetic moments and facilitating the FM coupling, alkali metal doping would be the best choice to substitute the cation atoms. Indeed, recently, RT ferromagnetism is observed in alkali doped ZnO nanorods [84] and nanotubes [85]. Those authors attributed the origin of the RT ferromagnetism to the effect of cation substitution by alkali metal at Zn site. This is consistent with the theoretical reports for systems of cubic $\text{ZrO}_2\text{-K}$ [86-87], rutile $\text{TiO}_2\text{-K}$ [86], and $\text{SnO}_2\text{-Mg}$ [88]. As for the system of In_2O_3 , it is pointed out by Panguluri experimentally that the vital factor for the observed RT ferromagnetism in undoped In_2O_3 is the coexistence of V_{O} and V_{In} [80], which serve as carrier mediator and introduce local magnetic moment, respectively. This notion has been verified by the high quality scanning tunneling microscopy (STM) characterization.[82] However, theoretical work has yet to be established to solve the puzzles of local-moment formation and to provide atomic level understanding of the ferromagnetism in both undoped and nonmagnetic cation-doped In_2O_3 . Therefore, it is highly desirable to carry out the study on the roles that defect states play in mediating the magnetic coupling in order to improve the understanding on the observed magnetism.

In this chapter, we performed a systematical study for the electronic and magnetic properties in In_2O_3 by investigating the effects of intrinsic defects and nonmagnetic elements doping at In site. We demonstrate that In_2O_3 is one kind of the promising pristine spintronics material and alkali metals doping in In_2O_3 can promote robust RT ferromagnetism with a relatively small formation energy compared to $3d$ TMs and $2p$ elements (such as C and N) doping as well as the cation vacancy induced ferromagnetism in oxides- and nitride-based DMSs

6.2 Theoretical calculation details

The supercell we used contains 80 atoms, corresponding to 16 f.u. In_2O_3 . The supercell size is large enough to allow us to investigate various configurations of defect coupling as well as to eliminate the spurious interactions between periodic defect images of the supercell. According to the Wyckoff's notation, there are 8 In(1) atoms occupied the b sites, 24 In(2) atoms occupied the d sites, and 48 oxygen atoms occupied the e sites in such an 80-atoms supercell. The spin-polarized energy (ΔE_{spin}) is defined as the energy difference between spin-polarized and non spin-polarized states. In order to study the magnetic coupling between the defects, two defects are introduced. We fixed one defect (V_{In} or nonmagnetic atom, denoted by X1) at In(1). The second defect is varied within the fourth nearest-neighbor (NN) to X1, face-diagonal position and body-diagonal position with respect to X1 in the sub-lattice of the cubic In(1). These configurations are defined as a, b, c, d, f , and g , for first NN (1NN), second NN (2NN), third NN (3NN), fourth NN (4NN), face-diagonal and body-diagonal positions, respectively, as shown in Figure 6.1. All these dopant configurations are represented by a label, such as $b\text{-IO-X}_{\text{In}}$, where b represents the configuration of the two defects, and $X_{\text{In}} = V_{\text{In}}, \text{Li}, \text{Na}, \text{K}, \text{Mg}$ or Ca . For all configurations, the ferromagnetism stabilization energy: $\Delta E_{\text{FM}}(\mathbf{R}) = E_{\text{FM}}(\mathbf{R}) - E_{\text{AFM}}(\mathbf{R})$ are calculated, where $E_{\text{FM}}(\mathbf{R})$ and $E_{\text{AFM}}(\mathbf{R})$ are the total energies of the supercell with ferromagnetic (FM) and antiferromagnetic (AFM) aligned $X_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complex pairs (the defect with its 6 NN O atoms), respectively, with the $X_{\text{In}}\text{-}X_{\text{In}}$ separation distance of R . The difference in the two energies yields the J coupling, indicating relative stability of the AFM and FM states. Other calculation details can be referred to Chapter 4.

Figure 6.1. Crystal structure of In_2O_3 . Grey (big) and cyan (small) spheres are In and O atoms. For IO- X_{In} systems we examined, one of the two X dopants is fixed at the position labeled X1, and the other one locates at the positions labeled with a , b , c , d , f , and g for different configurations. ($\text{X}_{\text{In}} = \text{V}_{\text{In}}$, Li_{In} , Na_{In} , K_{In} , Mg_{In} , or Ca_{In}).

6.3 Results and discussion

6.3.1 Calculation results

6.3.1.1 Native defects induced ferromagnetism in In_2O_3

We first study the electronic and magnetic properties of pristine bulk In_2O_3 . The calculated spin-polarized total density of states (TDOS) shown in Figure 6.2(a) clearly indicates that the bulk In_2O_3 is a non-magnetic semiconductor, which is consistent with experimental results [79]. As seen from Figure 6.2(a), the O $2p$ orbitals compose the most of the valence band especially at the valence band maximum (VBM) which is a common character for many insulating metal oxides. On the other hand, the conduction band is mainly contributed by the In $5s$ and $5p$

orbitals and is empty.

Figure 6.2. The spin-polarized total DOS (TDOS, black solid curve) and partial DOS (PDOS) of O 2p (red dashed curve) of bulk In_2O_3 (IO) (a). TDOS of $\text{IO}-V_{\text{O}}$ and $\text{IO}-V_{\text{In}}$ are given in (b) and (c). PDOS of nearest-neighboring (NN) O 2p and NN In 4d and 5p of $\text{IO}-V_{\text{In}}$ are shown in (d) and (e). The vertical dashed line represents the E_F , which is set to zero.

Experimentally, many native defects can be introduced in traditional sample preparation process with highly non-equilibrium techniques. The defects are typically associated with open electron shell leading to the formation of local magnetic moments. If the local magnetic moments the defects introduced could couple in long-range, macroscopic magnetic material can be achieved. Generally, there are several kinds of possible native point defects in In_2O_3 such as vacancies and interstitials. For simplicity, we only consider the vacancies cases by removing O (oxygen vacancy, V_{O}) and In (In vacancy, V_{In}) atoms from the supercell. The

band structure after introducing V_O (IO- V_O) is nearly identical to pure In_2O_3 except that the Fermi level (E_F) is raised up into the bottom of conduction band, as shown in Figure 6.2(b), which confirms the electron donor nature of V_O . Based on the calculated total energies, the spin-polarized and non-spin-polarized states are degenerate indicating a non-magnetic ground state. The presence of V_O also leads to local lattice distortion, where the nearest-neighboring In atoms move outward by $0.02 \sim 0.12 \text{ \AA}$ due to the Coulomb repulsion effect. The fact that V_O introduces no magnetic moments agrees well with the theoretical results for other oxides system, such as ZrO_2 [87] and HfO_2 [124; 130]. When an In atom is removed, two of the O_{NN} move outward by $0.05 \text{ \AA}$, the other 4 O_{NN} atoms move away by $0.20 \text{ \AA}$ and the calculations show that V_{In} introduces the formation of local magnetic moments in the system. Strong interaction between V_{In} and its surrounding O atoms leads to the splitting of the energy levels near the E_F . The spin-up bands are fully occupied while the spin-down bands are partially filled, resulting in a half metallic system with a total magnetic moment of $3.0 \mu_B$ per supercell. This is in accord with the 3+ nominal valence state of In that three holes are therefore needed to charge compensate a V_{In} . Our total energy calculation favors a spin-polarized state for IO- V_{In} system with ΔE_{spin} as high as -368.5 meV . The moments are mostly localized to the dangling bonds of its 6 O_{NN} atoms. This localized nature of magnetic moments is verified by the spin-density distribution around the V_{In} as shown in Figure 6.3. The moments on the 2NN O atoms are an order of magnitude smaller than that on the 1NN ones but they are also important as to overcome the magnetic percolation threshold [131]. The observation of cation vacancies induced localized magnetic moments agrees with other reports in undoped oxides [128-129; 132], which have been demonstrated to lead to ferromagnetism.

Figure 6.3. Spatial spin-density distribution of In_2O_3 with single V_{In} .

The site-resolved partial DOS (PDOS) of $\text{In}_2\text{O}_3\text{-}V_{\text{In}}$ (IO- V_{In}) system are presented in Figures 6.2(d) and (e) for a 1NN O and a 2NN In. It is clear that the hole states are mainly contributed by the p orbitals of O_{NN} , which drive the magnetism. The hole induced magnetism has also been found in TiO_2 [133], ZnO [1] and SnO_2 [127].

As evidenced above, the magnetic moments in IO- V_{In} system are mainly derived from $V_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complex. To study the magnetic coupling between these $V_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complexes, we considered several unique configurations of two V_{In} with several possible separations in the supercell which are labeled by a , b , c , d , f , and g in Figure 6.1. The atomic positions in each case are fully optimized and the total energies are calculated for both FM and AFM ordering. Unlike the other systems such as TiO_2 and ZnO where the cation vacancies (V_{Ti} and V_{Zn}) tend to form clusters, our results show that V_{In} are reluctant to aggregate, which suggests a

homogeneous distribution of V_{In} . The main calculation results of IO- V_{In} systems are tabulated in Table 6.1.

Table 6.1. Calculation results for various configurations of IO- V_{In} . $|V_{\text{In}}-V_{\text{In}}|$, ΔE , ΔE_{FM} and M_{tot} are the separation distance, the relative stable energy, the FM stabilization energy and the total magnetic moments of the supercell in FM ordering, respectively.

Notation	$ V_{\text{In}}-V_{\text{In}} $ (Å)	ΔE (eV)	ΔE_{FM} (meV)	M_{tot} (μ_{B})
<i>a</i> -IO- V_{In}	3.41	0.59	-91.7	6.00
<i>b</i> -IO- V_{In}	3.93	0.43	-339.0	6.00
<i>c</i> -IO- V_{In}	5.12	0.00	-115.7	6.00
<i>d</i> -IO- V_{In}	6.20	0.49	-97.6	6.00
<i>f</i> -IO- V_{In}	7.32	0.63	-140.8	6.00
<i>g</i> -IO- V_{In}	8.97	0.68	-27.3	6.00

It is found that FM spin ordering predominates over the exchange interaction for all studied configurations. Note that even for the configurations of *g* and *f*, where the $V_{\text{In}}-V_{\text{In}}$ separations are as large as 7.32 and 8.97 Å, the ground state is found to be ferromagnetic. This indicates that long range FM coupling exists in this system to promote the collective magnetism. Our results are consistent with the work done on Mg vacancies in MgO [134], Ti vacancies in TiO₂ [133], and Sn vacancies in SnO₂ [127], where the FM coupling between cation vacancies is long-ranged. The spin-polarized total energy calculations for all configurations indicate the *c*-IO- V_{In} to be the most energetically favorable structure,

which is 0.68 eV more stable than g -IO- V_{In} configuration with ΔE_{FM} of -115.7 meV. This ΔE_{FM} is larger than, for example, that of Cu-doped ZnO (42 meV) which is known to be ferromagnetism at RT [115] as well as some other systems, such as C-ZnO [74]. The large ΔE_{FM} implies the RT ferromagnetism for IO- V_{In} is expected. In c configuration, the V_{In} defects are separated by ~ 5.12 Å. Generally speaking, this moderate $V_{\text{In}}-V_{\text{In}}$ distance implies a moderate V_{In} concentration.

6.3.1.2 Alkali metals doping induced ferromagnetism

Besides the cation vacancies, cationic substitution is another approach to introduce acceptor-like localized magnetic moments. Table 6.2 lists out the calculated formation energies (E_{form}), spin-polarized energy (ΔE_{spin}) and the total induced magnetic moments (M_{tot}) of an 80-atom supercell involving single V_{In} , single Li substitution at In site (Li_{In}) and single N substitution at O site (N_{O}). The formation energy E_{form} is calculated using the following equations:

$$E_{\text{form}}(\text{IO}-V_{\text{In}}) = E_{\text{tot}}(\text{IO}-V_{\text{In}}) - E_{\text{tot}}(\text{IO}) + \mu_{\text{In}};$$

$$E_{\text{form}}(\text{IO}-\text{N}_{\text{O}}) = E_{\text{tot}}(\text{IO}-\text{N}_{\text{O}}) - E_{\text{tot}}(\text{IO}) - \mu_{\text{N}} + \mu_{\text{O}}$$

$$E_{\text{form}}(\text{IO}-\text{Li}_{\text{In}}) = E_{\text{tot}}(\text{IO}-\text{Li}_{\text{In}}) - E_{\text{tot}}(\text{IO}) - \mu_{\text{Li}} + \mu_{\text{In}}$$

Where, $E_{\text{tot}}(\text{IO})$, $E_{\text{tot}}(\text{IO}-V_{\text{In}})$, $E_{\text{tot}}(\text{IO}-\text{N}_{\text{O}})$, and $E_{\text{tot}}(\text{IO}-\text{Li}_{\text{In}})$ are the total energies of In_2O_3 , IO- V_{In} IO- N_{O} and IO- Li_{In} systems, respectively. And μ_{In} , μ_{O} , μ_{N} , and μ_{Li} are the chemical potentials for Li, O, N and Li, respectively. For O-rich condition: $\mu_{\text{O}} = 1/2 E_{\text{tot}}(\text{O}_2)$, while in O-poor case, $\mu_{\text{O}} = 1/3 [E_{\text{tot}}(\text{IO}) - 2\mu_{\text{In}}]$.

Table 6.2. The calculation results of formation energy (E_{form}), spin-polarized energy (ΔE_{spin}) and total magnetic moments (M_{tot}) for an 80-atom In_2O_3 supercell involving one V_{In} (IO- V_{In}), one N_{O} (IO- N_{O}), and one Li_{In} defect (IO- Li_{In}), respectively. Only the lower values of E_{form} are given under the condition specified.

Notation	E_{form} (eV)	E_{spin} (meV)	M_{tot} (μ_{B})	Coupling strength
IO- V_{In}	4.52 (O-rich)	-368.5	3.00	Long range
IO- N_{O}	2.15 (In-rich)	-267.0	1.00	Short range
IO- Li_{In}	-0.67 (O-rich)	-128.1	2.00	Long range

The negative E_{form} of Li_{In} signifies that Li doping in In_2O_3 is more energetically favorable in practical sample preparation. In the following of this section, we will discuss the alkali metal doping effect for the In_2O_3 system in term of their magnetic properties. The bulk In_2O_3 doped with Li, Na and K (IO- X_{In} , $\text{X} = \text{Li, Na and K}$) atoms are considered that each introduces two holes. If the hole states are sufficiently localized, a spin-polarized ground state may be achieved. Our first-principles calculations confirm that the alkali metal substitutions indeed give rise to a $2.00 \mu_{\text{B}}$ local magnetic moment per defect and render the system magnetic ground state with ΔE_{spin} of -128.1 meV, -103.2 meV and -102.8 meV for Li, Na and K doping, respectively.

Similar to the V_{In} case, the magnetic moments are localized to the 1NN O atoms, which is evidenced by the spin density distribution (not shown) as well as the projected DOS for IO- Li_{In} in Figure 6.4. (Similar DOS spectra are observed for IO- Na_{In} and IO- K_{In}). In addition to the formation of the defects states, $2p$ states of the 1NN O atoms also contribute to the bulk states. The main feature of the DOS

spectra is that the E_F crosses the minority-spin of impurity levels. There is strong p - p hybridization between 1NN O atoms, which induces localized distributed holes in O $2p$ states. All these findings strongly suggest that the localized p holes of O atoms induced by alkali metal doping play a vital role for the magnetic exchange interaction among O atoms.

Figure 6.4. Total DOS (a), and partial DOSs of NN O (b), NN In (c) and Li (d) of In_2O_3 with single Li_{In} . The vertical dashed line represents the E_F , which is set to zero.

After introducing Li, Na and K ions into In_2O_3 , local structure distortions occur around the substitution sites. The distortion strength varies regarding to dopants. The optimized bond lengths of Li-O are within $\pm 0.1 \text{ \AA}$ of that of In-O bond, while Na-O and K-O bond lengths are increased by $0.05\sim 0.18 \text{ \AA}$ and

0.20~0.30 Å after lattice optimization, respectively. Note that the structure distortion introduced by Li and Na doping is smaller than that of V_{In} , which makes the former more suitable in practical use.

Table 6.3. Calculation results for various configurations of IO-Li_{In}. The specifications are the same as in Table 6.1.

Notation	Li - Li (Å)	ΔE (eV)	ΔE_{FM} (meV)	M_{tot} (μ_{B})
<i>a</i> - IO-Li _{In}	3.41	0.09	-74.3	3.95
<i>b</i> - IO-Li _{In}	3.93	0.12	-119.4	3.96
<i>c</i> - IO-Li _{In}	5.12	0.00	-96.5	3.96
<i>d</i> - IO-Li _{In}	6.20	0.12	-76.2	3.95
<i>f</i> - IO-Li _{In}	7.32	0.32	-87.0	3.96
<i>g</i> - IO-Li _{In}	8.97	0.31	-46.2	3.92

To further investigate the magnetic coupling between alkali metal dopants, two defects are created in the In₂O₃ supercell the same manner as discussed in V_{In} case. Our main calculation results for IO-Li_{In} are summarized in Table 6.3 involving the FM stabilization energy and magnetic moments for each configuration studied. As can be seen in Table 6.3, for all doping configurations, the system is in FM ground state and the values of ΔE_{FM} imply that the ferromagnetism can sustain even at RT. Again the *c*-configuration is the most stable one with ΔE_{FM} of -96.5 meV. The large ΔE_{FM} of *g*-configuration (-46.2 meV) suggests that long-range FM coupling exists in IO-Li_{In} system. The same calculations with two Na and two K dopants are also performed. The results are similar to that of Li doping and the main calculation results are tabulated in Table

6.4 and 6.5 for Na and K doping, respectively.

Table 6.4. Calculation results for various configurations of IO-Na_{In}. The specifications are the same as in Table 6.1.

Notation	Na- Na (Å)	ΔE (eV)	ΔE_{FM} (meV)	M_{tot} (μ_B)
<i>a</i> - IO-Na _{In}	3.41	0.24	-59.6	3.97
<i>b</i> - IO-Na _{In}	3.93	0.22	-158.9	3.96
<i>c</i> - IO-Na _{In}	5.12	0.00	-36.3	3.98
<i>d</i> - IO-Na _{In}	6.20	0.22	-76.9	3.96
<i>f</i> - IO-Na _{In}	7.32	0.31	-112.4	3.95
<i>g</i> - IO-Na _{In}	8.97	0.38	-45.4	3.91

Table 6.5. Calculation results for various configurations of IO-K_{In}. The specifications are the same as in Table 6.1.

Notation	K- K (Å)	ΔE (eV)	ΔE_{FM} (meV)	M_{tot} (μ_B)
<i>a</i> - IO-K _{In}	3.41	0.59	-51.6	3.98
<i>b</i> - IO-K _{In}	3.93	0.58	-54.1	3.97
<i>c</i> - IO-K _{In}	5.12	0.00	1.10	3.98
<i>d</i> - IO-K _{In}	6.20	0.75	-49.9	3.97
<i>f</i> - IO-K _{In}	7.32	0.56	-81.9	3.99
<i>g</i> - IO-K _{In}	8.97	0.45	-19.5	3.96

These results agree with the recent experimental results for Li and Na doped ZnO, which show RT ferromagnetism [84-85] as well as other theoretical calculations for K doped ZrO₂ [87], K doped SnO₂ [135], and K doped GaN [126]. It is noteworthy that, as a general trend, T_C (which is correlated with the value of ΔE_{FM}) decreases with the increase of atomic number as observed experimentally [85].

6.3.1.3 Magnetism in alkaline-earth metals doped In₂O₃

As discussed above, V_{In} or alkali metal doping in In₂O₃ system can promote FM coupling. We then consider a system involving alkaline-earth metal (Mg or Ca) doping, which introduces only one hole per substitution. Unlike the V_{In} and alkali metal doping, Mg and Ca doping do not introduce any magnetic moment and therefore no magnetic coupling exists in these systems. The results are consistent with the work done by Maca *et al.*, where Ca doping in ZrO₂ is non-magnetic but K doping is FM [87]. The reason for this observation is deliberated in next section.

6.3.2 Discussion

6.3.2.1 Mechanism of magnetic coupling

When local magnetic moments are brought forward to a system, the existence of long-range coupling among local moments is essential to achieve macroscopic magnetic ordering (collective magnetism). As reported, the O 2*p* hole states can couple with each other through *p-p* interaction [73-74], which serves as

the medium for the long-range magnetic coupling. The long-range coupling can align the spin moments of the hole states and result in a magnetic ground state.

Figure 6.5. Spatial spin-density distribution of f -IO-Li_{In} (a) and g -IO-Li_{In} in AFM ordering. Red and blue isosurfaces correspond to spin-up and spin-down region.

Using f -IO-Li_{In} as an example, we will demonstrate how the FM coupling is activated in IO-X_{In} (X_{In} = V_{In}, Li_{In}, Na_{In} and K_{In}) system. As given in Figure 6.5(a) for the spin density distribution of f -IO-Li_{In} in AFM ordering, coupling chains of Li_{In}-O_{NN}-In_{NN}-O_{NN}-Li_{In} can be easily recognized, which facilitates the p - p correlations in IO-X_{In} system. There exists dual spin distribution around some O atoms highlighted by arrows in Figure 6.5(a), which are in the range of 2NN to both Li_{In} defects. The dual spin density distribution indicates the long-range coupling between the two Li_{In}-6O_{NN} complexes and results in smaller magnetic moments of 2NN oxygen atoms in AFM ordering. The long-range coupling for alkali metal doping makes it superior to TMs and N doping where the coupling is short-ranged [75; 121]. However, in g -configuration as shown in Figure 6.5(b), the

spin for all O atoms is unitary. The diversity of the spin distribution with respect to separation demonstrates the complexity of magnetic interactions in this system, which involves both intra- and inter-correlation between O $2p$ orbitals inside the $\text{Li}_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complexes. A $\text{Li}_{\text{In}}\text{-O}_{\text{NN}}\text{-In}_{\text{NN}}\text{-O}_{\text{NN}}\text{-Li}_{\text{In}}$ chain is required to facilitate this long-range FM coupling. In g -configuration, the $\text{Li}_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complexes are too far to form this coupling chain and significant drop of magnetic stabilization energy is observed. Therefore, FM coupling is promoted when inter-correlation exists.

Figure 6.6. Schematic drawing of the magnetic mechanism in alkali metal doped In_2O_3 system.

In brief, as shown in Figure 6.6, the mechanism of the FM coupling in alkali doped In_2O_3 system is similar to BMP model. One alkali dopant can generate some magnetic moment localized within it 2NN O. Although the moments on 2NN O is smaller than that on 1NN O, they are important to contribute to the “polaron” radius. Only when the polarons overlap with each other, the long range FM can be realized. However, different from the conventional BMP

model, the magnetic moment is generated by O $2p$ holes in this case rather than the magnetic ion dopant.

Our results show that the FM coupling radius for cation vacancy as well as cation site alkali metal doping is larger and more robust than that of $2p$ element (like N) doping at anion site and even TM-doping at cation sites [73; 75-76]. Taking into account of the negative formation energy and less lattice distortion for alkali metal doping (discussed in the previous sections), we suggest here that alkali metals, Li and Na doped In_2O_3 are more promising for achieving practical spintronic applications.

6.3.2.2 The effect of carrier density

The non-magnetic ground state observed for Mg and Ca doping indicates that the long-range magnetic coupling as well as the local moment formation depend on the hole concentration. There is less hole for alkaline-earth metal doping due to the charge difference between host and impurity cation. The result is in agreement with the prediction that a threshold for hole concentration exists to induce local magnetic moments and to turn on the FM coupling [1]. Therefore, long-range FM ordering needs sufficient holes to active the magnetic coupling through $\text{X}_{\text{In}}\text{-O}_{\text{NN}}\text{-In}_{\text{NN}}\text{-O}_{\text{NN}}\text{-X}_{\text{In}}$ chain.

Figure 6.7. FM stabilization energy (ΔE_{FM}), magnetic moment of O_1 and O_2 (M_{I}) and other 4 O atoms (M_{II}) in one $V_{\text{In}}\text{-}6\text{O}_{\text{NN}}$ complex of $c\text{-IO-}V_{\text{In}}$ as a function of additional e -charge doping.

To verify the importance of hole concentration, we perform calculations with electron (e)-doping for $\text{IO-}V_{\text{In}}$ case in c -configuration, since it has been shown the most energetic stable. Jellium background is adopted to maintain charge neutrality for the e -doping studies as implemented in VASP. In $c\text{-IO-}V_{\text{In}}$ configuration, there are several $\text{O}_{\text{NN}}\text{-In}_{\text{NN}}\text{-O}_{\text{NN}}$ chains between the two V_{In} . Although the O atoms in the InO_6 octahedron are identical by symmetry, the magnetic moment distribution on them is different. The main results of $c\text{-IO-}V_{\text{In}}$ configuration with 1.0 e and 2.0 e doping are presented in Figure 6.7. As shown in Figure 6.7, ΔE_{FM} drops dramatically with the increase of e -charge. The magnetic

moments on O_1 and O_2 (notations are indicated in Figure 6.1, and represented as M_I in Figure 6.7) atoms are much smaller than that of the others (represented as M_{II} in Figure 6.7). Most importantly, M_I drops markedly with increasing of e -charge, while M_{II} is only slightly decreased with e -charge. It is therefore reasonable to correlate the drop of the ΔE_{FM} with the decreased magnetic moment on O_1 and O_2 atoms. When considering the interaction between two V_{In} - $6O_{NN}$ complexes, we find that the reduction of the moments on O_1 and O_2 atoms weakens the coupling strength of O_1 - In_{NN} - O_2 chain, O_1 - In_{NN} - O_{NN} chain, as well as O_{NN} - In_{NN} - O_2 chain, which results in the dramatic decrease of ΔE_{FM} . Therefore, the study of carrier density effect demonstrates the validity of the magnetic coupling mechanism for IO - X_{In} system proposed in section A. As discussed in section A, a strong ferromagnetism in IO - X_{In} system needs sufficient coupling between V_{In} - $6O_{NN}$ complexes which are mediated by O_{NN} - In_{NN} - O_{NN} chains.

It is known that In_2O_3 sample can be highly compensated, with the concentration of free carriers to the donor defects of about 1:5 [136]. Experimentally, In_2O_3 films are self-doped with donors (V_O) and self-compensated by magnetic acceptors (V_{In}) (V_{In} density $<$ V_O density). As we have shown above, the effect of V_O defects is purely electron doping and V_O does not create defect states inside the band gap. However, V_{In} generates empty states on top of valence band located at the NN O atoms. The n-type doping affects electronic properties, while the p-type doping leads to magnetic moments. Our results show even with electron doping, the ΔE_{FM} is still large enough (64.8 meV for 1.0 e doping case) to achieve RT ferromagnetism. Moreover, as demonstrated above, the electron doping decreases the ΔE_{FM} . Therefore, the ferromagnetism may be switch on/off by tuning the electron density, for example, by applying a gate voltage or Sn

doping. Indeed, the switch on/off by tuning the carrier density for In_2O_3 has been experimentally observed on Cr-doped In_2O_3 films [68; 137], Mn-doped In_2O_3 films [137] as well as Fe-doped In_2O_3 polycrystalline bulk samples [69] by controlling the carrier density via varying oxygen partial pressure or Sn concentration. These experimental results reveal that the carrier density and the net spin are two crucial factors for producing and tuning ferromagnetism.

6.4 Conclusions

In summary, we systematically studied the magnetism in In_2O_3 induced by native defects as well as alkali and alkaline-earth metals doping. It has been demonstrated that the experimental observed RT ferromagnetism in pristine In_2O_3 is attributed to V_{In} instead of V_{O} . The magnetic moments are mainly localized on the first shell of O atoms around the defects sites. A $X_{\text{In}}\text{-O}_{\text{NN}}\text{-In}_{\text{NN}}\text{-O}_{\text{NN}}\text{-X}_{\text{In}}$ chain is required to promote long-range FM coupling. We predict that alkali metals, Li, Na, and K-doped In_2O_3 can induce robust RT ferromagnetism. Compared to V_{In} , the alkali metal doped In_2O_3 is more favorable regarding to the low formation energy, which makes the latter more promising for spintronic applications.

Chapter seven

Summary and future work

7.1 Summary

The electronic structures and the FM stability in $\text{In}_2\text{O}_3\text{:Fe}$ (IFO) with additional Cu and V_{O} doping have been investigated using first-principles calculations within the framework of DFT. It is found that pure IFO has an AFM ground state, but the existence of V_{O} or with Cu co-doping could lead to a weak FM coupling in IFO system for some special configurations. The stability of the ferromagnetism is greatly enhanced by the coexistence of V_{O} and Cu co-doping in IFO system (IFCO- V_{O}). We demonstrate that the role of Cu ions is to act as superexchange mediators causing an indirect FM coupling between Fe cations through the hybridization of the Cu 3*d* states with the O 2*p* states. The delocalized hybridization consisted of Fe 3*d*, O 2*p*, and Cu 3*d* is found to be very efficient to mediate the FM exchange interaction. In favor of the FM state, Cu ions prefer to locate adjacent to the Fe ions in order to form Fe1-O1-Cu-O2-Fe2 coupling chain. The results of our calculations suggest the possibility of fabricating In_2O_3 based transparent spintronics by (Fe, Cu) co-doping in a reduced growth ambient. Our

calculations suggest that the ferromagnetism in IFCO system can be achieved with a large doping concentration of Fe with coexistence of V_O . The large Fe doping concentrations would result in an average smaller Fe-Cu separation distance, which increases the chance to form the Fe1-O1-Cu-O2-Fe2 coupling chains. The concentration of V_O , however, is not critical due to its long range coupling effect.

Beside the transition metal doping, the $2p$ non-magnetic element doping in In_2O_3 has also been studied. We found that, upon nitrogen doping, a total magnetic moment of $1.0 \mu_B$ per N can be introduced in the N- In_2O_3 system, which is mainly localized on the doped N atoms. FM coupling is possible to be activated between N dopants in short separation. Examination of spin density distribution and density of states spectra reveals that the spin-polarized holes introduced by N doping mediate the magnetic interaction in the N- In_2O_3 system. The FM coupling between N dopants is driven by the occurrence of coupling chains between a first N (N1)- $2p$ to a second N (N2)- $2p$ via a bridging In $5p$ and $4d$ orbitals ($\text{N1}:p\text{-In}_{\text{br}}:d/p\text{-N2}:p$).

Moreover, using In_2O_3 as a host matrix, extensive calculations based on DFT have been carried out to understand the electronic and magnetic properties of native defects, alkali and alkaline-earth metal elements substitutions as disputed in recent theoretical and experimental studies. Our calculations show that the magnetism in undoped In_2O_3 is originated from V_{In} instead of O vacancies. The FM coupling between the moments introduced by two V_{In} is found to be strong enough to achieve room temperature ferromagnetism. Moreover, FM coupling is also strongly favored for alkali doping with negative formation energy. For all X_{In} ($X = V_{\text{In}}, \text{Li}, \text{Na}$ and K) doped In_2O_3 , the induced magnetic moments are mainly localized on the first shell of O atoms around X_{In} sites. The FM coupling between the moments induced by X_{In} defects is activated by intra- and inter-correlation of

the $X_{\text{In}}-6\text{O}_{\text{NN}}$ complexes. A $X_{\text{In}}-\text{O}_{\text{NN}}-\text{In}_{\text{NN}}-\text{O}_{\text{NN}}-X_{\text{In}}$ chain is required to mediate the long range FM coupling. However, in cases of Mg or Ca doped In_2O_3 , the ground state is nonmagnetic.

7.2 Future work

Based on our current calculation results, we found that the In_2O_3 is a promising ODMS. We would continue to pursue further in future. The future work will contain both theoretical studies and potential experimental work with collaboration.

Currently, most of the experimental reports on the RTFM in In_2O_3 -based DMS are in form of thin film or nano-size materials, however their corresponding bulk materials are found to be diamagnetic or paramagnetic. These low-dimension materials exhibit many novel and significant properties due to the surface reconstruction, relaxation, adsorption and large surface to volume ratio characteristics. However, even for bulk materials, there are very few theoretical studies on the magnetic properties of TM-doped In_2O_3 . So far to our best knowledge, there is no theoretical study on nano-size effect on the magnetic properties of In_2O_3 -based DMS possibly due to the complicated crystal structures of In_2O_3 . On the other hand, it has been reported that, both O-terminated and In-terminated In_2O_3 (100) surfaces are possible in experiment by elaborately control the preparation conditions. The non-polar In_2O_3 (111) surface is the most stable surface and has a smallest surface reconstruction compared to O- and In-terminated In_2O_3 (100) surfaces. In our future work, we will perform various surface properties modeling and nano-size properties modeling to investigate the origin of the possible magnetic properties of the thin film and nano-size TM-doped

In₂O₃ systems, respectively.

Also, we will perform LDA+U study in parallel on this system since the system involves strong correlated electrons (*d* electrons of In and TMs). By carefully study, new insights are expected to be obtained on the mechanism of ferromagnetism in In₂O₃-based DMS system.

Although our theoretical calculations predict that the In₂O₃ is a promising DMS material, questions remain that whether we can experimentally prepare these materials. In order to make our theoretical work to the application level, we will collaborate with some experimentalists to carry out some experimental study to synthesize the In₂O₃ based DMSs. The synthesize method would be pulsed laser deposition (PLD), Molecular beam epitaxy (MBE), *etc*, as commonly used in this community.

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- 2) J. G. Tao, **L. X. Guan**, J. S. Pan, C. H. A. Huan, L. Wang and J. L. Kuo, "Possible room temperature ferromagnetism of Li-doped anatase TiO_2 : A first-principles study", *Phys. Lett. A*, 374 (2010) 4451.
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