STUDY OF FERROMAGNETISM IN DILUTED MAGNETIC SEMICONDUCTOR CaAs

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By

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The undersigned hereby certify that they have read and recommended to the Faculty of Science School of Graduate Studies for acceptance a thesis entitled "**STUDY OF FERROMAGNETISM IN DILUTED MAGNETIC SEMICONDUCTOR CaAs**" by **Merhawi Abreha** in partial fulfillment of the requirements for the degree of **Master of Science in Physics**.

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To My Departed Sister, Tsega.

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Abstract

In the present study we study ferromagnetism of a transition free diluted magnetic semiconductor CaAs. Ferromagnetism in this curious material is due to the spin polarization of *p*-orbitals of the As atom. This mechanism is different from that of the CrAs in which Cr atoms possess magnetic moments [20, 23]. Ca atom does not have magnetic moments; its role is just to provide electrons with As atoms at the fcc site and to sustain crystal symmetry. The Curie temperature is estimated within an improvement over the mean-field approximation RKKY interaction for homogeneous systems with randomly distributed localized spins and is obtained to be approximately proportional to the spin concentration.

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Introduction

The information technology we use today utilizes the mass, charge and spin of electrons in the solid state. Integrated circuits and high-frequency devices which are used for information processing and communications are made up of semiconductors such as silicon (Si), germanium (Ge) and gallium arsenide (GaAs). These devices have had great success using the charge of electrons. Mass storage of information is carried out by magnetic recording using spins of electrons in ferromagnetic materials. These include hard disks, magnetic tapes and magneto-optical disks. It is then quite natural to ask whether both the charge and spin of electrons can be used to further enhance the performance of devices so that we may be able to use the capability of mass storage and information processing at the same time [1].

Recently, the possibility of using electron's spins in addition to their charge in information technology has created much enthusiasm for a new branch of theoretical research on spin electronics (spintronics). Particular semiconducting materials which are considered to be ideal materials for spintronics are commonly known as diluted magnetic semiconductors (DMSs) or semimagnetic semiconductors (SMSCs).

Almost complete search for possible magnetic materials has been performed utilizing transition metal doping into II-VI compounds, like CdTe, CdSe, CdS, ZnSe, etc, or III-V crystals such as GaAs and InSb. For example, DMSs such as $In_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$ type were discovered by Munekata *et al* and Ohno *et al* where a small concentration of Mn atoms, or in general of transition metal atoms, are randomly distributed on the cation sites of the host material [2]. In this case the transition metal ions, used as the magnetic atoms, substitute the original cations of the host crystal. In fact, the strong magnetism is realized when the *d*-shell is partially occupied by electrons and is not half-filled.

In a hypothetical zinc-blende structure compounds of II-V elements such as CaAs, CaP, CaC, SrAs, SrC, BaC and CaSb are found to be possible ferromagnetic materials excluding transition metal atoms. In this case the *d*-orbitals on atoms of the G-II elements play essential roles for the magnetism [3, 13, 20, 21, 22]. Thus the half-metalicity and ferromagnetic properties appearing in the zinc-blende Ca compounds are new findings .

In the first chapter of this thesis a brief review of semiconductors is given. We shall define semiconductors and discuss a few important concepts which distinguish them from other solids. We shall also consider carrier concentration and electrical conductivity in semiconductors.

The discussion of magnetic properties of semiconductors comes under the second chapter. In this chapter we have included reviews of spontaneous magnetism, Curie-Weiss law of magnetization and different types of magnetization. In fact, the focus of this chapter shall be on ferromagnetism.

The third chapter of this paper concentrates on diluted magnetic semiconductors (DMSs). Some important examples of DMSs, including II-VI, III-V and Calcium compounds, are shortly discussed under this chapter.

In chapter four, we focus on the electronic structure and magnetism of calcium arsenide (CaAs). We shall show pd hybridization exchange interaction to produce magnetization in the curious material CaAs without transition metal atoms. Magnetic properties of CaAs such as Curie-Weiss temperature, magnetic susceptibility, magnetization and magnetoresistance are discussed on the basis of mainly mean or molecular field theory.

Finally, the fifth chapter summarizes the results obtained and gives concluding points of the thesis.

Chapter 1

SEMICONDUCTORS

1.1 Introduction

The theory of electronic structure determines the type of solid and its macroscopic properties. Solids in which the highest occupied state in the state of lowest energy is the top end of a band are insulators, whereas those in which the last occupied level is somewhere inside a band are distinguished as metals. However, if the energy gap between the last full and the next empty band is small, a few electrons will be moved up by thermal agitation, so that there are a few conduction electrons, and a few holes in the lower band. In such substances the number of carriers should increase very rapidly with temperature, and hence their characteristic low electric conductivity increases with temperature. These substances are called semiconductors [4]. Silicon, Germanium and Gallium arsenide are good examples of semiconductors.

A pure semiconducting material such as Silicon at low temperature would exhibit a low conductivity. In contrast, a higher conductivity would result from the addition of very small amounts of an impurity such as phosphorus by doping. The properties of the pure material result from the intrinsic electronic structure and hence it is labeled as an intrinsic semiconductor. The doped material is called an extrinsic or impurity semiconductor since its properties are dependent on some extrinsic agent or impurity [5]. Next, we shall briefly discuss the case of intrinsic and extrinsic behaviours of semiconductors, and their electrical properties.

1.2 Intrinsic Semiconductors

The magnitude of a band gap E_g is of central importance in discussing semiconductor properties. In order to find out something about the electron and hole concentrations, it is so important to know the magnitude of the band gap. The conductivity of the bulk material at some chosen temperature is then determined from the knowledge of electron and hole concentrations and their respective mobilities. We shall also calculate the position of the Fermi level μ from a required knowledge of the carriers concentrations [4, 5].

To calculate the number of carriers in an intrinsic semiconductor, we assume that our chosen zero (at 0K) is at the top of the valence band and the Fermi level μ is arbitrarily placed in the band gap, as in fig 1.1. The density of states in the valence band and the conductance band is respectively $N_v(E)$ and $N_c(E)$. The effective mass of electrons near the bottom of the conductance band is designated by m_e and that of holes near the top of the valence band by m_h.

The occupation of electron states at any finite temperature T is determined by the

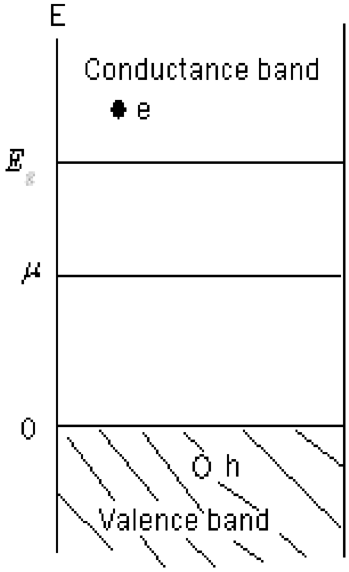


Figure 1.1: Conductance and valence bands in the semiconductor.

Fermi-Dirac function written as

$$f_e(E) = \{\exp[\beta(E-\mu)]+1\}^{-1} \tag{1.2.1}$$

where $\beta = \frac{1}{k_B T}$. We may assume that few electrons occupy the conductance band so that $f_e(E) << 1$. Thus, the classical limit of eqn (1.2.1) is

$$f_e(E) \simeq \exp[-\beta(E-\mu)] \tag{1.2.2}$$

where the unity of the denominator in (1.2.1) has been neglected. In contrast, $f_e \sim 1$ for electrons in the valence band so that we may expand the function to get approximately

$$f_e(E) \simeq 1 - \exp[\beta(E-\mu)] \tag{1.2.3}$$

The function for hole occupancy is therefore obviously

$$f_h(E) = 1 - f_e(E) = 1 - \{1 - \exp[\beta(E-\mu)]\} = \exp[\beta(E-\mu)] \tag{1.2.4}$$

The density of states functions for electrons near the bottom of the conductance band and holes near the top of the valence band from the free electron gas are simply

$$N_c(E) = \frac{V}{2\pi^2}(\frac{2m_e}{\hbar^2})^{\frac{3}{2}}(E-E_g)^{\frac{1}{2}} \tag{1.2.5}$$

and

$$N_v(E) = \frac{V}{2\pi^2}(\frac{2m_h}{\hbar^2})^{\frac{3}{2}}(-E)^{\frac{1}{2}} \tag{1.2.6}$$

The density of electrons in the conductance band n_c and that of holes in the valence band n_v are given by

$$n_c = \frac{1}{V}\int_{E_g}^{\infty} N_c(E) f_e(E) dE \tag{1.2.7}$$

and

$$n_v = \frac{1}{V}\int_{-\infty}^{0} N_v(E) f_h(E) dE \tag{1.2.8}$$

Substituting equations (1.2.2) and (1.2.5) in equation (1.2.7); (1.2.4) and (1.2.6) in (1.2.8), we find

$$n_c = \frac{1}{2\pi^2}(\frac{2m_e}{\hbar^2})^{\frac{3}{2}} \int_{E_g}^{\infty} (E - E_g)^{\frac{1}{2}} \exp[-\beta(E-\mu)] dE \tag{1.2.9}$$

and

$$n_v = \frac{1}{2\pi^2}(\frac{2m_h}{\hbar^2})^{\frac{3}{2}} \int_{-\infty}^{0} (-E)^{\frac{1}{2}} \exp[\beta(E-\mu)] dE \tag{1.2.10}$$

and by integrating we obtain

$$n_c = 2(\frac{m_e k_B T}{2\pi\hbar^2})^{\frac{3}{2}} \exp(\frac{\mu - E_g}{k_B T}) = N_c \exp(\frac{\mu - E_g}{k_B T}) \tag{1.2.11}$$

and

$$n_v = 2(\frac{m_h k_B T}{2\pi\hbar^2})^{\frac{3}{2}} \exp(\frac{-\mu}{k_B T}) = N_v \exp(\frac{-\mu}{k_B T}) \tag{1.2.12}$$

where N_c and N_v are respectively the effective density of states.

For an intrinsic semiconductor, where the carriers are all created by the thermal agitation, the number of electrons in the conductance band must be equal to the number of holes in the valence band so long as $E_g >> k_B T$. Thus

$$n_c = n_v \tag{1.2.13}$$

and hence

$$\mu = \frac{E_g}{2} + \frac{3}{4} k_B T \ln(\frac{m_h}{m_e}) \tag{1.2.14}$$

The relation between the product $n_c n_v$ and the energy gap E_g may easily be found by using (1.2.11) and (1.2.12).

$$n_c n_v = 4(\frac{k_B T}{2\pi\hbar^2})^3 (m_e m_h)^{\frac{3}{2}} \exp(-\frac{E_g}{k_B T}) \tag{1.2.15}$$

Thus

$$n_c = n_v = 2(\frac{k_B T}{2\pi\hbar^2})^{\frac{3}{2}} (m_e m_h)^{\frac{3}{4}} \exp(-\frac{E_g}{2k_B T}) \tag{1.2.16}$$

from (1.2.13) and (1.2.14), showing that the carrier density varies with a Boltzman factor, as if it required the energy $\frac{1}{2}E_g$ to activate an electron into the conduction band; and obviously it is dependent on temperature. Silicon's intrinsic carrier concentration, for example, is roughly $10^{10} cm^{-3}$ at room temperature (300K) [6].

1.3 Extrinsic Semiconductors

If a very small number of atoms of a Group V element such as phosphorus (P) are added to the intrinsic semiconductor silicon (Si) as substitutional atoms in the lattice, additional valence electrons are introduced into the material because each phosphorus atom has 5 valance electrons. These additional electrons are bound only to their parent impurity atoms, and even at very low temperatures these electrons can be promoted into the conductance band of the semiconductor [7]. The levels associated with the group V atoms are called *(electron) donor levels* and the impurity atoms are called *donor atoms*. In band diagrams the donor levels can be indicated schematically

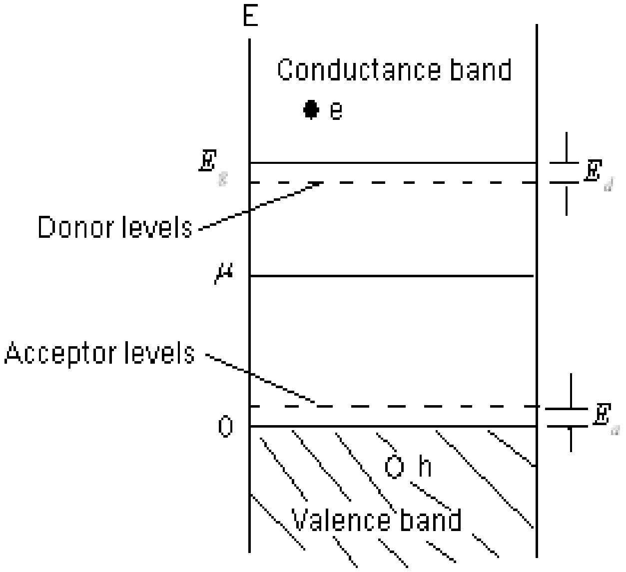


Figure 1.2: Electron donor and acceptor levels.

by a dashed line just below the bottom of the conductance band, as shown in fig 1.2. Note that the dashed line in the schematic diagram represents just the existence of additional electrons which may be easily excited into the conductance band. Semiconductors that have been doped in this way will have a surplus of electrons, and are called **N-type semiconductors**. In such semiconductors, electrons are the majority carriers.

Conversely, if a group III element, such as aluminium (Al), is used to substitute for some of the atoms in silicon, there will be a deficit in the number of valance electrons in the material. This introduces electron-accepting levels just above the top of the valance band and attributes to the introduction of more holes into the valance band. In this case, the majority charge carriers are positive holes, and semiconductors doped in this way are termed **P-type semiconductors**.

In the case of impurity or extrinsic semiconductors, the activation energy for electrons to be donated by or accepted to impurity states is usually so low that at room temperature the concentration of majority charge carriers is similar to the concentration of impurities. It should be remembered that in such semiconductors there is a contribution to the total number of charge carriers from intrinsic electrons and holes, which at room temperature is often very small in comparison with the number of charge carriers introduced by the controlled impurity doping of the host material.

If we consider an n-type semiconductor with N_d donor levels per unit volume, which lie just below the bottom of the conductance band, the impurity ionization energy E_d being very small compared with E_g, and assume that all of the donor atoms are ionized and that $N_d >> n_{ci}$ (where n_{ci} is the density of electrons in the conductance band), we may neglect n_{ci} and have the relationship

$$n_c = N_d \tag{1.3.1}$$

Using (1.2.11) and (1.3.1), we may write

$$\mu = E_g + k_B T \ln(\frac{N_d}{N_c}) \tag{1.3.2}$$

showing that as N_d increases, the fermi level will rise from its mid-gap intrinsic position to one close to the bottom of the conductance band when $N_d \simeq N_c$.

For N_a acceptor levels per unit volume lying just above the top of the valance band we may assume that these levels are completely occupied by electrons from the valance band and that the intrinsic contribution is negligible so that

$$n_v = N_a \tag{1.3.3}$$

Thus, using (1.2.12) and (1.3.3), we have

$$\mu = E_a + k_B T \ln(\frac{N_v}{N_a}) \tag{1.3.4}$$

This equation shows that as N_a increases, the Fermi level μ decreases towards the top of the valance band [5].

1.4 Electrical Properties

The ease with which electrons in a semiconductor can be excited from the valence band to the conductance band depends on the band gap between the bands. The electrons must move between states to conduct electric current, and so due to the Pauli's Exclusion Principle full bands do not contribute to the electrical conductivity. However, as the temperature of a semiconductor rises above absolute zero, the states of the electrons are increasingly randomized and some electrons are likely to be found in states of the conductance band.

Electrons excited to the conductance band also leave behind electron holes in the valance band. Both the electrons and the holes contribute to electrical conductivity.

The holes themselves do not actually move, but a neighboring electron can move to fill the hole, leaving a hole at the place it has just come from, and in this way the holes appear to move, and the holes behave as if they were actual positively charged particles, as depicted in the **E-K** diagram shown in fig. 1.3 [7].

The energy distribution of the electrons, which is described by Fermi Dirac statistics, determines which of the states are filled and which are empty. The distribution is characterized by the temperature of the electrons and the Fermi energy or Fermi level. The dependence of the electron energy distribution on temperature also explains why the conductivity of a semiconductor has a strong temperature dependency, as a semiconductor operating at lower temperatures will have fewer available free electrons and holes to do the work.

The energy-momentum dispersion relationship determines the effective mass, m_*, of electrons or holes in the semiconductor according to the formula:

$$m^* = \hbar^2 [\frac{d^2E(k)}{dk^2}]^{-1} \tag{1.4.1}$$

The effective mass is important as it affects many of the electrical properties of the semiconductor, such as the electron or hole mobility, which in turn influences the diffusivity of the charge carriers and the electrical conductivity of the semiconductor [6].

The property of semiconductors that makes them most useful for constructing electronic devices is that their conductivity may easily be modified by introducing impurities into their crystal lattice. The concentration of dopant (impurity) added to

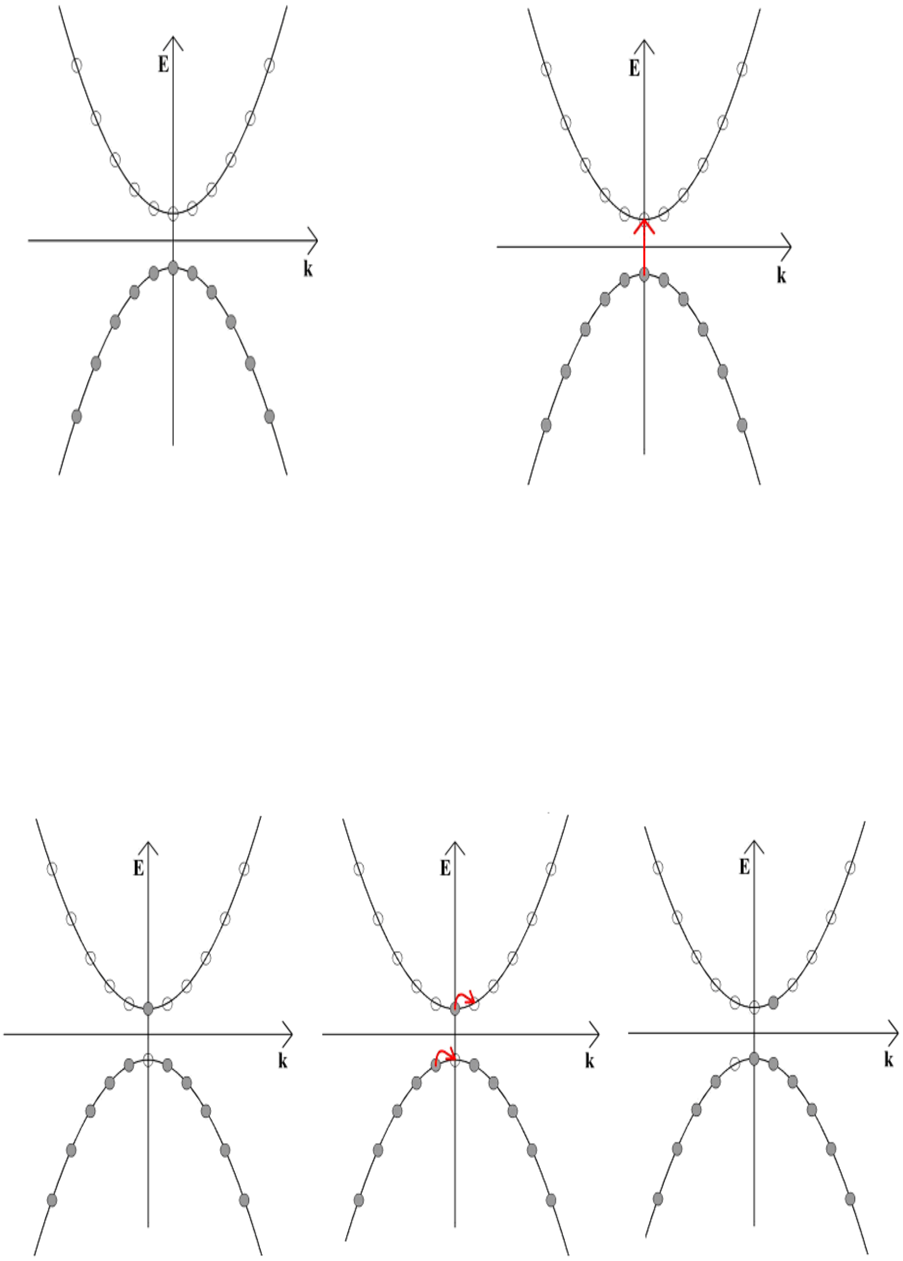


Figure 1.3: Thermal excitation of electrons from the valence band into the conductance band. Shaded circles represent filled momentum states and empty circles unfilled momentum states.

an intrinsic semiconductor affects many of its electrical properties. In general, an increase in doping concentration affords an increase in conductivity due to the higher concentration of carriers available for conduction. Very highly doped semiconductors have conductivity levels comparable to metals and are often used in modern integrated circuits as a replacement for metal.

Chapter 2

MAGNETIC PROPERTIES OF SEMICONDUCTORS

2.1 Introduction

Study of magnetism in insulators is much easier than in semiconductor or in metals due to absence of conduction electrons. Firstly, estimation of angular momentum of such electrons is difficult except when they could be treated as free gas. Secondly, they ”mediate” in many particle ion-ion interaction and make things more subtle.

At low temperatures undoped semiconductors would behave similar to insulators. But at higher temperature or with doped semiconductors or in metals, conduction electrons play very important role in magnetism and cannot be ignored. Similarly for diluted magnetic semiconductors, situation is not that simple.

Conduction electrons can contribute dipole moment due to orbital motion (Landau Diamagnetism) or spin (Pauli Paramagnetism). When a magnetic dipole moment is inside a dilutely alloyed semiconductor or in metallic alloys, the net magnetic moment on the ion might be quite different from that of the free ion depending on the position of the Fermi level (thermalization) [8].

2.2 Spontaneous Magnetization

Spontaneous magnetization can be of two types- **localized magnetism** and **itinerant magnetism**. Localized magnetism occurs due to the interaction between sufficiently localized and tightly bound inner shell electrons of atoms/ions at close by lattice sites. Assuming there are no free carriers, the interaction could be either dipolar which is magnetic in origin or it could be exchange interaction due to Pauli's exclusion principle which is purely electrostatic or Coulombic in origin.

Usually exchange interaction is much stronger compared to the dipolar interaction. Dipolar interaction can never explain spontaneous magnetization where electron-electron interaction is a must. First of all, they are much smaller in magnitude and cannot explain extremely strong spontaneous magnetizations at moderate temperatures. Moreover, dipolar interactions have opposite sign. They would like to keep the moments antiparallel to lower the energy of the system.

There could be many types of exchange interactions. When paramagnetic ion or atom cores are next to each other on the lattice sites and if they are not sufficiently tightly bound so that their electron clouds do overlap, then they can have direct exchange interaction. In the sea of conduction electrons two paramagnetic ions/atoms can interact with each other by the mediation of free electrons. This type of interaction is called **indirect exchange interaction**, and is dominant in metallic and semi conducting surroundings.

When two paramagnetic ions/atoms interact with the mediation of non-paramagnetic ion/atom sitting in between so that the paramagnetic ion/atom electron clouds do not overlap, we call such interactions **super exchange interaction**. Electrons that are not well localized and are shared by the entire crystal can have exchange interactions called **itinerant exchange interaction**.

Itinerant spontaneous magnetism occurs due to exchange interactions among free electrons which are shared by the entire crystal [8].

2.3 Diamagnetism and Paramagnetism

A diamagnetic substance has no free magnetic dipole moment in its constituent atoms. When an electron moving in an atomic orbit is in a magnetic field **B**, the force exerted on the electron produces a small change in the orbital motion. Each electron in the field acquires an additional angular momentum that contributes to the magnetization of the sample. The magnetic susceptibility of the substance containing N atoms per unit volume is given by

$$\chi = -\mu_0 N(\frac{e^2}{6m})\sum\langle r^2\rangle \tag{2.3.1}$$

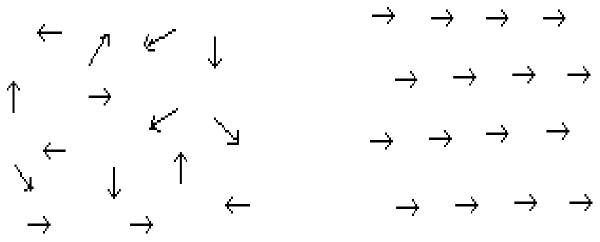
where e and m are the charge and mass of the electron, $\sum\langle r^2\rangle$ is the sum of the mean square radii of all electron orbits in each atom, and the negative sign is a direct consequence of Lenz's law (i.e. the induced magnetic moment is directed opposite to **B**). Hence, susceptibility of diamagnetic substances is independent of both field strength and temperature. Rare gases of the atmosphere show diamagnetism [9].

Substances with free magnetic dipole moments have not net magnetization since the orientation of their moments is normally random. In a magnetic field, the dipoles are no longer completely randomly oriented; more dipoles point with the field than against the field. In this case, the substance will have a net positive magnetization in the direction of the field. Such substances have positive susceptibility and are classified as paramagnetic.

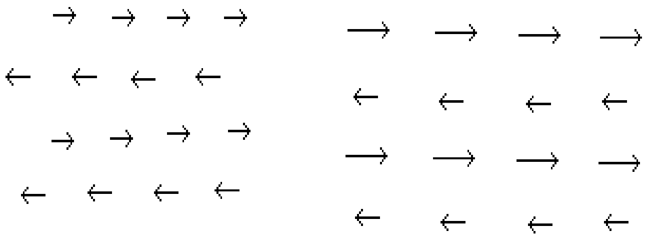
The magnitude of magnetization M of paramagnetic matter depends on the ratio of the magnetic energy mB of the individual dipoles to the thermal energy $k_B T$. At low magnetic fields, the magnetization is linearly proportional to the field, and Curie's law should hold provided that no other forces act on the dipoles. When the magnetic energy is much greater than the thermal energy, the magnetization reaches its maximum saturation value [9]. Some examples of paramagnets include alkali metals and Aluminium.

2.4 Ferromagnetism and Antiferromagnetism

At sufficiently low temperatures many paramagnetic materials undergo a transition to a state where all the spins align co-operatively and strongly enhance the magnetic properties of the material. When the neighboring spins align in the same direction



(a) Paramagnetism (b) Ferromagnetism



(c) Antiferromagnetism (d) Ferrimagnetism

Figure 2.1: Atomic dipoles in different magnetic materials.

throughout a reasonably extensive region (a domain) of the sample, a strong magnetization is obtained and remains after the magnetizing field is removed. This is the **ferromagnetic phase** [10].

The magnetic susceptibility of Ferromagnets above the Curie temperature T_c follows the Curie-Weiss law, $\chi = \frac{C}{T-T_c}$, in the mean field approximation, and at such temperatures the substance is still paramagnetic. When the temperature reaches the Curie temperature T_c, $\frac{1}{\chi}$ becomes zero and hence the magnetization $\mathbf{M}$ at this temperature must be finite even when the magnetic field $\mathbf{H}$ is zero. Thus, the substance exhibits a spontaneous magnetization $\mathbf{M}$ at and below the Curie temperature in the absence of an external field, which is the essential property of a Ferromagnet [7, 9, 10]. Common examples are iron ($T_c = 1043K$), cobalt ($T_c = 1403K$) and nickel.

Some group of materials such as NiO show a transition from the paramagnetic state at high temperatures to an antiferromagnetic state below a certain characteristic temperature, known as the **Neel temperature** T_N, in which neighboring spins are aligned in an ordered and antiparallel manner. At zero temperature the net spontaneous magnetization of antiferromagnetic substance vanishes and it increases with temperature. At or near the transition temperature its value depends on the applied field, higher the field higher the magnetization [8, 9, 10].

2.5 Ferrimagnetism

In some substances like the magnetite Fe_3O_4, the atomic dipoles are of different magnitudes and those pointing in one direction are all different in size from those pointing in the opposite direction. In this case there exists permanent magnetization on a macroscopic scale in an effect known as **ferrimagnetism**.

2.6 Ferromagnetic Spin Waves

In the case of an elastic solid, we know that if an atom is displaced from its equilibrium position, it will oscillate with the motion and frequencies associated with the harmonic oscillators of the crystal. The effect of quantum mechanics on this motion is to quantize the amplitudes of the normal modes, or the harmonic oscillators with the resulting quanta, phonons. Similarly, the elementary excitations in a ferromagnetic material result in spin waves of motion, which are analogous to the normal modes of the crystal. By analogy with phonons, such elementary excitations are called magnons [11, 12].

The ground state of a simple ferromagnet has all spins parallel. The excitations of the system correspond to states in which a single spin is deviated, as in fig. 2.2. However, each spin interacts with its neighbour and hence the spin deviation has to be exchanged with the neighbouring spin. Spin deviations keep moving about through the system; like the process by which electrons are handed on from one atom to the next in the tight binding model of Bloch states [4, 7, 11].

2.7 Role of Exchange Interaction in Ferromagnetism

A quantum mechanical effect known as the exchange interaction is involved in the spontaneous alignment of electrons in ferromagnetic materials, in addition to the

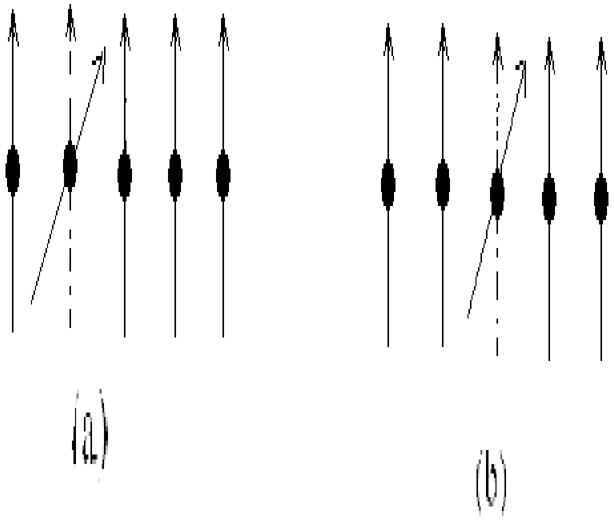


Figure 2.2: Spin deviation exchanges

dipolar interaction. The exchange interaction is due to Pauli's exclusion principle which is purely electrostatic or coulombic in origin, and is usually much stronger compared to the dipolar interaction.

In metallic and semiconducting materials, the indirect exchange interaction is usually dominant. One of the main mechanisms for indirect exchange interactions in diluted magnetic semiconductors (DMSs) is the RKKY (Runderman-Kittel-Kasaya-Yosida) mechanism [8, 9, 11].

The magnetic properties of iron (Fe), an example of ferromagnet, are thought to be the result of the magnetic moment associated with the spin of an electron in an outer atomic shell, specifically the 3d-shell. The effect of the spin Pauli's exclusion principle is opposite that required to align the electrons responsible for the spontaneous magnetization in the iron domains and can be viewed as "repulsive" mechanism for spins in the same direction. However, other electrons with spins in the opposite direction, primarily in the 4*s*-shell, interact at close range with the magnetization electrons (in the 3*d-shell*). This interaction is attractive. Hence the s-shell electrons influence the magnetization electrons (d-shell electrons) of a number of the iron atoms and align them with each other [9].

For the exchange interaction between the spins of the electrons on neighboring atoms in zero magnetic field, the spin Hamiltonian can be written in the form

$$H = -\sum_{ij} J_{ij} S_i \cdot S_j \tag{2.7.1}$$

where J_{ij} is a ferromagnetic exchange integral and $\mathbf{S}_i$ a total spin operator to the atom on the i^{th} lattice site. J_{ij} is a function of the relative positions of the sites i and j (i.e, $\mathbf{r}_i - \mathbf{r}_j$). Equation (2.7.1) is true for the strictly localized model of Heisenberg and Dirac.

However, the origin of ferromagnetism in CaAs is believed to be due to an exchange interaction between spin of conduction electrons and localized spin of the electrons in the unfilled shell, as it will be discussed in the 4^{th} chapter. The form of the Hamiltonian in this case can be written in the form

$$H = -\sum_{ij} J_{ij} \hat{\sigma}_i \cdot \mathbf{S}_j \tag{2.7.2}$$

where J_{ij} in this case is the p-d exchange integral, $\hat{\sigma}_i$ is the total spin operator of the conduction (mobile) electrons to the atom on the site i , and S_j is the total localized spin operator to the atom/ion on the site j [3, 8, 11, 13].

A simple empirical representation of the effect of exchange interactions invokes the idea of an effective internal or molecular field H_I, which is proportional in size to the magnetization M_I, i.e, $\mathrm{H}_I = \lambda M$ in which λ is an empirical parameter. The resulting magnetization is thus given by

$$M = \chi_p(H + \lambda M) \tag{2.7.3}$$

where χ_p is the susceptibility that the substance would have in the absence of the internal field, and H is an external field [9].

Chapter 3

DILUTED MAGNETIC SEMICONDUCTORS

3.1 Introduction

Do you ask yourself every time you turn on your computer while waiting for the operating system and programs to load from the hard drive into random access memory (RAM) the question ”When will this finally be as easy as switching on the light?”. The answer might be ”not far in the future.” Currently, most information is stored in a nonvolatile way in magnetic bits on hard drives that make use of electrons’ spin (their orientation up or down), while semiconductor devices like RAM operate by manipulating electron charge. But the ability to manipulate electrons’ spin together with controlling their charge flow could create a host of new capabilities for computer technology-like eliminating the need for lengthy boot-up times. This is the topic of an exciting research field known as ”spintronics”, in which electron (or nuclear) spin is utilized instead of or in addition to charge for the application of quantum computing and communications.

Manipulating an electron's magnetic state in a semiconductor device is the key to successful spintronics, and the simplest way to do that is by using a semiconductor material such as gallium arsenide (GaAs), which incorporates magnetic elements like manganese (Mn). A major obstacle to developing such devices is creating magnetic semiconductor materials that work at room temperature. In their research, Edmonds *et al.* correlate the electronic and magnetic characteristics of electrons in manganese-doped gallium arsenide. Their results are crucial for understanding and further development of a new class of semiconductors, dilute magnetic semiconductors (DMSs), which are obtained by the random substitution of a fraction of the original atoms by magnetic atoms [1, 2, 3, 8].

3.2 II-VI Ferromagnetic DMSs:

Studies of DMSs and their heterostructures have centered mostly on II-VI semiconductors, such as CdTe, CdSe and ZnSe, in which the valence of the cations matches that of the common magnetic ions such as Mn, Fe, or Co. Although this phenomenon makes these DMSs relatively easy to prepare in bulk form as well as in thin epitaxial layers, II-VI based DMSs have been difficult to dope to create p- and n-type semiconductors, which made the material less attractive for applications. Moreover, the magnetic interaction in II-VI DMSs is dominated by the antiferromagnetic exchange among the dopant Mn spins, which results in the paramagnetic, antiferromagnetic, or spin-glass behavior of the material [8].

3.3 III-V Ferromagnetic DMSs:

An approach compatible with the semiconductors used in present-day electronics is to make nonmagnetic III-V semiconductors magnetic, and even ferromagnetic, by introducing a high concentration of magnetic ions. The III-V semiconductors such as GaAs are already in use in a wide variety of electronic equipment in the form of electronic and optoelectronic devices, including cellular phones (microwave transistors), compact disks (semiconductor lasers), and in many other applications. Therefore, the introduction of magnetic III-V semiconductors opens up the possibility of using a variety of magnetic phenomena not present in conventional nonmagnetic III-V semiconductors in the optical and electrical devices already established.

The major obstacle in making III-V semiconductors magnetic has been the low solubility of magnetic elements (such as Mn) in the compounds. Because the magnetic effects are roughly proportional to the concentration of the magnetic ions, one would not expect a major change in properties with limited solubility of magnetic impurities, of the order of $10^{18}cm^{-3}$ or less. A breakthrough was made by using molecular beam epitaxy (MBE), a thin-film growth technique in vacuum that allows one to work far from equilibrium. When a high concentration of magnetic elements is introduced in excess of the solubility limit, formation of the second phase occurs if conditions are near equilibrium.

However, when the crystal is grown at low temperature by MBE, there is not enough thermal energy available to form the second phase, and yet there still exists a local potential landscape that allows epitaxial growth of a single-crystal alloy. The effort to grow new III-V based DMSs by low-temperature MBE was rewarded with successful epitaxial growth of uniform (In,Mn)As films on GaAs substrates in 1989, where partial ferromagnetic order was found, and ferromagnetic (Ga,Mn)As in 1996 [8].

Currie temperature, T_c, for these alloys can be calculated from the exchange constant, and the hole concentration can be determined from the magnetotransport measurements. The calculated T_c is found to be in good agreement with the experimentally determined T_c (by Ohno *et.al*) justifying RKKY to be the most likely reason for ferromagnetism. The understanding of the ferromagnetism of (Ga,Mn)As is not adequate, however. There are issues remaining to be studied such as to what extent the pure RKKY interaction is applicable to the present material system. It was pointed out, for example, that the behavior of the critical scattering may be qualitatively different when the spin-spin interaction is of long range (present case) as opposed to the short range interaction (magnetic semiconductors) [1, 8].

3.4 Calcium Pnictides:

Very recently, new candidates for ferromagnetic DMSs were theoretically designed by Geshi *et al* [13]. These materials are compounds of calcium and Group V elements including phosphorus (P), aresenic (As), and antimony (Sb). In doing so the zincblende structure was assumed.

The interest of this thesis is, in fact, to study the magnetic property of CaAs without doping process with any magnetic impurity. These materials are curious in that none of their components possess magnetic moment. It was found that ferromagnetism is the dominant magnetic property of these curious compounds [3, 8, 13, 14].

Chapter 4

MECHANISM OF MAGNETISM IN CaAs

4.1 Introduction

Significant theoretical activities have been devoted to the study of the electronic and magnetic properties of some DMSs including CrAs, GaAs and CrTe in the zinc blende lattice structure (by Kenmochi *et al* and Seike *et al*) [15] and the mechanism of the ferromagnetism is reported to be attributed to Zener's double-exchange mechanism. As reported by Elfimov *et al* [16] rock-salt CaO is found to be ferromagnetic due to interorbital exchange interaction between doubly degenerate molecular orbitals in O^{2-} cluster surrounding a Ca vacancy. A similar argument was proposed for CaB_6 by R. Monnier *et al* [17] in which the vacancies in the B_6^{2-} cluster were supposed to be the origin of magnetism.

But in zb-CaAs there are no such vacancies in the crystal and the ferromagnetism mechanism has to be studied differently. In fact focus will be on the intra-atomic exchange between p-electrons of the As atom.

4.2 The Ferromagnetic Interaction Hamiltonian

Calcium is a metal with the atomic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ that when combined with arsenic ($[Ar]3d^{10}4s^2 4p^3$) forms an ionic compound, calcium arsenide. In the zinc-blende structure of CaAs (zb-CaAs), 2 4s electrons of Ca and 3 4p electrons of As contribute to bond formation. Since there are no localized d spins in zb-CaAs, the double exchange nor p-d exchange like that induced by the 3d-transition metals do not work. The magnetism must be understood by another mechanism: the exchange interaction between conduction (mobile) electron spin of Ca and localized electron spin of As in which the localized electrons provide the definite spin and the conduction electrons are polarized by them. The interaction between the As atoms is provided by the conduction electrons.

The resultant spin polarization of the Ca conduction electrons, constrained by the Pauli exclusion principle, is not well localized in the vicinity of the As atoms, but is oscillatory. The As atoms which polarize the spins of the conduction electrons in their nighbourhood, at arbitrary distances from the latter suffer an exchange interaction with each other either in the trough or on the crest of the polarization wave via the conduction electrons.

Now we formulate the theory of the conduction Ca electrons interacting with the localized As atoms. To avoid dealing with wave functions and eigenvalues explicitly, the Hamiltonian describing the exchange interaction in the system will be expressed in terms of the creation and the annihilation operators.

In the absence of external magnetic field, the ferromagnetic interaction Hamiltonian can be written as

$$H_{pd} = -\sum_{ij} J_{pd}\hat{\sigma}_i(\mathbf{r}_i) \cdot \mathbf{S}_j(\mathbf{R}_j) \tag{4.2.1}$$

where the exchange integral J_{pd} is positive for ferromagnetic ordering; $\hat{\sigma}_i$ and $\mathbf{S}_j$ are total spin operators of each of the conduction electrons and localized atoms located at lattice sites $\mathbf{r}_i$ and $\mathbf{R}_j$, respectively. It describes the exchange interaction or spin dependent coupling in the p-d hybridization between d orbitals of Ca and localized p orbitals of As.

We define new spin operators at the sites $\mathbf{r}_i$ and $\mathbf{R}_j$ as

$$\sigma_i^+ = \sigma_i^x + i\sigma_i^y; \qquad \sigma_i^- = \sigma_i^x - i\sigma_i^y \tag{4.2.2}$$

$$S_j^+ = S_j^x + iS_j^y; \qquad S_j^- = S_j^x - iS_j^y \tag{4.2.3}$$

from which one obtains

$$\sigma_i^x = \frac{1}{2}(\sigma_i^+ + \sigma_i^-); \qquad \sigma_i^y = \frac{1}{2i}(\sigma_i^+ - \sigma_i^-) \tag{4.2.4}$$

$$S_j^x = \frac{1}{2}(S_j^+ + S_j^-); \qquad S_j^y = \frac{1}{2i}(S_j^+ - S_j^-) \tag{4.2.5}$$

Thus $_i \cdot \mathbf{S}_j = \sigma_i^x S_j^x + \sigma_i^y S_j^y + \sigma_i^z S_j^z \;\; = 1\frac{}{4(\sigma_i^+ + \sigma_i^-)(S_j^+ + S_j^-) - \frac{1}{4}(\sigma_i^+ - \sigma_i^-)(S_j^+ - S_j^-) + \sigma_i^z S_j^z}$

$$= \frac{1}{2}(\sigma_i^+ S_j^- + \sigma_i^- S_j^+) + \sigma_i^z S_j^z \tag{4.2.6}$$

where equations (4.2.4) and (4.2.5) have been utilized. Substituting (4.2.6) in (4.2.1), we find

$$H_{pd} = -\sum_{ij} J_{pd}[\frac{1}{2}(\sigma_i^+ S_j^- + \sigma_i^- S_j^+) + \sigma_i^z S_j^z] \tag{4.2.7}$$

The conduction-band spin operators, $\sigma_i^{\pm}$ and σ_i^z, are recognized as the Fermion representation of the spin one-half operators, given by

$$\sigma_i^+ = a_{k'\uparrow}^+ a_{k\downarrow}; \quad \sigma_i^- = a_{k'\downarrow}^+ a_{k\uparrow}; \quad \sigma_i^z = \frac{1}{2}(a_{k'\uparrow}^+ a_{k\uparrow} - a_{k'\downarrow}^+ a_{k\downarrow}) \tag{4.2.8}$$

with a_k^+ and a_k satisfying the anticommutation relations and $\hbar = 1$, and the localized spin operators can be expressed in terms of the boson creation and annihilation operators a_j^+ and a_j obeying the commutation relations by using the Holstein-Primakoff transformation as

$$S_j^+ = \sqrt{2S}(1-\frac{a_j^+ a_j}{2S})^{\frac{1}{2}} a_j \simeq \sqrt{2S} a_j; \quad S_j^- = \sqrt{2S} a_j^+ (1-\frac{a_j^+ a_j}{2S})^{\frac{1}{2}} \simeq \sqrt{2S} a_j^+; \quad S_j^z = S - a_j^+ a_j \tag{4.2.9}$$

where

$$a_j = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} a_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_j}; \quad a_j^+ = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} a_{\mathbf{k}}^+ e^{i\mathbf{k}\cdot\mathbf{R}_j} \tag{4.2.10}$$

for very small thermal excitations (very small temperatures) and S is the total spin quantum number of each localized moment.

4.3 Ferromagnetic Transition Temperature

The dependence of magnetization **M** on the magnetic field **H** and the total electronic spin quantum number S of the magnetic moments of the atom or ion can be described by the Brillouin function $B_S(x)$ according to

$$\mathbf{M}(\mathbf{H}, T) = ng\mu_B S B_S(x) \tag{4.3.1}$$

where n is the spin concentration, g the Landé g-factor, and μ_B the Bohr magneton. The Brillouin function which varies from -1 to 1 is given by

$$B_S(x) = \frac{2S+1}{2S}\coth(\frac{2S+1}{2S}x) - \frac{1}{2S}\coth(\frac{1}{2S}x) \tag{4.3.2}$$

with x=gS$\mu_B H_{\overline{k_BT,}}$ the Zeeman energy of the magnetic moments in the total field H, k_B the Boltzmann constant and T the temperature. Since we are dealing with a ferromagnetic specimen, H=H$_{app} + \lambda M$, where λ is the molecular field constant.

If we focus our attention on a particular spin $\hat{\sigma}_i$, the interaction Hamiltonian in (4.2.1) may be written as

$$H_{pd} = -J_{pd}\hat{\sigma}_i \cdot \sum_j \mathbf{S}_j = \frac{J_{pd}}{g\mu_B}\hat{\sigma}_i \cdot \sum_j \mathbf{M}_j(\mathbf{R}_j) \tag{4.3.3}$$

where $\mathbf{M}_j(\mathbf{R}_j)$, the magnetization of the localized spins, carry magnetic moment $-g\mu_B\mathbf{S}_j$. The effective magnetic field $\mathbf{H}(\mathbf{r}_i)$ acting on the spin $\hat{\sigma}_i(\mathbf{r}_i)$ in the absence of applied field is

$$H(r_i) = \frac{J_{pd}}{(g\mu_B)}\sum_j \mathbf{S}_j \tag{4.3.4}$$

In the MFA the operator $\mathbf{H}(\mathbf{r}_i)$ is replaced by its thermal equilibrium mean value. In the case of a ferromagnet, every spin has the same mean value, which can be represented in terms of the total magnetization as

$$\langle\hat{\sigma}_i(\mathbf{r}_i)\rangle = -\frac{1}{g\mu_B}\sum_j \mathbf{M}_j(\mathbf{r}_i - \mathbf{R}_j) \tag{4.3.5}$$

Expressing the magnetization as a function of H, (4.3.5) becomes

$$\langle\hat{\sigma}_i(\mathbf{r}_i)\rangle = -\frac{J_{pd}}{(g\mu_B)^2}\sum_j \chi(\mathbf{r}_i - \mathbf{R}_j)\hat{\sigma}_i(\mathbf{r}_i) \tag{4.3.6}$$

where χ is the electronic spin susceptibility. With all operators replaced by their mean value and recalling that $\mathbf{M}_j(\mathbf{R}_j) = -g\mu_B \mathbf{S}_j(\mathbf{R}_j)$, one obtains $\mathrm{H}_{pd} = \frac{J_{pd}^2}{(g\mu_B)^2} \sum_j \chi(\mathbf{r}_i - \mathbf{R}_j)\hat{\sigma}_i \cdot \mathbf{S}_j$ or

$$g\mu_B H(r_i) = \frac{J_{pd}^2}{(g\mu_B)^2} \sum_j \chi(\mathbf{r}_i - \mathbf{R}_j)\langle S_j \rangle \tag{4.3.7}$$

Near magnetic transition temperature, the magnetization is small and hence $\frac{g\mu_B S}{k_B T} H << 1$, which upon expansion leads to

$$B_S(\frac{g\mu_B S}{k_B T} H)_{T \to T_c} \simeq [\frac{(S+1)g\mu_B H}{3k_B T_c}] \tag{4.3.8}$$

Now we consider equation (4.3.1) to find $\langle S_i \rangle$ as

$$\langle S_i \rangle = S\frac{(S+1)ng\mu_B H(r_i)}{3k_B T_c} \tag{4.3.9}$$

where (4.3.8) has been utilized. Combining (4.3.7) and (4.3.9), we obtain

$$\langle S_i \rangle = nS\frac{(S+1)}{3k_B T_c}\frac{J_{pd}^2}{(g\mu_B)^2} \sum_j \chi(r_i - R_j)\langle S_j \rangle \tag{4.3.10}$$

To estimate the Curie-Weiss Temperature, we consider the Fourier Transform of (4.3.10), i.e,

$$\langle S_q \rangle = S\frac{(S+1)}{3k_B T_c}\frac{J_{pd}^2}{(g\mu_B)^2} n\chi(q)\langle S_q \rangle \tag{4.3.11}$$

Thus

$$T_c = S\frac{(S+1)}{3k_B}\frac{J_{pd}^2}{(g\mu_B)^2} n\chi(q) = An \tag{4.3.12}$$

where A is a constant and q the wave vector for which $\chi(q)$ is maximum.

As it can be seen from (4.3.12), the Curie temperature vs spin concentration graph has to be a straight line because other quantities are constant in a very weak (negligible) magnetic field.

4.4 Magnetoresistance

The magnetoresistance of a certain metal, semiconductor or alloy describes the increase in electrical resistance of the material when an external magnetic field is applied upon it. It is usually measured as the change of resistance ΔR relative to the zero-field resistance R(0). For most metals the transverse magnetoresistance is positive, but there are a few cases for which it is negative, notably ferromagnetic materials and some diluted alloys.

The increase in resistance of a specimen for weak fields ($|\omega_c|\tau << 1$) acting perpendicular to the current direction as measured by $\frac{\Delta R}{R}$ is proportional to H^2. In strong magnetic fields, it is proportional to H, i.e, $\Delta R\frac{}{R=\frac{R(H)-R(0)}{R(0)}\propto H^2 \qquad (forsmallfields),and}$ $\Delta R\frac{}{R=\frac{R(H)-R(0)}{R(0)}\propto H \qquad (forlargefields)}$

The magnetoresistance effect observed when the magnetic field is applied parallel to the current direction is smaller than the transverse effect [18, 19].

The equation of motion of the drift velocity **v** of a gas of charge carriers having mass m in the presence of an electric field **E** and a magnetic field $\mathbf{H} = H\hat{z}$ is

$$m\frac{d\mathbf{v}}{dt} = q\mathbf{E} + \frac{q}{c}(\mathbf{v} \times \mathbf{H}) - \frac{m}{\tau}\mathbf{v} \qquad (4.4.1)$$

where τ is the relaxation time.

In the steady state, $\frac{d\mathbf{v}}{dt} = 0$, assuming current flows in the x-direction and introducing the cuurent density components, $j_\alpha = \sigma_{\alpha\beta}E_\beta = nqv_\alpha$, n being the carrier concentration and $\sigma_{\alpha\beta}$ the conductivity tensor, we find the Hall field as

$$E_y = (\frac{H}{nqc})j_x \tag{4.4.2}$$

and thus the Hall coefficient is

$$R_H = \frac{E_y}{j_x H} = \frac{1}{nqc} \tag{4.4.3}$$

The transverse magnetoresistance $\rho(H)$ can be found by taking the ratio of the electric field along the x-direction to the current density j_x,

$$\rho(H) = \frac{E_x}{j_x} \tag{4.4.4}$$

For two-carrier types, electrons of effective mass m_e, relaxation time τ_e and concentration n_e, and holes of mass m_h, relaxation time τ_h and concentration n_h, of semiconductors in the high field limit,we have

$$j_y = \frac{(n_h - n_e)ec}{H}E_x \tag{4.4.5}$$

and

$$\sigma_{yx} = (n_h - n_e)\frac{ec}{H} \tag{4.4.6}$$

In the case when $n_h = n_e = n$, $\sigma_{yx} = 0$ which results in $E_y = 0$ as $j_y = 0$. Hence the effective magnetic conductivity is found approximately as

$$\sigma_{xx} = \frac{n|e|}{H^2}(\frac{m_e}{|e|\tau_e} + \frac{m_h}{|e|\tau_h}) \tag{4.4.7}$$

In this case the effective magnetic resistivity $\rho(H)$ may easily be found by taking the reciprocal of the effective conductivity σ_{xx}, i.e, $\rho(H) = \frac{1}{\sigma_{xx}}$ The experimental datum is not yet available on CaAs to see the validity of the above obtained result.

4.5 The Origin of Magnetism

The compound investigated has a total magnetic moment M of $1\mu_B$ per formula unit. This can be determined by the general rule, $M = |Z_v - 8|\mu_B$, where Z_v is the total number of valence electrons per formula unit. This indicates that the slightly hybridized localized anion p band is completely filled with the exception of a single hole. Clearly this hole is responsible for the $1\mu_B$ magnetic moment of CaAs.

To confirm this we compare two hypothetical model crystals. The first one is the fcc lattice of As, and the second is zb-CaAs. We assume both have the same lattice constant. The p-electrons in the first model align their spins in the same direction and the local magnetic moment is $3\mu_B$. If we add two more electrons to this hypothetical model the magnetic moment would be $1\mu_B$ which is the same as that of the zb-CaAs. This implies that the role of Ca atom in zb-CaAs is to provide two electrons with As atoms at the fcc sites. Ca plays the same role in the case of rock-salt-CaAs with a different equilibrium lattice constant in which its position is different from that in zb-CaAs. Equilibrium lattice constants of CaAs obtained by spin generalized gradient approximation (spin-GGA) calculations for the ferromagnetic state in the zinc-blende, rock-salt and CsCl type are, respectively, 6.75, 6.03 and 3.65 $\mathring{A}$ [20]. It seems that Ca atom determines the equilibrium lattice constant of the crystals.

The ferromagnetic state in zb-CaAs is localized where the unpaired spins are positioned in well defined orbitals and appears as an undispersed band. The magnetic moment of the compound can be attributed mainly to the anion (arsenide) [$\simeq 0.46\mu_B$], the cation (Ca ion) contributes a very small amount [$\simeq 0.11\mu_B$] as given by Geshi *et al* [3]. The interstitial region contributes a relatively considerable amount of magnetic moment [$\simeq 0.43\mu_B$] created due to mainly the slight hybridization of d states of Ca with p states of As. Hence the density of spins is well localized at the arsenic (As) sites in the zb-CaAs crystal.

The cation moments are aligned parallel to the anion (localized spin) moments because of p-d hybridization. The hybridization of d orbitals of Ca with the p orbitals of As results in a flat p band near the Fermi energy E_F. Thus the flat band ferromagnetism in zb-CaAs is favoured by the presence of the d states of Ca. If we remove the Ca atoms from the system, spin polarization will not take place; therefore, Ca atoms play an important role.

Chapter 5

Conclusion

We investigated that the ionic compound composed of Ca metal and group V element As is a promising ferromagnetic material if a zinc-blende crystal structure is assumed. The origin of ferromagnetic order of this material depends on the appearance of a flat arsenic p-electron band at the Fermi energy in the fully ordered compound. This is in contrast to most other diluted magnetic semiconductors like CrAs and Mn-doped GaAs where they possess magnetic moments or magnetic transition metal impurities are inserted into a host crystal. An expression for the Curie-Wiess temperature T_c below which ferromagnetic order will ensure have been obtained. In the absence of parameter values, numerical estimates have not been made.

The strange ferromagnetic order in zb-CaAs is favored by large lattice constants and empty 3d orbitals that are present due to the Ca cations. The mechanism of magnetism has been confirmed by studying fcc-As with two electrons added and by this it is considered that the role of Ca is to provide two electrons with the hypothetical crystal and to adjust the atomic distances between the As atoms. The slightly hybridized p states of As atom interact with each other via the exchange interaction.

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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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