CHAPTER-I

INTRODUCTION AND LITERATURE SURVEY
1.1 DILUTED MAGNETIC SEMICONDUCTORS

Diluted Magnetic Semiconductors (DMS) or semi magnetic semiconductors are formed when a fraction of the host cations are substitutionally replaced by magnetic ions or appropriate rare earth ions. Transition metals that have partially filled d states (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu) and rare earth elements that have partially filled f states (e.g. Eu, Gd, Er) have been used as substituent magnetic atoms in DMS. The partially filled d states or f states contain unpaired electrons, in terms of their spin, and are responsible for their magnetic behavior. Examples of such materials are alloys of the type $A^{II}_{1-x}TM_{x}B^{VI}$ or $A^{II}_{1-x}RE_{x}B^{VI}$ [1]. Crystal structure of a typical diluted magnetic semiconductor with the wurtzite type host with transition metal ions (brown circle) doped at cation site in tetrahedral symmetry of anions is shown in Fig. 1.1.

In DMS materials the delocalized conduction band electrons and valence band holes interact with the localized magnetic moments associated with the magnetic atoms. Generally, when 3d transition metal ions are substituted for the cations of the host, the resultant electronic structure is influenced by strong hybridization of the 3d orbitals of the magnetic ion and mainly the p orbitals of the neighboring host anions. This hybridization gives rise to the strong magnetic interaction between the localized 3d spins and the carriers in the host valence band [1, 20]. Due to the necessity that the DMS materials must exhibit ferromagnetism with a critical temperature above room temperature in order to have practical applications in spintronic devices, this is deemed to be the bottleneck issue. The nascent field of spin electronics or spintronics stands to assimilate the two fundamental properties of the electron, charge and spin, to form the basis for a new class of device design. Operating by the manipulation, transport, and detection of charge carrier spins, spintronics is expected to improve upon traditional electronic and photonic devices, allowing for enhancements in the form of reduced power consumption, faster device operation, and new forms of information computation [21, 22]. Spintronics may lead to devices such as spin-polarized LEDs, spin-FETs, and spin-based qubits for quantum computers. Increased functionalities are also expected, such as integrated magnetic/electronic operations on the same chip. Schematic overview of spintronics which combines both charge (electronics) and spin (magnetism) into a novel field of research and applications is shown in Fig. 1.2.
Fig. 1.1 General crystal structure of diluted magnetic semiconductors.

Fig. 1.2 Schematic overview of spintronics which combines both charge (electronics) and spin (magnetism) into a novel field of research and applications.
1.2 MODELS DESCRIBING MAGNETISM IN DMS

The basic model for DMS is a magnetically inert host semiconductor doped with localized spins, which may then be doped with electrons or holes. The magnetic spins are localized on much smaller scales than the carriers. The magnetic interactions seen in DMS are governed by an sp-d exchange interaction, which allows carrier mediated magnetic order and leads to such effects as giant Faraday rotation and formation of bound magnetic polarons. Several models and mechanisms have been suggested to explain the origin of magnetism in DMS. Most of the theories attempt to identify the various spin coupling energies in a system and by plugging in the material parameters, attempt to estimate if the energies lead to ferromagnetic, antiferromagnetic or spin-glass like interactions between individual atomic spins.

(i) Mean field theory

Zener originally proposed a model for ferromagnetism in dilute alloys of transition metals, driven by the exchange interaction between carriers and localized spins [23]. The three important ideas behind the model are:

1. In an isolated atom, the lowest energy state is given by the electronic state where an incomplete d-shell has the highest spin - meaning that all the spins are aligned.
2. The exchange integral between d-shells of adjacent atoms always leads to antiferromagnetic order.
3. The spin of an incomplete shell is strongly coupled to the conduction electrons. When this coupling dominates over the direct exchange, ferromagnetism is made possible. The net spin coupling energy in such a system is a combination of three terms. The first one is the direct exchange between incomplete d-shell electrons while the second is the exchange between the d-shell electrons and the conduction electrons. The third interaction is the Fermi kinetic energy of the conduction electrons. This is at a minimum (0) when there is an even number of spin up and spin down electrons, since the spin distribution at the Fermi level is balanced. A combination of these three terms is given by:

\[ E_{\text{spin}} = \frac{1}{2} \alpha S_d^2 - \beta S_d S_c + \frac{1}{2} \gamma S_c^2 \] (1.1)

Here, \( S_c \) and \( S_d \) are the net spin polarizations of the conduction electrons and the d-shell electrons respectively. The sign of \( E_{\text{spin}} \) determines the nature of magnetic order, while a
positive sign is indicative of antiferromagnetic order, a negative sign implies ferromagnetism.

(ii) Bound magnetic polaron

An important attribute of diluted magnetic semiconductors is the sp-d exchange coupling between spins of magnetic ions and those of the impurity electrons in the semiconductor band. This results in phenomena such as valence band splitting under magnetic field and polaron effects. A bound magnetic polaron (BMP) is a collection of electrons (or holes) bound to impurity atoms through exchange interactions within an orbit [24]. These interactions can render carriers parallel or anti-parallel to the magnetic impurity, depending upon the system. These two configurations differ in energy and result in a non-zero spin flip energy which is a characteristic of BMPs. The net energy of the system can be lowered if the ions are aligned parallel to each other, since they all interact with carriers the same way. At low temperatures, where the s-d exchange energy exceeds \( k_B T \), mutual alignment of the ions and carriers results in a ferromagnetic “bubble”. At higher temperatures, however, the spins of the magnetic ions are not constant anymore. A nonzero magnetization results from the spin fluctuations within any carrier orbit. While the former instance comprises the “collective” regime, the latter is a characteristic of the “fluctuation” regime. The temperature up to which a BMP can facilitate magnetic order depends upon the nature of the interactions between the atomic spins and the charge carriers. The net exchange has been computed by Durst et al. [25] based on the polaron-pair model. This model considers the interaction between a pair of BMPs via a shared interstitial area, where the magnetic ions interact with carriers belonging to both the polarons. Such an area is crucial for carrier mediated ordering of the individual polarons. Fig. 1.3 shows a schematic of the polaron pair model. The Hamiltonian that results from this model is given by:

\[
H_{\text{in}} = K \sqrt{(s_1 + s_2)^2} + K' (s_1 + s_2) S_1 + J s_1 s_2 \tag{1.2}
\]

where \( K \) is the intra polaron ion-carrier exchange constant, \( K' \) is the interstitial ion-carrier exchange constant, \( J \) is the direct carrier-carrier exchange constant, \( s_1 \) and \( s_2 \) are the carrier spins, \( S_1 \) and \( S_2 \) are the net polaron spins, and \( S_I \) is the collective spin of the interstitial region.
(iii) The spin glass phase

The spin-glass phase transition of DMS is observed at low temperatures. This conclusion is based on the characteristic exhibited by the low-field magnetic susceptibility at some temperature $T_f$. The low temperature phase is a disordered phase, but "frozen" state, such as a spin glass. For a diluted magnetic fcc lattice with nearest neighbor interactions a spin glass transition becomes possible only when magnetic ion concentration exceeds a percolation threshold of $x \approx 0.19$. The spin-glass phase can form for arbitrarily small "$x$" at low temperatures [26].

1.3 CLASSIFICATION OF DMS

The DMS alloys are generally classified into two categories, by virtue of the type of interaction of 'd' electrons with the band electrons / holes as narrow gap and wide gap diluted magnetic semiconductors. Mercury and lead chalcogenides along with indium based III-V compounds are narrow gap DMS and many of the remaining are wide band gap DMS. Most common DMS are II-VI compounds (like ZnTe, CdTe, ZnSe, CdS, ZnS,
etc.) with transitional metal ions (e.g., Mn, Fe, Co etc.). The exhibition of antiferro/ferromagnetic behavior critically depends on the specific host and magnetic atoms.

1.3.1 IMPORTANCE OF II-VI DMS

The most thoroughly understood DMS species are the alloys of $A_{1-x}^{II}, TM_x B^{VI}$ (where the TM = Sc$^{2+}$, Ti$^{3+}$, V$^{2+}$, Cr$^{3+}$, Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ or rare earth such as Eu, Gd, Er) compounds. Among II-VI compounds most extensively studied materials are CdTe, ZnSe and ZnS. This is because +2 magnetic ions are easily incorporated into the host II-VI crystals by replacing group II cations, which gives rise to localized magnetic moment in the host semiconductor. Among all the II-VI DMS, Mn doped II-VI DMS have attracted special attention due to the highest miscibility of Mn ($x = 0.86$), electrical neutrality of magnetic atoms and maximum spin value ($S = 5/2$). The highest miscibilities of Fe, Co and Cr in II-VI compounds are only 0.26, 0.14 and 0.005 [27].

The diluted magnetic semiconductors of $A_{1-x}^{II}, TM_x B^{VI}$ type are of great interest for several distinct reasons [1]:

a) Their ternary nature gives us the possibility of “tuning” the lattice constant and band parameters by varying the composition of the material and hence they are excellent candidates for the fabrication of quantum wells, super lattices and other configurations which involve band-gap engineering.

b) The substitutional transition metal ions like Mn in the $A^{II} B^{VI}$ structure are also characterized by highly efficient electroluminescence and render dilute magnetic semiconductor alloys important in the context of optical flat panel display applications.

c) The random distribution of magnetic ions over the cation sub-lattice leads to important magnetic effects, e.g., the formation of the spin-glass-like phase at low temperatures.

d) The spin dependent properties lead to dramatic effects, such as the giant Faraday rotation, the magnetic field induced metal-insulator transition, and the formation of bound magnetic polarons.
1.3.2 PROPERTIES OF II-VI DMS

(i) Crystal structure of II-VI DMS

Most of the properties of DMS are strongly dependent on their equilibrium crystal structure [1, 28]. The ternary alloys formed by substituting magnetic elements for the group II elements in the $A^{II}B^{VI}$ lattice retain the crystal structure of the “parent” $A^{II}B^{VI}$ compound up to a critical value of the dopant concentration in their crystal structure. The mechanical, optical and electrical properties of DMS are qualitatively similar to their nonmagnetic “parent” compounds. However, when the concentration of the magnetic element becomes appreciable, the lattice becomes strained and structural transitions become imminent. Most of the II-VI based DMS crystallize in zincblende structure, although in some both wurtzite and zincblende structures co-exist. These structures are shown in Fig. 1.4.

The crystal structures (zincblende and wurtzite) of DMS are very closely related inspite of difference in their symmetry. They are formed with tetrahedral (s-p$^3$) bonding, involving the two valence s electrons of the group II element and the six valence p electrons of the group VI element. The transitional metals can contribute their 4s$^2$ electrons to the s-p$^3$ hybridization and can substitutionally replace the group elements in tetrahedral structures of II-VI lattice.

![Fig. 1.4 Unit cells in the (a) zincblende (b) wurtzite structures](image-url)
(ii) BAND STRUCTURE OF II-VI DMS

Fig. 1.5 shows a typical band structure diagram of a wide gap II-VI DMS [1]. The band structure in DMS is essentially same as that of the host lattice except that the d-electron states are split in the presence of crystal field. The ‘d-d’ and ‘sp-d’ exchange interactions determine the bulk magnetization and hence the relative positions of these energy levels are of great importance. As these DMS are alloys, the energy level positions in the band structure are tailorable as a function of concentration of the magnetic atoms leading to the tailability of the magnetic properties of DMS. In Fig.1.5 $\tau^0$ and $\tau^1$ are the usual conduction and valence band edges and these are called the sp bands. When magnetic atoms are incorporated, sp-d hybridization broadens the ‘d’ levels into relatively flat and narrow bands. The lower lying occupied band at $e_{d^5}+(d^5-d^4)$ and the higher occupied $e_{d^6}^-$ (d$^5$-d$^6$) band are of great importance [1].

Qualitatively the band diagram of narrow gap DMS is similar to that of wide gap DMS. But the band structure of the host is not similar and shows band inversion at some composition of the magnetic atoms leading to zero band gap. In some DMS (Hg$_{1-x}$Mn$_x$Te), the band gap variation with composition is very much higher compared to their non magnetic counterpart (Hg$_{1-x}$Cd$_x$Te). Effective mass and the large spin splitting factor considerably increase the cyclotron splitting. These splitting energies are appreciable and hence no longer can be neglected. Fig. 1.6 shows the spin splitting of conduction and valence bands for wide gap DMS in the presence of magnetic field [1, 29]. In the absence of magnetic field such split in energy levels will not affect the properties of the DMS. However, an applied magnetic field brings about dramatic changes.
1.5 Schematic band structure of wide gap zincblende DMS crystals.

1.6 Band structure near the $\Gamma$ point for three cases: an open gap Zincblende semiconductor, a zero-gap zincblende semiconductor and a wurtzite semiconductor.
(III) MAGNETIC PROPERTIES

This section presents a qualitative discussion of the magnetic properties of DMSs. In particular, the theoretical background of the magnetic interaction will be described. The Hamiltonian including the various interactions is of the form:

\[ H = H_{sp} + H_d + H_{sp-d} + H_{d-d} \]  

(1.3)

Where \( H_{sp} \) is the unperturbed Hamiltonian of the host material and gives rise to the band structure. \( H_d \) is the Hamiltonian for the divalent magnetic atom with localized \( d \)-levels. The exchange interaction of these ions with the band electrons or holes, is denoted by the \( H_{sp-d} \) (sp-d interaction), where as with other magnetic ions, is denoted by \( H_{d-d} \) (d-d interaction). Diluted magnetic semiconductors consist of two subsystems, namely, (a) the magnetic subsystem with 3d electrons of magnetic ions and (b) the electronic subsystem consisting of s-like electrons and p-like electrons in the conduction band and valence band respectively. The unique optical and transport properties observed in DMS materials are due to the sp-d interaction between the magnetic and electronic subsystems [30].

(a) sp-d exchange interaction

The sp-d exchange interaction involves the conduction and valence band electrons as well as the 3d levels of the local magnetic ions. In Eq.1.3, the \( H_{sp-d} \) contribution to energies of the two spin substates of \( l \)-th Landau level in a parabolic conduction band is given by [30]

\[ E_{\pm} = E_{q} + (l + 1/2) \hbar W \pm \frac{1}{2} g_{eff} \mu_B \]  

(1.4)

Here, \( W \) is the cyclotron frequency and \( g_{eff} \) is given by

\[ g_{eff} = g^* - N_0 a \langle S_z \rangle / \mu_0 H \]  

(1.5)

where \( g^* \) is the band g-factor, \( N_0 \) is the number of cations, and “\( a \)” is the exchange interaction constant for s-like electrons normalized by the volume of an elementary cell. A similar expression can be obtained for the valence band holes, with the exchange integral \( \beta \) instead of \( \alpha \). The principal difference between \( \alpha \) and \( \beta \) stems from the symmetry of the electron wave function within the band structure. The factor \( N_0 a \langle S_z \rangle \) is proportional to the macroscopic magnetization of the system. Consequently, the magnetic field, temperature, and composition contribute to the electronic properties of a
DMS material. Effects like large Faraday rotation and giant negative magneto-resistance arise from this exchange interaction.

(b) \textit{d-d Exchange Interaction} \\
(i) \textbf{Super exchange:} \\

Super exchange is a two-hole process where the interaction between \textit{d} electrons of the Mn$^{2+}$ ions is mediated through the valence band. As a result of the \textit{sp-d} exchange interaction, the electrons residing in the valence band are either attracted to or repulsed by a given magnetic ion, depending on their spin orientation. This results in a spatial separation of spin-down and spin-up electrons if the band is entirely occupied, as in insulators or intrinsic semiconductors. Such separation leads to an antiferromagnetic interaction between neighboring localized spins, a mechanism known as super exchange interaction. Indeed, in the absence of holes, localized spins are antiferromagnetically coupled in Mn based \textit{II-VI} and \textit{III-V} DMSs [1, 31]. However, it has been suggested that super exchange in Cr and V based \textit{II-VI} compounds can lead to a ferromagnetic order [32].

(ii) \textbf{Zener/RKKY Models} \\

This is a two-electron process where the interaction is mediated through two electrons in the conduction band. This reasoning implies the appearance of spin-polarized carrier clouds around each localized spin in extrinsic DMSs. Since the spins of all carriers can assume the same direction if the band is unfilled, a ferromagnetic ordering can emerge, as noted by Zener [33] in the context of magnetic metals. This ordering can be viewed as driven by lowering of the carriers’ energy associated with their redistribution between spin sub bands split apart in energy by the exchange interaction. A more detailed quantum treatment indicates, however, that the sign of the interaction between localized spin oscillates with distance, according to the celebrated RKKY (Ruderman-Kittel-Kasuya-Yoshida) model [34]. Nevertheless, as long as the carrier concentration is smaller than that of the localized spins, the RKKY and Zener models lead to the same values of $T_c$ in the mean-field approximation.
(iii) Double exchange

This mechanism operates if the width of the carrier band (V) is smaller than the exchange energy, a situation expected for bands formed from d states. As noted in another work by Zener, [35] spin ordering facilitates carrier hopping over the d states, so that the ferromagnetic transition is driven by the lowering of the carrier energy due to an increase in V. Accordingly, in such systems spin ordering is always accompanied by a strong increase in the conductivity, an effect leading to so called colossal magneto resistance, typically orders of magnitude greater than the giant magneto resistance occurring in multi layers of magnetic metals. So far, there is no evidence for d-band transport or for the associated colossal magneto resistance in III-V and II-VI DMSs.

1.4 DMS NANOSTRUCTURES

In recent years DMS in the nanoform have attracted considerable attention of the scientific community, because of their unique properties and innovative applications in miniature technology and spintronics, DMS nanostructured materials are currently considered to have potential technological applications in optoelectronic devices such as semiconductor quantum dots and photodiodes and are also used as window layers in solar cells. Magnetic applications of these include fabrication of devices with giant magneto resistance (GMR) effects, the property used by magnetic heads to read data on computer hard drives as well as the development of magnetic refrigerators that use solid magnets as refrigerants rather than compressed ozone-destroying chlorofluorocarbons [36]. Single nano sized magnetic particles are mono-domains and one expects that in magnetic nanophase materials also the grains correspond to domains, while boundaries on the contrary correspond to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to super-paramagnetism. Magnetic nano composites have been used for mechanical force transfer (ferro fluids), for high density information storage. In addition, nanostructured metals and ceramics seem to be candidates for new catalytic applications [37-39].

The development of semiconductor nanoclusters is an area of intense research. These nanoclusters are often referred to as quantum dots, nanocrystals and Q-particles [40]. In the nanometer size regime, electron-hole confinement in nanosized spherical
semiconductor particles results in three dimensional size quantization. Band gap engineering by size and dimension quantization is important because it leads to electrical, optical, magnetic, optoelectronic and magneto optoelectronic properties substantially different from those observed in the bulk materials [36]. As an example, quantum dots can be developed to emit and absorb a desired wavelength of light by changing the particle diameters. This feature allows the construction of finely tunable and efficient semiconductor lasers, owing to the phenomenon of “quantum size effects” caused by the spatial confinement of delocalized electrons in confined grain sizes [41, 42]. The properties of nano DMS depend on the following four common micro structural features: (i) fine grain size and size distribution (< 100 nm); (ii) the chemical composition of the constituent phases (iii) the presence of interfaces, more specifically, grain boundaries, hetero phase interfaces, or the free surface and (iv) interactions between the constituent domains. Hence these materials exhibit unusual mechanical, electrical, optical and magnetic properties. Mainly the following two principal factors cause the properties of nanomaterials to differ significantly from other materials.

(i) **Increase in surface Area to Volume ratio**

Surface area to volume ratio is one of the key concepts for understanding of the size-dependent properties and behaviors and changes that are at the core of nanoscience. Not only the size of objects or system changes with scale, but also the way in which they function or behave also reflects the changes. For example, even small changes in linear size yield larger relative changes in area, and even larger changes in volume. Thus, if a property is dependent on volume (e.g., heat capacity, mass), then it will change much faster than properties dependent on area (e.g., cooling surface, absorptivity for a given change in size) [36].

(ii) **Quantum Confinement**

The properties of materials are studied based on their energy levels. For isolated atoms the energy levels are discrete and for materials consisting of a large number of close atoms, the energy levels split and form bands. Nanomaterials are intermediate to isolated atoms and the bulk materials. When the size of the material is reduced to
nanoscale, energy levels of electrons change, this effect is called quantum confinement. This affects the optical, electrical and magnetic properties of nanomaterials [36].

1.5 SOME PRESENT AND FUTURE APPLICATIONS OF DMS NANOSTRUCTURES

DMS in crystalline, thin film, multi layer and nano-structure forms find a wide variety of applications. The device applications can be classified as (i) Composition and band gap dependent applications (ii) Devices using optical transitions of Mn$^{2+}$ ions (iii) Devices based on sp-d exchange interaction. These include magnetic sensors [43], isolators, polarisers and light modulators throughout the infrared and visible spectral regions [44], IR detectors tunable both by temperature and magnetic field [45], solar cells and visible and near IR lasers [46] that compliment III-V lasers and Kerr mirrors with inherent low-light absorption in the active medium. The advantages of these materials as magnetic field sensors in sensitive optical-fiber-fed dielectric magnetometers for static and dynamic magnetic fields are due to large Faraday rotation and flexible magnetic domain walls. Transition metal-doped crystals are very attractive in the development of tunable mid-infrared solid state lasers owing to their simplicity and compactness. The presence of Mn in ZnS and ZnSe gives electroluminescence, which finds application in flat panel display technology [47]. Cr$^{2+}$ doped Cd$_{0.85}$Mn$_{0.15}$Te is of great importance as tunable laser for use in medicine and environmental studies [48]. Recently observed lasing action near 2.5 µm in Cr doped ZnS, and ZnSe is of great interest for medical and other applications [49, 50]. Nanostructure DMS have revolutionary applications in non-linear optics, fast optical switching and memory devices and a new area of spintronics has already begun with the observation of polarized light in a light emitting diode when the polarized electrons are made to pass through an LED [51].

As well known today, integrated circuits and high-frequency devices, used for information processing and communications, have had great success through controlling the charge of electrons in semiconductors. Mass storage of information (indispensable for information technology) is carried out by magnetic recording (hard disks, magnetic disks) using electronic spins in ferromagnetic materials. It is then quite natural to ask if both the charge and spin of electrons can be used at the same time to enhance the performance of
devices. This is the main idea of spintronics, which is widely expected to be the future solution to downsize current microelectronic devices into size of even nanometers. The realization of functional spintronic devices requires materials with ferromagnetic ordering at operational temperatures compatible with existing semiconductor materials. A ferromagnetic dilute magnetic semiconductor with favorable experimental properties, will promisingly suit this need [52].

(a) Spintronic solar cells

One possible application of spin-polarized p-n junction is something we call the spin-polarized solar cell. As in ordinary solar cells, light illuminates the depletion layer of a semiconductor (such as gallium arsenide), generating electron-hole pairs. The huge built-in electric field in the layer (typically 104 volts per centimeter) swiftly sweeps electrons into the region and holes into the p region. If a wire connects the edges of the junction, a current flows. If the light is circularly polarized (from filtered solar photons, for instance), the generated electrons are spin polarized. Holes in III-V semiconductors for example, gallium arsenide, indium arsenide and others which are most useful for opto-spin-electronic purposes lose their spin very quickly, so that their polarization can be neglected. As the spin-polarized electrons created in the depletion layer pump the spin into the n region, the resulting current is spin polarized. Hence, photons of light are converted into oriented spins [53].

Fig.1.7 shows the spin based solar cell process. Sunlight passes through a filter to produce circularly polarized light, which is absorbed in the region between p-type and n-type semiconductors. This creates spin polarized electron hole pairs in this so-called “depletion” layer, but if a semiconductor of the III-V variety is used (gallium arsenide, for example), the polarization is only retained by the electrons. The inherent electric field at the layer boundaries sweeps the holes to the p side and the electrons to the n side. Just as with a conventional solar cell, a wire connected from the p electrode to the “n” electrode will now have a current flowing in it, but in this case the current is spin polarized [52].
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(b) Field effect transistor

In a conventional field effect transistor, electric charge is introduced via a source electrode and collected at a drain electrode. A third electrode, the gate, generates an electric field that changes the size of the channel through which the source-drain current can flow, akin to stepping on a garden hose. This results in a very small electric field being able to control large currents. In this device, a structure made from indium-aluminum-arsenide and indium-gallium-arsenide provides a channel for two-dimensional electron transport between two ferromagnetic electrodes. One electrode acts as an emitter, the other as collector (similar, in effect, to the source and drain, respectively, in a field effect transistor). The emitter emits electrons with their spins oriented along the direction of the electrode's magnetization, while the collector (with the same electrode magnetization) acts as a spin filter and accepts electrons with the same spin only. In the absence of any changes to the spins during transport, every emitted electron enters the collector. In this device, the gate electrode produces a field that forces the electron spins to precess, just like the precession of a spinning top under the force of gravity. The electron current is modulated by the degree of precession in electron spin introduced by
the gate field: An electron passes through the collector if its spin is parallel, and does not if it is antiparallel, to the magnetization. The Das effect [54] should be most visible for narrow band-gap semiconductors such as InGaAs, which have relatively large spin-orbit interactions (that is, a magnetic field introduced by the gate current has a relatively large effect on electron spin). Despite several years of effort, however, the effect has yet to be convincingly demonstrated experimentally.

Das spin transistor was the first spintronic device to be proposed for fabrication in a metal-oxide-semiconductor geometry familiar in conventional microelectronics [54].

Fig.1.8 shows the spin based field effect transistor. An electrode made of a ferromagnetic material (purple) emits spin-aligned electrons (red spheres), which pass through a narrow channel (blue) controlled by the gate electrode (gold) and are collected by another ferromagnetic electrode (top). With the gate voltage off, the aligned spins pass through the channel and are collected at the other side (middle). With the gate voltage on, the field produces magnetic interaction that causes the spins to precess, like spinning tops in a gravity field. If the spins are not aligned with the direction of magnetization of the collector, no current can pass. In this way, the emitter-collector current is modulated by the gate electrode [52].

(c) Quantum computer

One of the most influential schemes is the nuclear spin based quantum computer. Here silicon donor nuclei serve as qubits, while donor electrons together with external gates provide single qubit (using an external magnetic field) and two-qubit operations (using electron-nuclear and electron-electron spin interactions). The donor electrons are essentially shuttles between different nuclear qubits and are controlled by external gate voltages. In addition, the final measurement is also supplied by the donor electrons by converting spin information into charge information. A significant advantage of silicon is that its most abundant isotope is spinless, thus providing a “quiet” environment for donor nuclear spin qubits [55]. In general, nuclear spins have very long coherence times because they do not strongly couple with their environment and are thus good candidates for qubits. However, this isolation from the environment also brings with it the baggage that individual nuclear spins are difficult to control. This is why donor electrons play a crucial role in the silicon computer scheme. Another potential advantage of a quantum
computer based on silicon is the prospect of using the vast resources available from the semiconductor chip industry.

![Fig. 1.8 Spin based Field effect transistor](image_url)
Fig. 1.9 Spin based quantum computer processor

Fig.1.9 shows the spin based quantum computer processor. Here the phosphorus atoms doped into a silicon substrate act as the quantum computing elements. The diagram shows one part of a larger array of phosphorus atoms in a hypothetical quantum computer. Each phosphorus nucleus embedded in the substrate has its own nuclear spin and each donates an electron, which in turn has its own spin. The state of the nuclear spins can be read and written by the outer electrodes, called “A gates” and the nuclear spins can be allowed to interact via the electrons, which are controlled with the center, or
"J gates". In a typical series of steps, the nuclear spins would be set with a pulse of a radio frequency magnetic field (top panel). Next, the electrons (red spheres) would be activated with the J gates to move between the phosphorus atoms (black circles with arrows), creating a quantum mechanical "entangled" state (middle panel). Finally, the gates are used again to read out the final quantum state of the array of phosphorus atoms via the spin state of the electrons (bottom panel) [52].

1.6 IMPORTANCE OF ZnS

There are generally eight II-VI semiconductors materials like ZnO, ZnS, ZnSe, ZnTe, CdO, CdS and CdTe, which are widely recognized. Among these materials, ZnS has been realized to be the potential material for extensive research, possible applications in optoelectronics and the potential generalization of results to other nanomaterials. ZnS is a wide band gap material with band gaps of 3.68 eV (zincblende) and 3.91eV (wurtzite). It displays a high refractive index of 2.2 and high transmittance of light in the visible region of the spectrum [56]. These properties make ZnS a strong candidate for optoelectronic devices. Wurtzite ZnS is one of the most important materials in photonics due to its high transmittance in the visible range and high index of refraction (~2.2). In recent years, nanocrystalline ZnS has been reported to have some characteristics, different from the bulk properties, which may extend its application range. Therefore, much attention has been focused on the synthesis of ZnS nanoparticles and films, and the exploration of their novel properties. Several approaches are available to obtain nanocrystalline ZnS. ZnS has been synthesized as nanowires, nanobelts, nanocombs, nanowindmills and nanohelices [57-60]. All of these are one-dimensional nanostructures. ZnS doped with Mn exhibits attractive light-emitting properties with increased optically active sites for application as efficient phosphors [61]. ZnS shows various luminescence properties such as photoluminescence [62], electroluminescence [63], mechanoluminescence and thermo luminescence [64], which enable it to be used in the fields of optical displays, sensors and lasers. Many efforts were made to study the electroluminescence properties of pure and rare earth doped ZnS nanocrystals [65, 66]. Furthermore, ZnS one dimensional nanostructures have been shown to facilitate optically pumped lasing [67]. Moreover, zinc sulfide is also widely used in photo catalysis [68].
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Recently much attention has been focused on the nanocrystalline ZnS layers because of the advantages and benefits offered by these layers in thin film solar cells. In these the effective optical path for absorption is much larger than the actual film thickness due to multiple reflections, light generated electrons and holes need to travel over a much shorter path and thus recombination losses are greatly reduced. This reduces the thickness of the constituent layers in nanostructured thin films solar cell to a few nanometers instead of several micrometers in the traditional thin film solar cells and tailors the energy band gap to a desired value by varying the particle size [69] there by allowing more design flexibility in the absorber window layers in the solar cell. Higher solar conversion efficiency of 10 % have been achieved using ZnS in nanoform in solar cells [70]. ZnS particles with nanometer dimensions showed novel electro-optical properties that arise from quantum confinement effects, which can be tuned with particle size. This feature highlights the interest on ZnS and enhances its applications in various fields. ZnS offers the advantages of wide energy band gap, higher optical transmittance, low cost and abundancy of the constituent elements that are less toxic and tunability of the energy band gap, lattice parameter and electron affinity by the addition of suitable dopant that could be perfectly matched with the absorber material, with a band gap between 1.3 eV and 1.6 eV. Therefore, it is worth to investigate undoped and doped ZnS as an alternative buffer/window layer to CdS.

ZnS based DMS in bulk, thin film and nanoforms have been widely investigated as ZnS has been identified as an excellent host semiconductor for supporting room-temperature ferromagnetism when doped with a variety of 3d transition metal ions.

1.7 FUNDAMENTAL PROPERTIES OF ZnS

(i) Crystal structure

The physical properties of a semiconductor are mostly structure derived. The crystal structure of ZnS compound is complicated due to the propensity to crystallize in two polymorphic structures. Some compounds crystallize in cubic zincblende structure and some others exhibit hexagonal structure. These two crystal structures are closely related being made up of tetrahedral bonding atoms. Structural transformation from one type to another can also occur in these compounds at high temperatures and high
pressures. For instance, ZnS exhibits a stable zincblende structure at room temperature with a few observations of stable wurtzite ZnS. The cubic zincblende and hexagonal wurtzite crystal structures are shown in Fig.1.10. In fact, the cubic zincblende and wurtzite crystal structures of ZnS (and also other II-VI semiconductors) are quite similar. In case of zincblende structure, stacking sequence of the close-packed planes, the (111) planes, within the zincblende crystal can be represented by a sequence of ABCABCABCABCABC. Each letter represents a different placement of the plane. This pattern continues through the entire crystal. However, if the stacking sequence of the (111) planes is altered from ABCABCABCABCABC pattern to ABABABABABAB, the crystal structure is said to be wurtzite crystal structure. Here, the stacking planes represent the (001) planes along the c-direction. The structure of wurtzite ZnS can be described as a number of alternating planes composed of tetrahedrally coordinated $S^{2-}$ and $Zn^{2+}$ ions, stacked alternatively along the c-axis. Because of this close relationship, wurtzite and zincblend can often be transformed from one to another. Although wurtzite is not stable in bulk ZnS, this hexagonal crystal structure can be formed at elevated temperatures. The transformation from zincblend to wurtzite ZnS occurs at 1020 °C. There are reports on the stable wurtzite ZnS, but all of them involve nanoscale materials [71].

(ii) Lattice parameters

Lattice parameters are considered important, when one has to develop semiconductor devices. There are mainly four factors which determine the lattice parameters of the semiconductors. (i) Free-electron concentration which affects the potential of the bottom of conduction band normally occupied by electrons. (ii) Concentration of impurities and defects and the difference in ionic radii between these defects and impurities with respect to substituted matrix ions. (iii) External strains, for example, those induced by temperature. On the other hand, the strict periodicity of the lattice is disturbed by many imperfections or defects. These imperfections or defects have a considerable controlling influence on mechanical, thermal, electrical and optical properties of semiconductors. They determine the plasticity, hardness, thermal and electrical conductivities. Commonly the lattice parameters of any crystalline material are
measured accurately by high-resolution X-ray diffraction (HRXRD). The lattice constant is 5.41 Å for the cubic form while the a-axis is 3.81 Å and the c-axis is 6.23 Å for the hexagonal form [72].

![Zinc blend and Wurtzite Crystal Structures](image)

Figure 1.10 The zincblend and wurtzite crystal structures. The blue represents the zinc atoms and the black represents the sulfur atoms.

(iii) Electronic band structure

The successful operation of any practical device critically depends on the band structure characteristics [73]. The transport properties of semiconducting compounds are sensitive to the band structure of valance band that contains more electrons and the structure of conduction band into which the electrons can be excited. The positions and form of the bands in a crystal are determined by its chemical composition, its symmetry and the nature of the constituent elements. These bands are also sensitive to temperature. The band structure can be determined by photoemission, photo reflection, cyclotron resonance, de Hass-Van Alphen effect, etc.

Depending upon the relative positions of the conduction and valence band edges in k-space, semiconductors are classified into direct and indirect band gap semiconductors. If the valence band maximum and conduction band minimum are situated at the same values of k or if \( k_f - k_i = 0 \) where \( k_i \) and \( k_f \) are the initial and final state
wave vectors of the electron respectively then it represents the direct band gap semiconductor. On the other hand, if the valence band maximum and conduction band minimum are situated at different values of k such that \( k_r k_i \neq 0 \) then it represents indirect band gap semiconductor. In this type of electron transition the excitation of electron from the top of the valence band to the bottom of the conduction band occurs with the aid of a phonon of right momentum. Since for ZnS the valence band and the conduction band edges occur at the same k-values, the material is called a direct band gap semiconductor. Recently the band structure was calculated using an empirical tight-binding Hamiltonian. Band gap between the occupied band and empty bands, optical band gap \( (E_g) \), of ZnS is about 3.68 eV.

(iv) Optical Properties

The optical properties of a semiconductor are associated with both intrinsic and extrinsic effects. Intrinsic effects include optical transitions that take place between the electrons in the conduction band and holes in the valence band and excitonic effects due to the Coulomb interaction. Extrinsic properties are related to dopants or defects, which usually create discrete electronic states in the band gap, and therefore influence both optical absorption and emission processes. As already mentioned ZnS is a direct band gap and transparent semiconductor material. ZnS films are transparent in the wavelength range of 0.3 - 2.5 \( \mu m \), and plasma edge lies between 2 and 4 \( \mu m \) depending on the carrier concentration. It is well known that a shift in the band gap edge appears with an increase in the carrier concentration. This shift is known as Burstein-Moss shift. Optical transitions in ZnS have been studied by a variety of experimental techniques such as optical absorption, transmission, reflection, spectroscopic, ellipsometry, photoluminescence, cathode luminescence, calorimetric spectroscopy, etc.

Room temperature PL spectrum of ZnS nanocrystals exhibits various visible emission properties and have been investigated extensively. The electron–phonon
Fig. 1.11 (a) Schematics of point defects that may occur in pure ZnS. (b) Schematic energy level diagram for the point defects in ZnS: \( I_s = \) interstitial sulfur, \( I_{Zn} = \) interstitial zinc, \( V_s = \) sulfur vacancy, and \( V_{Zn} = \) zinc vacancy. The levels are drawn corresponding to the peaks in the PL spectra of ZnS.
coupling in ZnS increases with the increase in crystallite size. The enhancement of electron-phonon coupling affects the optical properties of ZnS. The blue (430 nm), green (515 nm) and orange (620 nm) luminescence are exhibited for these ZnS nanocrystals due to different defect properties [74]. The blue emission is attributed to surface states of ZnS without any treatment, while the green and orange emission bands are assigned to the electron transfer from sulfur vacancies to interstitial sulfur states and the recombination between interstitial zinc states and zinc vacancies, respectively. The orange emission exhibits slower relaxation processes than the green luminescence because of the longer distance between luminescent sites. In summary, various visible emission characteristics are obtained in ZnS nanocrystals by changing the nature of defects in ZnS. Therefore, it is indispensable to design and control defect states to tune the emission properties of ZnS for application in light emitting displays, optoelectronic devices, etc. The schematic energy level diagram with the four types of point defects is shown in Fig. 1.11.

(v) Magnetic Properties

ZnS is a potential candidate for device applications because of its wide band gap (3.68 eV), large exciton binding energy (40 meV), high index of refraction (2.27 at 1 µm) and ZnS has been identified as an excellent host semiconductor for supporting room temperature ferromagnetism when doped with a variety of 3d transition metal ions. Recently sulfur vacancies-related \( d^0 \) ferromagnetism in undoped sphalerite ZnS nanoparticles is also observed [75].

1.8 REVIEW OF EARLIER WORK ON ZnS:Cr DMS NANOPARTICLES

Among the family of II–VI semiconductors, zinc sulfide (ZnS) is a technologically versatile and important semiconducting material for many photonic and optoelectronic applications, especially in nanocrystalline form. In particular luminescence studies showed that the physical properties of individual nanoparticles could be different from those of their bulk counterparts, originating from surface and quantum confinement effects [36]. Doping with optically active luminescent materials, the band-gap, PL
emissions, magnetic properties etc. in nanoparticles may be tailored depending on the impurity type, concentration and crystal dimensions. For example, ZnS:Te, ZnS:Cu$^{2+}$, ZnS:Ni$^{2+}$, ZnS:Mn$^{2+}$ nanocrystals show blue, green, orange emissions respectively [76-79]. These doped semiconducting nanocrystals can yield both high luminescence efficiencies and lifetime shortening from microseconds to nanoseconds at the same time. These spectacular results suggested that doped semiconductor nanocrystals form a new class of luminescent materials, with a wide range of applications in optoelectronic devices. Room temperature ferromagnetism in doped ZnS Nanoparticles reported in literature pave the way for applications in new generation spintronic devices. Till now room-temperature ferromagnetism has been reported in ZnS doped with various TM, such as Mn [17], Co [18], and Fe [19]. On the other hand, co-doping under appropriate conditions can also modulate the intrinsic point defects of the TM-doped DMS and influence the properties of the carriers to regulate the magnetism. Similarly presence of two different kinds of ions simultaneously in a host material produces luminescence which is completely different from the emission due to single ion and this property is very beneficial for optoelectronic device applications. Recently, many researchers have tried to dope two different types of ions into the ZnS based semiconductor nanocrystals to tune their luminescent properties.

Nanocrystalline ZnS doped with various transition metal and rare earth ions has been studied extensively by a large number of workers and the data available is voluminous. It is not possible to review all the work here. Only studies relevant to the present work are outlined here. Surprisingly, in spite of both applied and academic interests, Cr-doped ZnS has been least studied. In fact as per literature, there are only a few reports on Cr-doped ZnS. Even, the available data is of piece meal type and the earlier workers have studied only one or two aspects on ZnS:Cr nanocrystals/Films with just a few compositions of Cr. No single paper reports the complete characterization of ZnS:Cr nanoparticles over a wide range of compositions. In this context, a review of work done on Cr doped ZnS is presented in Table.1.1, whereas Table 1.2 presents the work done on co-doped ZnS samples.
<table>
<thead>
<tr>
<th>Authors and Ref. No.</th>
<th>Title of the paper</th>
<th>Form</th>
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<td>Kelley et al. [80]</td>
<td>Optical Absorption Spectra of Chromium-Doped Zinc Sulfide Crystals</td>
<td>Bulk Crystals</td>
<td>Optical absorption spectra of twinned cubic crystals of Cr doped zinc sulfide between 5000 and 29000 cm(^{-1}) investigated.</td>
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<td>Goetz et al. [81]</td>
<td>Influence of the impurity concentration on the microstructure of compound semiconductors - the example of ZnS:Cr optical spectra</td>
<td>Bulk Crystals</td>
<td>Cr concentration dependent emission and structural properties are reported.</td>
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<td>Graham et al. [82]</td>
<td>Laser performance of Cr(^{2+}) doped ZnS</td>
<td>Crystals</td>
<td>Laser performance of gas phase grown and diffusion doped Cr(^{2+}):ZnS crystals was investigated.</td>
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<td>Sato et al. [83]</td>
<td>Materials Design of Transparent and Half-Metallic Ferromagnets in V- or Cr-Doped ZnS, ZnSe and ZnTe without P- or N-type Doping Treatment</td>
<td>Thin Films</td>
<td>Materials design to fabricate the transparent and half-metallic ferromagnets in V or Cr-doped ZnS, ZnSe and ZnTe based upon ab initio electronic structure calculation with the local-spin-density-functional approximation was proposed.</td>
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<tr>
<td>Wang et al. [84]</td>
<td>Synthesis and spectroscopic properties of Cr doped ZnS crystalline thin films</td>
<td>Thin Films</td>
<td>Cr doped and undoped ZnS crystalline thin films of thicknesses from 100 nm to 20 (\mu)m were synthesized by PLD on (100) oriented Si substrates. Studied the Structural, Morphological and optical properties.</td>
</tr>
<tr>
<td>Ichino et al. [85]</td>
<td>Molecular beam epitaxy and structural properties of ZnCrS</td>
<td>Thin films</td>
<td>Zn(_{1-x})Cr(_x)S thin films were grown on GaP substrates by molecular beam epitaxy. Structural properties were carried out upto Cr content (x=0.04)</td>
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<td>Tablero et al. [86]</td>
<td>Electronic and magnetic properties of ZnS doped with Cr</td>
<td>Crystals</td>
<td>Photo-EPR and optical absorption measurements are presented for chromium doped ZnS</td>
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<td>Kim et al. [87]</td>
<td>Middle-infrared random lasing of Cr(^{2+}) doped ZnSe, ZnS, CdSe powders, powders imbedded in polymer liquid solutions, and polymer films</td>
<td>Polymer Films</td>
<td>Studied Mid-IR Photoluminescence and output emission intensity versus pump energy density</td>
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<tr>
<td>Gogoi et al. [88]</td>
<td>Chromium Doped ZnS Nanostructures: Structural and Optical Characteristics</td>
<td>Nanoparticles</td>
<td>Cr doped ZnS nanoparticles were fabricated by using physico-chemical route, Structural and optical studies were carried out</td>
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<tr>
<td>Martyshkin et al. [49]</td>
<td>Mid-IR random lasing of Cr-doped ZnS Nanocrystals</td>
<td>Nanoparticles</td>
<td>Cr doped ZnS formed by laser ablation of Cr doped polycrystalline ZnS targets in Ar atmosphere. PL and lasing in the mid-IR spectral region studied</td>
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<td>Gogoi et al. [89]</td>
<td>ZnS:Cr Nanostructures Building Fractals and Their Properties</td>
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<td>Synthesized by colloidal solution route, Structural and optical and morphological studies were carried out</td>
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<td>Rahdar et al. [90]</td>
<td>Study of structural and optical properties of ZnS:Cr nanoparticles synthesized by co-precipitation method</td>
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<td>Effect of Cr content on structural and optical properties of ZnS Nanoparticles investigated. Reported concentration dependent reduced crystallite size.</td>
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<td>Zhang et al. [91]</td>
<td>Laser diode end-pumped passively Q-switched Tm,Ho:YLF laser with Cr:ZnS as a saturable absorber</td>
<td>Crystal</td>
<td>Output performance of a continuous-wave laser diode end-pumped passively Q-switched Tm, Ho:YLF laser is demonstrated with a Cr:ZnS crystal as the saturable absorber</td>
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<td>Zeng et al. [92]</td>
<td>Optical and magnetic properties of Cr-doped ZnS nanocrystallites</td>
<td>Nanoparticles</td>
<td>Cr-doped ZnS (molar between 0.51% and 19.69%) nanocrystallites have been prepared through co-precipitation method. Structural optical and magnetic properties are studied.</td>
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Table 1.2 Earlier work done on co-doped ZnS

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<td>Yang et al. [93]</td>
<td>PL characteristics of ZnS nanocrystallites co-doped with Co(^{2+}) and Cu(^{2+})</td>
<td>Nanoparticles</td>
<td>High emission intensity in co-doped samples with different emission wavelengths varying with change in the impurity mole ratio of Cu(^{2+}) and Co(^{2+}).</td>
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<td>Yang et al. [94]</td>
<td>Photoluminescence properties of ZnS nanoparticles co-doped with Pb(^{2+}) and Cu(^{2+})</td>
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<td>Photoluminescence intensity increases as the ZnS nanoparticles co-doped with Pb(^{2+}) and Cu(^{2+})</td>
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<td>Yang et al. [95]</td>
<td>Luminescence of Cu(^{2+}) and In(^{3+}) co-activated ZnS nanoparticles</td>
<td>Nanoparticles</td>
<td>The emission wavelength and PL intensity of the co-doped samples varied with changing the impurity ratio of Cu(^{2+}) and In(^{3+}) ions.</td>
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<tr>
<td>Yang et al. [96]</td>
<td>Luminescence characteristics of ZnS nanoparticles co-doped with Ni(^{2+}) and Mn(^{2+})</td>
<td>Nanoparticles</td>
<td>Studied the luminescence properties of Ni(^{2+}) and Mn(^{2+}) co-doped ZnS nanocrystals. And observed that co-doping has remarkably enhanced the emission intensity.</td>
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<td>Yang et al. [97]</td>
<td>Photoluminescence characteristics of ZnS nanocrystallites co-doped with Cu(^{2+}) and Cd(^{2+})</td>
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<td>Novel luminescence phenomena (green emission) have been observed from the co-doped ZnS nanocrystals.</td>
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<td>Lee et al. [98]</td>
<td>Photoluminescence Characteristics of Mn- and Pr-doped ZnS Nanoparticles Optically Annealed with UV Illumination</td>
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<td>The integrated PL intensities for the nanoparticles annealed in air increased more markedly with the optical annealing time than those for the nanoparticles annealed in vacuum.</td>
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<td>Liu et al. [99]</td>
<td>Red light photoluminescence emission from Mn and Cd co-doped ZnS one-dimensional nanostructures</td>
<td>Nanorods</td>
<td>Red light emission from Mn and Cd co-doped ZnS one-dimensional nanostructures.</td>
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<td>Experiment Description</td>
<td>Nanoparticles</td>
<td>Notes</td>
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<td>Wang et al. [100]</td>
<td>Photo physical and photoluminescence properties of co-activated ZnS:Cu, Mn phosphors</td>
<td>Nanoparticles</td>
<td>Green luminescence of ZnS:Cu is quenched significantly when co-doped with Mn.</td>
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<td>Rao et al. [101]</td>
<td>Structural, optical and electrical properties of luminescent (ZnS)(_{1-x})(MnTe)(_x) powders</td>
<td>Powders</td>
<td>Optical, luminescence and electrical properties are investigated</td>
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<td>Rao et al. [102]</td>
<td>EPR and susceptibility studies on (ZnS)(_{1-x})(MnTe)(_x) powders</td>
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<td>Magnetic studies reported</td>
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<td>Thiyagarajan et al. [103]</td>
<td>A new red colour emitting phosphor – ZnS:Mn co-doped with Ba for electroluminescent (EL) displays</td>
<td>Powders</td>
<td>A new red emission in the range 538–623 nm in ZnS(_{1-x})Ba(_x)S:Mn(_0.01) (0 &lt; x &lt; 0.10) synthesized by carbothermal reduction method.</td>
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<td>Ma et al. [104]</td>
<td>ZnS:Cu,Co water-soluble after glow nanoparticles: synthesis, luminescence and potential applications</td>
<td>Nanoparticles</td>
<td>Luminescence properties reported</td>
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<td>Yang et al. [105]</td>
<td>Preparation and characteristics of yellow ZnS:Mn, Ce phosphor</td>
<td>Nanoparticles</td>
<td>Enhanced emission is induced in ZnS: (Mn, Ce) phosphor by indirect excitation,</td>
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<td>Mall et al. [106]</td>
<td>Optical studies of Cd(^{2+}) and Mn(^{2+}) Co-doped ZnS nanocrystals</td>
<td>Nanoparticles</td>
<td>In contrast to single-ion doped crystals, co-doped material exhibit red shift in PL spectrum.</td>
</tr>
<tr>
<td>Divya et al. [107]</td>
<td>Structural and optical characterization of ZnS nanoparticles co-doped with Mn and Te</td>
<td>Nanoparticles</td>
<td>Samples co-doped with Mn and Te, showed red emission with emission wavelength increasing with (Mn,Te) content in a narrow range of 605–611 nm.</td>
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<td>Murugadosss et al. [108]</td>
<td>Luminescence properties of co-doped ZnS:Ni,Mn and ZnS:Cu,Cd nanoparticles</td>
<td>Nanoparticles</td>
<td>Enhancement of luminescence reported</td>
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<tr>
<td>Ummartyotin et al. [109]</td>
<td>Synthesis and luminescence properties of ZnS and metal (Mn, Cu)-doped-ZnS ceramic powder</td>
<td>Nanoparticles</td>
<td>ZnS and metal-doped-ZnS exhibited intense, stable, and tunable emission covering the blue to red end of the visible spectrum.</td>
</tr>
</tbody>
</table>
1.9 JUSTIFICATION OF THE DOPANT SELECTION

(i) Reasons for selecting Cr as dopant

- Theoretical research on chromium based DMS supports the prospect of room temperature Ferromagnetism.
- Cr is an important transition-metal element with especially abundant electron shell structures, and its ionic radius (0.63 Å) is close to that of Zn$^{2+}$ (0.74 Å) which means Cr ion can easily penetrate into ZnS crystal lattice and substitute for Zn$^{2+}$ in the lattice.
- It possesses a high magnetic moment.

(ii) Reasons for selecting Cu as co-dopant

- Ionic radius of Cu$^{2+}$ (0.73 Å) is close to Zn$^{2+}$ (0.74 Å) it can easily penetrate into ZnS
- Theoretical research on Cu co-doped DMS supports the prospect of enhanced room temperature ferromagnetism

(iii) Reasons for selecting Mn as co-dopant

- It can be incorporated into a ZnS host in large proportions without altering the crystal structure.
- It has a relatively large magnetic moment and also creates stable polarized state due to its half filled 3d bands.
- It is electrically neutral in ZnS host, thus avoiding the formation of any acceptor or donor impurities in the crystal
- Mn is antiferromagnetic, which makes this system more clean in terms of metal precipitate induced ferromagnetism.
- The chemistry of the Mn atom is governed by its 4s$^2$ electrons, while its magnetic properties are determined by the 3d$^5$ shell. No other transition metal shows this dichotomy of behavior.
Chapter-I
Introduction and Literature Survey

1.10 SCOPE OF THE PRESENT WORK

Although ZnS based DMS in nanoform has been widely studied doped with a wide verity of transition metals and rare earth ions, investigations on Cr doped ZnS nanocrystals are sporadic. The review presented in section 1.8 on ZnS:Cr and co-doped DMS systems obviously shows that studies carried out by different workers seemed to have been narrowed down to a few characterization aspects only. Also no reports are available on co-doped samples of ZnS:Cr Nanoparticles. Surprisingly none of the earlier authors has used the chemical synthesis, although chemical route is simple and is capable of yielding nanoparticles of highest purity. Lack of data on Cr doped ZnS formed by chemical synthesis and also absence of reports on co-doped ZnS: Cr have motivated the present author to synthesize Zn$_{1-x}$Cr$_x$S, Zn$_{0.97-x}$Cu$_x$Cr$_{0.03}$S and Zn$_{0.97-x}$Mn$_x$Cr$_{0.03}$S nanoparticles using wet chemical method. In view of the spectacular phenomena exhibited by ZnS:Cr and co-doped ZnS nanoparticles and realizing their application potential, a systematic investigation on the preparation and characterization of the technologically promising ZnS:Cr and co-doped ZnS nanoparticles have been undertaken in the present investigation. The work reported in this thesis is therefore an attempt made to carry out comprehensive study on the preparation and characterization studies on ZnS:Cr and co-doped ZnS DMS quantum dots with facilities available/accessible to the authors in the country. This thesis reports room temperature ferromagnetism (RTFM) for the first time in Zn$_{1-x}$Cr$_x$S, Zn$_{0.97-x}$Cu$_x$Cr$_{0.03}$S and Zn$_{0.97-x}$Mn$_x$Cr$_{0.03}$S nanoparticles.

(i) In the present investigation, an attempt has been made to synthesize the DMS materials Zn$_{1-x}$Cr$_x$S ($x=0.00, 0.005, 0.01, 0.02, 0.03$ and $0.04$), Zn$_{0.97-x}$Cu$_x$Cr$_{0.03}$S ($x=0.01, 0.02, 0.03, 0.04$ and $0.05$) and Zn$_{0.97-x}$Mn$_x$Cr$_{0.03}$S ($x=0.00$ and $0.03$) in nanoform by chemical co-precipitation method at room temperature using EDTA as the capping agent.

(ii) In order to confirm the presence of chemical species in the synthesized nanoparticles, EDS measurements were performed.

(iii) Surface morphological studies were carried out using Scanning Electron Micro Scope (SEM).
(iii) Powder X-ray diffraction study was undertaken to investigate the structure and crystallite size of ZnS nanoparticles.

(iv) Grain size and structure of the nanoparticles were confirmed by transmission electron microscopy.

(v) DRS studies on all the samples were undertaken to investigate the variation in the band-gap with dopant concentrations.

(vi) Photoluminescence measurements on all the samples were carried out.

(vii) Molecular information of the samples was obtained by FTIR spectra.

(viii) Magnetisation studies were carried out using vibrating sample magnetometer (VSM) at room temperature to understand the magnetic behavior of the samples.

(ix) ESR measurements were done to confirm the magnetic nature of the samples.

The method of synthesis of the samples and the results of the above characterization studies are presented in the present thesis. The thesis comprises five chapters. The first chapter, while updating the understanding of DMS nanomaterials, presents a brief literature survey on ZnS based DMS systems relevant to the present study. The second chapter reviews briefly the synthesis and characterization techniques and describes the relevant working principles and design details of the techniques employed in the present work. Chapter III presents the results and discussion on Cr doped ZnS samples, whereas chapter IV comprises the results and discussion on co-doped ZnS:Cr samples. Chapter V presents the summary and important conclusions of the present investigation in a nutshell.
REFERENCES


Chapter I

Introduction and Literature Survey


