

## Chapter 1

### Magnetic Phenomena in Dilute Systems and Theoretical Considerations

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## **1.1 Introduction**

Dilute Magnetic semiconductors are composed of inert host semiconductor doped with localized spins and carriers (electron or holes) that are either itinerant, or localized on much longer length scale. In that sense they belong to the general family of correlated systems, which include a number of fascinating materials such as Cuprates, Manganites, Heavy fermions, and other Kondo lattice systems. The name dilute magnetic semiconductor implies that the system has only a small percentage of localized spins (Magnetic Impurities) [1].

The materials are obtained by alloying magnetic ions like transition metals or rare earths in the semiconductors. The host semiconductors are generally III-V, II-VI, IV-VI compounds or elemental semiconductors like Si and Ge. These semiconductors are crystallizing in Zinc blende, wurtzite or cubic structure and the crystallographic structure after alloying in dilute limit of impurity doping remains same. The magnetic ion substitutes at cation sites in the crystal or at interstitial depending on its size compared to the host. DMS shows a variety of physical phenomena and have semiconducting and magnetic characteristics together. These properties can be tuned by controlled doping of impurity [2].

Studies of magnetic interactions in Dilute Magnetic Semiconductor (DMS) systems are of great importance due to their potential application in SPINTRONICS. The electrical spin injection into the semiconductor

heterostructures has boosted the magnetic semiconductor research [3-6]. In order to use electron spin as information carrier, long spin coherence times are desirable [7]. Most of the studies are devoted to materials based on III-V and II-VI semiconductors [3]. Doping with transition metal impurities of suitable valance gives rise to ferromagnetic ordering in these dilute magnetic semiconductors.

The physical understanding of ferromagnetism was first established by T. Dietl et. al. [8,9]. He explained the phenomena of ferromagnetism through carrier mediation of charge carriers. The discovery of ferromagnetism in (In, Mn)As and (Ga, Mn)As prompted dilute magnetic semiconductors to be elementary materials for Spintronics [10,11], in addition they have a compatibility with semiconductors used in the present day electronic devices.

However, their curie temperatures ( $T_c$ ) are not high enough for real applications. Recently room temperature ferromagnetism has been reported by several groups in Mn: Ga-N [12-14] and Mn: Zn-O [15], where Mn substituting at Ga / Zn site brings holes in to the system. Varying the magnetic ion concentration varies the carrier densities in all these systems. Complication arises mostly due to the solubility of transition metals. It is difficult to achieve the desired concentration of TM in these systems either without clustering or without compound formation. Heavy doping of the magnetic impurities into semiconductors

without stable compound results in segregation or clustering of transition metals, viz results in uncertain Tc value [16].

The actual phase of compound responsible for ferromagnetic order and that contributes to the spin transport is not isolated so far. The objective is to synthesize materials which can have anisotropic band picture, which can be used for Spintronics application. Serious possible limitations of spin coherence in semiconductors are (a) Scattering of electrons at metal semiconductor interface. (b) Scattering due to lattice imperfection. (c) The interaction of electron spins with non-zero nuclear magnetic moment of host ions through Hyperfine Interaction [17].

In order to achieve carrier-mediated magnetism at room temperature, it is of great importance to increase the carrier densities by keeping TM impurities at low concentration. Conventionally magnetic ion concentration is varied to vary the charge carrier density. Mostly the semiconductors are of sp group metals or compounds and the conduction electron density can be varied by replacing the sp metals with different valence states. There may not be trouble of metal semiconductor interface and lattice imperfection if the host and impurities are of same chemical nature.

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We have studied the system  $\text{Fe}_{0.08}\text{Ge}_{0.992-x}\text{M}_x$  ( $\text{M} = \text{S, Se, Te, As, Sb, Bi, Sn, In}$ ), Depending on the valence of M in comparison to host, M represents Donor, Acceptor or Neutral states.

Work includes (I) Study of Hyperfine Interactions like Electric Quadrupole and Magnetic dipole Interactions at room temp and higher temp through  $\text{Fe}^{57}$  Mossbauer spectroscopy in  $\text{Fe}_{0.08}\text{Ge}_{0.992-x}\text{M}_x$ .

(II) The bulk properties with different characterization techniques like XRD, Hall effect, Magnetoresistance, resistivity and Magnetization measurement in  $\text{Fe}_{0.08}\text{Ge}_{0.992-x}\text{M}_x$ .

Chapter I gives the general introduction and brief summary of similar work done earlier in DMS. It includes Exchange interactions and various phenomenon related to dilute system.

Chapter II gives the theoretical background of Hyperfine interactions and concise details of Mossbauer spectroscopy. It shows experimental set up of Mossbauer spectrometer and development of instrumentation like temperature furnace which is used for recording Mossbauer data insitu.

Chapter III Describes techniques and theory of Hall effect and experimental setup, Four probe resistivity set up and comment on resistivity versus

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temperature, theory of Magnetoresistance measurement (Liq. He to Rt) and introduces fermisurface topology and some interpretation using Magnetoresistance measurement and AC susceptibility setup.

Chapter IV shows the data for the characterization in  $\text{Fe}_{0.008}\text{Ge}_{0.992-x}\text{M}_x$  Dilute Magnetic Semiconductor, where M is an impurity that is (In, Sn, As, Sb, Bi, S, Se, Te ). This Chapter also includes the results and discussion of the systems under investigation.

Chapter V Gives brief summary to the work and Future scope.

#### **1.2 Dilute alloys**

Alloys in which the solute atoms are in sufficiently small concentration, such that they have no/least effect on the electronic/crystal structure or phonon spectrum of the host. Though localized perturbation may result due to doping, in this regime the impurity atoms will act as independent scattering centers for conduction electrons. Hence the effect of N number of impurity atoms is just N times that of single impurity. This will only be possible if the solute atoms are widely separated, in other words there is no direct overlap interaction between them. In practice the composition range of the dilute alloys is restricted to  $< 2$  atomic % of solute atoms.

At higher solute concentrations the electronic structure or the phonon spectrum of the bulk alloys will start to suffer perturbations and the solute atoms may no longer be randomly distributed, such alloys will be described as concentrated alloys.

### **1.3 Shallow and Deep levels in semiconductors**

Chemical trend gives the variation of electronic structure of impurity doped crystals depending on the chemical property of the substituting atom. The impurities versus the chemical features of the host allow distinguishing between the deep and shallow impurity states. The fundamental properties of shallow level are described by the effective mass theory and are determined by the electron spectrum of the host [18,19]. The levels are tightly attached to the extrema either of the conduction band (donors) or of the valance band (acceptor). Properties of shallow level are determined by the long range tail of impurity potential [20]. The fundamental characteristic of shallow impurity levels is that their electron wave functions typically extend over many primitive unit cells.

Deep centers on the other hand, have a localized wave function over a large region of momentum space. Impurities with highly localized potential are expected to form deep centers. Such localized potentials can be caused by broken bonds, strain associated with the displacement of the atoms, and difference in electronegativity or core potentials between the impurity and host atoms[21-24].

#### **1.4 Transition metal Impurities in semiconductors**

The transition metals are the special group of impurities where the states of unfilled d shells play an important part in the formation of deep levels in semiconductors [25, 26]. They occur in different electronic configurations and charge states, depending on the positions of their energies within the band gap relative to Fermi level as discussed by Kikoin et. al.[27]. They greatly influence the electrical and optical properties of semiconductors. The determination of electronic states, the charge state as well as configuration and their dynamics are quite important for understanding the role of impurity atoms in such isolated states in semiconductor materials. The deep level in semiconductor system results from resonance scattering of the band electrons by the d levels of the unfilled shells rather than from the potential scattering as it takes place in the case of iso-electronic impurities. As a result these levels should have d rather than s or p character.

When the TM becomes part of some lattice the electron and spin density are redistributed between impurity atoms and its neighbors [28]. The covalent effect is the overlap of the impurity d - orbitals and host p - orbitals, it plays an important role in the formation of  $t_{2g}$  and  $e_g$  states of the unfilled d shells. The magnetic behavior is directly reflected by the configuration of electrons in the unfilled shells which is furthermore influenced by the neighboring ions. Therefore the local magnetism of isolated transition metal ions in semiconductors



can be used to investigate and identify their electronic states. Besides optical spectroscopy and electron resonance techniques, the nuclear methods can also determine the electronic configurations via the hyperfine interaction. In addition to the magnetically active configuration, it can detect the non magnetic states also.

### **1.5 Magnetic Anisotropy Energy (MAE)**

The tendency of the magnetization is to align along a specific spatial direction rather than randomly fluctuate over time. The MAE determines the stability of magnetization in bulk as well as in nano particle systems. MAE depends upon crystal structure (symmetry) and atomic composition. The exchange interaction among the electron spins is purely isotropic, the orbital magnetization via spin orbit interaction connects the spin magnetization to the atomic structure of magnetic material, and hence it gives magnetic anisotropy.

MAE is the interaction energy of magnetic moment of magnetic ion with its surrounding magnetic fields. Major contribution to it is from internal field and field which is applied externally.

$$\text{MAE } U = m_j g \mu (B_L + B_E)$$

Where  $B_L$  = Local or internal fields.

$B_E$  = Externally applied fields.

### 1.6 Local Moments

The system containing transition metal atoms show a rich variety of magnetic phenomena. The basic building blocks of these magnetic systems are the magnetic moments on the individual transition metal ions. The study of formation and stability of magnetic moment on an impurity in a host are of considerable importance in the area of magnetism. The susceptibility of these systems follows a Curie-Weiss behavior at high temperature [29].

$$\chi = \chi_0 + C / (T + \theta)$$

The first term is temperature independent Pauli susceptibility of host and the second term is the contribution from magnetic impurity. The parameter  $\theta$  is positive constant, called spin fluctuation temperature which is measure of moment stability.

The interest of theoretical and experimental investigations in this area is, under what condition does a moment on an impurity survive? And how it affects the conduction band electrons?

The mean local moment per magnetic atom in a random alloy as discussed by Rossister et. al. [30] is given by

$$\bar{\mu} = \mu_m \sum_{n=p}^N \frac{N!}{n!(N-n)!} C_A^n C_B^{N-n}$$

Where  $N$  is co-ordination number. If the impurity has a strong attractive potential, one or more electrons will be permanently trapped and localized in the potential well and form bound state. It will form bound state at energies below that of the conduction band with strong repulsive energy, it can also form at energy above the top of the band. If these states are far from the top of the conduction band they are of no consequence to the electrical resistivity. If the potential of the impurity is such that the localized energy level lies within the conduction band, its interaction can be accounted. Electron can enter into the impurity state from conduction band and leak back in to it. This interaction with the conduction electron can be regarded as scattering mechanism. As the impurity is a TM there is interaction in the d wave part of conduction electron wave function at energies near to d level.

This mechanism supports a magnetic moment or not is determined by the inter atomic coulomb interaction ( $U$ ) between occupying states. According to Anderson (1961) model the localized energy level can be occupied at most by two electrons, one having spin up and another having spin down. The interaction between these electrons causes splitting of level, if the energy of the state is above  $E_F$  it will be empty leading to net spin polarization. The product of coulomb interaction energy  $U$  and local density of states at impurity  $N_d(E_F)$  i.e. if  $U N_d(E_F) > 1$  a local moment will exist [31].

### **1.7 Spin Glass**

System comprising randomly frozen magnetic moments is called spin glass. If the concentration of magnetic impurities increases, they may start to interact with each other via the conduction electrons. The basis of this interaction lies in the exchange interaction. The absence of long range magnetic order is a direct consequence of randomness of spins. They fall into the class of disordered system with competing ferromagnetic and antiferromagnetic interactions, which generates frustration. In these systems the dominating exchange interaction is RKKY interaction via conduction electrons. They exhibit freezing transition to a low temperature phase where spins are aligned in fixed but random directions. At elevated temperature this alignment can be unfrozen corresponds to  $k_B T_0 \approx \Delta_s$ , where  $\Delta_s$  is the average interaction strength and  $T_0$  is spin glass freezing temperature [32]. The range of the interaction depends on the conduction electron mean free path, such behavior is typically observed at impurity concentration in range 0.1 to 10 % in the system.

### **1.8 Magnetic Clusters**

At concentration range 10 – 15% of magnetic ions the interaction become strong enough to condense small regions into magnetically aligned state. These regions will be associated with composition, concentration of magnetic species and the spin ordering results from the direct (Heisenberg) exchange. For each concentration of TM impurities there is separate situation that should be

identified. If the spin glass state exists the magnetic clusters will interact with spins in the surrounding matrix, which results in micromagnetic structure [33].

Above the freezing temperature the system becomes superparamagnetic until at higher temperature the magnetic alignment within the cluster destroys. If the particle concentration is small they can act as independent entities in non magnetic matrix.

In all situations for randomly distributed magnetic clusters there will be magnetic anisotropy described by an anisotropy constant  $k$  ( J/ m<sup>3</sup> ).If the volume of the particle is  $V$  then the energy required to alter the magnetization is  $\Delta E = kV$ . The rate of change of magnetization is given by

$$\frac{dM}{dt} = \frac{M}{\tau} = 10^9 M \exp \left( -\frac{\Delta E}{KBT} \right)$$

This equation allows to evaluate superparamagnetic freezing or blocking temperature  $T_B$  which gives a relaxation time  $\tau$ , typically it is of the order of 10<sup>2</sup> sec and can be measured by bulk magnetization measurements. Presence of magnetic field  $H$  causes reduction in height of energy barrier to

$$\Delta E = \left( 1 - \frac{HM_s}{2K} \right)$$

Here  $M_s$  is the magnetic moment associated with cluster.

### **1.9 Kondo Effect**

It is usually connected with the interaction between localized spin moments and itinerant electrons. This interaction leads to the formation of narrow resonance at Fermi level, which is called Abrikosov - suhl or Kondo resonance [34]. In the alloys that have a simple metal host and transition metal impurity, the resistivity results from the scattering of conduction electrons by localized spin fluctuation.

The additional scattering by thermal excitations of the spin fluctuations drives them off resonance and the resistivity decreases as temperature increases. This is possible only if the spin fluctuation time is long compared to their thermal fluctuations.

The transition from unitary limit to zero occurs through the temperature range  $T < T_{sf}$  to  $T > T_{sf}$  [35]. The resistivity increase or decrease with temperature depends upon their band structure and particularly the host conduction states are orthogonal to the impurity states [36]. For the spin  $s$  of conduction electrons and the spin  $S$  of impurity, interaction Hamiltonian involves local antiferromagnetic exchange is given by

$$H = J_k s \cdot S$$

where the kondo exchange interaction  $J_k$  is positive. In a static picture, the antiferromagnetic interaction gives rise to a screening of the local spin by

surrounding cloud of conduction electrons with opposite spins due to this magnetic field vanishes at low temperature  $T < T_{sf}$ .

### **1.10 Magnetic Properties.**

The magnetic properties of solids are important and attempts to understand them have led to deep insight into fundamental structure of metallic and non metallic solids. The transition elements and the rare earths show variety of magnetic phenomena, the ferromagnetism seen in TM and that in rare earths is quite different. In transition metals the partly filled 3d shells gives rise to magnetism whereas in the case of rare earths it is partly filled 4f states. The 4f states are deep inside but the d shells are more exposed to outer environment of atom, and hence it interacts more during bond formation. Thus the magnetism in TM impurity doped systems reflects wandering nature of these electrons interaction.

Ferromagnetism is the case of long-range interaction and ordered state, where spontaneous magnetization assumes large value. Where as antiferromagnetism is highly aligned state, the individual moments are arranged in self-compensatory way so that the overall spontaneous magnetism has got very small magnitude. The spins of the adjacent moments are antiparallel so that over all magnetism is zero. In ferrimagnetic materials the spins of two nearby sublattice ions are in opposite direction, but they are of unequal magnitude. Hence there is net

spontaneous magnetization. The temperature behavior of magnetization allows classifying the nature of these materials.

According Ewing [37] atom is permanent magnet free to align in any direction, in substance the orientation of each magnet was supposed to be due to mutual magnetic forces. Phenomena like hysteresis could be explained, a serious discrepancy was found when the thermal energy was comparable to magnetic potential energy estimated by this model. The thermal energy was found to be  $10^2$  times higher than that of magnetic anisotropy energy. It indicates that thermal energy will not allow stabilizing atomic magnets to any stable configuration, is in contrast to magnetic ordering. Hence one can say that there must be some additional force which makes the material ferromagnetic. Interaction of an atom with the rest of the crystal is represented by various exchange interactions

## **1.11 Exchange Interactions**

### **1.11.1 Direct exchange interactions**

The two neighboring atoms with direct overlap of electrons density can be explained by direct exchange interaction. The idea of exchange coupling between the spins of atoms first appeared in the work of Heitler and London (1927). The lobes of charge density of adjacent atoms has a tendency to form overlap regions and follows Pauli exclusion principle. Heisenberg [38] tried to explain the theory



of ferromagnetism. The magnetic coupling between two ions with a spin quantum number  $s$  can be represented by Heisenberg Hamiltonian

$$H_{ij} = -2J_{ij} s_i s_j$$

The exchange interaction  $J_{ij}$  is positive for ferromagnetic interaction and negative for antiferromagnetic interaction between two ions  $i$  and  $j$  and it falls rapidly with increase in distance.

### **1.11.2 Super-exchange Interactions**

The magnetic interactions in many magnetic oxides like NiO, MnO, FeO and other materials can not be explained by direct exchange interaction, because the ions on which the magnetic moment located are not in direct contact with each other.

Crystal structure of such material infers that the nonmagnetic anion such as oxygen is connected with two magnetic ions; spins of magnetic cations are coupled indirectly through intervening anion. Electron transfer can take place between a  $p_\sigma$  and the  $e_g$  orbitals or  $p_\pi$  and  $t_{2g}$  orbitals. Picture shows the electronic charge distribution round the cation and anion.

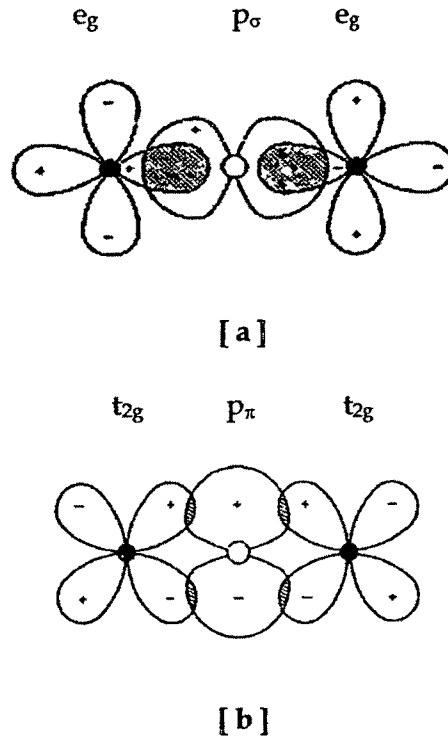


Fig :1.1 (a) and (b) shows orbital overlap in super-exchange interaction.

The interaction Hamiltonian yields

$$E = J S(S+1)/2 \pm B(S + 1/2)$$

Where the first term corresponds to spin exchange interaction energy, and the second term is displacement energy. For  $J > B$  the S electron cloud is symmetric round the anion, and hence no net transfer of charge from adjacent atom. Super-exchange interaction results in anti ferromagnetism.

### 1.11.3 Double exchange Interactions

The double exchange mechanism was proposed by Clarence Zener [39], for explaining the conductivity property of mixed valence solids. It is the

delocalization of electron cloud due to spin coupling with nearest neighbours. Doped perovskites in which two Mn ions with different charge states are attached to each other via oxygen ion  $O^{2-}$ . The transfer of electrons takes place in two steps, The movement of electron from oxygen to Mn followed by second electron transfer from Mn to empty orbital of oxygen hence the term double exchange is used. The interaction yields the values of displacement energy (B) higher than the exchange energy (J), For  $B > J$  the s electron cloud is not symmetric round the central oxygen atom. Double exchange results in ferromagnetism or Ferrimagnetism.

#### 1.11.4 RKKY Interactions

This is an important mechanism of coupling between localized magnetic moments, the magnetic moments can interact with each other via conduction electrons. The basis of this interaction lies in exchange interaction proposed by Ruderman and Kittel [40] viz. later on extended by Kasuya and Yosida [41] and now known as RKKY interaction. The exchange energy can be written as

$$E_{ex} = -J(r)\sigma \cdot s$$

$$J(r) = \text{exchange parameter}$$

Interaction results in Ferromagnetism or Anti ferromagnetism depending on the value of J. The exchange parameter is function of r and has asymptotic form

$$J(r) = \frac{\cos(2kr)}{r^3}$$

Equation shows that conduction electrons with spin antiparallel to the magnetic ion can have a lowest energy. Magnetic impurities polarize conduction electron spins in its vicinity; the distribution of electron spins has an oscillatory nature which decays with increasing distance as shown schematically in figure 2 below.

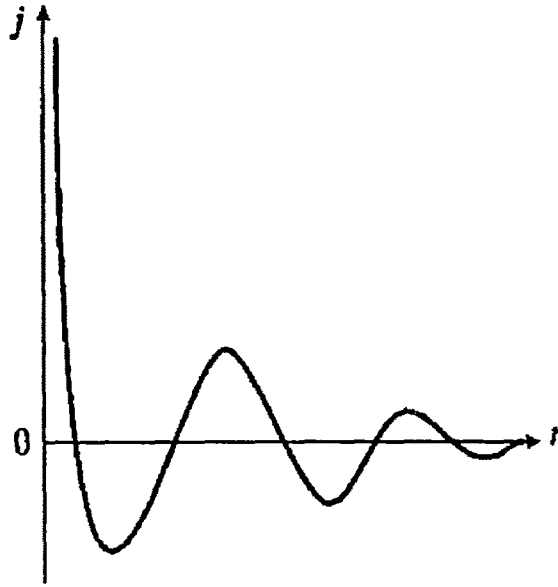


Fig :1.2 : the variation exchange parameter  $j$  with distance.

This effect mainly concerns with spins of conduction electrons and the charge density remains uniform in the system. For a magnetic ion situated in some solid if the another magnetic ion is in its spin density oscillation region, it will be a point of lower energy state.

### 1.12 Jahn Teller Effect

According to Jahn-Teller Theorem. If the ground state of an ion in a crystal is orbitally degenerate, with no other perturbation present, the crystal will distort to one of the lower symmetry in order to remove the degeneracy [42].

This effect is only seen if the orbital angular momentum is quenched by ligand fields. Orbital moments are normally quenched by ligand field when the  $t_{2g}$  orbitals are partially filled. The spin orbit energy due to unquenched orbital angular momentum can become comparable to Jahn Teller stabilization energy. In an ordered system the orbital state gets coupled with ordered spin through spin-orbital interaction gives rise to crystal distortion.

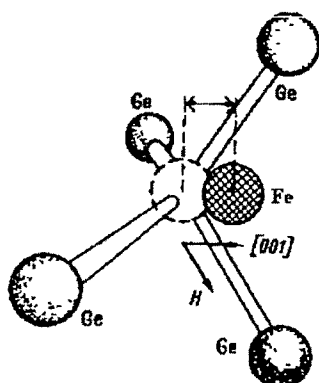


Fig :1.3 : Shows the Model of Jahn -Teller distortion in Fe substitutional in Ge  
The orbital contribution to the magnetic moments is quenched in cubic fields for many ions, and the observed moments are close to their spin values only. In a tetrahedral  $d^3, d^4, d^8$  and  $d^9$  orbital configuration splitting can occur through Jahn-

Teller distortion from cubic symmetry. For e.g. Tetrahedral Fe<sup>+2</sup> ions may give rise to Orthorhombic distortion, Figure 3 shows a Model picture in the Fe doped Germanium.

### 1.13 Hyperfine interaction

Hyperfine interactions are the interactions between nuclear moments and the surrounding electromagnetic fields. The interactions predominantly caused by the contribution of Overlap Polarization (OP), Conduction electron Polarization (CEP) and Core Polarization (CP).

$$B_{HF} = B_{CEP} + B_{CP} + B_{OP}$$

The overlap polarization is due to direct overlap of orbital between nearest neighbors. The long range exchange interaction can cause the conduction electron polarization (CEP). Core polarization occurs when a partly filled atomic d-shell is polarized by conduction electrons of the host. This polarization in turn polarizes the s electron of the atom.

An electron J at point  $r_j$  and having angular momentum (I) and spin s induces the field on the nucleus at  $r = 0$ , represented by an operator [43]

$$H'_{hf} = -2\beta \left\{ \frac{I_j}{r_j^3} + \frac{3r_j(r_j S_j)}{r_j^5} - \frac{S_j}{r_j^3} + \frac{8\pi^2}{3} S_j \delta(r_j) \right\}$$

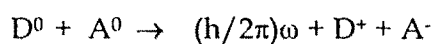
Where  $\beta$  is the Bohr Magneton. The first term describes the contribution of orbital current and is the contribution from (OP), second and third terms are

magnetic dipole contributions due to (CEP), Last term is contribution of (CP) known as Fermi Contact interaction [44 - 46]. The s electron has its probability distribution at nucleus. It turns out that closed s shell of these ions is polarized by exchange interaction with 3d uncompensated spins.

The electron density at the nucleus and interactions can be studied by Mossbauer effect. This technique is useful to investigate the interactions in solid materials from which the properties of extra nuclear electrons and about the solid state interatomic interactions can be deduced.

#### **1.14 Donor-Acceptor Pair**

The semiconductor doped with both the donor and the acceptor impurities are called compensated semiconductors. Some of the electrons from donors will be captured by vacancy or holes created by acceptors under the equilibrium condition. Optical excitation creates an electron and a hole in the conduction and valance band, respectively and these carriers can be trapped at donor (  $D^+$  ) and acceptor (  $A^-$  ) sites due to coulomb interaction which results in neutral (  $D^0$  ) and (  $A^0$  ) state. While returning from this state some of the electrons at neutral donors (  $D^0$  ) recombine with neutral acceptor (  $A^0$  ) by radiative transition. The electronic property of host can be strongly affected by this process. It can be represented by the equation



The donor acceptor pairs interaction is considered as the quasi-hydrogen molecules [ 47 ], which can exist in singlet or triplet state depending on spin orientation. The coulomb energy associated with donor-acceptor pair can be given by  $-e^2/\epsilon R$ . The energy associated with radiative transition is given by

$$(\hbar/2\pi)\omega = E_g - E_A - E_D + e^2/\epsilon R$$

$E_g$  is the band gap and  $E_A$ ,  $E_D$  are energy associated with acceptors and donors. Efros and Shklovskii [48] proposed the theory of percolation to magnetism of interacting donors. TM in semiconductors have a different magnetic moments depending on their position and charge state, the crystal field setup by DAP can cause considerable changes in magnetic properties.

### **1.15 General Mechanism of Ferromagnetism in DMS**

Ferromagnetisms is due to collection of identical magnetic spins of magnitude  $S$ , placed adjacent on an ordered lattice. The simplest one is isotropic case where the spin interactions are well described by Heisenberg Interaction Hamiltonian  $H_{ij} = -2J_{ij} s_i s_j$ . The exchange integral is  $J_{ij}$  depends only on the distance between spins. When the magnetic atom becomes part of some non magnetic host the exchange integral exponentially decay with increasing distance. For a magnetic ion the orbital causing magnetic moment is d or f and they are localized in a  $1-2 \text{ \AA}$  [1].



The most relevant feature of the DMS is the existence and interaction of two different electronic subsystems, the localized conduction (s band) and valence (p band) electrons of the host and localized (d or f state) electrons of magnetic ions. A model based on the mean field theory explains the ferromagnetism on the basis of sp-d exchange interaction also known as Zener ferromagnetism [49]. The spontaneous magnetization present in a hole/electron system, splits a valence/conduction band and the energy of carrier reduces. At the same time the free energy of localized spins increases due to the spontaneous magnetization. The localized hole or electron polarizes the surrounding magnetic ions through sp-d exchange interaction. At a certain temperature increase in free energy of localized spins and decrease in energy of carrier due to splitting balances and magnetic ordering could be observed.

Recent theoretical calculation as well as experimental work on (Ga, Mn)As and (Zn, Mn)Te by H. Ohno et. al. [7] strongly indicates that ferromagnetism is due to hole mediated p-d exchange interactions. According to this model the electron mediated system has got smaller magnitude of s-d exchange integral, hence ferromagnetism is difficult to occur in n type system.

Theoretical calculations of Ferromagnetism and its stability in (In, Mn)As discussed by H. Akai[50] shows that the ferromagnetic state is stable due to the double exchange at lower concentration of As. In higher concentration of As the

d holes created by Mn ion nearly compensates, which gives rise to spin glass like state. In the frame work of band structure when the exchange splitting is larger than band gap the double exchange mechanism dominates. The stability of ferromagnetism over antiferromagnetism depends on the ratio  $t^2/J_H$  i.e. square of nearest neighbors hopping ( $t$ ) and intra atomic exchange coupling  $J_H$ . According to this mechanism the energy gained for antiferromagnetism is nearly constant for low concentrations of the holes, and increase in hole density will stabilize the ferromagnetic state.

Considerable amount of experimental and theoretical investigations data has been accumulated for dilute magnetic semiconductors. Though the actual mechanism responsible for ferromagnetism observed are still in the preliminary state.

The attempts are made on the basis of model that ferromagnetism is due to local moments of magnetic ions interacts with each other via RKKY type interactions in a low carrier density regime. Explanation of this mechanism is still at question when carriers are holes instead of electrons.

In an elemental semiconductor [Si, Ge] doped with donor as well as acceptor, each of the hole and the electrons binds themselves to form shallow hydrogenic state. In a 1s state radial function is represented by

$$\phi_r \sim \exp \frac{-r}{a_b} \quad (1)$$

The characteristic Bohr radius  $a_b \sim 10^{-20} \text{ \AA}^3$ . Here the acceptor atoms are of magnetic (d or f) group elements. The exchange interactions arise between the spins of charge carriers and the spins of the magnetic impurity. And are represented by Hamiltonian [51]

$$H = \sum_{i,j} J(r_i, R_j) s_i S_j \quad (2)$$

Where  $s_i$  is the spin of donor at  $r_i$ , and  $S_j$  is the spin of the magnetic impurity at  $R_j$ . The exchange integral  $J(r_i, R_j)$  depends on orbital overlap between charge carrier and magnetic impurity. For the localized d, the charge carrier density nearer to it is given by

$$J(r_i, R_j) = J_0 \exp \frac{-2|r_i - R_j|}{a_b} \quad (3)$$

Where  $J_0$  is characteristic strength of exchange coupling,  $J_0 < 0$  for electron mediated system and  $0 < J_0$  for hole mediated system. For very low concentration of magnetic impurity concentration, the possibility direct overlap between orbital and hence possibility of anti ferromagnetic coupling can be neglected.

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