

STUDY OF FERROMAGNETISM IN A NEW HIGH T_C
FERROMAGNETIC SEMICONDUCTOR $K_2(S, Ge)$
WITHOUT TRANSITION METAL ELEMENT

By
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DECLARATION

I hereby declare that this thesis is my original work and has not been presented for a degree in any other University. All sources of material used for the thesis have been duly acknowledged.

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Getahun Kitil

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To
*My Father: **Kitil Dakssa***
and
*My Daughter: **Hawwii Bilisummaa***

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Abstract

In the present work we have studied the ferromagnetic properties of a high temperature magnetic semiconductor $K_2S(Si/Ge)$ which is free from any transition metal element. A model Hamiltonian taking into account, the exchange interaction of conduction electrons with localized electrons coming from Si/Ge and the host is studied using quantum field theory formalism of Green functions and also using spin wave theory to find expression for Curie temperature, T_C , magnetic susceptibility, χ and specific heat capacity of magnons excited. T_C, χ , and C are plotted with concentration of dopants (Si/Ge). The direct proportionality relation of the Curie temperature, T_c and concentration, x of Ge in $K_2(S, Ge)$ have been shown. The reduced magnetization vs the reduced temperature graph has been plotted. The plot shows convex curvature. The heat capacity vs temperature has also been plotted. The plot has got parabolic curve nature for low concentration, $x = 0.02$ and become linear for high concentration, $x > 0.08$, which are in good agreement with available experiments. We also plotted the graph for the reciprocal of the susceptibility versus temperature difference. As can be seen from the graph the material is in its ferromagnetic state for $T < 299.9K$. And $(1/\chi) = 0$ at $T = T_C = 300K$, and the graph is straight line after $T = 300K$. Which shows the material leaves its ferromagnetic state for $T = T_C$. Which are in good agreement with available experiments.

The study of ferromagnetism in a new high- T_c diluted
magnetic Semiconductor K_2S : Ge without Transition
metal element

Getahun Kitil Dakssa

February 2007

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Part I

Introduction

Semiconductor physics and magnetism are established subfields of condensed-matter physics that continue to reveal a rich variety of unusual phenomena, often in new types of solid-state materials. The properties of semiconductors are extraordinarily sensitive to impurity atoms, defects, and charges on external gates. Magnetism is a collective electronic phenomena with an ordered state that is often stable to exceptionally high temperatures. Magnetic orders when it is present, has a large impact on other material properties including transport and optical properties. In both semiconductor and magnetic cases, sophisticated and economically important technologies have been developed to exploit the unique electronic properties mainly for information storage and retrieval in the case of magnetism. The realization of materials that combine semiconducting behavior with robust magnetism has long been a dream of material physicists. One strategy for creating systems that are simultaneously semiconducting and magnetic, initiated in the late 1940s (Ga J et al, 1978; Kaczynski et al, 1978), is to introduce local moments into well understood semiconductors. The result is a new class of materials known as diluted magnetic semiconductors (DMSs)[1]. Over the past 15 years, building on a series of pioneering publications in the 1990s (Hayashi et al. 1997; Munekata et al, 1989, 1993; Ohno, 1998; ohno et al. 1992, 1996b; Van Esch et al. 1997), it has been established that several (*III-V*) compound semi conductors become ferromagnetic when heavily doped with Mn(*III-V*,Mn), and that the ferromagnetic transition temperatures can be well above 100 K. In semiconductors like GaAs and InAs the host semiconductor is doped with magnetic impurities, generally atoms of a transition metal such as manganese, iron, cobalt or chromium there is considerable current interest in these materials,because they appear to have great potential for use in spin-polarized electronics (spintronics) or in non-volatile computer memory (Ohno, 1998; Prinz, 1998). The discovery of ferromagnetism in (Ga,Mn)As at a relatively high temperature has sparked a rapid increase in the number and variety of such materials studied[2].

Most of the early work in the field focused on II-VI semiconductors, in which a semiconductor composed of a groupII and a groupVI element, such as CdTe, is doped with Mn. In the II-VI case, Mn and Cd have the same valence, hence each Mn ion introduces a spin-5/2 moment, but does not introduce any carriers, unless another dopant with a different valence,

such as N (a p -type dopant) is introduced. Undoped II-VI materials show spin glass behavior at low temperatures when the Mn concentration is above around 10%. Ferromagnetism with a Curie temperature of 2.5 K was observed in modulation-doped p -type $(Cd, Mn)Te$ (Diet et al. 1999). A major advance in the field occurred with the ability to dope Mn into $III - V$ semiconductors such as InAs and GaAs. These materials differ from the II-VI DMS because Mn has a different valence to group III elements, and whilst it still introduces a spin-5/2 moment, Mn plays the dual role of magnetic ion and acceptor. The low solubility of Mn in $III-V$ semiconductors was the main barrier to fabrication and it has only recently become possible to grow such materials using low-temperature molecular beam epitaxy (H. Ohno, 1996). Apart from their technological interest, from physics point of view the challenge is to understand their interesting magnetic properties and the interplay of this magnetism with their transport properties. The highest Curie temperatures (T_c s) found to date have been in $(Ga, Mn)N$, at 940 K (Sonoda et al, 2001; Diet, Matsukura and H. Ohno, 2001) and in $(Ga, Mn)P$: C, at 270 K (Theodoropolon et al, 2002). The $III - V$ DMS which has had the greatest amount of attention is $Ga_{1-x}Mn_xAs$, for which the Curie temperature has been found to be as high as 110 K in a sample with $x = 0.053$ (Matsukura et al, 1998). The presence of two metal insulator transitions (MITs) within the range $0.01 < x < 0.09$, at $x \sim 0.035$ and $x \sim 0.07$ (Van Esch et al, 1997; Ohno, 1999) is also quite unusual.

Ferromagnetism does not appear to be greatly affected by the metal-insulator transitions. Interestingly, the measured hole concentration appears to be about 10% to 30% of the Mn concentration whereas naively one would expect the hole and Mn concentrations to be equal. There also appears to be some x dependence of the ratio of the hole concentration to the Mn concentration, but this has not been systematically established (Ohno, 1999). The basic model for DMS is of a magnetically inert host semiconductor doped with localized spins, which may then be doped with carriers-electrons or holes. This is either through addition of another element, or, as is the case for Mn in $III-V$ materials, the magnetic ion can itself be an acceptor. If the carriers are localized, it is on much longer length scales than the localized spins. These materials are very interesting on a theoretical level because they are in a different limit from other magnetic systems that have been studied previously. There are a number of related magnetic systems in the general family of correlated electron systems: the cuprates, manganites, heavy fermions and Kondo lattice materials (Bhatt, Berciu, Kennett and Wan, 2002). In each of these systems there are small to moderate concentrations of localized spins. However, in many cases the magnetic impurities are a perturbation on the Fermi liquid of carriers in the host, and the magnetism can be understood as arising from a dilute Kondo system or an amorphous magnetic system with a carrier mediated spin-spin coupling described by the Ruderman-Kittel-Kasuya-Yosida (Ruderman and Kittel, 1954; Kasuya, 1956; Yosida, 1957) (RKKY) interaction. The essential difference is that the concentration of carriers here is either comparable to, or less than the concentration of magnetic impurities [1].

Hence an accurate description of the system requires carrier (fermions) and spin degree of freedom to be treated on equal footing. The observed ferromagnetism in (Ga,Mn)As is widely accepted to be due to anti-ferromagnetic exchange between itinerant holes and d-electrons localized on the Mn sites. The itinerant nature of the holes leads to an effective ferromagnetic coupling between Mn spins, which overwhelms the anti-ferromagnetic Mn-Mn super exchange interaction. There is less agreement on the detailed model, which can describe the observed ferromagnetism quantitatively. Terms in the Hamiltonian that should be taken into account include the kinetic energy of the holes, their Coulomb interactions with the Mn ions, the exchange between Mn spins and holes, the exchange (nearest-neighbour) between Mn spins, hole-hole interactions and disorder in the position of the Mn ions (Chattopadhyay et al., 2001). In the insulating (low x) regime, one expects hole-hole interactions and Mn-Mn super exchange to be relatively unimportant due to the low concentrations of Mn ions and holes, while the effects of the Coulomb interaction between Mn impurities and holes should lead to impurity orbital. A model that incorporates these features has been studied by Bericu and Bhatt (2001a, 2001b) the proximity to a MIT suggests that fluctuations due to disorder could be important for dopant densities up to 3-5 times those at the MIT, as is the case in non-magnetic semiconductors. Emphasis on K₂S based DMS, as it is the system for which there is no experimental data available. This is similar to the situation in high T_c cuprates, but unlike the cuprates there is a lower local moment density that is in common state saturation with the lattice, and the carriers and spins are local moment density.

The carriers and spins are not in the same band. Ge has been shown to act as an acceptor and as a source of local moments. These K₂S based material a phase we reserve for magnetic systems in which ferromagnetism is due primarily to coupling between magnetic element moments that is mediated by conduction-band electrons or valence-band holes. This definition implies that, in ferromagnetic semiconductors, magnetic properties can be influenced by the same assortment of variables that are available for other more conventional semiconductor electronic properties. In the best studied arsenide DMSs, semiconductor valence-band holes for formation of a ferromagnetic state. Efforts to increase their critical temperatures further run into incompletely understood fundamental limits on the ratio of the magnetic transition temperature to the Fermi temperature of the free-carrier systems and are also affected by the role of disorder in these heavily doped materials. The tension between achieving high curie temperatures and the desire for low, and therefore gate able, carrier densities is among the major issues in the study of these materials. After (In,Mn)As and (Ga,Mn)As were reported by (H. Ohno, 1998; H. Akinaga, 1997), many researchers have tried to discovery of high-curie temperature ferromagnetism experimentally as the first step for practical application of spintronics. So far not only experimentally but also theoretically [4] new DMSs have been proposed by first principles electronic structure calculations.

Stato and Katayama-Yoshida have proposed materials designs for high- T_c DMSs such as 3d-transition-metal (3d-TM) doped II-VI(ZnO,ZnS,ZnSe and ZnTe) and III-V(GaN,GaP,GaAs and GaSb) compound semiconductors. Some (3d-TM) doped $II-VI$ are experimentally synthesized like (Ga,Cr)N,(Zn,Cr)Te,(Zn,V)O and (Zn,Co)O[5]. However, it should be pointed out that these well-known DMSs include TM and their ferromagnetism is due to existence of 3d-electrons from transition metal elements. H.Katayama-Yoshida and his group investigate ferromagnetism in *Ge*-doped K_2S with out TM impurities

K_2S is an insulator[5] Its wide band-gap, and its transparency with visible light allows us to use it for an optical application. Moreover, such DMSs are environmentally friendly because it doesn't have any poisonous elements. In a similar manner to the case of K_2S , K. Kenmochii and K. Sato have reported *CaO*-related ferromagnetism. There are two guidelines to realize transparent, half-metallic and high- T_c DMSs. One is to satisfy the condition to form the localized magnetic moment in the highly correlated and deep-impurity band in K_2S . The other is to satisfy the condition to stabilize the half-metallic ferromagnetism by using Zener's double-exchange mechanism. Ferromagnetic semiconductors with out TM elements have great impact and potential for realization of the semiconductor spintronics in the next generation of high-speed, high-density and low power electronics.

The objectives of this work is to investigate ferromagnetism in Ge doped K_2S .

In the first chapter we have briefly discussed over the back ground of the diluted magnetic semiconductors, spin glasses, Half metallicferromagnets, Magnetic ordering, the classes of diluted magnetic semiconductors, Curie temperature of diluted magnetic semiconductors, exchange integral and ferromagnetic spin waves.

Chapter two wediscussed the therotical systems to solve the problem in chapter three we tried to solve the problem for the material under discussion and we give conculssion for the results obtained.

Chapter 1

BACKGROUND

1.1 Diluted Magnetic Semiconductors (DMSs)

Diluted magnetic semiconductors (DMSs) are alloys between non-magnetic semiconductor (eg *GaAs*) and a magnetic element, usually manganese (Mn)[1]. Therefore semiconductors and ferromagnetic properties coexist in these materials. This leads to important technological application since the charge and the spin of the electron could be used on the same device. At the same time, the underlying solid-state system has an enormous interest for basic science. The possibility of controlling both the charge and the spin of the electron has attracted the interest of researcher for several decades. Magnetic semiconductors, such as Europium chalcogenides and semi conducting spiels that have a periodic array of magnetic atoms were extensively studied in the 1960s. However ,the crystal structure of such magnetic semiconductors is completely different from that of the most commonly used semiconductors(eg .Si and GaAs) and the crystal growth of those materials is not notoriously difficult. On the other hand diluted magnetic semiconductors are based on widely known semiconductors like Ga as that can be doped with impurities to change their properties, usually to *p*- or *n* type. *II – VI* DMSs which have a host semiconductor made up of a group *II* and a group *VI* element of the periodic table, for example CdTe and *ZnS*. *III – V* DMSs are defined in an analogous way and the most important DMSs studied mainly due to their Curie temperature (*T_c*), the highest of all DMSs[3].

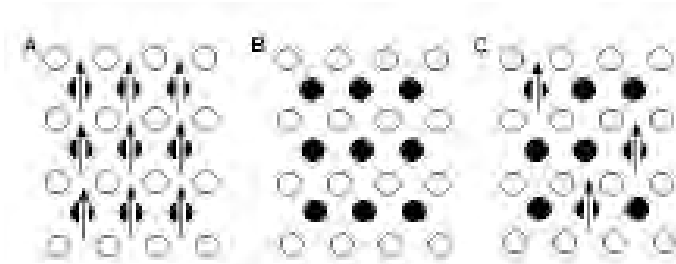


Figure.1.1 Three types of semiconductors: (a) amagnetic semiconductor , which has a prridic array of a magnetic element,(b) a non magnetic semiconductor ,which contains no

magnetic ions. and(c) diluted magnetic semiconductor (DMS), an alloy between nonmagnetic semiconductor and a magnetic element

In fact the interest in this field was boosted by the demonstration [16] in 1996 that ferromagnetic transition temperatures in excess of 100 K can be achieved in manganese doped gallium arsenide, (Ga,Mn)As, much higher than the previous record of only 7.5 K for (In,Mn)As [17]. Among the problems in the production of DMS samples is the low solubility of magnetic elements in III-V semiconductors. Since the magnetic effects are often proportional to the concentration of magnetic ions x , it is necessary to introduce disagreements (a few percent or not) for the material to develop cooperative effects. This requires doping that exceeds the solubility limit of III-V semiconductors. This problem was overcome by low-temperature non-equilibrium Molecular Beam epitaxial (MBE) growth. MBE is a physical deposition process (basically evaporation) that is carried out in ultra-high vacuum and at substrate temperature typically not exceeding 800 °C to the unobstructed molecular flow of the species to be deposited and the chemical cleanliness of the substrate surface, highly controlled growth of very thin epitaxial layers is possible. However, segregation of impurities during MBE growth is an obstacle in obtaining high concentration of magnetic ions. In addition after the sample is prepared and found to be ferromagnetic below T_c , it is usually necessary to show that ferromagnetism is not caused by the segregation of purely magnetic components, E.g. Mn as during the fabrication of (Ga,Mn)As but that Mn has been randomly substituted in the host semiconductor instead. Usually, the quality of the samples is examined by observing the reflection High-energy electron Diffraction (RHEED) patterns, which help determine if there is any phase segregation [1]. Despite all these difficulties, various DMSs have been fabricated. Higher T_c 's have been achieved by annealing. Optimally annealed samples of (Ga,Mn)As with $x > 0.08$ have been found to be ferromagnetic below $T_c = 127$ K [2]. More details will be presented. Another DMS that could find important applications is gallium nitride (Ga,Mn)N, with a reported T_c of 500 K [14].

1.1.1 Why We Study DMSs?

Technological Applications

As mentioned before, the possibility of using the spin as well as the charge of the electron for information processing will be a tremendous application in the technology and it is the basic idea of spin electronic or spintronics. In order for spintronics devices (the most cited example is the transistor of Datta and Das [9] to work, polarized carriers have to be introduced into a semiconductor, for example using ferromagnetic contacts. However, these devices have not been fabricated yet. The main reason is that it is very difficult to inject net spin polarization directly from a metal into a semiconductor [18], due to conductance mismatch between the

two materials that will cause big suppression of spintronic effects. It is at this point, where DMSs would become extremely useful because they would substitute the metallic contact and provide a FM contact that has a conductance similar to that of the semiconductor spintronic devices. A theory of spin- polarized transport in inhomogeneous magnetic semiconductors has been developed [19] similar to the standard theory of charge transport for p- n junctions. It is likely that these proposed applications for DMS would be realized only if ferromagnetism at room temperature can be achieved. The focus of this work, however, is on the physics of this ferromagnetism and there are indeed important motivations for their study from the point of view of basic science also.

Theoretical Interest

Diluted magnetic semiconductors bring together many topics of current interest in condensed matter theory. First, DMSs are correlated electron systems because ferromagnetism is carrier mediated i.e. the carriers interact with the localized spins of the magnetic ions. The physics of correlated electrons is without doubt one of the most important areas of research in condensed matter, and many other materials fall in this category e.g.. Superconductors and magnetes in addition there is now consensus[10] the effects of disorder are important to understand the physics of DMSs. The study of disordered systems has an enormous interest per. Se of particular importance is to understand the interplay between disorder and strong correlations and the role that disorder plays is important in transport and magnetism.

1.1.2 Motivation for numerical studies

There have a few theoretical studies of DMSs using a mean field approach [6,7,8]. They report the dependence of T_c on the carrier density, n , at fixed Mn concentration x . and calculate the magnetization as function of the temperature. However, it is well known that mean field theory (MFT) has sever limitations: (i) MFT calculation tend to overestimate the critical temperatures mainly because it neglects thermal fluctuation (ii) disorder in the Mn position is not taken into account within the Mn continuum approximation which can have a substantial impact on the ferromagnetism. Theoretical descriptions of DMS materials could be roughly classified in two categories. On other hand, the multi band nature of the problem is emphasized as a crucial aspect to quantitatively understand them. In this context the lattice does not play a key role and a continuum formulation is sufficient based on the disorder is considered on average, on the other hand, formulations based on the possible strong localization of carriers at the Mn- spin sites have also been proposed [4]. In this context a single impurity band description is considered sufficient for these materials. Still with in the impurity-band description is consider hopping not restricted to the Mn locations, some approaches to the or blew have used dynamical mean field [20] or reduced-

basis [21] approximations. An effective Hamiltonian for (Ga,Mn)As was derived in the dilute limit and studies in [22]. All these calculations are important in our effort to understand DMSs. However; it is desirable to obtain a more general view of the problem of ferromagnetism induced by a diluted set of spins and holes. To reach this goal it would be better to use techniques that do not rely on mean-field approximations and, in addition, select a model that has both the continuum and impurity band formulations as limiting cases, such an approach would provide information on potential procedures to further enhance T_c and clarify the role of the many parameters in the problem. In addition, these general considerations will be useful beyond the specific details of allowing us to reach conclusions for other DMSs. That is why a Monte Carlo study is strongly localized and free electron pictures explained before and it will help test their validity and provide information about the intermediate regime.

1.1.3 Why We Dilute Magnetic Semiconductors?

Diluted magnetic semiconductors (DMS's) have attracted considerable attention, because they hold the promise of using electron spin, in addition to its charge, for creating a new class of “spintronic” semiconductor devices with unprecedented functionality[10]. The suggested applications include, spin field effect transistors, which could allow for software reprogramming of the microprocessor hardware during run times semiconductor-based “spin valves” which would result in high-density non-volatile semiconductor memory chips and even “spin qubits” to be used as the basic building block for quantum computing. The attention was paid primarily to $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ for several reasons:

i) Significant breakthrough the non equilibrium growth of $\text{Mn}_x\text{Ga}_{1-x}\text{As}$, pioneered by H. Ohno and Co-workers, has enabled its practical growth with stoichiometric amount of Mn[11]. ii) this material has been experimentally confirmed to be ferromagnetic, with Curie temperature as high as 110 K. iii) $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ alloys are recently compatible with existing GaAs technology, resulting in the practical realization of device structure combining ferromagnetic and non-magnetic layers. Last, but by no means least, injection of spin-polarized holes has been observed experimentally and supported theoretically, proving that “spintronic” devices are feasible. Data storage media such as hard disks use the spin of electrons in a magnetic study interesting and it is of great technological importance to find DMS system with Curie temperature, T_c above room temperature (RT)[11] it was predicted theoretically, based on a Zener model, that an alloy of $\text{Mn}_x\text{Ga}_{1-x}\text{As}$, with an amount of Mn comparable to that used in $\text{Mn}_x\text{Ga}_{1-x}\text{As}$, should result in a Curie temperature exceeding room temperature. Of course, GaN is a technologically important material in its own right due to its applications in numerous devices, most notably the blue solid-state laser. A successful operation of spintronic devices requires more than a ferromagnetic semiconductor. It requires the support of spin-polarized transport so that spin polarized charge carriers may be injected into non-magnetic semiconductor. It was found by Korring-Kohn-Kostoker (KKR) that Mn

3d and N 2p hybridization results in an impurity band that makes the material half-metallic and therefore ideal for spin injection. This group also examined the theoretical limits to spin polarized transport in $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ with realistic $x = 0.063$ which was experimentally obtained by wurtzite by using first- principles calculations based on spin.

1.2 Spintronics

In course of years spintronics research has spread over all branches of condensed matter physics and materials science, Indeed, because of asymmetry in abundance of electric and magnetic elementary charges, random magnetic fields are weaker than random electric fields, so that electron spin may at the end be better information carrier than the electron charge in both classical and quantum information technologies[8]. With no doubt the most advanced are studies on metal magnetic multilayer, in which spin dependent electron scattering and tunneling are employed in reading heads of hard disks and random access magnetic memories (MRAMs) that are now reaching the production stage. However, particularly interesting appear ferromagnetic semiconductors as they combine resources of magnetic and semi conducting systems. Now we discuss issues we encounter developing wide-band gap semiconductor systems in which spontaneous magnetization persists to above room temperature . We are interested to describe advances in spintronics research on non-magnetic semiconductors in narrow-band gap semiconductors can serve for spin manipulation, while it is weakness in wide-band gap dielectric constant, and offer a worthwhile opportunity for developing functional quantum gates. Owing to a short-range character of the direct exchange interaction between tightly localized magnetic orbital, the coupling between d spins proceeds indirectly, via sp bands in tetra hardly coordinated diluted magnetic semiconductors (DMS) . Such a coupling is usually anti ferromagnetic if the sp bands are either entirely occupied or totally empty (super exchange) but can acquire a ferromagnetic character in the presence of free carriers (zener or RKKY mechanism). The discovery of carrier-induced ferromagnetism in Zinc-blend $III - V$ compounds containing a few percent of Mn in which T_c can exceed 100K followed by the prediction and the observation of ferromagnetism in p-type (II,Mn)-VI materials, opened up new areas for exploration. Spintronics[9]: exploits the electron spin along with its charge. In this material, there is a need for manipulating of spin and charge degrees of freedom to yield a desired electronic out come. All spintronic devices act in order that:

- i) Information is stored (written) in to spin as a particular spin orientations (up or down).
- ii) The spins, being attached to mobile electrons, carry the information along a wire, and
- iii) The information is read at the terminal. Spin orientation of conduction electrons survives for a relatively long time (nano seconds compared to tens of femto seconds during which electron momentum and energy decay), which make spintronic devices particularly attractive for memory, storage and potentially for quantum computing where electron spins

would represent a bit (called qubit) of information.

What is expected from these materials is to have a large commercial and economical impact in non-volatile memories (the information stays in the memory even if the electronic power is switched off, in contrast to semi conductor memories that we use). How we talk about previously, two the most important successfully technologies today in the world has been the Si integrated circuit (ICs) and the Data storage industry. Both continue to advance at a rapid pace. On the other hands, the data Storage industry has had a great and significant advance in the elaboration of different devices for this end. For example for magnetic hard disk driver Technology, a typical desktop computer drive today has a 40 GB, whereas in 1995 this capacity was approximately 1GB [2]. All integrate circuits operate controlling the flow of the carrier charge in this Case (electron and hole) through the semiconductor when we applied an electric field. This is the dominant parameter in this type of devices. For the case of Magnetic data storage, the dominant parameter is the spin of the electron where this characteristic intrinsic can be considered as the fundamental origin of the Magnetic moment. Into of the characteristic more important of ICs consist in your high speed Signal processing and excellent trustworthy, but the memory elements are volatile (The stored information is lost when the power is switched-off, as data is stored in Capacitors, i.e. (DRAMs).

A big advantage of magnetic memories technologies is that these are non-volatile since they employ ferromagnetic materials that by nature have reminiscend. A new field of the electronic opens the possibility for the study and understands of the properties a new material that tries combining the two-promise characteristic (charge and spin). This branch of the electronics is now like, semiconductor, spin transfer electronics” (spintronics). Spintronics or spin electronics, consist in the study of actives control and manipulation of spin degrees of freedom in solid-state system[10]. On this base several group of investigator in the world are trying looking for material which combining both properties, to create an amazing new generation of electronic devices. This characteristic open the possibility of developing spintronics devices that could be much smaller, (less than 100 nanometers) which consume less electricity and be more powerful for certain types of computations than is possible with electron-charge based system. The scientific community hope understand the behavior of electron spin in this kind of material, in order to provide something foundations new about solid state physics that will lead to a new generation of electronic devices based on the flow of spin in addition of the flow of charge.

1.3 The Spin Glasses

A spin glass has been defined [6,7] as a random metallic magnetic system in non-magnetic host characterized by a random freezing of moments without long-range order. It is well known that the magnetic coupling of the s and d electrons for the isolated impurities give rise to the so-called Kondo effect; the RKKY theory tells us that the effective coupling between the magnetic moments can be either ferromagnetic or antiferromagnetic; depending on the separation between two impurities. The spin glass state is defined as the state where the direction of the local magnetic moments is 0 [6]. The electronic structure of ferromagnetic and the spin glass states are calculated by using the Korringa-Kohn-Kostoker coherent potential approximation and local spin density approximation (KKR-CPA-LSDA) method [11]. A long-range interaction of spin glass interaction via the conduction electrons causes the freezing process, [9,11] at $T=T_f$ the independent isolated spins freeze out in random directions, these spins are, however, difficult to detect experimentally because of their very low concentration. However, their freezing reacts on the largest of the clusters, and they become rigid. These materials also possess some form of disorder in which the temperature variation of the magnetic susceptibility undergoes an unexpected change in shape that is, a cusp, at low magnetic field and zero frequency, at the freezing Temperature. And is characterized by Edwards and Anderson spin glass order parameter.

1.4 Half Metallic Ferromagnets

De Groot et al., [12] introduced the concept of half-metallic Ferromagnets, based on band structure phases. Due to the ferromagnetic decoupling, one of the spin subbands (generally the majority spin or up-spin subband) is metallic, whereas the Fermi level falls into the gap of the other (down-spin) subband. Obvious conditions for the occurrence of these new materials are the existence of narrow bands and energy gaps in the energy spectrum, and of strong ferromagnetic interactions. Half metals are the extreme case of strong Ferromagnets (or saturated Hubbard Ferromagnets), where not only 3d electrons are fully polarized, but also other (sp) down spin bands do not cross the Fermi level. These conditions can be met in Mn compounds particularly, as the large intra-atomic exchange results in the full alignment of local spins and thus in the exclusion of down spin electrons from the 3d shell [13]. Half-metallic behavior is found in CrO_2 and in $(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3$ ferromagnetic manganites. However, the high temperature paramagnetic states of these materials are very different, and will influence the thermal dependence of their properties. Fe_3O_4 is thought to be a ferromagnetic half metal [14].

Half-metallic system in EuO arises from the magnetic decoupling and band crossing in

paramagnetic semiconducting compound. The spin polarization of electrons for half metals is 100% at the Fermi level [13] the majority spins have a large density of states (DOS) which exhibits the metallic Fermi cut off at E_f , already seen by classical photoemission [12], where as the minority band spectrum shows a vanishing DOS from about 0.4 eV below E_F up to the Fermi level is the gap between E_F and the top of the occupied valance band for the minority band. Another more important feature is the gap between E_F and bottom of the conduction band for the minority band, which measures the minimum energy for an individual electronic spin reversal is similar than the overall exchange splitting between the two sub bands, and will vanish when the magnetic splitting is reduced. Only 50% polarization has been measured in NiMnSb [13] at low temperature, probably because the surface of this material is not so well ordered as buck for stoichiometric compounds, the least occupied down-spin band is filled and contains an integer number of electrons n . hence the magnetization is an integer (apart from a weak polarization of internal shells). For instance, the magnetization of NiMnSb and PtMnSb is $4.05\mu_B$ that of CrO_2 is $2.0\mu_B$. Note that the magnetization may be shared between atoms, for instance $3.8\mu_B$ for Mn, $0.2\mu_B$ for Ni respectively in NiMnSb. For solid solutions like intermediate-valiant manganities, each electron added at the Fermi level goes into the up spin band, thus the magnetization increases at the same rate as the number of electrons. For ferromagnetic solutions around $(\text{La}_{0.7}\text{Sr}_{0.3})\text{MnO}_3$, the magnetization increases with the slope (+1) as a function of La content. It is worth noting that the half-metal gap has nothing in common with the spin wave gap energy E_g that may arise from the magneto crystalline anisotropy. In the case of NiMnSb [12] as well as for ferromagnetic manganites [12], inelastic neutron scattering experiments show classical magnon excitations at low temperature, the analysis of which demonstrates that these systems are 3D Heisenberg magnets rather than 3D Ising systems. Θ is of the order of 10 K in NiMnSb and no more than 15 K in $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ respectively, these values are much smaller than those estimated for (about 600 K for NiMnSb at low temperatures). The magnetization for CrO_2 [12] follows a nice $T^{3/2}$ law between 2 and 60 K, thus the anisotropy gap should be small. Additional excitations (diffusive modes for manganites, Stoner-like modes for NiMnSb) have been observed at high energies and close to the Curie temperature. The analogy stops there, as paramagnetic states are different for both systems. Some exceptions may arise, magnetization will become localized when additional electrons in internal magnetic shell (as for instance in rare earths). Rather than being added at the Fermi level. The magnetization is fully saturated at low temperature i.e., the superposed high. Field susceptibility is ravishing by small, at least for a single crystal and magnetic field applied along the easy magnetization axis; the applied field slightly increases the half-metallic gap, but does not modify the occupation of both sub bands. Thermal excitation will destroy the half-metallic character below the Curie temperature T_C , as the splitting between the two sub bands decreases.

The half-metal gap can vanish well below T_c , before substantial decrease of magnetization [20]. A question is whether ferromagnetic materials can turn directly from half metallic to semi conducting behavior or not. In the paramagnetic state, atomic correlations still maintain a high local moment and expel the local minority- spin density, but the behavior of the disordered magnetic system and the exact nature of the gap are still not completely understood. The answer will be certainly brought by temperature dependent spin-resolved photoemission experiments, but also by the complete analysis of the resistivity and magnetic resistance. It is worth noting that the half-metal gap has nothing in common with the spin wave gap Δ that may arise from the magneto crystalline anisotropy. In the case of NiMnSb [13], as well as for ferromagnetic manganites [13], inelastic neutron scattering experiments show classical magnon excitations at low temperature, the analysis of which demonstrates that these systems are Heisenberg magnets rather than 3D Ising systems. Johnson et al. [13], and his group described half metals are applicable in a magneto optical effects, GMR application, spin electronic, etc. The current tunneling out of a ferromagnetic material is spin polarized. The largest polarization will of course be obtained with half metals. This can be used in:

- i) The spin injection in a normal metal can give information on the spin diffusion length in this metal.
- ii) Spin injection may act as a spin-breaking agent in superconductor, T.V entakesan et al., [15] have shown that the injection of a 100% polarized current in $YBaCuO$ leads to drastic decrease of the superconducting current I_c .
- iii) Half metals can also be used to build a spin transistor
- iv) STM, in order to visualize the orientation of the magnetic domains (as polarized tips).

1.5 Magnetic Ordering

Among the paramagnetic materials, it is possible especially at low temperatures to distinguish three different sub classes of magnetic materials called Ferro magnets, Anti Ferro magnets, or Ferri magnets. The basis for the distinction is provided by magnetic ordering with spontaneous magnetization, i.e. the alignment of spontaneous atomic or molecular moments with respect to one another and with respect to the crystallographic axes. The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials response to magnetic fields. This may be surprising to some, but all matter is magnetic It is just that some materials are much more magnetic than others are. The main distinction is that in materials there is a very strong interaction between moments. The magnetic behavior of materials can be classified in to the following five major groups; diamagnetism, para magnetism, ferromagnetism, ferromagnetic anti ferromagnetism. Dia-

magnetism and para magnetism are those that exhibit no collective magnetic interaction and are not magnetically ordered ferromagnetism, ferrimagnetisms and Anti ferromagnetism exhibit long-range magnetic order below certain critical temperature. Ferromagnetic and ferromagnetic materials are usually what we consider as being magnetic (i.e. be having like iron) where as diamagnetic, paramagnetic and anti ferromagnetic materials are so weakly magnetic that they are usually thought of as “nonmagnetic”.

1.5.1 Diamagnetism

It is a fundamental property of all matter, although it is usually very weak. It is due to the non cooperative behavior of orbiting electrons when exposed to an applied magnetic field. Diamagnetic substances are composed of atoms which have no magnetic moments (i.e. all the orbital shells are filled and there are no up paired electrons) .However when exposed to a field a negative magnetization is produced and thus the susceptibility is negative.

When the field is zero, the magnification is zero. The other characteristic behavior of diamagnetic materials is that the susceptibility is temperature in dependent. Some well known substances, in units of $10^{-8} \text{ m}^3 / \text{kg}$ include quartz (SiO_2), calcite (CaCO_3) and water (H_2O)

1.5.2 Paramagnetism

It is the class of materials that have a net magnetic moment due to on paired electrons in a partially filled orbital. One of the most important atoms with up paired electrons iron. However the individual magnetic moments do not interact magnetically, and like diamagnetism, the magnetization is zero with the field is removed. In the presence of a field, there is now a partial alignment of the atomic magnetic moments in the direction and positive susceptibility fig [7] In addition, the efficiency of the field in aligning the moments is opposed by the random dominating effects of temperature. This result in temperature dependent susceptibility is small (but larger than the Diamagnetic contribution) unless the temperature is very low ($\ll 100 \text{ K}$) or the field is varying. High paramagnetic susceptibility is independent of the applied field. Under these conditions, paramagnetic susceptibility is proportion to the total iron content. Many iron-bearing minerals are paramagnetic at room temperature. Some of them, in unit of $10^{-8} \text{ m}^3 / \text{kg}$ include montcorillonite (clay), Nontronite (Fe - rich clay) Biotitic (silicate) siderite (carbonate) and pyrite (sulfide).

1.5.3 Ferromagnetism

It is the properties of substances, which are capable of having magnetization in absence of external magnetic field. Even in absence of external magnetic field. The magnetization in a domain of ferromagnetic material has saturation value (M_s) The electron spin are

the sources of permanent magnetic moment. Ferromagnetism is found only in elements that have incomplete energy level such as 3d in *Fe*, *Ni* and *Co*; 4f level in *Gd*. However, not all elements possessing magnetic moment are ferromagnetic. Ferromagnetism and semiconducting properties coexist in magnetic Semiconductors, such as Europium Chalcogenides and Semiconducting spinels that have a periodic array of magnetic elements. Magnetic order exists only below certain Critical temperature (T_c) called the Curie point; $T_c = 774$ K, 1131 K, and 372 K for *Fe*, *Co*, and *Ni* respectively. Above T_c , all Ferro magnets show normal paramagnetic behavior. Ferromagnetic susceptibility which is high at the point can be expressed as, which means. This implies susceptibility obeys the Curie Weiss law. Below the Curie point, a ferromagnetic substance is composed of small, spontaneously magnetized regions called ferromagnetic domains. The total magnetic moment of the material is the vector sum of the magnetic moment of the individual domains. It is now known that these assumed domains really exist and are usually between 0.01 and 0.1 cm wide (ref. Fig.1.2).

1.5.4 Ferrimagnetism

In ionic compounds such as oxides, more complex forms of magnetic ordering can occur as a result of the crystal structure called ferrimagnetism. Ferrimagnetism is only special case of ferromagnetism, for example Fe_3O_4 is a well known ferrimagnetic material, Magnetite is a well-known ferrimagnetic material. It was considered ferrimagnetic until Neel in the 1940's provided the theoretical framework for understanding ferrimagnetism. The Curie temperature of ferrimagnetic materials is usually quite higher than the room temperature and saturation magnetization at 0 K can be the orders of 500 G. Fig.1.2d shows this property.

1.5.5 Antiferromagnetism

A more common situation is when the crystal symmetry is such that the localized dipole moment alignment at different lattice sites results in no net macroscopic magnetic field then such solid is referred to as antiferromagnetism. *MnO*, *FeO*, *CoO*, and *NiO*, are few well-known examples of antiferromagnetic ally ordered solids. The sub lattice moments of antiferromagnetic materials are exactly equal but opposite, the net magnetization is zero. The clue to antiferromagnetism is the behavior of susceptibility above a critical temperature (T_N). Above T_N , the susceptibility obeys the Curie Weiss law for Paramagnets but with a negative intercept in dictating negative exchange interactions (Fig.1.2b shows this group).

1.6 Curie Temperature

Even though electronic exchange forces in ferromagnets are very large, thermal energy eventually overcome the exchange and produce a randomizing effect. This occurs at a particular

temperature called curie temperature (T_c) below the Curie temperature, the ferromagnetism is ordered and above it, disordered that means the saturation magnetization goes to zero at the curie temperature. Atypical plot of magnetization vs. temperature for ferromagnetic material is shown below fig (1.2)

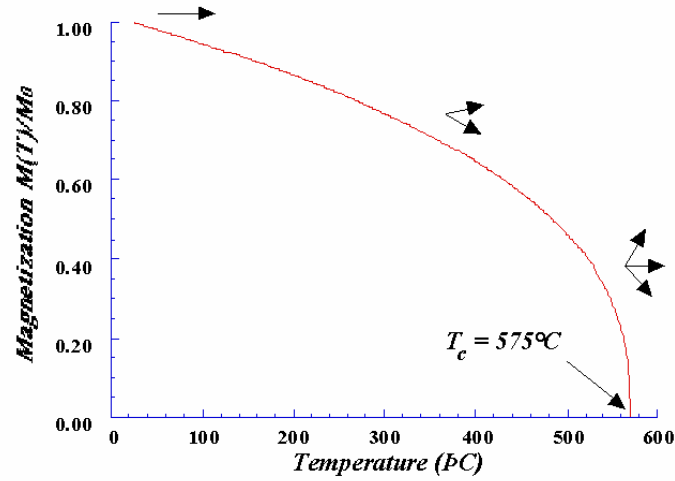


Fig1.2 spontaneous magnetization vs temperature.

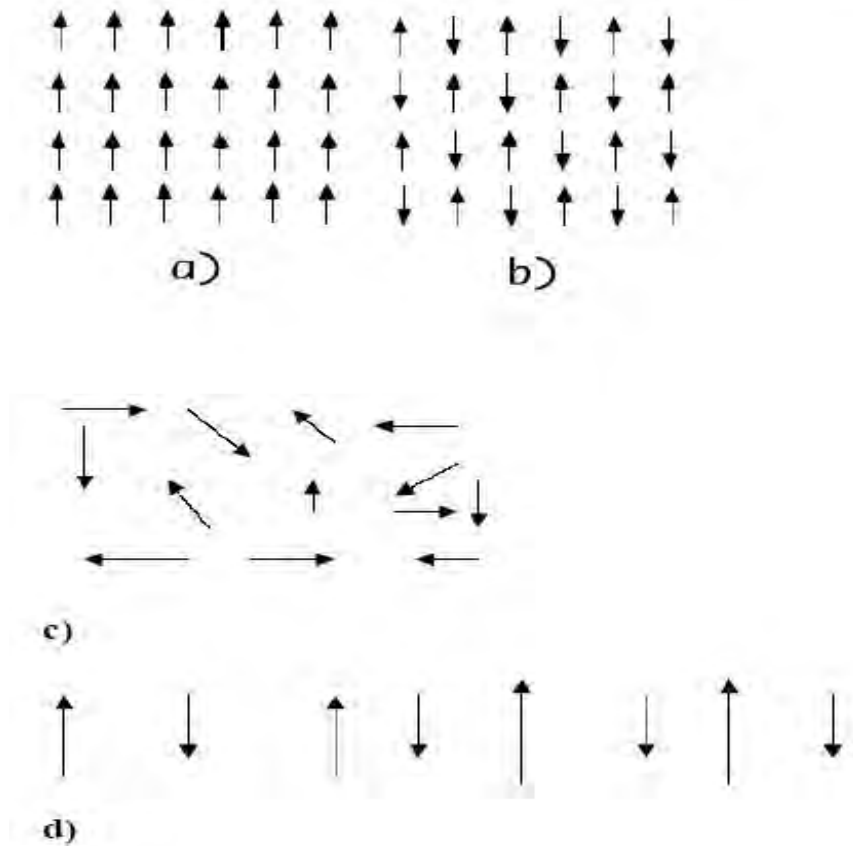


Fig.1.3: a) Ferromagnetic ordering. b) Antiferromagnetic ordering. c) diamagnetic

ordering. d) ferrimagnetic ordering.

The magnetic moments of the Fe^{3+} ions are Ferromagnetically coupled within specific c - planes, but anti ferromagnetically coupled between the planes. Above $-10^\circ C$, the spin moments lie in the c - plane but are slightly canted. This produces a weak spontaneous magnetization with the C - plane ($G_s = 0.4 Am/kg$); below $-10^\circ C$, the direction of the antiferromagnetism changes and becomes parallel to the c - axis there is no spin canting and hematite become a perfect antiferromagnet.

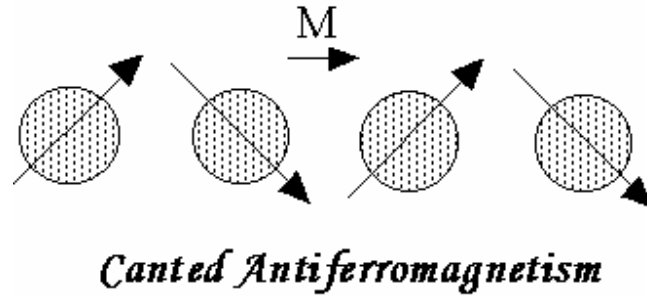


Fig1.4.The canted antiferromagnetism

1.7 The classification of Diluted Magnetic Semiconductors.

1.7.1 The II-VI Diluted Magnetic Semiconductors

These are the class of DMSs with a long-range ferro magnetic order and whose ferromagnetism is induced by holes ($10^{19} - 10^{20} cm^{-3}$) that are self supplied from doped Mn ions. Such a large number of holes inevitably change their transport and optical properties from semiconducting to metallic. They are obtained by doping Mn into non-magnetic semiconductors, such as ZnSe, ZnS, CdTe, CdSe, and HgSe[5]. The materials can be expressed as $(II_{1-x}Mn_x)VI$, which become $(Zn_{1-x}Mn_x)Se$, $(Cd_{1-x}Mn_x)Te$, and so on; where x is fraction of Mn that substitutes the II element ion at cation site. Mn substitutes on cat ion sites where it provides local moments but alters the host semiconductor valance and conduction bands very weakly. The magnetic interaction in II-VI DMSs is dominated by antiferromagnetic exchange among the Mn spins, which results in the paramagnetic, antiferromagnetic, or spin glass behavior of the material. It was not possible until very recently to make II-VI DMS ferromagnetic at low temperature ($< 2 K$). Doped II-VI materials show spin glass behavior at low temperature when the Mn concentration is above 10% . The most extensively studied

and understood DMS are based on II-VI materials in which Mn[9] has replaced a fraction of group II- element.

1.7.2 III-V Diluted Magnetic Semiconductors

An approach compatible with the semiconductors used in present- day electronics is to make non-magnetic III-V semiconductors magnetic, and even ferromagnetic, by introducing a high concentration of magnetic ions. The III-V diluted magnetic semiconductors (DMS) are materials, which exhibit spontaneous ferromagnetism mediated by holes in the valence band of the host semiconductor and thus represent new materials with promising applications in spintronics. They have attracted a great deal of attention from both experimental and theoretical points of view [9,11] and have distorted zinc-blend structure [6]. This shows that there is an open opportunity to achieve a proper ferromagnetic semiconductor device material for spintronics. they are obtained by doping Mn^{2+} into non magnetic semiconductor. And can be expressed as $(\text{III}_{1-x}\text{Mn}_x)\text{V}$. the commonly known examples of such DMSs are $(\text{Ga}_{1-x}\text{Mn}_x)\text{As}$, $(\text{In}_{1-x}\text{Mn}_x)\text{As}$, $(\text{Ga}_{1-x}\text{Mn}_x)\text{P}$, $(\text{Ga}_{1-x}\text{Mn}_x)\text{N}$, and $(\text{Ga}_{1-x}\text{Mn}_x)\text{Sb}$.

1.7.3 Oxide-Based Semiconductors

In contrast non-oxide semiconductors, the oxide semiconductors have many advantages[25]. Their wide band gaps make them transparent and suitable for application with shortwave length. They can be easily grown at low temperature even on a plastic substrate and are ecologically safe and durable besides being low in cost. In addition, the strong p-d exchange spins, and prerequisite are ZnO-based dms, TiO_2 based dms, and CaO based dms. Nano structured ZnO materials have received broad affection due to their distinguished in electronic, optics and photonics synthesis of ZnO thin film has been received on active field because of their application as sensor transducers and catalysts[26]. ZnO is semiconductor material of II-VI compound of the periodic table whose ionic city resides at the borderline between covalent and ionic semiconductor. The electro negative difference between zinc and oxygen produce a high degree of ionicity in its bond, which is considered in one of the compound much ions of this family. This characteristic causes a considerable repulsion of its electronic of charge; causing that their electronic more stable is wurtzite. In this structure the atoms are completely remote to be able to compensate this repulsion. Thus each atoms of zinc is surrounded by four cations of oxygen at the corners of a tetrahedron and vice versa. This tetrahedral coordination is typical of sp^3 covalent bonding.

1.7.4 New Ferromagnetic Materials Without Transition Metal Impurities

These groups of DMSs have been proposed by the first principle electronic structure calculations [6]. DMSs have been considered to be fundamental materials for spintronics. However, the highest Curie temperature T_c of (Ga,Mn)As is about 180 K, which is much lower than the room temperature. Therefore, many researchers have tried to fabricate high- T_c ferromagnets as a first step for a practical application of spintronics. Ferromagnetic semiconductors without TM elements have great impact and potential for realization of the semiconductor spintronics in the next generation of high speed, high density, low power and high frequency electronic [8]. The semiconductor spintronics as a practical technology was triggered by the discovery of the ferromagnetism in DMSs like Mn doped InAs or GaAs [7]. Most of the ferromagnetic DMSs are 3d TM doped ones [6]. Reports concerned with non-TM doped ferromagnetic DMSs are rare and these mechanisms or their validity of ferromagnetism remain the issue under discussion. I. S. Elfimov et al., proposed that CaO with a small concentration of Ca vacancies could exhibit ferromagnetism using model Hamiltonian and tight binding linear muffin-tin orbital (TBLMTO) band structure calculation. However non-magnetic solution is obtained due to the shallow and broad impurity band, which merges with the valance band. The hybridization between p orbital (or 4d orbital) of the impurities and the orbital of the host material is extremely larger than that of 3d TM in semiconductors since the p orbital (or 4d orbital) is more delocalized than 3d TM doped $III - V$ and $II - VI$ compound semiconductors are materials designed and some of them are tried for the fabrication and realized a room temperature ferromagnetism, such as $K_2(S,Ge)$, $(CaO)N$, $(CaO)C$, $(Ga,Cr)N$, $(Zn,Cr)Te$, $(Zn,V)O$, and $(Zn,Co)O$. We discussed about the new DMSs without transition metal element, now we are going to fix our discussion to the Ge doped DMS.

1.7.5 Ge Doped K_2S Magnetic Semiconductor

The discovery of carrier induced ferromagnetism in (In,Mn)As and (Ga,Mn)As has triggered the semiconductor spintronics as a promising technology[6,7,8] and diluted magnetic semiconductors (DMSs) have been considered to be fundamental material for spintronics[6]. However the highest Curie temperature (T_c) of (Ga,Mn,)As is about 180K, which is much lower than room temperature. Therefore researchers have tried to fabricate a high T_c ferromagnetic materials as the first step for practical application of spintronics with DMSs such as zinc-blend $CrAs$, $(Ti,Co)O_2$ and Mn-doped $CdGeP_2$. Sato and Katayama-yoshida have systematically investigated ferromagnetism in $K_2(S,Ge)$ DMS[8]. Number of tetrahedral sites just double the number of atoms per unit cell(lattice point)[28]. K_2S is an ionic solid (insulator or magnetic semiconductor)[6]. Number of tetrahedral sites just double the number

of atoms per unit cell (lattice point)[28]. It also has large lattice spacing and wide band gap due to the large ionic radius of K^+ and S^{2-} [28]. Its wide band gap make it transparent, half metallic and suitable for application with short wave length, high speed, high density, high frequency and low electric power. It is well known that the hybridization between p orbital (or $4d$ orbital) of impurities and orbital of the host material is extremely larger than that of $3d$ TM in the semiconductors since the P orbital (or $4d$ orbital) is more delocalized than $3d$ orbital [8]. In order to stabilize this the narrow p - impurity band was designed in the band gap of the semiconductor by controlling the hybridization [7]. The hybridization between the orbital of the host material can be controlled by changing the lattice spacing and p - impurity concentration [6]. K_2S is a transparent material with large band gap and anti CaF_2 crystal structure[8]. and has lattice spacing, $a = 7.391 \text{ \AA}$. Owing to its wide band gap and its large lattice spacing, a narrow $4d$ -impurity band in the band gap is achieved for stabilizing ferromagnetic state by using $4d$ impurity band in the band of semiconductors. From this result, We have possibility to create the localized magnetic moment at the impurity site in ferromagnetic state $K_2(S,Ge)$ and to design and to realize the ferromagnetic semiconductors without TM elements. The ion S^{2-} has been described [28]. This chalcogenic ion forms simple ionic lattice type with alkali and alkaline Earth metal cations. The coordination number of $K^+ = 4$ and $S^{2-} = 8$, and the $4S^{2-}$ ions form FCC structure and the 8 tetragonal site in FCC structure are present and occupied by K^+ ions. In order to estimate the stability of the ferromagnetic state the electronic structure and the total energy (E) of the ferromagnetic state and of the spin glass state were calculated in pseudo- binary systems by LSDA-KKR-CPA calculation to estimate the density of the ferromagnetic state [6].

T_C was estimated based up on the mean field approximations. Zener's double-exchange interaction in the present systems was long-range one and the magnetic and transport properties were not discussed. Ge impurity defects were controlled by thermal non-equilibrium crystal growth like low temperature molecular Beam epitaxy (MBE). The form of the potential was restricted to the muffin tin type [7]. The wave functions in respective muffin-tin spheres were expanded with the real harmonics up to $l = 2$ here l was the angular momentum defined at each site. The number of the calculated independently Sampling points in the first Brillion was 145 point [7] the adopted manners have been well utilized for treating magnetic property of DMSs. A lot of high- T_C DMS for $3d$ -TM doped $III - V$ and $II - VI$ compound semiconductors [6,7] are materials designed. That Shows the curie temperature of $K_2(S,Ge)$ as function of concentration of Ge impurities. The T_C 's fastly increase, approximately proportional to the concentration of Ge impurities due to the impurity screening effect indicating that the main contribution of ferromagnetism comes from Ziner's double-exchange interaction. For the compound, room temperature ferromagnetism is predicated around 8% impurity concentration. It is found that $K_2(S,Ge)$ is promising candidate for high- T_C ($T_C \sim 300 \text{ K}$) for 0.08 doping of Ge . The ferromagnetic double exchange mechanism gives T_C .

T_C is proportional to the impurity concentration x . Fluctuation of the magnetization direction in which low temperature is required is dominated by magnons and Stoner's excitations can be neglected. The origin of the ferromagnetic interaction in the p-impurity band which is partially occupied are introduced by substitution of the vacancies on k sites in the compound. The calculated T_C 's are shown as a function of additional hole doping in $K_2(S,Ge)$ on carrier concentration is understood by analyzing their DOS. According to Zener's double exchange mechanism, the ferromagnetic interaction originates from kinetic energy gain of itinerant $Ge - 4p$ electrons [7] this means that the ferromagnetic state is the most stable one when E_F is located at the higher impurity density of state in the impurity band with increasing hole concentration E_F is shifted to lower energy. The exchange splitting energy between up and down spin state becomes smaller with increasing electron concentration. However, at low concentration E_F is still located near the higher energy side of the impurity peak, then T_C 's remain around 300K. Based up on first-principles calculations of $K_2(S,Ge)$, it was demonstrated that, transparent, half metallic and room temperature ferromagnetic DMS could be designed even without transition metal elements. The results show that it is possible to fabricate the room temperature ferromagnets in $K_2(S,Ge)$ around 0.08 impurity concentration [8]. It was found that ferromagnetic ground states were readily achieved in $K_2(S,Ge)$ DMS without any transition metal elements [7].

1.8 Properties of $K_2(S,Ge)$ DMS

This section is devoted to the discussion of important properties of $K_2(S,Ge)$ DMS that have been established experimentally. Detailed reviews of the properties of these materials have been presented by H. Katayama-Yoshida and the coworkers [6,7]. And a more experimentally oriented discussion is given in [6]. Here the focus will be on the observations that are most important in considering theoretical models. It is generally accepted that the origin of ferromagnetism in $K_2(S,Ge)$ is due to Zener's double exchange interaction in the p-impurity band in the wide band gap of K_2S since this band is partially occupied by electrons.

It is also generally accepted that ferromagnetism occurs in this materials because of interactions that originates from kinetic energy gain of itinerant electrons or hole of the impurity band near the half filled states [7]. This shows an intimate connection between carriers and impurity spins. In contrast, in non magnetic doped semiconductors, such as phosphorus doped silicon, there has been no evidence for ferromagnetism due to carriers. This carrier mediated interaction in DMSs has a direct and important implication in the theoretical formulations will be described in chapter three. For $K_2(S,Ge)$ the Ge spin is $S=1$, as reported from electron paramagnetic resonance [4] and optical experiments [5]. Therefore, fundamental theories should be able to predict that $K_2(S,Ge)$ has ferromagnetic properties at a certain temperature below the Curie temperature and the ferromagnetic susceptibility

obeys Curie Weiss law.

1.9 Curie Temperature of Diluted Magnetic Semiconductors

The normal condition to DMSs will be realized when the materials are made to have T_c greater than room temperature since spintronic devices eventually have to be operated at room temperature[27].

The curie temperature of DMSs is studied from its first principles. We map total energies associated with rotation of the dopant atom magnetic moments on to the effective classical Heisenberg Hamiltonian which is treated in the mean-field approximation to find the curie temperature. The presence of donors strongly reduces the Curie temperature and gives rise to a ground state with a partial disorder of local moments.

1. It is in (Ga,Mn)N that the highest curie temperature, T_c of 940 K with $x = 0.03 - 0.05$ observed but controversial due to the deep acceptor level in (Ga,Mn)N, the carrier mediated ferromagnetism which has been thought as the origin of ferromagnetic transition temperature, $T_c = 10 - 110$ K for $x = 0.01 - 0.07$ where the value of x corresponding to the highest T_c is 111 K for $x = 0.053$ and continually rising to 160 K [5]. Unlike *II - VI* DMSs the *III - V* DMSs show ferromagnetic with relatively high Curie temperature[11] it has been shown that T_c and x , concentration of Mn in (GaMn)As, have direct proportionality approximated as $T_c \sim 2000x$ K up to $x = 0.053$ and the origin of ferromagnetic order in (GaMn)As is shown to be the Rudermann- kittel-kasuya-Yosida (RKKY) interaction [9,11] that is not very low density of carriers [28].

The exchange interactions in (GaMn)As have been calculated by Kudrnovsky et al, 2004 [5], using electronic calculations have utilized to estimate Curie temperature of the system as in the form

$$K_B T_c^{MFA} = \frac{2}{3} x \sum_{i(i \neq 0)} J_{i0}^{M_n, M_n} \quad (1.1)$$

The approaches that have been considered fall into a few general classes. Some groups have followed the approach treating ferromagnetism as arising from RKKY interactions. In the Heisenberg model [23].

T_c is readily found,

$$K_B T_c = \frac{\Delta E_F M(x) Z J (J + 1)}{6} \quad (1.2)$$

According to Weiss molecular-field approximation,

T_c is found to be [29],

$$K_B T_c = \frac{2nJS(S+1)}{3} \quad (1.3)$$

It should be emphasized that yet there does not appear to be any one approach or model that gives an adequate description of all properties for the entire phase diagram. The impurity band model is most likely to be applicable in the metallic phase, and cannot describe the insulating phase unless impurity states are included explicitly [35]. The highest Curie temperature of (Ga,Mn)As is about 180 K, which is much lower than room temperature [30]. Therefore, many researchers have tried to fabricate a high T_c Ferro magnet as the first step for a practical application of spintronics with DMSs such as Zinc blend CrAs, (TiCo)O₂ and Mn-doped *CdGeP₂*. So far, not only experimentally but also theoretically new

DMSs have been proposed by the first-principles electronic calculations. T_c is estimated based up on the mean field approximation (MFA) by mapping total energy difference ΔE on the Heisenberg model. Where x was the concentration of the do pant atom. It is not obvious if the magnetic interaction is long-ranged in the present Ca(O,C), Ca(O,N) or K₂(S,Ge). If it is 20, MFA gives accurate T_c . MFA estimates T_c for DMSs with in 5 – 10% errors compared to the random phase approximation (RPA) in which the spin wave fluctuation is taken into account [8]. The dependence of T_c of K₂(S,Ge) on carrier concentration is understood by analyzing their DOS [8]. Hiroshi Katayama- Yoshida and this team reported. *Ge* doped K₂S are promising candidate for high T_c ($T_c \sim 350$ K for 5% doping of Ge) [7].

1.10 Exchange Interaction

The Pauli exclusion principle exerts a powerful influence on the energetic of a collection of electrons through their relative intrinsic spin orientations [31,32]. The columbic repulsion energy between pairs of electrons with a parallel spin configuration is lower than for pairs of electrons with anti parallel spins: in this case, ferromagnetic (parallel) spin ordering is favored. This difference in columbic energies for different spin configuration is the exchange interaction energy [33]. The Hartree-Folck exchange-interactions responsible for ferromagnetism and anti ferromagnetism may be readily appreciated by considering the singlets (electron spins anti Para ell) and the triplet (electron spins Parallel) states of the H_2 molecule [31]. This is a two electrons problem for a system of two atoms at sites i and j ; where the exchange integral J_{ij} is given by;

$$J_{ij} = \frac{1}{2} (E_s - E_t) \quad (1.4)$$

i.e. half the energy difference between the singlets (symmetric) and the triplet (anti symmetric) state. It is apparent that the anti system metric state has the lowest energy if $J_{ij} > 0$, and the symmetric state has the lowest energy if $J_{ij} < 0$. These correspond respectively, to an elementary ferromagnetic parallel in the anti-ferromagnetic states, the

spins being Parallel in ferromagnetic state and anti parallel in the anti-ferromagnetic states. We may write the energy difference in equ. (1.4) in the form:

$$E_{exch} = -2J_{ij}S_i.S_j \quad (1.5)$$

Where $S_i = S_j = \frac{1}{2}$ for the case of single electron. For the case where several spins interact, we write the total exchange energy as;

$$H_{exch} = -2 \sum_{ij} J_{ij}S_i.S_j \quad (1.6)$$

This is Heisenberg Hamiltonian[35]. The value of J_{ij} depends on the ratio $\frac{R}{R_0}$, where $R = R_i - r_j$ which we shall replace later on by δ is the inter atomic distance and R_0 is the radius of the orbit of the electrons (d electrons in transition metals) Heisenberg in his original work introduces J_{jj} as the direct exchange integral between electrons on different orbital on different neighboring atoms). In practice it appears that this mechanism is small; in ionic crystal J_{jj} is due to super exchange; and in rare earth metals it is an indirect exchange, mechanism. The mean field theory of ferromagnetism predicts an exponential temperature dependence of the magnetization at very low temperature [31,36] in disagreement with $T^{3/2}$ power-law observed experimentally. This discrepancy arises because mean-field theory does not properly take account of low energy excitation. The magnetic coupling of the impurity spin is most probably caused by exchange of the $J_{ij}S_i.S_j$, where S_j is the spin of the localized carrier [32]. This exchange interaction between the conduction carriers and the localized moment of the magnetic ions can alter drastically the transport, optical and magnetic properties of the host semiconductor. In the extreme case, the interaction may induce ferromagnetic phase transition where RKKY interaction between the impurity spins via delocalized carriers is responsible for transition. The anti-ferromagnetic exchange between the impurity spin S_i and the charge carriers S_j is proportional to the probability of finding the charge carriers trapped at r_j near the impurity spin at r_i [4]. Pair exchange interaction in DMS between magnetic atoms and the impurity concentrations allows one to address in detail the character of magnetic excitations [37,39]. We can establish an approximate connection between the exchange integral J and the Curie temperature T_c . Suppose that the atom under consideration has Z nearest neighbors, each connected with the central atom by the interaction J . For more distinct neighbors we can take J as zero.

1.11 Spin Wave excitation and Magnetization

In solid-state physics, Bloch established the concept of spin waves in 1930[27,33,36]. The spin waves exist in magnetic materials and are important excitations. It is a common experimen-

tal observation that the magnetization M of a ferromagnetic material decreases when the temperature is raised from absolute zero. At the absolute zero the ionic magnetic moments are all oriented parallel to the applied field. If the temperature is raised, there will be some misalign the total magnetization will decrease from its value at absolute zero. The simple relation can represent the decrease from its value at a very low temperature.

$$M = M_0 (1 - \alpha T^n) \quad (1.7)$$

Where M_0 the magnetization at the 0 K, and $n = \frac{3}{2}$. This is known as the famous $T^{3/2}$ law of Bloch. The low-lying energy states of spin system coupled by exchange interactions are wave like, as shown by Bloch for ferromagnetism [49] the waves are called the spin waves. The quantized spin wave is called a magnon. The spin waves have been studied for all types of ordered spin arrays including ferromagnetic arrays.

Chapter 2

Analytical Techniques

In the present work we have used the Green's function formalism and Mean field theory of ferromagnetism to obtain the expression for ferromagnetic transition temperature and the number of magnons excited at temperature T , and the thermodynamic properties of magnons, magnon heat capacity. There is a great deal of similarity between the quantum field theory and the theories based on statistical mechanics as far as the many body aspect are concerned. The starting point for attacking the many body problems is to express the Hamiltonian describing the system in terms of the creation and annihilation operation. Both quantum mechanical operators and statistical Mechanics are concerned with the averages of the quantum-mechanical operators, but in quantum field theory one usually considers averages over the ground state of the system ($T = 0$), where as in statistical mechanics one is interested in the ensemble averages ($T - T_c$).

2.1 The Green's Function Formalism

The Green functions play the most important part in the field theoretical treatment of the many body problem, and are especially useful for summing over the restricted classes of perturbation theory of diagrams, and also are very powerful when combined with spectral representations. and also they are flexible enough to describe the effects of retarded interactions and all quantities of physical interest like thermodynamic properties can be derived from them. There are different types of Green functions, or propagators: one particle, two-particle... n particles, advanced, retarded, zero temperature, finite-temperature, real-time, imaginary time[40],

$$G_{kk'}(t - t') = \ll b_k(t); b_{k'}^{\dagger}(t') \gg = -i\theta(t - t') - \langle [b_k(t), b_{k'}^{\dagger}(t')] \rangle \quad (2.1)$$

denotes a Heaviside step function, and given by[41]

$$\begin{aligned}\theta(t - t') &= 1 \text{ if } t > t' \\ \theta(t - t') &= 0 \text{ if } t < t'\end{aligned}\tag{2.2}$$

$$G_{kk'}(t - t') = \langle \langle b_k(t), b_{k'}^+(t') \rangle \rangle = \langle \langle b_k, b_{k'}^+ \rangle \rangle\tag{2.3}$$

In order to obtain equation of motion we differentiate equ. (2.1) With respect to t and multiplying both sides of 2.3 by i

$$i \frac{d}{dt} G_{kk'}(t, t') = i \frac{d}{dt} \langle \langle b_k(t), b_{k'}^+(t') \rangle \rangle_r = \delta(t - t') \langle [b_k(t), b_{k'}^+(t')] \rangle + \langle \langle [b_k(t), H], b_{k'}^+(t') \rangle \rangle\tag{2.4}$$

To solve equ. (2.4) it is convenient to work with the Fourier transformation of this equation.

Now let $G_{kk'}(\omega)$ be the Fourier transform of $G_{kk'}(t - t')$, such that

$$G_{kk'}(t - t') = \int_{-\infty}^{\infty} G_{kk'}(\omega) e^{-i\omega(t-t')} d\omega,\tag{2.5}$$

and

$$G_{kk'}(\omega) = \int_{-\infty}^{\infty} G_{kk'}(t = t') e^{i\omega(t-t')} d(t - t')\tag{2.6}$$

In addition, the delta function can be defined as

$$\delta(t - t') = \int_{-\infty}^{\infty} e^{-i\omega(t-t')} d\omega,\tag{2.7}$$

Using equation (2.5), (2.6) and (2.7) in equation 2.4

we have got,

$$\omega G_{kk'}(\omega) = \langle [b_k(t), b_{k'}^+(t')] \rangle \omega + \langle \langle [b_k(t), H], b_{k'}^+(t') \rangle \rangle \omega\tag{2.8}$$

Where $i \frac{d}{dt} b_k(t) = [b_k(t), H]$ and $H = \langle H^{magnon} \rangle = \omega_k \langle b_k^+; b_k \rangle$. We will write as b_k dropping t

Here, $\langle \langle \dots \rangle \rangle$ is the abbreviated notation for the Fourier transform of the corresponding Green function, and $\langle \dots \rangle$ denotes averaging over a grand canonical ensemble[24]. The commuting and anticommuting relation for the two operators is also given by $[b_k b_{k'}] = b_k b_{k'} - \eta b_{k'} b_k$. Where $\eta = 1$ for Boson operators, and $\eta = -1$ for fermions operators. That is

$$[b_k, b_{k'}^+] = b_{k\sigma} b_{k'\sigma}^+ - b_{k'\sigma}^+ b_{k\sigma}\tag{2.9}$$

For two boson operators

and

$$[b_{k\sigma} b_{k'\sigma'}] = [b_{k\sigma}^+, b_{k'\sigma'}^+] = 0 \quad (2.10)$$

For two fermions operators:

$$\{b_{k\sigma}, b_{k'\sigma'}^+\} = b_{k\sigma} b_{k'\sigma'}^+ + b_{k'\sigma'}^+ b_{k\sigma} = \delta_{kk'} \delta_{\sigma\sigma'} \quad (2.11)$$

$$\{b_{k\sigma}, b_{k'\sigma'}\} = \{b_{k\sigma}^+, b_{k'\sigma'}^+\} = 0 \quad (2.12)$$

The Correlation function $\langle b_{k'}(t), b_k(t) \rangle$ is related to the analytic property of Green's function by

$$\langle b_{k'}^+(t) b_k(t) \rangle = i \lim_{\delta \rightarrow 0} i \int_{-\infty}^{\infty} \frac{[\langle \langle b_k, b_{k'}^+ \rangle \rangle \omega + i\delta - \langle \langle b_k b_{k'}^+ \rangle \rangle \omega - i\delta] e^{\omega(t-t')d\omega dt}}{e^{\beta\omega} - 1}$$

$$\begin{aligned} \text{Now } i \frac{d}{dt} b_k &= [b_k, \sum_k \omega_k b_{k'}^+ b_k] \\ &= \sum_k \omega_k [b_k, b_{k'}^+ b_k] \\ &= \sum_{kk'} \omega_k [b_k, b_{k'}^+] b_k + \sum_{kk'} \omega_k b_{k'}^+ [b_k, b_k] \\ &= \sum_{kk'} \omega_k b_k \delta_{kk'} + 0 = \omega_k b_k, \quad k = k' \end{aligned}$$

Taking the Fourier transformation (2.6), we get

$$\omega G_{kk'} = \frac{\delta_{kk'}}{2\pi} + \langle \langle [b_k, H], b_{k'}^+ \rangle \rangle_{\omega} \quad (2.13)$$

$[b_k, H]$ is the Commutation relation of b_k with the magnon Hamiltonian, H_{magnon} where $[b_k, H_{\text{magnon}}] = \omega_k b_k$ and for $k=k', \delta_{kk'} = 1$. These gives

$$\omega G_{kk}(\omega) = \frac{1}{2\pi} + \langle \langle \omega_k b_k, b_k^+ \rangle \rangle_{\omega} \quad (2.14)$$

$$\text{Where } \langle \langle \omega_k b_k, b_k^+ \rangle \rangle_{\omega} = \omega_k \langle \langle b_k, b_k^+ \rangle \rangle = \omega_k G_{kk}(\omega)$$

From which we obtain

$$(\omega = \omega_k) G_{kk}(\omega) = \frac{1}{2\pi}, \quad G_{kk}(\omega) = \frac{1}{2\pi(\omega - \omega_k)} \quad (2.15)$$

Poles of the Green function will be given by $\omega - \omega_k$ from which we find dispersion.

Again considering equ (2.13) and taking $t = t'$ equal time correlation gives the number operator;

$$\langle \langle b_k, b_k^+ \rangle \rangle \omega + i\delta = \frac{1}{2\pi(\omega + i\delta) - \omega_k} = \frac{1}{2\pi} \left[\frac{p}{\omega - \omega_k} - i\pi\delta(\omega - \omega_k) \right] \quad (2.16)$$

$$\langle\langle b_k, b_k^+ \rangle\rangle \omega - i\delta = \frac{1}{2\pi (\omega - i\delta) - \omega_k} = \frac{1}{2\pi} \left[\frac{p}{\omega - \omega_k} + i\pi\delta (\omega - \omega_k) \right] \quad (2.17)$$

Where p is the principal part of the integral finally,

$$\langle b_k b_k \rangle = \lim_{\delta \rightarrow 0} i \int \frac{\delta (\omega - \omega_k) d\omega}{e^{\beta\omega} - 1}$$

this can be expesered as

$$\check{n}_k = \frac{1}{e^{\beta\omega} - 1} \quad (2.18)$$

Where $\overline{n_k} = \langle b_k^+ b_k \rangle$ is the number of magnons in state k .

2.2 Mean Field Theory of Ferromagnetism

One possibility to describe observed properties of magnetic structure is to start with Heisenberg spin Hamiltonian. Although no complete solution has been found even to this simplified problem. It is possible to extract much partial information in avidity of important cases, with two interesting approaches like the spin wave theory and the molecular field theory, which is our interest of magnetic susceptibility. When we vary the external applied magnetic field H acting an a solid, its change of magnetization M will be a function of the temperature T , hence the scueptibility $\chi(T)$ is given by

$$\chi(T) = \lim_{|H| \rightarrow 0} \left(\frac{\partial M}{\partial H} \right) \quad (2.19)$$

Thus, the susceptibility of a solid $\chi(T)$ is measured and it is used to categorize different kinds of solids like ferromagnetism in which all magnetic moments are in parallel alignment, anti ferromagnetism, in which all magnetic moments line antiparallel alignment, spiral and helical processes around a cone or circle as or moves from one site to the next and spin glasses in which the magnetic moments lie in frozen random arrangements[42]. The starting point in many treatments of ferromagnetism is to treat the interaction of an atomic moment with its neighboring atomic moments, as if there were an additional component of the magnetic filed, and no account taken of vibrations (fluctuations) from sites to site[42]. The effective filed ensures the effect of ordering of the system experienced by each atomic site and therefore is give by

$$H_{eff} = H + \lambda M \quad (2.20)$$

Where $\lambda > 0$ is a constant that parameterize the strength of the molecular filed as function of the magnetization. The mean magnetic moment or magnetization for N atoms is also given by

$$M = N \sum_i \mu_i p_i = N \sum_{-s}^s \frac{(-m_s g \mu_B) e^{-\beta m_s g H_{eff}}}{\sum_{-s}^s e^{-\beta \mu_B g H_{eff}}} \quad (2.21)$$

$Ng\mu_B S B_s(x)$ where $B_s(x)$ is the Brillouin function given by

$$B_s(x) = \frac{1}{S} \left[\left(S + \frac{1}{2} \right) \coth \left[\left(S + \frac{1}{2} \right) x \right] - \frac{1}{2} \coth \frac{x}{2} \right] \quad (2.22)$$

and $x = \frac{g\mu_B H_{eff}}{k_B T}$, and g is the Landé factor which depends on the magnitude of L and S . For $x \ll 1$, $B_s(x) = \frac{(S+1)x}{3}$, and using $H_{eff} = H + \lambda M$, we have a self-consistent Equation for M as

$$M = \frac{Ng^2 \mu_B^2 S(S+1)(H + \lambda M)}{3k_B T} \quad (2.23)$$

Equation (2.1.26.) can be rewritten as

$$M \left[1 - \frac{C\lambda}{T} \right] = \left(\frac{C}{T} \right) H \quad (2.24)$$

But $M = \chi H$ so that the magnetic susceptibility is given by

$$\chi = \frac{C}{T - C\lambda} \quad (2.25)$$

And obtaining the Curie–Weiss law as

$$\chi = \frac{C}{T - T_c} \quad (2.26)$$

Which is valid for $T \gg T_c$ and in which the constant $C\lambda$, which is independent of T , the Curie temperature is given by,

$$T_c = C\lambda \quad (2.27)$$

We also assumed that an idealized spin system in terms of localized spins on a lattice.

The starting point of the mean field theory as well as the spin wave theory is the Heisenberg Hamiltonian of the spin system that is given by,

$$H = - \sum_{ij} J(r_i - r_j) S_i \cdot S_j \quad (2.28)$$

In the mean field approximation we assume each magnetic atom experiences a field proportional to the magnetization;

$$B_E = \lambda M \quad (2.29)$$

Where BE is the mean field or Weiss field, λ is the mean field constant, independent of temperature.

According to equation (2.1.34), each spin sees the average magnetization of all other spins. The Curie temperature, T_c is the temperature above which the spontaneous magnetization vanishes; it separates the disordered paramagnetic phase at $T > T_c$ from the ordered ferromagnetic phase at $T < T_c$ [33]. The mean field constant,

$$\lambda = \frac{T_c}{C} = \frac{3k_B T_c}{N g^2 S(S+1) \mu_B^2} \quad (2.30)$$

where C is the Curie constant.

$$T_c = C\lambda = \frac{\lambda N g^2 S(S+1) \mu_B^2}{3k_B} \quad (2.31)$$

Considering $HM_j = \frac{-2Z_j S_j}{g\mu_B} = \lambda M_j$, So the Curie temperature can be [29],

$$T_c = \frac{2ZJS(S+1)}{3K_B} \quad (2.32)$$

Chapter 3

Theoretical Formulation

The Diluted magnetic semi conductors have attracted the attention of many solid-state physicists[46]. DMSs bring together many topics of current interest in Condensed matter theory. First DMSs are correlated electron systems because ferromagnetism is carrier mediated, i.e., the carriers interact with the localized spins of the magnetic ions[47]. Now let us formulate a model Hamiltonian to study theoretically the existence of ferromagnetism of a new high-Tc diluted ferromagnetic semiconductor $K_2S:Ge$ with out transition metal elements and ferromagnetic properties of Ge doped K_2S by constructing model Hamiltonian in this chapter. Let us consider a system of Conduction electrons and an impurity on which a magnetic moment is localized in avery small region. The so-called Sp-d exchange interaction acts between the conduction electrons and the localized magnetic moment. Then the ferromagnetic behavior can be reasonably well described by the Zener model[48], in which ant ferromagnetic exchange coupling practically spin polarizes the holes, which intern causes an alignment of the local semiconductor Ge) spins. With in the zener model When a semiconductor in question contains localized magnetic moments (after doping) its band structure will be modified by the indirect exchange interaction of the moments (i.e. the $4p^2$ electrons) with band (i.e. sp) electrons. The total Hamiltonian expresses such interaction.

$$\mathbf{H} = \mathbf{H}_s + H_d + H_{ex}^{(sp-d)} \quad (3.1)$$

Where we have not written the direct exchange effects between the localized d electrons and the effects arising from d-d transfer and correlation. Here

$$H_s = \sum_{\mathbf{k}, \sigma} E_k (a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma}) \quad (3.2)$$

Is the Hamiltonian of the conduction electrons: are the electron creation and annihilation operators for the Bloch states $\mathbf{k}$, where $\mathbf{k}$ is the electron wabe vector and the spin index. E_k is a single particle unperturbed energy of an electron in this conduction state.

$$H_d = \sum_{i\sigma} E_i a_{i\sigma}^+ a_{i\sigma} \quad (3.3)$$

Where E_i is the one electron energy of an on-degenerated orbital ϕ_i at the site R_i . a^+ , a are the corresponding electron creation and annihilation operators. The Sp-d exchange Hamiltonian is expressed as

$$\mathbf{H}_{ex(sp-d)} = \sum_{R_i} J^{(sp-d)} (r - R_i) \mathbf{S}_i \cdot \boldsymbol{\sigma} \quad (3.4)$$

Where J is the electron ion sp-d coupling constant; $\mathbf{r}$ and $\mathbf{R}_i$ the Coordinates of the band electron and of the dopant ion (i.e. Ge), equation (3.4) can be expressed as

$$\sum_i J^{sp-d} (r - R_i) = J \sum_i \overline{\delta(r - R_i)} = xJ \quad (3.5)$$

x is the impurity percentage concentration. The summation is only over the lattice sites occupied by the semiconductor or dopant ions. Using Pauli matrices and Holstein-Primakoff transformations,

$$\sigma = \sigma_i^x + \sigma_j^y + \sigma_k^z \quad (3.6)$$

and

$$\sigma^x + i\sigma^y = \sigma^+ \rightarrow a^+ \uparrow a \downarrow \quad (3.7)$$

$$\sigma^x - i\sigma^y = a^+ \downarrow a \uparrow \quad (3.8)$$

$$\sigma^z \rightarrow (a^+ \uparrow a \uparrow) - (a^+ \downarrow a \downarrow) \quad (3.9)$$

$$a_k^+ \uparrow a_k \uparrow + a_k^+ \downarrow a_k \downarrow = 1 = N_k \uparrow + N_k \downarrow \text{ (for single occupied orbitals)} \quad (3.10)$$

$$(a_k^+ \uparrow a_k \uparrow - a_k^+ \downarrow a_k \downarrow) = 2S_j^z \quad (3.11)$$

$$a_k^+ \uparrow a_k \downarrow = S_i^+ = S^x + iS^y \quad (3.12)$$

$$a_k^+ \downarrow a_k \uparrow = S_i^- = S^x - iS^y \quad (3.13)$$

and

$$S = S_i^x + S_j^y + S_k^z \quad (3.14)$$

$$S_i^+ = \sqrt{2S} \left[a_i - \frac{a_i^+ a_i a_i}{4S} + - - - \right] = \sqrt{2S} \left[1 - \frac{a_i^+ a_i}{4S} \right] a_i \quad (3.15)$$

Similarly

$$S_i^- = \sqrt{2S} \left[1 - \frac{a_i^+ a_i}{4S} \right] a_i^+ \quad (3.16)$$

and

$$S_i^z = S - a_i^+ a_i \quad (3.17)$$

It is possible to verify that $S^\pm$ gives the corect commutation relations $[S_x, S_y] = iS^z$ if the boson commutation relations $[a_k, a_{k'}^+] = \delta_{kk'}$ are obeyed on the given lattice.

$$[a_k^+, a_{k'}] = \delta_{kk'} = 1, \quad \text{for } k = k' \quad (3.18)$$

It is convenient to make a transformation form the atomic $a_i^+ a_i$ to the magnon Variables defined

$$a_i = \frac{1}{N^{\frac{1}{2}}} \sum_k e^{-ik \cdot r_i} b_k \quad (3.19)$$

$$a_i^+ = \frac{1}{N^{\frac{1}{2}}} \sum_k e^{ik \cdot r_i} b_k^+ \quad (3.20)$$

$$a_j = \frac{1}{N^{\frac{1}{2}}} \sum_k e^{-ik \cdot (r_i + \delta)} b_k \quad (3.21)$$

$$a_j^+ = \frac{1}{N^{\frac{1}{2}}} \sum_k e^{ik \cdot (r_i + \delta)}$$

Here $\mathbf{r}_i$ is the position vector of the atom i the inverse transformation is given by

$$b_k = \frac{1}{N} \sum_i e^{-ik \cdot r_i} \quad (3.22)$$

$$b_{k'}^+ = \frac{1}{N} \sum_i e^{ik \cdot r_i} \quad (3.23)$$

The Commentator also satisfies the Bosonic relations

$$[b_k, b_{k'}^+] = \delta_{kk'} \quad (3.24)$$

and

$$[b_k, b_k] = [b_{k'}^+, b_{k'}^+] = 0 \quad (3.25)$$

Here the operator $b_{k'}^+$ creates a magnon of wave vector k , and the operator b_k destroys amagnon of the wave vector k . The discrete values of k summed over are those obtained

from periodic boundary conditions[43]. We will be concerned chiefly with low-lying states of the system; such that the fractional spin reversal is small;

$$\frac{\langle a_i^+ a_i \rangle}{S_i} = \frac{\langle n \rangle}{S} \ll 1 \quad (3.26)$$

Note that the expansion is formally an expansion in substituting for from Eq. [3.15] and considering low temperature excitations it reduces to:

$$S_i^+ \cong \sqrt{2S} a_i \quad (3.27)$$

Similarly

$$S_i^- = \sqrt{2S} a_i^+ \quad (3.28)$$

$$S_i^z = S - a_i^+ a_i = S - \frac{1}{N} e^{i(k-k') \cdot r_i} b_k^+ b_{k'} \quad (3.29)$$

From equation (3.12) and (3.13) we get

$$S_x = \frac{S^+ + S^-}{2} \quad (3.30)$$

and

$$S_y = -\frac{S^+ - S^-}{2i} \quad (3.31)$$

but

$$S = S_i^x + S_j^y + S_k^z \quad (3.32)$$

Substituting equation (3.30) and (3.31) in Eq. (3.32) we get

$$S = \left(\frac{S^+ + S^-}{2} \right) \mathbf{i} + \left(\frac{S^+ - S^-}{2i} \right) \mathbf{j} + \mathbf{S}_k^z \quad (3.33)$$

Again substituting eq. (3.15) and (3.16) in eq. (3.30) and (3.31)

We get

$$S_x = \frac{1}{2} \left(\frac{2S}{N} \right)^{\frac{1}{2}} \sum_k e^{-ik \cdot r_i} b_k \quad (3.34)$$

and

$$S_y = \frac{1}{2i} \left(\frac{2S}{N} \right)^{\frac{1}{2}} \sum_k e^{ik \cdot r_i} b_{k'}^+ \quad (3.35)$$

The Hamiltonian describes our diluted magnetic semiconductor $K_2(S, Ge)$ which is known

to show ferromagnetism experimentally and brought by electron interaction with $S = 1$ and dopant (Ge) Since a semiconductor contains localized magnetic moment (after doping) its band structure will be modified by exchange interaction of these localized magnetic moments created at the impurity site with the exchange splitting energy (i.e. $4p$) unfilled electrons with band (s) electrons. Such interaction is the electron sp-d interaction [8] which is expressed formally by the total Hamiltonian of eq.(3.1)and

$$H = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \boldsymbol{\sigma}_j \quad (3.36)$$

$$H = - \sum_{ij} J_{ij} (S_i^x + S_j^y + S_k^z) \cdot (\sigma_i^x + \sigma_j^y + \sigma_k^z) \quad (3.37)$$

$$H = - \sum_{ij} J_{ij} (S_i^x \sigma_i^x + S_j^y \sigma_j^y + S_k^z \sigma_k^z) \quad (3.38)$$

$$\mathbf{H} = \sum_{ij} J_{ij} \left[\frac{1}{2} (S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z \right] \quad (3.39)$$

Again

Substituting Eq. (3.27) in Eq. (3.32) for S^+ , S^- and S^z .

$$\mathbf{H} = - \sum_{ij} J_{ij} S^2 - \sum_{ij} J_{ij} S \left[a_i a_j^+ a_i^+ a_j - 2a_j^+ a_j - 2a_i^+ a_i - \sum_{ij} J_{ij} (a_i^+ a_i a_j a_j^+) \right] \quad (3.40)$$

The terms in the square bracket are operators expressing explicitly the handing of spin deviations from one site to the next. The term of order $a_i^+ a_i a_j^+ a_j$ is ignored, since they represent scattering of spin waves, which are unimportant at low temperatures. Therefore, denoting the ground state energy in the external field by $\mathbf{H}_0$ that is,

$$H_0 = - \sum_{ij} J_{ij} S^2 \quad (3.41)$$

and

Substituting equ.(3.19-3.32)in equ(3.4)we get,

$$\begin{aligned} \mathbf{H} - \mathbf{H}_0 &= H^{magnon} = - \sum_{j\delta k k'} \frac{J(\delta) S}{N} e^{-i(k-k') \cdot r_i} e^{ik \cdot \delta} b_k b_{k'}^+ + e^{i(k-k') \cdot r_j} e^{-ik' \cdot \delta} b_k^+ b_{k'} \\ &\quad - 2e^{i(k-k') \cdot r_j} b_k^+ b_{k'} - 2e^{-i(k-k') \cdot (r_i + \delta)} b_k^+ b_{k'} \end{aligned} \quad (3.42)$$

At $k = k'$ we get,

This becomes, on summing over j and substituting

$$\mathbf{H} = - \sum_k J(\delta) S Z \{ \gamma_k b_k b_k^+ + \gamma_{-k} b_k^+ b_k - 2b_k^+ b_k - 2b_k^+ b_k \}, \quad (3.43)$$

$$\begin{aligned} \text{taking } k = -k \text{ we get } H &= - \sum_k J(\delta) S Z \{ \gamma_k b_k b_k^+ + \gamma_k b_k^+ b_k - 4b_k^+ b_k \} \\ &= - \sum_k J(\delta) S Z \{ 2\gamma_k b_k b_{k-4b_k^+} b_k \} \\ &= - \sum_k J(\delta) S Z 2 \{ \gamma_k b_k b_k^+ - 2b_k^+ b_k \} \\ &= \sum_{\delta k} J(\delta) S Z [2 - \gamma_k] b_k^+ b_k, \\ \gamma_k &= \frac{1}{Z} \sum_{\delta} e^{ik \cdot \delta} \end{aligned} \quad (3.44)$$

Where (3.44) is the magnon dispersion function, which in this approximation depends only on the positions of the nearest neighbor spins. We assumed that $\gamma_k = \gamma_{-k}$, which is true for lattices with inversion symmetry. For bcc lattice structure in our case in 3D with lattice constant $a = 7.391 \text{ \AA}$; γ_k is clearly an even function of k . Under these simple assumptions, the magnon part of the Hamiltonian is remarkably simple, and can be written like a harmonic oscillator or phonon type Hamiltonian. Since the frequency is real, only the real part of the exponential is retained so that

$$\gamma_k = \frac{1}{Z} \sum_{\delta} \cos(k \cdot \delta) \quad (3.45)$$

The summation is over the $\mathbf{z}$ vectors denoted by $\boldsymbol{\delta}$ which join the central atom to its nearest neighbor's. For $\mathbf{k} \cdot \boldsymbol{\delta} \ll 1$

$$\gamma_k = 1 - \frac{k^2 \delta^2}{Z6} \quad (3.46)$$

Where $Z\delta^2 = 6a^2$. We neglected higher order terms in magnon operators, since we consider the low excitations. Substituting equ. (3.46) into equ. (3.43)

$$\begin{aligned} H^{magnon} &= \sum_{\delta k} 2J(\delta) S Z (2 - 1 + \frac{k^2 \delta^2}{6}) b_k^+ b_k \\ H^{magnon} &= 2 \sum_{\delta} J(\delta) S (1 + \frac{k^2 \delta^2}{6}) b_k^+ b_k \end{aligned} \quad (3.47)$$

In its simplified form it can be rewritten as

$$H^{magnon} = \sum_k \sum_{\delta} [2J(\delta) S + 2J(\delta) S \left(\frac{k^2 \delta^2}{6} \right)] b_k^+ b_k \quad (3.48)$$

$$\langle H^{magnon} \rangle = \langle \sum_k [2J(\delta)S + 2J(\delta)S \left(\frac{k^2 \delta^2}{6} \right)] b_k^+ b_k \rangle$$

Averaging over the impurities gives the following,

$$\langle \mathbf{H}^{magnon} \rangle = \langle \sum_k [2ZxJS + 2xJSk^2a^2] b_k^+ b_k \rangle \quad (3.49)$$

Where $\omega_k = 2ZxJS + 2xJSk^2a^2$

(3.49) is the dispersion relation for magnons in spin system forming a bcc lattice.

Where $2xZJS$ is anisotropic term which is very small so that $\langle \sum_k 2ZxJS b_k^+ b_k \rangle$ contribution is less than that can also be neglected; in which the dispersion relation becomes, .

$$\omega_k = 2xJSa^2k^2 \quad (3.50)$$

$$\langle \mathbf{H}^{magnon} \rangle = \langle \sum_k (2xJSk^2a^2) b_k^+ b_k \rangle \quad (3.51)$$

In this work ferromagnetic ordering is considered where externally applied field is very small and negligible.

3.1 Magnon Distributions Function

A magnon is a quantized spin wave[11]. The ground state of a simple ferromagnet has all spins parallel. At long wave lengths $ka \ll 1$ so that, the frequency of magnon ω_k is proportional to k^2 ; in the same limit the frequency of a phonon is proportional to k . The quantization of spin waves proceeds exactly as for photons and phonons. The energy of a mode of frequency ω_k with $\tilde{n}_k$ magnons can also be equated to,

$$E_k = \left(n + \frac{1}{2} \right) \hbar \omega_k \quad (3.52)$$

The excitation of magnon corresponds to the reversal of one spin $\frac{1}{2}$. Equ. (2.18) is the Bose-Einstein distribution that magnons also obey. The total number of magnons in all modes excited at temperature T can be calculated as:

$$\sum_k \langle \tilde{n}_k \rangle = \int D(\omega) n(\omega) d\omega \quad (3.53)$$

Where $D(\omega)$ is the number of magnon modes per unit frequency range. The integral is taken over the allowed range of k , which is the first Brillouin zone. At sufficiently low

temperature we may carry the integral between 0 and ∞ because $\langle n(\omega) \rangle \rightarrow 0$ exponentially as $\omega \rightarrow \infty$. Magnons have a single polarization for each value of $\mathbf{k}$ [33]. In three dimensions the number of modes of wave vector less than $\mathbf{k}$ is $\left(\frac{1}{2\pi}\right)^3 \left(\frac{4\pi k^3}{3}\right)$ per-unit volume, whence the number of magnons with frequency in $d\omega$ at ω is

$$\left(\frac{1}{2\pi}\right)^3 (4\pi k^2) \left(\frac{dk}{d\omega}\right) \quad (3.54)$$

Under these assumptions, the magnon part of the Hamiltonian can simply be written like a harmonic oscillator or phonon type Hamiltonian:

$$\langle \mathbf{H}^{magnon} \rangle = \sum_k \bar{n}_k \omega_k \quad (3.55)$$

where $\bar{n} = \langle b_k^\dagger b_k \rangle$ is the average number of magnons in state $\mathbf{k}$ and, $\omega_k = 2xJSa^2k^2$, is the long wave length magnon dispersion. Substituting equation () into equation () for ω_k we get

$$\langle b_k^\dagger b_k \rangle = \frac{1}{e^{\frac{2xJSk^2a^2}{k_B T}} - 1} \quad (3.56)$$

$$\sum_k \langle \bar{n}_k \rangle = \frac{1}{(2\pi)^3} \int_0^\infty \frac{4\pi k^2 dk}{e^{\frac{2xJSa^2k^2}{k_B T}} - 1} \quad (3.57)$$

$$\frac{1}{2\pi^2} \int_0^\infty \frac{k^2 dk}{e^{\frac{2xJSk^2a^2}{k_B T}} - 1} \quad (3.58)$$

let $y = \frac{2xJSk^2a^2}{k_B}$ and, $dy = \frac{4xJSa^2k dk}{k_B}$
solving for k ,

$$k = \left(\frac{k_B T}{2xJSa^2} \right)^{\frac{1}{2}} y^{\frac{1}{2}} \quad (3.59)$$

and

$$k^2 dk = \left(\frac{k_B T}{2xJSa^2} \right)^{\frac{3}{2}} \frac{y^{\frac{1}{2}}}{2} \quad (3.60)$$

substituting equation (3.58) in to equ. (3.60) we get

$$\sum_k \bar{n}_k = \frac{1}{2\pi^2} \int_0^\infty \left(\frac{k_B T}{2xJSa^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{y^{\frac{1}{2}}}{e^{y-1}} \quad (3.61)$$

Where the integration $\int_0^\infty \frac{y^{\frac{1}{2}}}{e^{y-1}} = 2.3174$. Hence,

$$\sum_k \bar{n}_k = (2.3174) \left(\frac{1}{4\pi^2} \right) \left(\frac{k_B T}{2xJSa^2} \right)^{\frac{3}{2}} \quad (3.62)$$

$$\sum_k \tilde{n}_k = (0,0587) \left(\frac{k_B T}{2xJSa^2} \right)^{\frac{3}{2}} \quad (3.63)$$

Where equ. (3.63) gives us the number of reversed spins given by the ensemble average of the spin wave occupancy numbers. The average magnons excitation energy at low temperature is given by:

$$\langle \mathbf{H}^{magnon} \rangle = \sum_k \langle n_k \rangle \omega_k \quad (3.64)$$

3.2 Ferromagnetic Transition Temperature

The mean magnetic moment per unit volume (magnetization at a temperature T , which is $M(T)$ of the system is obtained in the following form:

$$M(T) = g\mu_B \left(NS - \sum_k \langle b_k^+ b_k \rangle \right) \quad (3.65)$$

where, $g = 2$, $\langle n_k \rangle = \langle b_k^+ b_k \rangle$.

$$M(T) = M(0) - 2\mu_B \sum_k \langle \tilde{n}_k \rangle \quad (3.66)$$

Where $M(0) = 2\mu_B nS$, which is ground state magnetization or magnetization at absolute zero, ferromagnetic state where all spins can exploit their mutual exchange energy by being preferentially aligned parallel to each other has lower free energy than the state where $H_m = 0$.

Equation, Eq. (3.66) can be written as:

$$M(T) = 2\mu_B nS - 2\mu_B \sum_k \langle \tilde{n}_k \rangle \quad (3.67)$$

$$M(T) = 2\mu_k nS \left(1 - \frac{1}{nS} \right) \sum_k \langle \tilde{n}_k \rangle \quad (3.68)$$

Where is the lattice cell volume

$$M(T) = 2\mu_{BnS} \left(1 - \frac{1}{nS} \right) (0.0587) \left(\frac{K_B T}{2xJSa^2} \right)^{\frac{3}{2}} \quad (3.69)$$

where $n = \frac{N}{V}$, V is the lattice cell volume $= a^3$.

so

$$M(T) = M(0) \left(1 - \frac{1}{nS} \right) (0.0587) \left(\frac{K_B T}{2xJSa^2} \right)^{\frac{3}{2}} \quad (3.70)$$

then,

$$\frac{M(T)}{M(0)} = 1 - \frac{0.0587}{na^3S} \left(\frac{K_B T}{2xJS} \right)^{\frac{3}{2}} \quad (3.71)$$

The number N of atoms per unit volume is na^3 where $N = 1, 2, 4$ for *sc*, *bcc*, *fcc* lattices, respectively.

Here $na^3 = 1$, and $a = 7.391 \text{ \AA}$ in our case.

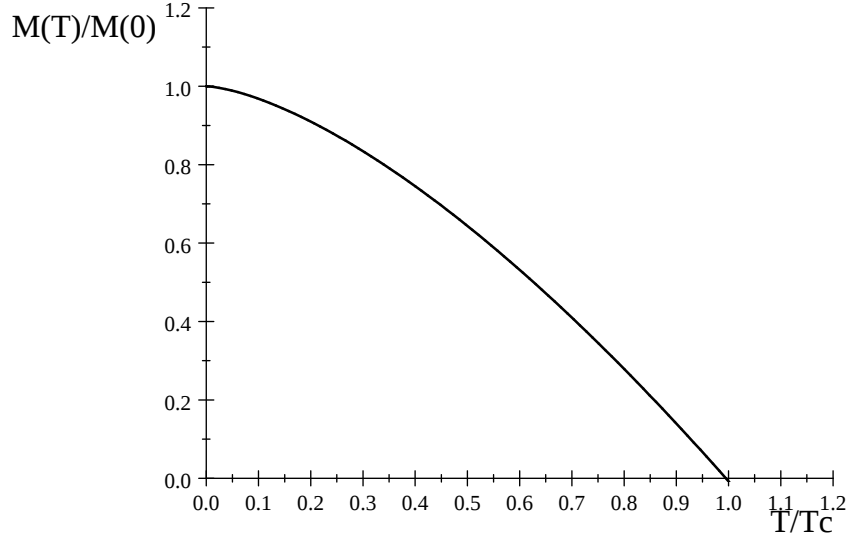


Fig 3.1. The reduced magnetization versus reduced temperature (the spontaneous magnetization),

The figure 3.1 shows $\frac{M(T)}{M(0)}$ (reduced magnetization) *vs* $\frac{T}{T_c}$ (reduced temperature) graph drawn for $x = 0.08$ where we can possibly see that as T increases ($T \rightarrow T_c$) the magnetization decreases smoothly; to zero at $T = T_c$. This behavior classifies the usual ferromagnetic/paramagnetic transition as a second order transition.

Now $\sum_k \frac{\langle \tilde{n}_K \rangle}{NS}$ is equal to the fractional change of magnetization.

Whence,

$$\frac{M(T)}{M(0)} = 1 - \frac{0.0587}{na^3S} \left(\frac{K_B T}{2xJS} \right)^{\frac{3}{2}} \quad (3.72)$$

As $\frac{M(T)}{M(0)} \rightarrow 0$ then, $T \rightarrow T_c$ which gives

$$T_c = x \left(\frac{2JS}{K_B} \right) \left(\frac{na^3S}{0.0587} \right)^{\frac{2}{3}}$$

, thus, there exists the possibility of ferromagnetism below a certain Critical temperature T_c called the “Curie temperature” which is directly proportional to the concentration of the impurity atom. i.e. T_c is proportional x . At temperature below T_c the ferromagnetic state

is therefore the stable one. For $T \rightarrow 0$, the magnetic moment when all spins are aligned completely parallel.

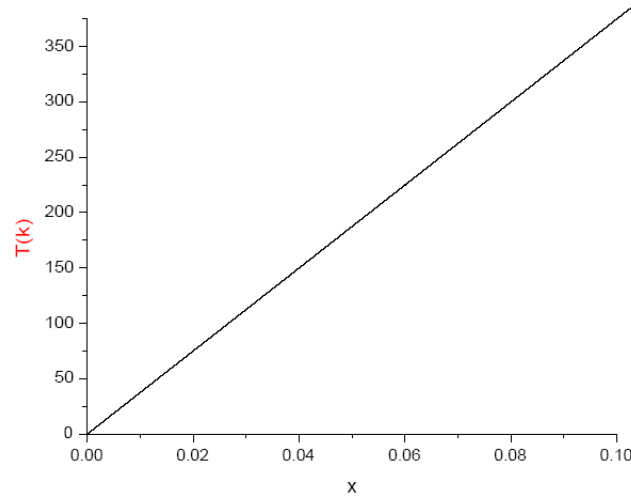


Fig.3.2 Curie temperature, T_c versus concentration of the impurity semiconductor Ge x in $K_2(S, Ge)$.

3.3 Magnon Heat Capacity

The internal energy of unit Volume of the magnon gas in thermal equilibrium at temperature T_i neglecting magnon-magnon interaction, at very low external field, and considering $\mathbf{k}a \ll 1$ is given by:

$$U = \sum_k \omega_k \langle \tilde{n}_k \rangle_T \quad (3.73)$$

$$\sum_k \frac{\omega_k}{e^{\beta\omega} - 1} \quad (3.74)$$

Taking , $\omega_k = 2xJSa^2k^2$

$$U = \frac{1}{(2\pi)^3} \int_0^\infty \frac{\omega_k 4\pi k^2 dk}{e^{\frac{2xJSa^2k^2}{k_B T}} - 1} \quad (3.75)$$

Again from equ.(3.49) $d\omega_k = 2xJSa^2(2k)dk$ and $dk^2 = \frac{\omega_k}{2xJSa^2}$ we get $dk = \left(\frac{1}{8xJSa^2}\right) \omega_k^{\frac{1}{2}} d\omega_k$

$$U = \left(\frac{1}{2xJSa^2}\right)^{\frac{1}{2}} \frac{1}{4\pi^2} \int_0^\infty \frac{\omega_k^{\frac{3}{2}}}{e^{\frac{2xJSa^2k^2}{k_B T}} - 1} \quad (3.76)$$

let $y = \frac{\omega_k}{k_B T}$ and $\frac{d\omega_k}{k_B T} = dy \Rightarrow dy k_B T = d\omega_k$

and

$$K_B T = \frac{d\omega_k}{dy} \quad (3.77)$$

Where $\frac{1}{4\pi^2} \int_0^\infty \frac{y^{\frac{3}{2}} dy}{e^y - 1} = 0.0456$. Then

$$U = 0.0456 \left(\frac{1}{2xJSa^3} \right)^{\frac{3}{2}} K_B^{\frac{5}{2}} T^{\frac{5}{2}} \quad (3.78)$$

Specific heat capacity of magnons will be calculated as:

$$C^{magnon} = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \sum_k \omega_k \langle \tilde{n}_k \rangle_T \quad (3.79)$$

$$C^{magnon} = \frac{\partial}{\partial T} \left[0.0456 \left(\frac{1}{2xJSa^2} \right)^{\frac{3}{2}} K_B^{\frac{5}{2}} T^{\frac{5}{2}} \right] \quad (3.80)$$

$$C^{magnon} = \frac{5}{2} (0.0456) \left(\frac{1}{2xJSa^2} \right)^{\frac{3}{2}} K_B^{\frac{5}{2}} T^{\frac{3}{2}} \quad (3.81)$$

$$C^{magnon} = 0.113 \left(\frac{1}{2xJSa^2} \right)^{\frac{3}{2}} K_B^{\frac{5}{2}} T^{\frac{3}{2}} \quad (3.82)$$

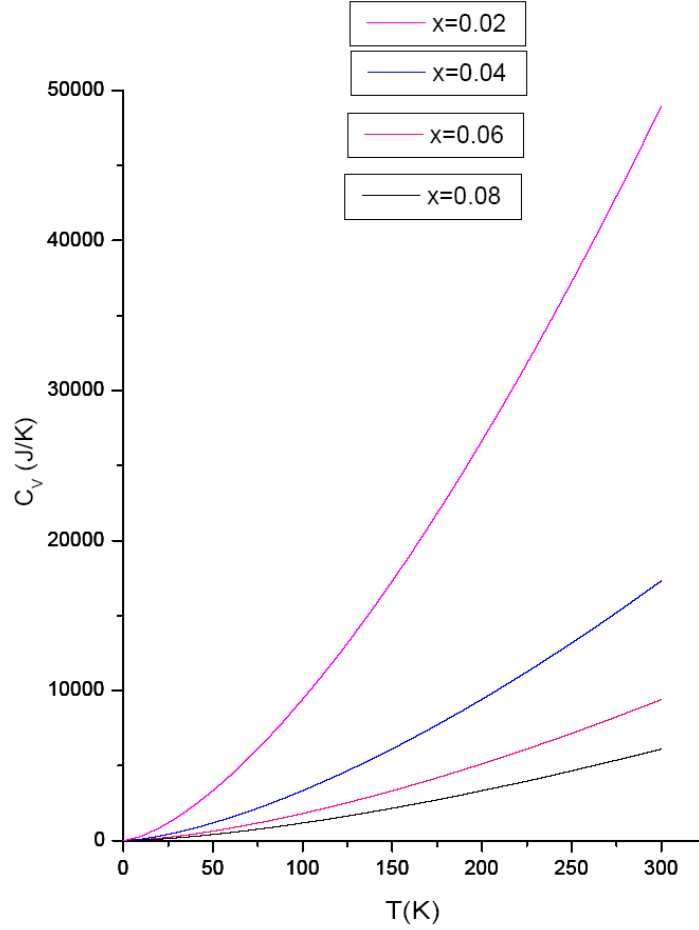


Fig.3.3: Heat capacity vs Curie temperature where the values of x are kept constant for each correspondingly.

3.4 The Ferromagnetic Suceptibility

The magnetization, which is the mean magnetic moment per unit volume, is given by

$$M = Ng\mu_B S B_s(x) \quad (3.83)$$

Where $B_s(x)$ is the Brillouin function for s spins which is given by

$$B_s(x) = \frac{1}{S} \left(S + \frac{1}{2} \right) \coth \left(S + \frac{1}{2} \right) x - \frac{1}{2} \coth \left(\frac{x}{2} \right) \quad (3.84)$$

It has the limiting behavior for large and small values of the parameter x .

The hyperbolic cotangent is defined as

$$\coth y = \frac{\cosh y}{\sinh y} = \frac{e^y + e^{-y}}{e^y - e^{-y}} \quad (3.85)$$

For $y \gg 1$, $e^{-y} e^y$ and $\coth y = 1$.

Conversely, for $y \ll 1$ both e^y and e^{-y} can be expanded in power series. Retaining all terms quadratic in y , the result is

$$\begin{aligned} \coth y &= \frac{1 + \frac{1}{2}y^2 + \dots}{y + \frac{1}{6}y^3 + \dots} \\ &= \left(1 + \frac{1}{2}y^2\right) \left[\frac{1}{y} \left(1 + \frac{1}{6}y^2\right)^{-1}\right] \\ &= \frac{1}{y} \left(1 + \frac{1}{3}y^2\right) \end{aligned} \quad (3.86)$$

For $y \ll 1$,

$$\cot hy = \frac{1}{y} + \frac{1}{3}y \quad (3.87)$$

Applying the results of equ. (3.83) to the function $B_s(x)$

For $x \gg 1$,

$$B_s(x) = \frac{1}{S} \left[\left(S + \frac{1}{2}\right) - \frac{1}{2} \right] = 1 \quad (3.88)$$

In the opposite limit where, $x \ll 1$

$$B_s(x) = \frac{1}{S} \left\{ \left(S + \frac{1}{2}\right) \left[\frac{1}{\left(S + \frac{1}{2}\right)x} + \frac{1}{3} \left(S + \frac{1}{2}\right)x - \frac{1}{2} \left(\frac{2}{x} + \frac{x}{6}\right) \right] \right\} \quad (3.89)$$

$$= \frac{1}{S} \left\{ \frac{1}{3} \left(S + \frac{1}{2}\right)^2 x - \frac{1}{12}x \right\} \quad (3.90)$$

$$= \frac{x}{3S} \left(S^2 + S + \frac{1}{4} - \frac{1}{4} \right) \quad (3.91)$$

Hence for $x \ll 1$

$$B_s(x) = \left(\frac{S+1}{3} \right) x \quad (3.92)$$

The energy levels of the central j th atom are given by

$$E_m = -g\mu_B (H_0 + H_m) m_s, m_s = -S, (-S+1), \dots, S \quad (3.93)$$

We can immediately calculate the mean Z component of spin of this atom

$$S_{jz} = SB_s(x) \quad (3.94)$$

Where

$$x = \frac{g\mu_B (H_0 + H_m)}{K_B T} \quad (3.95)$$

From the molecular field approximation, we know that

$$2J \sum_{K=1}^n S_{Kz} = g\mu_B H_m \quad (3.96)$$

To obtain self-consistency we must then require reducing

$$g\mu_B H_m = 2JnSB_s(x) \quad (3.97)$$

Since x is related to H_m by (3.94).

Expressing H_m in terms of x (3.96) becomes

$$B_s(x) = \frac{K_B T}{2nJS} \left(x - \frac{g\mu_B H_0}{K_B T} \right) \quad (3.98)$$

In the absence of external field (3.97) becomes,

$$B_s(x) = \frac{K_B T}{2JnS} x \quad (3.99)$$

Once the molecular field H_m is determined, the total magnetic moment can be given by

$$M = g\mu_B \sum_j S_{jz} = Ng\mu_B SB_s(x) \quad (3.100)$$

Using the approximation (3.98) we can write

$$\frac{1}{3}(S+1)x = \frac{K_B T}{2JnS} \left(x - \frac{g\mu_B H_0}{3K_B T} \right) \quad (3.101)$$

Solving this for x gives, using the quantity $K_B T_c$

$$x = \frac{g\mu_B H_0}{K_B(T-T_c)}$$

Thus (3.97) yields

$$\begin{aligned} M &= \frac{1}{3}Ng\mu_B S(S+1)x \\ &= \frac{1}{3} \frac{Ng^2\mu_B^2 S(S+1)H_0}{K_B(T-T_c)} \end{aligned} \quad (3.102)$$

So that

$$\chi = \frac{M}{H_0} = \frac{1Ng^2\mu_B^2 S(S+1)}{3K_B(T-T_c)} \quad (3.103)$$

we define $d\gamma^2 = \mu_B^2 g^2$, then equation (3.102) becomes,

$$\chi = \frac{\gamma^2 S(S+1)}{3K(T-T_c)} \quad (3.104)$$

i.e the high-temperature susceptibility. A $\frac{1}{T}$ susceptibility at high T is generally taken as evidence for free paramagnetic spins, and the size of the moment. Thus χ becomes infinite when $T \rightarrow T_c$ i.e., at the Curie temperature where the substance, $K_2(S, Ge)$ becomes ferromagnetic; and the magnetic susceptibility increases with the transition temperature decrease. From equation (3.103) one can see that $\chi \sim \frac{1}{(T-T_c)}$.

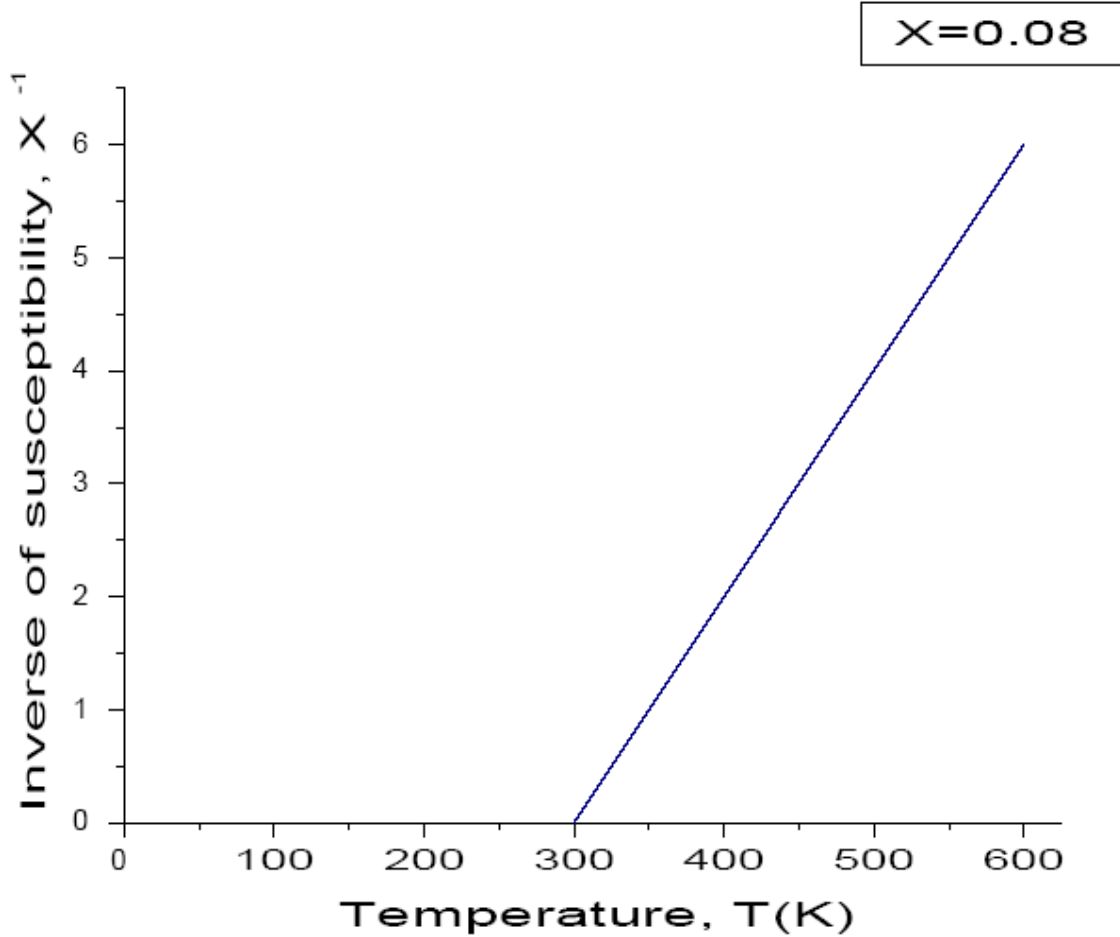


Fig3.4. The reciprocal of susceptibility versus temperature. The curve is (except for some slight departures at high temperatures) a straight line, in accord with what would be expected from Curie-Weiss law. The material becomes ferromagnetic below 300 K. (as we predicted theoretically). Magnetic susceptibility becomes infinite when $T \rightarrow T_C$, i.e., at the Curie temperature where the substance becomes ferromagnetic. We also can see from the graph that $\frac{1}{\chi} = (T - T_C) = 0$ at the point $T = T_C$.

Chapter 4

Discussion and Conclusion

4.1 Discussion

This part of our study is devoted to the investigation of Curie temperature T_c , magnon heat capacity and the magnetic susceptibility. For this purpose we have studied a model Hamiltonian which contains interactions involving the mobile electrons with localized spins due to $4p$ unpaired electrons of the dopant semiconductor, Ge . We have found the results for the problem based on spin wave theory by implementing the mean field theory and using Holstein-Primakoff transformation. Replacing the up and down impurity spins with boson creation and annihilation operators. The spin problems are transferred to a many body interaction through the use of both quantum field theory and statistical mechanics. The proportionality relation of Curie temperature, T_c and concentration, x of the Ge impurity is shown where the obtained result agrees with what is experimentally obtained by Katayama-yoshida and his coworkers based up on the mean field theory approximation (MFA) by mapping on the Heisenberg model, we took the total spin of the dopant (impurity) atoms $S = 1$ and $na^3 = N = 1$. We assumed that K_2S possesses a sc lattice structure, where N is the number of atoms per unit volume, and the experimentally obtained Curie temperature is enhanced for the value of exchange integral $J = 15.3871meV$. Assuming the values for our numerical parameters as the lattice constant, $a = 7.391 \text{ \AA}$, $S = 1$ the orbital radius of the $4d$ electrons of the impurity semiconductor which is large as compared to the Bohr radius for hydrogen atom. which arises due to the large lattice spacing of K_2S , which raised due to its large ionic radius of K^+ and S^{2-} . For which the theoretically calculated T_c is found to be $300k$. for $x = 0.08$ in our case and experimentally too. This implies that the theoretically obtained result is almost the same as was experimentally obtained. From the result obtained, we assumed that the material is in its ordered stable ferromagnetic state for $x < 0.08$ for which $T < T_c$ and enters the disordered Paramagnetic state for $x > 0.08$ for which $T > T_c$. The T_c 's slightly go up with increasing electron concentrations and

the ferromagnetism disappears and disordered Para magnetism appears at $x = 0.1$. Room temperature ferromagnetism is predicted at $x = 0.08$ impurity concentration. T_c has been evaluated numerically as a function of impurity concentration.

4.2 Conclusion

In the present investigation we have studied the ferromagnetism of $K_2S(Si/Ge)$ which is free from any transition metal element. We introduced the relation and role of solid-state physics to study ferromagnetism and the origin of ferromagnetism and local magnetic moment. Chapter one is devoted to the back-ground of spintronics, spin-glasses, half metallic properties, diluted magnetic semiconductor, the importance of studying DMSs, the reason why we dilute DMSs, types of DMSs and new high- T_c DMSs in general, which has been carried out in recent years. In chapter two, we have had a brief account about double time temperature dependent Green's functions formalism of quantum field theory and the mean field theory, which are a tool to solve our main problem. Under chapter three, we devoted on the calculation of the number of magnons excited, the dispersion relations for magnons. And calculation of magnetization at different temperature to realize the saturation of magnetization and also the magnetic susceptibility to understand for which susceptibility point (range) high- T_c ferromagnetism will be stable and disappear. We finally calculated the Curie temperature for $K_2S : Ge$ DMS to confirm the relation between concentrations of the deep-impurity of semiconductor, Ge . Using spin wave theory an expression for T_c as a function of x has been obtained and which has been plotted. T_c varies with the deep impurity concentration of the semiconductor, Ge x in $K_2(S, Ge)$ as linearly and the two parameters have a direct proportionality relation such that T_c increases with the concentration x regard less of the remaining parameters and this is in good agreement with experimental observation [36]. Magnetization increases with increasing the Ge concentration, x with other parameters remaining constant. In a reduced magnetization, versus reduced temperature graph, the reduced magnetization decreases and goes to zero with increasing reduced temperature. At $T < T_c$ there is saturation magnetization (ferromagnetic state) and at $T > T_c$ there is a Paramagnetic region. The bandwidth W and the electron correlation energy U in the deep-impurity-band are controlled to satisfy the stoner's condition. This new route could open a new way to fabricate the high T_c , transparent and half-metallic DMS with the wide-band gap semiconductors with out magnetic elements. In a reduced magnetization $m(T) = \frac{M(T)}{M(0)}$ versus reduced temperature graph $\frac{M(T)}{M(0)}$ decreases. For larger values of x the ferromagnetic order is seen increasing and the graph becomes less convex. Where as in reduced magnetization versus reduced temperature case the nature of the graph does not change much with concentration. The graph of the magnon heat capacity versus temperature graph is also plotted. From this graph we found that the curve has got a parabolic shape for small concentration

$x=0.02$ in our case and becomes linear for high concentration of Ge $x=0.08$. And it can be found that the curve is straight line for higher concentration of the impurity. We also plotted the graph for the reciprocal the susceptibility versus temperature difference. As can be seen from the graph the material is in its ferromagnetic state for $T < 300$ K. And $\frac{1}{\chi} = 0$ at $T = T_c = 300$ K. And the graph is straight line after $T = 300$ K Which shows that the material leaves its ferromagnetic state for $T = T_c$. The results obtained are broadly in agreement with experimental values.

4.3 Suggestion For Further Study

. There are fertile grounds to study ferromagnetism in new ferromagnetic materials without any transition metal element.

CaO based DMSs

MgO based DMSs

CaAs based DMSs

BaO based DMSs

It is also interesting to study the following properties of new ferromagnetic materials without any transition metal element to realize:

the existence of ferromagnetism in them.

the resistivity

the conductivity

magnetic property of new DMSs.

transparent property of new DMSs.

half metallic property of new DMSs.

optical property of new DMSs.

effects of impurity types (n-types or p-types) on new DMSs.

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