Basic Introduction
1.1 Spintronics

Spintronics is a multidisciplinary field involving physics, chemistry and engineering, and is a new research area for solid-state scientists. A variety of new materials must be found to satisfy different demands. The search for ferromagnetic semiconductors and stable half-metallic ferromagnets with Curie temperature higher than room temperature remains a priority for solid state chemistry. A general understanding of structural property relationships is a necessary prerequisite for the design of new materials.

After the development of transistor in the last half of the 20th century, the microelectronics industry has made marvelous progress in the integrated circuit chips which have large number of applications these days. The communication between these microelectronic devices occurs by the binary flow of electric charges. This charge is only the basic unit in the microelectronics for processing and storage of data. The transistor is the smallest electronic components of such a chip. In 1965, Moore [1] proposed a fundamental law, according to which the power of the devices would double in every 18 months as electronic devices shrink and more logic is packed into every chip. This would provide us the key point for improving performance and profitability of the microelectronic devices. In this way, Moore’s Law will run out of momentum one day as the size of individual bits (1 and 0 represented by the existence or absence of electric charge) approaches the dimension of atoms. This will be termed as the end of the silicon road map.

During last 60 years period, the world witnessed a possibility to utilize the spin of the electrons in addition to their charge in order to enhance the multifunctionality of devices on the same chip. The movement of spin like the flow of charge can also carry information among devices. There are various
advantages of doing this; first is that, comparatively spin can be easily manipulated by externally applied magnetic fields, this property is very useful in magnetic storage technology. Another advantage of spin is that its long coherence or relaxation time which allows the magnetic materials to remember their spin state, without any refresh. In other words, we can say once spin (with orientation up or down) is created, it can store in a non-volatile way in magnetic bits on hard drive unlike charge states which are easily destroyed by scattering or collision with defects, impurities or other charges. This could allow us to integrate logic and storage processes and potentially lead to “instant-on” computers, where no boot up is required. This property of spin is able to develop devices which could be much smaller, non volatility of data storage, consume less electricity and increased speed of data processing than the electron charge based conventional electronics. The possibility of using such electron spin in addition to their charge in information technology has created much enthusiasm for a new field of electronics properly known as “Spintronics”.

If a computer is turned on, we have to wait for the operating system to start and other programs to load from the hard drive into random access memory (RAM). But with the help of spintronics, it would finally be easy as switching on the light in the future. Due to the ability of manipulating electron-spins together with controlling their charge flow, could create a host of new capabilities for computer technology which eradicates the lengthy boot-up times. The key elements of spintronics are injection, manipulation, transfer and detection (i.e. how the spin is created or destroyed and moves in metal and semiconductor) of spin-polarized carriers across a semiconductor device.

A breakthrough came into picture in 1988 when Baibich et al. [2] and Binash et al. [3] independently, discovered giant magnetoresistance (GMR) effect. This discovery led to an explosion of research in the field of GMR comparable to that experienced in the field of high-temperature superconductivity. It can be considered one of the first real applications of the promising field of
nanotechnology. Although the term "giant" in GMR seems incongruous for a nanotechnology device, it refers to large change in resistance (typically 10-20 %) when the devices are subjected to a magnetic field. The GMR structures consist of alternating ferromagnetic (i.e. permanently magnetized) and nonmagnetic metal layers. Depending on the relative orientation of the magnetizations in the magnetic layers, the electrical resistance through the layers changes from small value to (parallel magnetizations) large (antiparallel magnetizations). They are used in magnetic sensors and in nearly all hard-disk read heads, and can permit the storage of tens of gigabytes of data on notebook computer hard drives. The works to develop non-volatile memory elements from these materials, possibly a route to instant-on computers are in progress by many research groups. To exploit the full potential of spintronics, the development of new magnetic materials, magnetic semiconductor and half metallic (HM) ferromagnets are necessary. Out of these, the HM ferromagnets attract the interest of research community as these are the ideal candidates for spintronics or magneto-electronics due to their exceptional electronic structure [4].

The spintronics materials can be classified as:

- Heusler alloys
- Perovskite compounds
- Transition metal oxides
- DMS compounds
- Organic compounds
- Binary compounds with Zinc blende (ZB) and Wurzite (WZ) structure.

### 1.2 Half metallic Ferromagnetism (HMF)

The concept of half metallic ferromagnets was introduced by de Groot et al. [5], on the basis of band structure calculations in NiMnSb and PtMnSb semi-Heusler alloys. Due to the ferromagnetic decoupling, these materials have an unequal density of states (DOS) of spin-up and spin-down states at the Fermi level.
(E\(_F\)) and behave like metals for one electron spin direction and like semiconductors for other spin direction. The spin polarization at E\(_F\) for half metallic ferromagnets, as shown in Fig. 1.1, is 100 % and might be able to yield a 100 % spin injection and thus maximize the efficiency of spintronic devices [6].

![Diagram showing DOS for metals, paramagnetics, ferromagnetics, and semiconductors.](image)

**Fig. 1.1** Schematic representation of DOS for a half metal compared to a normal metal (Paramagnetic and ferromagnetic) and a semiconductor.

It is useful, for both technological and scientific reason, to define the electron spin polarization at E\(_F\) of a material, although it is quite cumbersome to measure [7]. The empirically relation of degree of polarization at E\(_F\) is given by:

\[
P = \frac{N_\uparrow(E_F) - N_\downarrow(E_F)}{N_\uparrow(E_F) + N_\downarrow(E_F)}
\]  

where \(N_\uparrow(E_F)\) and \(N_\downarrow(E_F)\) are the spin dependent density of states of majority (\(\uparrow\)) and minority (\(\downarrow\)) spins at the E\(_F\), respectively. For paramagnetic or
antiferromagnetic material, P vanishes completely. However, it has a finite value in ferromagnetic or ferrimagnetic material below the Curie temperature. The spin-polarization is 100% or electrons are fully spin polarized at $E_F$ if $N_\uparrow(E_F)$ or $N_\downarrow(E_F)$ equals to zero.

In 2002, Coey et al. [8] proposed the broad classification scheme for half metals. There are four types of half metals and according to proposed scheme; the types of HM ferromagnets depend upon the localized and itinerant nature of the conduction electrons. It has been found that the localized states are well described by atomic theory, including the Hund’s rule, with corrections due to the influence of the crystal fields. The itinerant magnetism is caused by the exchange interaction between valence electrons. This interaction originates from the Pauli Exclusion principle and favors spin polarization.

The first class of half metals is type I, where only one type of spin polarized electrons (either $\uparrow$ or $\downarrow$) contributes to the conductivity and a gap is encountered at $E_F$ in the DOS for other spin direction. If the half metallic gap appears in the minority DOS, we have a type IA half metal and only the majority electrons, which are itinerant, contribute to the conductivity. In type IB, the majority DOS vanishes at $E_F$ and minority electrons are itinerant. In type I half metals, the electrons at $E_F$ are itinerant but in type II, these are localized at $E_F$. In type III half metals, no gap appears at $E_F$ and one has at $E_F$ itinerant electrons for one spin direction and localized electrons for the other. In type IV half metals, the conductivity is semi-metallic rather than metallic like in type III. Type IIIA (IVA) and type IIIB (IVB) distinguish half metals with the localized (or itinerant) states in opposite spin channels. In type III or IV half metals, a gap may appear in one of the spin channels that are located below or above $E_F$. In types I and II half metals, the spin polarization P is always 100%, whereas lower values appear in types III and IV. A brief summary of description of half metals is given in Table 1.1. It is important here to note that the half-metallic conductivity is quite different from
semi-metallic conductivity. In semimetals (e.g. graphite or bismuth), there is small overlap between valence and conduction bands. Due to this, they have small and equal numbers of electrons and holes. There is a noticeable anisotropy in the conductivity of semimetals.

**Table 1.1: Classification of half metals**

<table>
<thead>
<tr>
<th>Type</th>
<th>DOS</th>
<th>Conductivity</th>
<th>$\uparrow$ electrons at $E_F$</th>
<th>$\downarrow$ electrons at $E_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I A</td>
<td>Half metallic</td>
<td>Metallic</td>
<td>Itinerant</td>
<td>Not present</td>
</tr>
<tr>
<td>I B</td>
<td>Half metallic</td>
<td>Metallic</td>
<td>Not present</td>
<td>Itinerant</td>
</tr>
<tr>
<td>II A</td>
<td>Half metallic</td>
<td>Nonmetallic</td>
<td>Localized</td>
<td>Not present</td>
</tr>
<tr>
<td>II B</td>
<td>Half metallic</td>
<td>Nonmetallic</td>
<td>Not present</td>
<td>Localized</td>
</tr>
<tr>
<td>III A</td>
<td>Metallic</td>
<td>Metallic</td>
<td>Itinerant</td>
<td>Localized</td>
</tr>
<tr>
<td>III B</td>
<td>Metallic</td>
<td>Metallic</td>
<td>Localized</td>
<td>Itinerant</td>
</tr>
<tr>
<td>IV A</td>
<td>Semimetallic</td>
<td>Metallic</td>
<td>Itinerant</td>
<td>Localized</td>
</tr>
<tr>
<td>IV B</td>
<td>Semimetallic</td>
<td>Metallic</td>
<td>Localized</td>
<td>Itinerant</td>
</tr>
</tbody>
</table>

In this thesis, we have decided to remain focused on the magnetism in the various Dilute Magnetic Semiconductor compounds.

### 1.3 Magnetic semiconductors

There is a long history of research on this category of materials. The general interest in these ferromagnetic semiconductors and semimetals are due to their larger spin-flip length which is favorable for laterally patterned spin devices. The first generation materials are Europium (Eu) chalcogenides [9] and multinary chalcogenides of Chromium [10], which were studied intensively in the late 60’s and early 70’s. These multinary chalcogenides with spinel structures, such as CdCr$_2$Se$_4$, are the most extensively studied species of magnetic semiconductor.
Chemical vapor transport using halogen or halides as transporting agents was the most widely used technique for bulk crystal growth of chalcogenide spinels. On the other hand, Europium mono-chalcogenides EuX (X = O, S, Se, Te) crystallize in a NaCl-type fcc structure. EuO and EuS compounds show ferromagnetism with Curie temperature of 68K and 16.2K, respectively. EuSe is metamagnetic whereas EuTe exists in antiferromagnetic state \[11\]. Due to melting point higher than 2000°C, growth of Europium chalcogenides from the melt is quite difficult. e.g. EuS single crystals was grown by a normal freezing technique using a high-pressure furnace, in which the temperature was raised above 2500 °C. Good-quality single crystals of several millimeters in size were cleaved out from the ingot. Moreover, CrBr$_3$, transition metal, rare earth oxides, fluorides, phosphides and few other ferromagnetic semiconductors such as BiMnO$_3$, MSeO$_3$ and MTeO$_3$ (M = Mg, Mn, Co, Ni, Cu, and Zn) \[12-14\] also belongs to the same generation of magnetic semiconductors. Interesting physical properties of these magnetic semiconductors, such as magnetic red shift of the absorption edge and huge negative magneto-resistance (MR) were discovered at that time. However, researcher lost interest in these materials due to their low Curie temperatures which were far below the room temperature and the growth of good quality single crystals was very difficult.

After that, a lot of theoretical and experimental efforts have been focused on the new class of semiconductors which has some unique properties that enhance their potential for use in wide verities of optoelectronic device applications. The researchers tried to understand the underlying physics of the unusual phenomenon associated with these special semiconductors. In 1977, Komarov et al. \[15\] first reported the giant enhancement of magnetic-optical effects in CdMnTe. That was the birth of second generation of magnetic semiconductors, called Dilute Magnetic Semiconductors (DMS). These materials are particularly important due to their capability to accommodate a high
percentage of Mn atoms (as high as 77%) and its appropriate energy gap for optical application.

The active research on DMS has been started after the development of III-V based diluted semiconductors, in which magnetic properties have been found to be strongly dependent on the carrier concentration in the material [16-19]. That was the third generation of magnetic semiconductors. This series of materials can only be produced by using an MBE technique with very low substrate temperatures and are widely used in electronic devices.

1.3.1 Dilute Magnetic Semiconductors

The DMS compounds are the conventional semiconductors in which appropriate fraction of atoms is substituted by the elements which are capable to add localized magnetic moment. Due to this substitution, these materials not only retain the semiconducting properties but can also possess well-defined magnetic properties (e.g., paramagnetic, anti-ferromagnetic or ferromagnetic) that the conventional semiconductors do not have. In general, these can be expressed by numbers of different ways such as $A_{1-x}M_xB$ or $AB (M)$ or $(AB)_{1-x}(MB)_x$. Here $x$ indicates the fraction of the non-magnetic cations ($A$) of the semiconductor $AB$, which is randomly replaced by magnetic 3d and 4f ions ($M$). The formation of the DMS can also be described as alloying an ordinary semiconductor $AB$ with a magnetic semiconductor $MB$ in the required proportion. Alternatively, we can also define DMS as the mixed crystals of ordinary and magnetic semiconductors. A consequence of resultant ternary nature is that the lattice constants, energy gap and other band parameters of the DMS can be tuned between the values applicable to the primary binaries $AB$ and $MB$ by varying the value of $x$. The choice of suitable host (semiconductor) material is very important to make DMS compound because the properties and composition of host material influences the properties of resultant DMS compound.
1.3.1.1 Promising DMS candidates

The foremost characteristics in novel DMS materials are; it’s magnetic behavior, high Curie temperature and a well established growth technology. The various DMS candidates at different doping concentration is listed in Table 1.2

Table 1.2: Classification of DMS compounds

<table>
<thead>
<tr>
<th>Material</th>
<th>Doping Concentration (x)</th>
<th>Synthesis method</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$_{1-x}$Mn$_x$ [20]</td>
<td>0.05</td>
<td>Deposition and annealing</td>
<td>&gt; 400</td>
</tr>
<tr>
<td>Ge$_{1-x}$Cr$_x$ [21]</td>
<td>0.01</td>
<td>Vertical gradient solidification</td>
<td>126</td>
</tr>
<tr>
<td>Ge$_{1-x}$Fe$_x$ [22]</td>
<td>0.175</td>
<td>MBE</td>
<td>170</td>
</tr>
<tr>
<td>[23]</td>
<td>0.05</td>
<td>Vertical gradient solidification</td>
<td>233</td>
</tr>
<tr>
<td>Ge$_{1-x}$Mn$_x$ [24]</td>
<td>0.06</td>
<td>MBE</td>
<td>&gt; 400</td>
</tr>
<tr>
<td>[25]</td>
<td>0.57</td>
<td>Sputtering</td>
<td>213</td>
</tr>
<tr>
<td>[26]</td>
<td>0.15</td>
<td>MBE</td>
<td>100</td>
</tr>
<tr>
<td>III-V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_{1-x}$Cr$_x$N [27]</td>
<td>0.07</td>
<td>MBE</td>
<td>&gt; 900</td>
</tr>
<tr>
<td>Al$_{1-x}$Mn$_x$N[28]</td>
<td>0.028</td>
<td>MBE</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Ga$_{1-x}$Cr$_x$N[27]</td>
<td>0.02</td>
<td>MBE</td>
<td>&gt; 900</td>
</tr>
<tr>
<td>Ga$_{1-x}$Fe$_x$N[29]</td>
<td>0.068</td>
<td>MBE</td>
<td>~ 100</td>
</tr>
<tr>
<td>[30]</td>
<td>0.03</td>
<td>Ion implantation</td>
<td>~ 250</td>
</tr>
<tr>
<td>Ga$_{1-x}$Mn$_x$N[31]</td>
<td>0.045</td>
<td>MBE</td>
<td>~940</td>
</tr>
<tr>
<td>Ga$_{1-x}$Mn$_x$P [32]</td>
<td>0.03</td>
<td>Ion implantation</td>
<td>270</td>
</tr>
<tr>
<td>Ga$_{1-x}$Cr$_x$As [33]</td>
<td>0.11</td>
<td>MBE</td>
<td>~40</td>
</tr>
<tr>
<td>Ga$_{1-x}$Mn$_x$As [34]</td>
<td>0.09</td>
<td>MBE</td>
<td>173</td>
</tr>
<tr>
<td>Material</td>
<td>Composition</td>
<td>Method</td>
<td>Temperature</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>(Ga$_{1-x}$Mn$_x$Sb [35])</td>
<td>0.023</td>
<td>MBE</td>
<td>25</td>
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<tr>
<td>In$_{1-x}$Mn$_x$P [36]</td>
<td>0.035</td>
<td>Diffusion</td>
<td>~300</td>
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<tr>
<td>In$_{1-x}$Mn$_x$As [37]</td>
<td>0.127</td>
<td>MBE</td>
<td>90</td>
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<tr>
<td>In$_{1-x}$Mn$_x$Sb [38]</td>
<td>0.1</td>
<td>MBE</td>
<td>20</td>
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**II-VI**

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Method</th>
<th>Temperature</th>
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</thead>
<tbody>
<tr>
<td>Zn$_{1-x}$Co$_x$O [39]</td>
<td>0.15</td>
<td>PLD</td>
<td>~300</td>
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<tr>
<td>Zn$_{1-x}$Cr$_x$O [40]</td>
<td>0.095</td>
<td>Sputtering</td>
<td>&gt;365</td>
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<tr>
<td>Zn$_{1-x}$Cu$_x$O [41]</td>
<td>0.02-0.10</td>
<td>PLD</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Zn$_{1-x}$Fe$_x$O [42]</td>
<td>0.12</td>
<td>Ion implantation</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Zn$_{1-x}$Mn$_x$O [43]</td>
<td>0.3</td>
<td>PLD</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>Ion implantation</td>
<td>~250</td>
</tr>
<tr>
<td>Zn$_{1-x}$V$_x$O [45]</td>
<td>0.05-0.15</td>
<td>PLD</td>
<td>&gt;350</td>
</tr>
<tr>
<td>Zn$_{1-x}$Cr$_x$Te [46]</td>
<td>0.2</td>
<td>MBE</td>
<td>300</td>
</tr>
<tr>
<td>Zn$_{1-x}$Mn$_x$Te [47]</td>
<td>0.015</td>
<td>MBE</td>
<td>1.45</td>
</tr>
<tr>
<td>Cd$_{1-x}$Mn$_x$Te [48]</td>
<td>0.024</td>
<td>MBE</td>
<td>~2</td>
</tr>
</tbody>
</table>

**IV-VI**

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Method</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$_{1-x}$Cr$_x$Te [49]</td>
<td>0.08</td>
<td>MBE</td>
<td>140</td>
</tr>
<tr>
<td>Ge$_{1-x}$Fe$_x$Te [50]</td>
<td>0.18</td>
<td>Sputtering</td>
<td>100</td>
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<tr>
<td>Ge$_{1-x}$Mn$_x$Te [51]</td>
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<td>ICB</td>
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**II-VI-V$_2$**

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</tr>
</thead>
<tbody>
<tr>
<td>Zn$_{1-x}$Mn$_x$GeP$_2$ [52]</td>
<td>0.2</td>
<td>Solid state reaction</td>
<td>350</td>
</tr>
<tr>
<td>Cd$_{1-x}$Mn$_x$GeP$_2$ [53]</td>
<td>0.2</td>
<td>Solid state reaction</td>
<td>320</td>
</tr>
<tr>
<td>Zn$_{1-x}$Mn$_x$SnAs$_2$ [54]</td>
<td>0.13</td>
<td>Vertical Bridgman</td>
<td>329</td>
</tr>
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**Oxides**

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Method</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-TiO$_2$:Co [55]</td>
<td>0.08</td>
<td>PLD</td>
<td>&gt; 400</td>
</tr>
</tbody>
</table>
### Basic Introduction

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition</th>
<th>Process</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-TiO₂:Cr [56]</td>
<td>0.01</td>
<td>PLD</td>
<td>&gt;300</td>
</tr>
<tr>
<td>A-TiO₂:Fe [57]</td>
<td>0.081</td>
<td>PLD</td>
<td>&gt;400</td>
</tr>
<tr>
<td>A-TiO₂:Mn [58]</td>
<td>0.02</td>
<td>PLD</td>
<td>&gt;400</td>
</tr>
<tr>
<td>A-TiO₂:V [59]</td>
<td>0.05</td>
<td>PLD</td>
<td>&gt;300</td>
</tr>
<tr>
<td>R-TiO₂:Co [60]</td>
<td>0.05</td>
<td>PLD</td>
<td>&gt;400</td>
</tr>
<tr>
<td>R-TiO₂:Fe [61]</td>
<td>0.02-0.08</td>
<td>PLD</td>
<td>&gt;300</td>
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<tr>
<td>R-TiO₂:Mn [62]</td>
<td>0.02-0.12</td>
<td>PLD</td>
<td>&gt;300</td>
</tr>
<tr>
<td>SnO₂:Co [63, 64]</td>
<td>0.01</td>
<td>Wet chemical method</td>
<td>440</td>
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<td>SnO₂:Fe [65]</td>
<td>0.05</td>
<td>PLD</td>
<td>610</td>
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<tr>
<td>SnO₂:Mn [66]</td>
<td>0.01</td>
<td>Wet chemical method</td>
<td>850</td>
</tr>
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<td>SnO₂:Mn [64]</td>
<td>0.05</td>
<td>Sintering</td>
<td>360</td>
</tr>
<tr>
<td>In₂O₃:Ni [67]</td>
<td>0.05-0.08</td>
<td>PLD</td>
<td>&gt;400</td>
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<tr>
<td>In₂O₃:Ni [68]</td>
<td>0.02</td>
<td>Reactive evaporation</td>
<td>850-930</td>
</tr>
<tr>
<td>InSnO₃:Co [69]</td>
<td>0.3</td>
<td>Sputtering</td>
<td>&gt;300</td>
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<td>InSnO₃:Mn [70]</td>
<td>0.05</td>
<td>Reactive evaporation</td>
<td>&gt;300</td>
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<td>Zincblende Metal</td>
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<td></td>
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<tr>
<td>CrAs [71]</td>
<td></td>
<td>MBE</td>
<td>&gt;400</td>
</tr>
<tr>
<td>CrSb [72]</td>
<td></td>
<td>MBE</td>
<td>&gt;400</td>
</tr>
</tbody>
</table>

We have decided to confine ourselves to the following compounds for the present work.

**A) Host Semiconductors suitable for DMS: Improving band gap**

The rutile type dioxide materials and chalcopyrite compounds are the appropriate host semiconductors for DMS materials. Due to large discrepancy between the experimental and theoretical band gap, these compounds attract much attention to the research community in order to analyze the exact electronic band
structure. But many theoretical predictions could not predict the correct ground state. We tried to fill this gap by using more efficient and exact mBJLDA XC potential in our calculations. This work is concerned with the study of electronic properties of rutile RO$_2$ (R = Si, Ge, Sn and Pb) compounds and ABAs$_2$ (A = Zn, Cd; B = Ge, Sn) compounds existing in the chalcopyrite structure.

B) **Cr-doped GaP:**

The GaP compound as host semiconductor is of great interest due to the low solubility limit of transition metals. These are the exciting DMS materials for spintronic applications due to their predicted 100% spin polarization along with high Curie temperature. In this work, we have studied the electronic and magnetic properties, with an emphasis on HMF, of Ga$_{1-x}$Cr$_x$P ($x = 0.25$, $0.125$, $0.06$ and $0.03$).

C) **Cr-doped Cd-chalcogenides:**

These Cd-based chalcogenides semiconductors show interesting magnetic properties after appropriate doping with 3d transition metal. Therefore, these materials are of considerable interest on account of their electronic and magnetic properties. Due to the considerable half metallicity, these compounds are promising candidates for the applications of spintronic devices. In this work, we have studied the ground state properties of Cd$_{1-x}$Cr$_x$Z ($Z = S$, Se and Te) compound for doping concentrations, $x = 0.25$ and $0.125$.

D) **Fe-doped CeO$_2$ DMO compound:** In this work, we have performed the full potential calculations of Ce$_{1-x}$Fe$_x$O$_2$ ($x = 0.125$ and $0.06$) rare-earth oxides with the aim to study the effect of reducing dopant (Fe) concentration on their electronic and magnetic properties. Due to the well known catalytic properties, the CeO$_2$ easily forms stable Oxygen vacancy. Thus, the presence of oxygen vacancy should not be ignored in the theoretical description. Hence, in order to present realistic predictions, the role of oxygen vacancy has also been analyzed for deciding the magnetic properties and half metallicity.
1.4 Density Functional Theory (DFT)

The study of Condensed Matter Physics and Material Science is fundamentally concerned with understanding and exploiting the properties of system of interacting electrons and atomic nuclei. Quantum mechanics provides suitable computational techniques for solving this particular problem. But, unfortunately, a real material consists of strongly interacting many-body system. This makes the solution of Schrödinger equation a completely impractical task. DFT is a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure (principally the ground state) of many body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functional i.e. function of another functions, which in this case is the spatially dependent electron density. Hence, the name DFT comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed matter physics, computational physics, and computational chemistry. The success of DFT not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes.

The main idea of DFT is to describe an interacting system of fermions via its density, $\rho(r)$ and not via its many-body wave function. For N-electrons in a solid, which obey the Pauli Exclusion Principle and repulse each other via Coulomb potential, this means that the basic variable of the system depends only on three spatial coordinates x, y and z rather than $3N$ degrees of freedom. While DFT in principle, gives a good description of ground state properties, practical applications of DFT are based on approximations for the so called exchange-correlation (XC) potential. The XC potential describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons. Possessing the exact XC potential means that we solved the many-body problem exactly, this is clearly not feasible in solids.
The electron density, \( \rho(r) \), at each point \( r \) which determines the ground-state properties of atomic or molecular systems was initially formulated by Thomas [73], Fermi [74] and Dirac [75] in the late 1920’s and 1930’s on the basis of free electron gas model. An important step toward the use of DFT in the study of molecules and the solid state was taken by Slater in the 1950s [76], where he used simple, one-parameter approximate exchange correlation functional, written in the form of an exchange-only functional. DFT became a full-fledged theory only after the formulation of the Hohenberg and Kohn (HK) theorems [77] in 1964 which have provided a formal justification for the use of density as a central quantity. Since then, a significant work has been done to carry out various modifications to DFT systems like atoms, molecules, metals, semiconductors, surfaces, and impurity problems etc. with remarkable success. In many cases, the results of DFT calculations for solid-state systems agree quite satisfactorily with experimental data. The computational costs are relatively low when compared to traditional methods such as Hartree-Fock [78], configuration interaction [79], coupled cluster theory [80] etc.

1.4.1 The Hohenberg-Kohn theorems

The first Hohenberg-Kohn (H–K) theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates. It lays the groundwork for reducing the many-body problem of \( N \) electrons with \( 3N \) spatial coordinates to \( 3 \) spatial coordinates, through the use of functionals of the electron density. This theorem can be extended to the time-dependent domain to develop time-dependent density functional theory (TDDFT), which can be used to describe excited states. The second H–K theorem defines energy functional for the system and proves that the correct ground state electron density minimizes this energy functional. The traditional formulation of these two theorems [77] is as follows:
**Theorem I:** For any system of interacting particles in an external potential \( V_{\text{ext}}(\vec{r}) \), the potential \( V_{\text{ext}}(\vec{r}) \) is determined uniquely, except for a constant, by the ground state particle density \( \rho_0(\vec{r}) \).

This theorem demonstrates the existence of a one-to-one mapping between the ground state electron density and ground state wave function of a many-particle system.

**Theorem II:** A universal functional for the energy \( E[\rho(\vec{r})] \), in terms of the density \( \rho(\vec{r}) \), can be defined, valid for any external potential \( V_{\text{ext}}(\vec{r}) \). For any particular \( V_{\text{ext}}(\vec{r}) \), the exact ground state energy of the system is the global minimum value of this functional and the density \( \rho(\vec{r}) \) that minimizes the functional is the exact ground state density \( \rho_0(\vec{r}) \).

\[
E = E[\rho_0(\vec{r})] = \min E[\rho(\vec{r})] \tag{1.2}
\]

i.e.

\[
\left. \frac{\delta E[\rho(\vec{r})]}{\delta \rho(\vec{r})} \right|_{\rho(\vec{r})=\rho_0(\vec{r})} = 0 \tag{1.3}
\]

It means that the true ground state density minimizes the total electronic energy of the system.

**1.4.2 The Kohn-Sham Approach**

The most obvious problem in utilizing the Hohenberg-Kohn formulation is that there is no known way to find any simple form for the functional \( E[\rho(\vec{r})] \). Thomas (1926) and Fermi (1928) independently used the kinetic energy of the free electrons [73,74] which is an important part of the energy functional \( E[\rho(\vec{r})] \). This is not correct because we cannot neglect the spatial variation of the electronic charge density. Kohn-Sham (KS) simply revised the kinetic energy functional and turns DFT into a practical tool. They provided a
practical procedure to obtain the ground state density. They introduced a way to
treat exactly the kinetic energy of non-interacting particles which is the dominant
part of the total kinetic energy. In KS approach, the much complicated electronic
wave function is replaced with quite simpler electronic density. The
implementation of DFT through KS approach reduced the intractable many-body
problem of the interacting electrons in a static potential to a tractable problem of
non-interacting electrons moving in an effective potential.

As mentioned earlier, an important step towards applicability of DFT has
been made by Kohn and Sham [81]. They proposed to write \( E[\rho(\vec{r})] \) as follows:

\[
E[\rho(\vec{r})] = T_{NI} [\rho(\vec{r})] + E_{HF} [\rho(\vec{r})] + E_{XC} [\rho(\vec{r})]
\]

The first term on R.H.S. is Kinetic energy of the non-interacting electrons
and the second term is the Hartree contribution, which describe the interaction
with the field obtained by averaging over the positions of the remaining electrons.
Although no on-site electron-electron interaction in taken into account,
\( E_{HF} [\rho(\vec{r})] \) is already a good approximation for the electron interaction. Assuming
we know the exchange-correlation functional, we can now write the total energy
as:

\[
E[\rho(\vec{r})] = T_{NI} [\rho(\vec{r})] + E_{HF} [\rho(\vec{r})] + E_{XC} [\rho(\vec{r})] + E_{ex} [\rho(\vec{r})]
\]

This equation can be interpreted as the energy functional of non-interacting
particles submitted to two external potentials \( V_{ex} [\rho(\vec{r})] \) and \( V_{xc} [\rho(\vec{r})] \), with
corresponding KS Hamiltonian

\[
H_{KS} = \frac{-\hbar^2}{2m} \nabla^2 + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc} [\rho(\vec{r})] + V_{ex} [\rho(\vec{r})]
\]

The exchange-correlation potential is given by the fundamental derivative of
\( E_{xc} [\rho(\vec{r})] \):

\[
V_{xc} = \frac{dE_{xc} [\rho(\vec{r})]}{d\rho(\vec{r})}
\]
The KS theorem can now be stated as follows:

The exact ground state density of an N particle system is

\[
\rho_0(r) = \sum_{i=1}^{N} \rho_i(r) = \sum_{i=1}^{N} \psi_i^*(r)\psi_i(r)
\]  

(1.8)

where the single particle wave functions \( \psi_i(r) \) are the N lowest-energy solutions of the KS equations.
\[
\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r})\right] \psi^{KS}_i(\vec{r}) = \varepsilon_i \psi^{KS}_i(\vec{r})
\] (1.9)

where

\[
V_{\text{eff}}(\vec{r}) = V_{\text{ext}}(\vec{r}) + U_{\text{coul}}(\vec{r}) + V_{\text{XC}}(\vec{r})
\] (1.10)

For LDA, the functional \( E_{\text{XC}}[\rho] \) is given by

\[
E^{\text{LDA}}_{\text{XC}}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{\text{XC}}[\rho(\vec{r})] d^3r
\] (1.12)

where \( \varepsilon_{\text{XC}}[\rho] \) is the XC energy per particle of a homogeneous electron with interacting electrons. Equation (1.12) may be interpreted as dividing the inhomogeneous electron system in infinitesimally small volumes with a constant density. The underlying idea is very simple. At each point in space, the XC
energy is approximated locally by the XC energy of a homogeneous electron gas with the same electron density as present at that point. LDA is based on the local nature of XC and the assumption that the density distribution does not vary too rapidly. In spite of its simplicity, LDA performs quite well even for more realistic systems.

1.4.4 Spin density functional theory

A formulation of the energy functional depending only on the total electron density should allow an exact description of real materials; however the treatment of magnetic systems is much simpler if the energy functional is explicitly considered as dependent on the two spin populations, separately. For magnetic systems, this total density can be calculated and, as stated by the first HK theorem, there exists a functional of $\rho(\vec{r})$ that gives the magnetic moments of the system. This is known as spin density functional theory (SDFT) [82], the total density $\rho(\vec{r})$ can be written as a function of the two so-called spin densities: $\rho(\vec{r}) = \rho^\uparrow(\vec{r}) - \rho^\downarrow(\vec{r})$. In other words, every observable property is a functional of the spin densities.

The equivalent of the LDA in spin-polarized system is the Local Spin Density Approximation (LSDA), which basically consists of replacing the XC energy density with a spin-polarized expression:

$$E_{xc}^{\text{LDA}} \left[ \rho^\uparrow(\vec{r}), \rho^\downarrow(\vec{r}) \right] = \int \left( \rho^\uparrow(\vec{r}) + \rho^\downarrow(\vec{r}) \right) E_{xc} \left[ \rho^\uparrow(\vec{r}), \rho^\downarrow(\vec{r}) \right] d^3r \quad (1.13)$$

One major problem with LDA/LSDA is that it underestimates consistently lattice parameter as a consequence of overestimating binding energies. LSDA also fails to explain physical properties of Fe and transition metal oxides.

1.4.5 Beyond the LDA/LSDA

Although exact DFT should be capable of obtaining ground state properties correctly, but the LSDA is not successful for all the systems. LSDA fails in
Chapter 1

describing the electronic structure and the conduction properties of strongly correlated materials which usually contain transition metal oxides or rare-earth metal compounds. Such transition metal oxides and rare-earth metal compounds normally have well-localized $f$ electrons and a sizable energy gap between occupied and unoccupied sub-bands. When such a system is treated with LSDA, which has an orbital-independent potential, a partially filled $f$ band with a metallic-type electronic structure and itinerant $f$ electrons is found. This behavior arises because in LSDA, the spin and orbital polarization are driven by the exchange interactions of the homogeneous electron gas instead of the screened on-site Coulomb interactions. As a consequence, LSDA fails in describing orbital polarization correctly. Several attempts have been made to improve on LSDA in order to take into account strong correlations and localizations of $f$ electrons. For example: the self-interaction correction-local spin density (SIC-LSD) formalism, which is important for rare earth systems. In the, SIC-LSD approximation, the localized electrons see a different potential (SIC potential) from that of the delocalized ones for which the self-interaction vanishes and whose potential therefore, reduces to that of the LSDA.

1.4.6 Self-Interaction Correction (SIC) to the LDA

To facilitate an accurate description of the localized $d$ and $f$ electrons in the solids, the self interaction correction is introduced. Within the LSDA, the spurious self-interaction tends to underestimate their localization. In SIC-LDA formalism, the localized electrons see a potential (SIC potential) different from that of the delocalized ones for which the self-interaction vanishes and whose potential therefore reduces to that of the LSDA. It is known that self-interaction is important only for localized states in the solid. The correction for extended states is proportional to $1/V$, where $V$ is the volume of the system. For extended states in an infinite system, the correction will vanish identically.
In the SIC-LSD approximation [83], the non-physical electron self-interaction, including both SIC Coulomb energy and corresponding SIC-XC energy, are subtracted from the LSDA Hamiltonian, and the energy functional is written as

\[
E_{\text{SIC}} = E_{\text{LSDA}} - \sum_{i}^{\text{occu}} (U[\rho_{i}] + E_{\text{XC}}[\rho_{i}])
\]  
(1.14)

\[
E_{\text{SIC}} = E_{\text{LSDA}} - \sum_{i}^{\text{occu}} \left( \int \rho_{i}(\vec{r}) \rho_{i}(\vec{r}') \frac{d^{3}\vec{r} \cdot d^{3}\vec{r}'}{|\vec{r} - \vec{r}'|} + \int \rho_{i}(\vec{r}) \rho_{\uparrow}(\vec{r}) e_{\text{XC}}[\rho_{\uparrow},\rho_{\downarrow}] d^{3}\vec{r}' \right)
\]  
(1.15)

where \(E_{\text{LSDA}}\) is the energy functional in LSDA approximation, \(\rho_{i}(\vec{r})\) is the charge density to the \(i^{th}\) solution of the SIC-LSD equation and \(e_{\text{XC}}(\rho_{\uparrow},\rho_{\downarrow})\) is the XC energy density of a homogeneous system with the spin densities \((\rho_{\uparrow} \text{ and } \rho_{\downarrow})\). The SIC approach generates an orbital-dependent potential which can be significant for localized states, yielding a much-improved description of the static Coulomb correlation effect compared to that provided by LSDA.

Another advantage of the SIC-LSD method is that the minimization of total energy, with respect to the number of localized electrons, leads to a determination of the nominal valence defined as the integer number of electrons available for band formation.

\[
N_{v} = Z - N_{\text{core}} - N_{\text{SIC}}
\]  
(1.16)

where \(Z\) is the atomic number, \(N_{\text{core}}\) and \(N_{\text{SIC}}\) is the number of core and localized states, respectively. This information is important to the analysis of the various properties of solid materials.

**1.4.7 Coulomb Corrected Local spin Density (LDA+U/LSDA+U) Approximation**

In the context of strongly correlated systems, for example those exhibiting narrow \(d\) or \(f\) bands, LDA has a limitation to describe strong onsite correlations of
the Hubbard type. These features have been introduced as a posteriori within the so-called LDA + U approach [84-86], one of the most popular methods.

This method considers the mean-field solution of the Hubbard model on top of the LDA solution, where the Hubbard on-site interaction U is computed for the d or f orbital by differentiating the LDA eigenvalues with respect to the occupation numbers. The main idea proposed by the LDA+U method is to correct the LDA approximation in order to make it able to approximately describe strong electronic correlations. The first expression of the LDA+U approach was formulated by Anisimov et al. [84]. An important contribution was given by Pickett et al. [87] who, while slightly refining the functionals, introduced a linear response technique for calculating the Hubbard parameter. Despite some different detail occurring among these approaches, the main physical idea behind these can be captured in a very elementary formulation of the total energy functional:

\[ E = E_{\text{LDA}} + \sum \left[ \frac{U}{2} \sum n_{m\sigma}^I n_{m'\sigma'}^I - \frac{U}{2} n^I \left(n^I - 1\right) \right] \] (1.17)

where \( n^I = \sum n_{m\sigma}^I \), are generalized atomic orbital occupations and U is the Hubbard parameter describing on-site correlation and second and third term on right hand side are, respectively, the correct on-site correlation functional (\( E_{\text{Hub}} \)) and the mean field approximation (\( E_{\text{dc}} \)) to it. If we derive this equation with respect to orbital occupation to obtain the corresponding orbital energy, we have:

\[ \varepsilon_{m\sigma}^I = \frac{\partial E}{\partial n_{m\sigma}^I} = \varepsilon_{m\sigma}^{0I} + U\left(\frac{1}{2} - n_{m\sigma}^I\right) \] (1.18)

(\( \varepsilon^{0I} \) is the corresponding LDA quantity) from which it is evident that a gap of width \( \approx U \) opens between occupied (\( n^I \approx 0 \)) and unoccupied (\( n^I \approx 0 \)) orbitals. If we define the atomic orbital occupation as the projection of the occupied valence manifold over the corresponding atomic state (\( n_{m\sigma}^I = \sum_{k,v} \langle \psi_{k,v}^\sigma | p_{k,v}^I | \psi_{k,v}^\sigma \rangle \)), we can easily extract the potential entering the KS equations which reads:
From this expression, we can see that if the occupation of a particular atomic orbital is initially larger than $\frac{1}{2}$ then the Hubbard contribution to the potential is attractive and encourages the electrons to localize on that particular atomic state, whereas the opposite happens when the initial occupation is smaller than $\frac{1}{2}$.

In practical calculations, the final result does not actually depend very strongly on the initial conditions as occupations greatly evolve during the self consistent iterations with possible changes in the sign of the Hubbard potential. In the final self consistent configuration, completely empty or completely filled atomic orbitals are not necessarily obtained because the LDA contribution to the energy functional contains the competing factor (the tendency to minimize kinetic energy through delocalization) which sometimes could turn out to be stronger than the effect due to the Hubbard $U$ term. Fractional occupation numbers (for atomic orbitals around the Fermi level) is indeed the situation, we would expect when applying this functional to a normal metal. Furthermore, even for localized electrons, we could observe fractional $n_{m\sigma}$ because localization may occur on hybridized orbital built by $d$ levels with states of other atoms (this situation is actually not taken into account by most models).

Despite the fact that this simple scheme already contains the main physical mechanism that could lead to gap opening in strongly correlated materials, it actually neglects the exchange coupling and the possible non spherical character of the effective interactions (the dependence of $U$ on the magnetic quantum number $m$) entering the model. It’s most serious inconsistency is, however, that the expression given in equation (1.17) is not invariant under rotation of the atomic orbital basis set used to define the occupancies $n_{m\sigma}$. To solve these problems, Anisimov and coworkers [84,85] introduced a basis set independent
formulation of LDA+U in which $E_{\text{Hub}}$ and $E_{dc}$ are given in a more general expression.

1.4.8 Generalized Gradient Approximation (GGA)

The basic concept used in LDA/LSDA, i.e. of homogeneous electron gas, is quite far away from realistic situation. In other words, we can say that the density in real system is varying rapidly. This shortcoming of LSDA [88] was overcome by GGA because the gradient of density will play a crucial role. The GGA accounts not only for the information about $\rho(\vec{r})$ at a particular point $\vec{r}$, but also for the non-homogeneity of the true electron density (with gradient of density, i.e. $\nabla \rho(\vec{r})$). First of all, Herman et al. [89] modify LDA by interpreting LDA as the first term of a Taylor expansion of the uniform density. By expanding the series with next lowest term [90, 91], the XC energy functional become [and this is known as Generalized Expansion Approximation (GEA)]

$$E_{\text{xc}}^{\text{GEA}}[\rho_\uparrow, \rho_\downarrow] = \int \rho(\vec{r}) \varepsilon_{\text{xc}}(\rho_\uparrow, \rho_\downarrow) d^3 r + \sum_{\sigma, \sigma'} \int C_{\text{xc}}^{\sigma, \sigma'}(\rho_\uparrow, \rho_\downarrow) \frac{\nabla \rho_\sigma}{\rho_\sigma^{2/3}} \frac{\nabla \rho_{\sigma'}}{\rho_{\sigma'}^{2/3}} d^3 r$$

where $\sigma$ and $\sigma'$ indicates, respectively, up and down components of spin. Unfortunately, this approximation could not served its purpose rather it turns out to be worst than simple LDA.

In GGA, behavior of large gradient is modified in such a way as to preserve desired properties. It is convenient [90] to define the functional as gradient of equation (1.12).

$$E_{\text{xc}}^{\text{GGA}}[\rho_\uparrow, \rho_\downarrow] = \int \rho(\vec{r}) \varepsilon_{\text{xc}}^{\text{hom}}(\rho_\uparrow, \rho_\downarrow) d^3 r$$

$$= \int \rho(\vec{r}) \varepsilon_{\text{xc}}^{\text{hom}}(\rho_\uparrow, \rho_\downarrow) F_{\text{xc}}(\rho_\uparrow, \rho_\downarrow) d^3 r$$

where $F_{\text{xc}}$ is a dimensionless quantity and $\varepsilon_{\text{xc}}^{\text{hom}}(\rho)$ is the exchange energy of the unpolarized gas. For exchange part:

$$E_x[\rho_\uparrow, \rho_\downarrow] = \frac{1}{2} \left[ E_x[2\rho_\uparrow] + E_x[2\rho_\downarrow] \right]$$
where $E_x[\rho]$ is the exchange energy of an unpolarized system of density $\rho(\hat{r})$, we need to consider $F_x(\rho, |\nabla \rho|)$.

Unlike LDA, GGA takes care of non-uniform charge density and this can be expressed in terms of the gradient and higher spatial derivative of the total charge density. The GGA also gives better results than LDA for systems in which the density is slowly varying.

### 1.4.9 Coulomb Corrected Generalized Gradient Approximation (GGA+U)

Within conventional GGA also, electron correlation due to intra-atomic coulomb repulsion of localized $d$ or $f$ electrons is not described very well. Different methods have been proposed to overcome this problem. One of the GGA+U methods has been applied successfully to a diversity of problems in strongly correlated systems where ordinary GGA does not give satisfactory results. The prominent examples are Mott insulators like 3d TM oxides.

For the GGA+U calculations, we have adopted a version proposed by Dudarev et al. [92]. In this implementation, the total energy depends on the difference $U-J$, i.e.

$$
E_{\text{GGA+U}} = E_{\text{GGA}} + \frac{U-J}{2} \sum_{m\sigma}(n_{m\sigma} - n_{m\sigma}^2) \tag{1.24}
$$

where $n_{m\sigma}$ is the occupancy of the orbital with magnetic quantum number $m$ and spin $\sigma$, $U$ and $J$ represent the spherically averaged on-site coulomb interaction and screened exchange integrals, respectively. It can be shown that within this formalism, unoccupied $d$ states are shifted towards higher energies by $(U-J)/2$, while the opposite is true for occupied $d$ states. For a comprehensive discussion, we refer to the literature [84,92]. Understandably, the GGA+U approach reduces to the pure GGA if we have $U - J = 0$ eV.
1.4.10 Modified Becke Johnson (mBJ) potential

On the theoretical side, one usually uses the DFT method with GGA and LDA to study the electronic structures of most the materials. But, these two approximations underestimate band gap of semiconductors or insulators. There are some alternative methods to improve the band gap with respect to the experimental values. Hybrid functionals (e.g., HSE) [93], in which a fraction of exact exchange replaces a fraction of the LDA or GGA exchange, also improve the band gap. However, the hybrid methods are more expensive and also not satisfactory in all cases. Another possibility is the DFT+U [84] method, but it can only be applied to correlated and localized electrons, e.g. 3d or 4f in transition and rare-earth oxides. Most successful methods are the combination of LDA with dynamical mean-field theory (LDA +DMFT) [94] and of course GW [95], but these methods need very expensive computational work. Recently, Tran and Blaha [96] proposed a semilocal modified Becke Johnson potential (mBJ) for the improvement in the results for band gaps. This new orbital independent mBJ potential in which mBJ exchange term is coupled with LDA correlation could catch the essentials of orbital dependent potentials (hybrid functionals) and predicts the energy bands more accurately such that calculated band gaps of the materials comes out in good agreement with experiments.

The modified Becke Johnson potential (MBJ) as proposed by Tran and Blaha [96] is

\[
v_{s,\sigma}(r) = cv_{s,\sigma}^{BB}(r) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \frac{2t_\sigma(r)}{\rho_\sigma(r)}
\]

(1.25)

where \( \rho_\sigma = \sum_{i=1}^{N_\sigma} |\psi_{i,\sigma}|^2 \) is the electronic density, \( t_\sigma = (1/2) \sum_{i=1}^{N_\sigma} \nabla \psi_{i,\sigma}^* \nabla \psi_{i,\sigma} \) is the kinetic energy density, and

\[
v_{s,\sigma}^{BB}(r) = -\frac{1}{b_\sigma(r)} \left( 1 - e^{-x_\sigma(r)} - \frac{1}{2} x_\sigma(r) e^{-x_\sigma(r)} \right)
\]

(1.26)
is the Becke Roussel (BR) potential [97] which was proposed to model the Coulomb potential created by the exchange hole. $x_\sigma$ is determined from an equation involving $\rho_\sigma$, $\nabla \rho_\sigma$, $\nabla^2 \rho_\sigma$, and $t_\sigma$. Then $b_\sigma$ is calculated by

$$b_\sigma = \left[ x_\sigma e^{-x_\sigma} / (8\pi \rho_\sigma) \right]^{1/3}.$$ 

In equation (1.27), $c$ is chosen such that it depends linearly on the square root of the average of $\sqrt{\nabla \rho / \rho}$:

$$c = \alpha + \beta \left( \frac{1}{V_\text{cell}} \int_{\text{cell}} \left| \frac{\nabla \rho(r')}{\rho(r')} \right| d^3 r' \right)^{1/2}$$

where $\alpha$ and $\beta$ are two free parameters, whose values are $\alpha = -0.012$ (dimensionless) and $\beta = 1.023$ bohr$^{1/2}$ and $V_\text{cell}$ is the unit cell volume.

Due to the second term in equation (1.25), the Becke Johnson potential reproduces very well the step structure and derivative discontinuity of the exact exchange potential, which is an important result since only the semilocal quantities are used.

### 1.5 Full Potential Linearized Augmented Plane Wave (FPLAPW) Method

The full potential linearized augmented plane wave (FPLAPW) method is a procedure for solving the KS equations for the ground state density, total energy and (KS) eigen values of a many electron system by introducing a suitable basis. The description of FPLAPW method is given below in two sub-sections.

#### 1.5.1 Linearized Augmented Plane Wave Method

There are different linear methods [98] for solving the KS equations. In all these methods the selection of a good basis set plays an important role. This is because the accuracy of approximation as well as the needed computation time strongly depends upon the basis set. For a basis set to be good enough, it should be efficient as well as unbiased i.e. it should be applicable for all systems. One such basis is the Linearized Augmented Plane Wave (LAPW) Basis [99].
Chapter 1

In LAPW method a unit cell is divided into two regions:

i) Non-overlapping atomic spheres (centered at the atomic sites) and

ii) An interstitial region

as shown in Fig. 1.3. Different basis sets are used in these two regions.

![Diagram of unit cell partitioning](image)

**Fig. 1.3** Schematic partitioning of the unit cell into atomic spheres (I) and interstitial region (II)

In the interstitial region, a plane wave expansion is used:

$$\Phi_{k_n} = \frac{1}{\sqrt{\Omega}} e^{i\tilde{k}_n \cdot \vec{r}}$$  \hspace{1cm} (1.28)

where $\tilde{k}_n = \vec{k} + \vec{K}_n$ and $\vec{k}$ is the wave vector in the Brillouin Zone (BZ), $\vec{K}_n$ is a reciprocal lattice vector and $\Omega$ is the volume of the unit cell.

Inside the atomic sphere, the potential is spherically symmetric. Therefore, the basis functions are spherical harmonics times the radial function $u_i(r, E)$.

The radial function, for a typical valence state with azimuthal quantum number $l$, is a regular at the origin and varies with energy as shown in Fig. 1.4. At the bottom of the band $E_{\text{bottom}}$, the wave function $u_i(r, E)$ has zero slopes (bonding state) but it has a zero value (anti-bonding) at the top of the band $E_{\text{top}}$. This energy dependence is linearized by selecting expansion energy $E_1$ near the centre of the band and writing the atomic function as:

$$\Phi_{k_n} = \sum_{lm} \left[ A_{lm,k_n} u_l(r, E_1) + B_{lm,k_n} \dot{u}_l(r, E_1) \right] Y_{lm}(\vec{r}). \hspace{1cm} (1.29)$$
Fig. 1.4 Schematic energy dependence of $u_l(r,E)$ and the corresponding density of states. The radius ($r$) goes up to the muffin-tin radius $R_{\text{MT}}$, which defines the atomic sphere [100].

Here $u_l$ is the solution of radial Schrödinger equation and $\dot{u}_l$ is its derivative; both these quantities are computed numerically. $A_{lm}$ and $B_{lm}$ are two free coefficients for each atom and $lm$ values which are chosen such that (at the sphere boundary) the plane wave with wave vector $\vec{k}_n$ joins continuously on to the atomic function value and slope.

The basic functions defined by equations (1.28) and (1.29) are of infinitely large size. Due to which they can not serve our purpose efficiently. So, to reduce their sizes, the two additional parameters have to be introduced. The first one is $l_{\text{max}}$ and it controls the size of LAPW augmentation which otherwise consist of an infinite sum over angular momentum ($l$). The second parameter is the plane wave cutoff $K_{\text{max}}$. It determines the size of the basis set. The basis set consists of the basis functions with only those $\vec{K}$ that satisfy the condition $|\vec{K}| \leq K_{\text{max}}$. Hence, $l_{\text{max}}$ and $K_{\text{max}}$ controls the accuracy of the calculation (completeness and quality). Therefore good choices of these parameters are very important. Further, $l_{\text{max}}$ and $K_{\text{max}}$ are not completely independent. Due to imposed boundary conditions, $l_{\text{max}}$
and $K_{\text{max}}$ must be selected in such a way that the truncation still match at the boundary. This can be done as follows, for a given $l_{\text{max}}$, $Y_m$ has at most $2l_{\text{max}}$ nodes along a large circle around the muffin-tin sphere, i.e. on a circle with contour equal to $2\pi R_{\text{MT}}$. This gives $l_{\text{max}}/(\pi R_{\text{MT}})$ nodes per unit length. On the other hand, $K_{\text{max}}$ describes a plane wave with $K_{\text{max}}/\pi$ nodes per unit length. On equating these, we get $R_{\text{MT}}K_{\text{max}} = l_{\text{max}}$. A good value $l_{\text{max}}$ thus can be chosen if $K_{\text{max}}$ is known. In general $l_{\text{max}}$ is fixed to a value of 10 and a well converged basis is obtained for $R_{\text{MT}}K_{\text{max}} = 7-9$ for most of the systems.

### 1.5.2 Full Potential and Charge Density

The muffin-tin approximation (MTA) is a good approximation for highly coordinated (metallic) systems e.g. face centered cubic (fcc) metal. However, its work is not up to level for covalently bonded systems. For such systems, full potential treatment is required. In full potential LAPW (FPLAPW) method, the potential and charge density are expanded into lattice harmonics (inside each atomic sphere) and as a Fourier series (in interstitial region) and thus they are completely general.

$$V(\hat{r}) = \begin{cases} \sum_{LM} V_{LM}(\hat{r}) Y_{LM}(\hat{r}) & \text{inside sphere} \\ \sum_{K} V_K \exp(iK\cdot\hat{r}) & \text{outside sphere} \end{cases}$$ (1.30)

In order to have few LM values in the lattice harmonics in equation (1.30), a local coordinate system for each atom sphere is defined, according to the point symmetry of the corresponding atom. This specifies a rotation matrix that reveals the local environment to the global coordinate system of the unit cell.

### 1.6 Electronic Structure Problem

Felix Bloch first discussed the eigen functions of the Schrödinger equation for an electron in a crystal. The theorems proved at that time (1928) are the
foundation of all subsequent work on the quantum theory of solids. The properties of matter under normal conditions are, at microscopic level, governed by the behavior of the electrons as these light particles in their motion almost immediately follow the heavier nuclei. A precise knowledge of the electronic band structures is thus the first step towards understanding the physical properties of matter. Historically, one may distinguish a phase, during which various methods cellular, orthogonalized plane wave (OPW), augmented plane wave (APW), Green’s function, etc. were invented but gave only limited results because of the enormous labour involved in implementing these schemes on band calculators. The next phase began in the 50’s with the advent of electronic computers. Very elaborate programs were constructed and set going, for various materials, but the outcome was often disappointing. Generally speaking, the different methods appeared to converge satisfactorily to match the same numerical results, but these were often a long way from the experimental information that was coming from Fermi surface and optical studies. The recognition of the sensitivity of the one-electron energies \( E(\vec{k}) \) to the form of potential \( V(\vec{r}) \) generated a new philosophy: the determination of band structure came to be regarded as an art, where one tried to build up a model of the energy surface represented by some parameters but consistent both with experimental and with some rough algebraic approximation to the solution of Schrödinger equation. The success of this procedure has revolutionized the whole theory of metals. To make further progress, however, it was essential to combine technique art with science. So we have learned to treat this problem as one where algebraic analysis, numerical computation and physical intention, all have their part.

The band structure problem is a many body problem corresponding to the motion of enormous number of electrons and of nuclear particles in the crystal. With the aid of DFT, the many-electron problem can be reduced to a problem
with one electron moving in an effective crystal potential. Once the effective one electron crystal potential \( V(\vec{r}) \) is constructed with the aid of certain approximations, e.g. one electron approximation [101] Born-Oppenheimer approximation [102], the problem remains of solving the KS equations like Schrödinger equation:

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \psi^{\text{KS}}_i(\vec{r}) = \epsilon_i \psi^{\text{KS}}_i(\vec{r})
\]

(1.31)

The energy band structure calculations are often done in a self-consistent manner. To achieve this one solves the Schrödinger equation and the electronic charge density is constructed as

\[
\rho(\vec{r}) = \sum_{i}^{\text{occ}} \left| \Psi_i(\vec{r}) \right|^2
\]

(1.32)

and then a new field is constructed by solving Poisson’s equation

\[
\nabla^2 u(\vec{r}) = -8\pi\rho(\vec{r})
\]

(1.33)

for the electronic contribution \( u(\vec{r}) \), to which is added the field from the nuclear point charges and exchange correlations. With a weighted average of new and old fields, the calculation is repeated and cycle iterated until the two fields are consistent as shown in Fig. 1.5.

Self-consistency is achieved by solving the Schrödinger equation at \( \vec{k} \) vectors chosen in a small part of the BZ, the so called irreducible part (governed by symmetry). By tracing the energy eigenvalues \( E_j(\vec{k}) \) for different high symmetry lines of \( \vec{k} \) points one can visualize the eigenvalues for the whole of the BZ. One often plots the density of states (DOS), which is defined by

\[
D(E) = \frac{1}{3\pi^2} \int \frac{ds}{|\nabla_{\vec{k}} E_{jk}|}
\]

(1.34)
where $ds$ is surface element and integral is performed over the surface of constant energy in the BZ.

![Flow chart for the $n^{th}$ iteration in the self-consistent procedure.](image)

**Fig. 1.5** Flow chart for the $n^{th}$ iteration in the self-consistent procedure.

In statistical and condensed matter physics, the DOS of a system describe the number of states at each level that are occupied (for energies $< E_F$) or are available to be occupied (for energies $> E_F$). A high DOS at a specific energy means that there exists many states at that energy, a zero DOS means none. In other words, the DOS indicates how closely quantum states for carriers in a
particular system are packed. This acts as a weight factor for an energy state and plays as important role in electronic and optical properties of a system.

1.7 Outline of the thesis

This thesis contains a detailed study on the Dilute Magnetic semiconductor compounds. The ground state properties like electronic band structure, DOS, half metallic ferromagnetism, magnetic moments have been studied theoretically. Since the choice of suitable host semiconductors are the foremost requirement for DMS, hence we are started with the natural choice to calculate the electronic properties of some semiconductors, being the promising hosts for the DMS. After a clear understanding of electronic properties and corrected band gap of host semiconductors, the introduction of TM as dopant in some host semiconductors have been analyzed. This induces strong magnetic moments and hence the TM based compounds are technologically more favorable for spintronic devices. The TM based compounds are widely used as half metallic ferromagnets with the largest Curie temperature. Hence, it is educative and worthwhile to work on various TM based DMS compounds and to study their electronic and magnetic properties. With this aim, in this thesis, we have studied the effect of different TMs on the magnetism of various DMS compounds substituted at the anion site of the host semiconductors.

This work is organized as follow: in **Second Chapter**, the electronic properties of some semiconductor compounds Rutile RO\(_2\) (R = Si,Ge,Sn and Pb) and ABAs\(_2\) (A = Zn, Cd; B = Ge, Sn) has been studied. The calculated electronic band gaps have been reported with a good agreement with experiments. In **Third Chapter**, Cr-doped Cd-based chalcogenides, Cd\(_{1-x}\)Cr\(_x\)Z (Z = S, Se and Te) at x = 0.25 and 0.125 in zinc blende structure have been studied. The **Fourth Chapter** concerned with the discussion of half metallic behavior of Cr-doped GaP at various doping concentration, x = 0.25, 0.0125, 0.06 and 0.06. In **fifth chapter**, we have chosen rare earth based semiconductor (CeO\(_2\)) and studied the doping of
Fe in it. The effects of oxygen vacancy on magnetic and half metallic characteristics have been discussed in details for Fe-doped CeO$_2$ DMS compound. Finally in Six Chapter, we summarize the results obtained in this thesis.
Chapter 1

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Chapter 1

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