Summary and Conclusions
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In this thesis, we have presented the calculations of electronic and magnetic properties of some Dilute Magnetic semiconductor (DMS) compounds. The transition metal (TM) based DMS compounds have an unequal density of states (DOS) of spin-up and spin-down electrons at the Fermi level ($E_F$) and behave like metals for one electron spin direction and like semiconductors for other spin direction. This property makes these materials promising to design new spintronics devices like spin valves, spin light emitting diodes, magnetic sensors, logic devices and ultra-fast optical switches. The ground state properties like electronic band structure, DOS, spin polarization, half metallic ferromagnetism, magnetic moments have been studied theoretically. The DFT based electronic band structure calculations in present work were performed by application of WIEN2k package in its Full Potential Augmented Plane Wave (FPLAPW) formulation for predicting the ground state. The exchange-correlation potential and energy were described within the various approximations such as mBJLDA, GGA and GGA+$U$. The Basic introduction constitutes Chapter 1 and our results follow in Chapter 2 to Chapter 5.

Since the choice of suitable host semiconductors are the foremost requirement for DMS compounds, hence we are started with the natural choice to calculate the electronic properties of some semiconductors, being the promising host materials for the DMS compounds. 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 large magnetic moment 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 very high 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, we have studied the effect of different TMs substituted at the anion site of the host semiconductors on the magnetism of various DMS compounds in this thesis. The second chapter deals with the some host semiconductor compounds suitable for DMS compounds. **Chapter 3** and **Chapter 4** contain the results on electronic and magnetic properties of some TM doped III-V and II-VI type DMS compounds such as Cr doped GaP and Cd-chalcogenides. **Chapter 5** deals with the ground state properties of Fe-doped CeO$_2$ rare earth compound. As we have used different doping concentrations of TM in the host semiconductors thus we have also studied the impact of the same on the ground state properties of the resulting compounds within Chapter 2 to Chapter 5.

We have demonstrated the electronic band gap of RO$_2$ (R =Si, Ge, Sn and Pb) and ABAs$_2$ (A = Zn, Cd; B = Ge, As$_2$) compounds in **Chapter 2**. In the first section, the physical state of RO$_2$ series has been altered with the change of R atom down the same group. Using FPLAPW method, we have observed that the ground state of the present compounds of RO$_2$ series has been changed from insulator (SiO$_2$) to semi-metal (PbO$_2$). We have predicted the large direct band gaps of all the semiconductors (except PbO$_2$) which are in very good agreement with the corresponding experimental values. We have noticed that the mBJLDA approach is flexible to reproduce accurately both, the XC energy and its charge derivative. Thus, the band gaps within mBJLDA come out to be very close to experimental values. On the other hand, GGA and EV-GGA formalisms underestimate the band gap. The covalent character of the R-O bond decreases with increase in size of R-atom. As the size of R atom increases which results in poorer orbitals overlap of R and O atoms and thus, leads to formation of longer and weaker bonds responsible for the semi-metallic nature of PbO$_2$. This poorer overlap produces a decrease in separation between valence and conduction bands. This overlap between R and O atom is strongest in case of SiO$_2$. The valence band
maximum is contributed by O-p, R-s and R-p states whereas conduction band minimum is dominated by R-s states mainly. The semimetallic nature of PbO$_2$ is governed by the partial occupation of lowest part of strongly hybridized conduction band at E$_F$. We have also observed that the charge transfer occurs mainly from R atom towards O atom. As we change the R atom down the group, the electron density in the interatomic region between R and O atoms decreases. This is due to the reason that the nearest neighbor distance between R and O atom increases from 3.31 a.u. (in SiO$_2$) to 4.04 a.u. (in PbO$_2$) which leads to longer bonds along the series. In other words, the ionicity of R-O bond increases along the series SiO$_2$ → PbO$_2$.

In the second section, the first principle calculations has been performed to calculate the electronic properties of ABAs$_2$ (A = Zn, Cd; B = Ge, Sn) compounds to see the effect of changing local environment. We have observed that the band gap of the reference compound, ZnGeAs$_2$ changes significantly by substituting cation(s) of corresponding next group element. We predict a direct band gap in all these compounds and this gap decreases with the change of either one or both cations in ZnGeAs$_2$. The calculated band gaps are in better agreement with corresponding experimental ones as compared to other calculations. The electronic band structure is analyzed in terms of contributions from various electrons and the covalency or ionicity of two bonds, A-As and B-As has been discussed with respect to the substitutions. This covalent/ionic character depends on Pauling’s electron-negativity difference of A/B and As atoms. These compounds are characterized as narrow band gap semiconductors with a maximum gap (1.27 eV) for ZnGeAs$_2$. A good agreement of band gaps with experiments indicates that mBJ functional is best suited for calculating electronic structure of semiconductors and insulators. The good agreement between theory and experiment for electronic properties allows a deep understanding of these compounds in terms of their band structures and DOS. This study could be very useful to provide a strong basis for the development of new DMS compounds for spintronic applications.
**In Chapter 3**, we have presented first principle predictions of electronic and magnetic properties of Cr-doped GaP at dopant concentration, \(x = 0.25, 0.125, 0.06\) and \(0.03\) using FPLAPW method within GGA to search new candidates showing half metallic ferromagnetism (HMF). The emphasis of this work is on the study of spin polarization at \(E_F\) in any one of the spin channels, as it is the essential requirement for the spintronic applications. The solubility limit of the studied compound should be very small \((< 8-10 \%)\) so that it can be used it as practical spintronic devices. The stable HMF at lower doping concentration is great challenge to the theoreticians because an expansive supercell calculation is needed for predicting the ground state properties of this DMS compound. We predict that it is HM ferromagnet at all dopant concentrations including solubility limit.

The most exciting characteristics of this compound is that the half metallicity remains intact on reducing the solubility limit of Cr atom with an enhanced HM gap at \(E_F\) in minority spin channel (MIC) for smallest dopant concentration \((x = 0.03)\). This property makes this compound suitable for practical spintronic devices and favors the need of growing it experimentally. The d-states of impurity atom (Cr) play a crucial role to induce the magnetism in the studied compound. The interaction between Cr-d states and P-p states pushes the symmetric d-states at \(E_F\) in majority spin channel and away from \(E_F\) in minority spin channel which originates a gap in the latter at all dopant concentrations. These Cr-d states are most localized at \(E_F\) for lowest doping concentration, \(x = 0.03\) results a large HM gap for that concentration. The double exchange mechanism is responsible for the emergence of ferromagnetism in this system. The HM character of this compound is consistent with the integral value of magnetic moment of the unit cell. We have also observed that the magnetic properties of this compound depend on the dopant concentrations and on its valence electron configuration. The main contribution in the total magnetic moment comes from Cr-d states. As the host, Ga and P atom are non magnetic and the magnetic
moments at these atoms in resultant DMS compounds are negligibly small and of induced character from Cr-atom. The p-d interaction between Cr and P atoms reduces the magnetic moment of Cr atom from its elemental value and induces small local spin magnetic moment on nonmagnetic Ga/P atom which aligns parallel/antiparallel to Cr atom. This induced magnetic moment decreases at both, Ga and P atoms on reducing the dopant concentration from 0.25 to 0.03 because lesser Cr-d states are available at lower concentration for p-d hybridization.

A full potential treatment of electronic and magnetic properties of Cr-doped Cd-chalcogenides, Cd\(_{1-x}\)Cr\(_x\)Z (Z = S, Se and Te) at dopant concentration, x = 0.25 and 0.125 constitutes Chapter 4. The main aim of this work is to elucidate the effect of decreasing dopant concentration and increasing size of the chalcogen atoms from S to Te along the same group on half metallicity and magnetism of studied compounds. We observe that our prediction of half metallic gaps and equilibrium lattice constants agree very well with the available theoretical data for dopant concentration, x = 0.25, but the results for x = 0.125 are reported first time in this work. The calculated result at equilibrium lattice constant show that the half metallicity remains intact on reducing the dilute limit for all the compounds with a band gap in minority spin channel. The analysis of DOS curves in the vicinity of \(E_F\) nicely explains the reason for the respective behavior. This property makes these compounds suitable for practical spintronic devices. The spin resolved band structure shows that the band gap is direct along \(\Gamma-\Gamma\) direction of the first Brillouin zone in all these compounds. The total magnetic moments for all compounds are almost similar and come out to be an integer value confirming the HM characteristics of compound, which is due to similar valence configuration of constituent atoms. The magnetism comes essentially from the d-states of impurity atom (Cr). The minority band gap decreases on reducing the dilute limit for all compounds. Moreover, the same also decreases on changing chalcogen atom (Z) by heavier ones in Cd\(_{1-x}\)Cr\(_x\)S compounds. The band gap in minority spin is a fingerprint of the Cr-d and Z-p interaction. This p-d interaction reduces the
magnetic moment of Cr from elemental value and induces small local spin magnetic moment on nonmagnetic Cd/Z atom which aligns parallel/antiparallel to Cr atom.

\( \text{CeO}_2 \) is a strongly correlated system in which Ce is heavy rare earth element and the theoretical description of Ce-f states is a challenge to the researchers due to their localization and extended behaviour. The standard density functional theory (DFT) calculations are inadequate to characterize the electronic structure of CeO\(_2\). So, the DFT + \( U \) is one of the effective schemes to cope with the correlation effects, in which a Hubbard-\( U \) term is added to the local density approximation (LDA) or generalized gradient approximation (GGA), which yields the correct ground state description of CeO\(_2\) in comparison with experiments. In order to support the experimental observations, we planned to remain focused on electronic and magnetic properties of Fe-doped CeO\(_2\) and to establish the DMS characteristics for the same at Fe-concentration (\( x = 0.125, 0.06 \)) in \textbf{fifth Chapter}. The half metallicity remains intact on reducing the dopant concentrations with a HM gap in minority/majority spin channel in all compounds with/without oxygen vacancy (\( V_O \)). This property makes these compounds suitable for practical spintronic devices. Moreover, the existence of HM gap is a striking feature of studied DMS compound. The moment in Fe-doped CeO\(_2\) with and without \( V_O \) comes essentially from the d-states of impurity atom (Fe). The HM gap decreases on reducing the dilute limit in all studied compounds. The HM gap in minority spin for Fe-doped CeO\(_2\) without \( V_O \) is a fingerprint of the Fe-d and O-p interaction and the emergence of ferromagnetism can be explained by Zener's double exchange mechanism for ferromagnetism as in other DMS compounds. On the other hand, interactions between O-p, Fe-d and Ce-f are accountable for the HMF in the majority spin channel for Fe-doped CeO\(_2\) with \( V_O \). The total magnetic moment is mainly governed by Fe-atom due to the presence of energetic Fe-d states. We believe that this study will serve as a groundbreaking step in the development of new spintronic devices.
The work presented in this thesis shows that the DMS compounds in the bulk form are considered highly impressive materials. A lot of work still remains to be done, in this area to search the new DMS compounds within the dilute limit. Moreover, a comprehensive investigation should be desired to elucidate the mechanism that results in appearance of the most important property i.e. half-metallicity in these compounds. It is quite important to access the effect of doping in DMS compounds on nano scale. So, the work is needed to explore the DFT calculations towards the nano DMS compounds. It may lead to many interesting physical properties. The rare earths, due to their partially filled f-orbitals, are also interesting subject to study electronic and magnetic properties. Therefore, a deep research in these compounds may lead to novel materials suitable for technological applications. The multiferroics are also the prime candidates for future spintronic devices because they can simultaneously exhibit both electric and magnetic properties. BiFeO$_3$, BiMnO$_3$ non-oxides such as BaNiF$_4$ and spinel chalcogenides like ZnCr$_2$Se$_4$ are some of the examples of this category. So, the search of magnetism and half metallicity in multiferroics by performing DFT calculations may be technologically important from spintronic point of view and will also be the one of the aims in future.