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Room temperature ferromagnetism in Dilute Magnetic Semiconductors

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Abstract*—Dilute magnetic semiconductors (DMS) has been attracting researchers due to their potential application in future spintronics applications. But most of practical applications require Curie temperature for DMS to be around room temperature or more. Hence significant research work has been carried out on finding suitable DMS which has high Curie temperature. In this article primarily we have tried to derive the expression for curie temperature by applying Coherent Potential Approximation to Mean Field theory for magnetism in DMS. Then based on the expression for curie temperature it's dependence on various parameters like carrier density, magnetic impurity density, carrier mean free path, type of impurity, defects etc has been found.

***Index Terms*— DMS, Ferromagnetism**

I. Introduction

Recently Dilute Magnetic Semiconductors have become focal point of researchers due to their promising applications in the field of spintronics . Although Magnetic semiconductors has been studied since early 1980's but still they have not been adopted for practical applications and are limited to laboratory experiments. One of the main reason which has hampered their usage in practical applications may be low curie temperature. Dilute magnetic semiconductors are broadly divided in two categories i.e II-VI DMS and III-V DMS. The II-VI semiconductor based DMS like Zn1-xMnxTe and Cd1-xMnxTe has not become so popular because most of these DMS are paramagnetic in nature. Still they have been used in some small applications like optical isolators. But unlike these III-V semiconductor based DMS like In1-xMnxAs and Ga1-xMnxAs are very popular because they show strong ferromagnetism and have higher curie temperature. Also their Curie temperature depends on carrier concentration which can be controlled by doping. Sometimes ternary semiconductors are also preferred due to ease in p-type doping and higher carrier mobility which results in strong double exchange interactions between transition metal ions (dopant). Dietl proposed several suitable candidates as hosts for DMS based on the mean field theory. All these materials were assumed to be exhibit p-type conductivity, and the carrier-mediated magnetism was expected to come about due to sp-d hybridization. However, most of the work published on high temperature magnetic order DMS materials has involved n-type materials such as Co-doped ZnO or Mn-doped GaN. Some of these materials have been shown in table 1. [5][9][11]

Recently Cu doped Zn1-xFexO based ferromagnetic semiconductors has been successfully synthesized with curie temperature of 550 K and saturation magnetization of 0.75μB per Fe at room temperature.[1] Recently spin-coated nickel-doped zinc oxide nano-crystalline thin films using high-quality colloidal diluted magnetic semiconductor (DMS) quantum dots as solution precursors has been successfully prepared. These films show robust ferromagnetism with Curie temperatures above 350 K and 300 K saturation moments up to 0.1 Bohr magnetrons per nickel.[2] Above room temperature ferromagnetic behavior has been achieved in Si through Mn ion implantation with saturation magnetization of 0.3 emu⁄g at 300 K. The saturation magnetization increased twice after annealing at 800 °C for 5 min. The Curie temperature for all samples was found to be greater than 400 K. A significant difference in the temperature-dependent remnant magnetization between the implanted p-type and n-type Si is observed, giving strong evidence that a Si-based diluted magnetic semiconductor can be achieved.[3]

Recently efforts has been carried out to control Ferromagnetic behavior of GaMnN-DMS using electric field . The exchange interaction between Mn ions and holes in GaMnN DMS results in FM ordering, which can be altered by controlling the number of interacting holes. However, Mn forms deep acceptor bands in GaMnN films resulting in an insulating film and even the doping with the Mg acceptor does not improve the film conductivity. Consequently, the electric

field controlled FM has been difficult to realize. But it has been observed that p-type AlGaN/GaN strained-layer superlattices (SLSs) forming p-SLS/GaMnN/p-SLS heterostructure overcome the problem of the highly resistive GaMnN films. A correlation between the FM of the film and the availability of holes in the p-type SLSs has been observed. The idea is to separate the DMS mediating hole carriers from the GaMnN films by growing GaMnN on a p-GaN layer. The source of mediating carriers is the p-GaN and the hole concentration can be controlled by applying an electric field.[12]

Table 1

Material	Eg (eV)	Doping	μ_B	T_C (K)
GaN	3.5	0.9% Mn Cr	0.9 0.9	940 > 400
AlN	4.3	7% Cr 5% V	1.2 4.2	> 600 > 400
TiO_2	3.2	1-2% Co 7% Co 2% Fe	0.3 1.4 2.4	> 300 650-700 > 300
SnO_2	3.5	5% Fe 5% Co	1.8 7.5	610 650
ZnO	3.3	15% V 5% Fe 1% Cu 10% Co 0.9% Ni	0.5 0.75 2.0 0.06	> 350 550 280-330 > 300
Cu_2O	2.0	5% Co 0.5% Al	0.2	> 300
$In_{1.8}Sn_{0.2}O_3$	3.8	5% Mn	0.8	> 300

Room temperature ferromagnetism has also been observed in Nb-doped $SrTiO_3$ (NSTO) single crystals. The ferromagnetism can be eliminated by air annealing and can be again recovered by subsequent vacuum annealing. The temperature dependence of magnetic moment intimately resembles the temperature dependence of carrier density suggesting an intrinsic origin of the ferromagnetism - carrier-mediated Ruderman-Kittel-Kasuya-Yosida interaction.[4]

Consider DMS of the type $A_{1-x}Mn_xB$, where the parent material AB is assumed to be a nonmagnetic III-V compound and both of the exchange interaction between carrier and impurity spins, and the direct exchange interaction between magnetic impurities are taken into account

$$H = \sum_{ij\sigma} t_{ij} a^{+}_{i\sigma} a_{j\sigma} + \sum_{i} u_i - J \sum_{<ij>} \overrightarrow{S_i} \overrightarrow{S_j}$$

where u_i is either u_i^A or u_i^M depending on the ion species occupying the i site

$$u_i = \begin{cases} E & \\ -A \sum_{\sigma} a^{+}_{i\sigma} a_{i\sigma} & i \in A \\ M \sum_{\sigma} a^{+}_{i\sigma} a_{i\sigma} - \Delta \sum_{\sigma} a^{+}_{i\sigma} a_{i\sigma}(\sigma S_i) & i \in Mn \end{cases}$$

Here $a^{+}_{i\sigma}(a_{i\sigma})$ is the creation (annihilation) operator for a carrier with spin σ at i site; S_i denotes the spin of localized impurity at i site; Δ is the effective coupling constant between the localized spin and itinerant spin; J is the coupling constant between the neighboring localized impurity spins, which depends on their distance and for the anti-ferromagnetic exchange interaction case J < 0. To consider the effect of the direct exchange interaction between magnetic impurities on Tc, dividing equation (1) into the

Impurity term and the itinerant carrier term

$$H_{imp} = -\sum_{i} h S_i^Z - J \sum_{<ij>} S_i^Z S_j^Z$$

$$H_{carr} = \sum_{ij\sigma} t_{ij} a^{+}_{i\sigma} a_{j\sigma} + \sum_{i} u_i$$

where h is the field induced by the polarization of the carrier spins. Where $S_i^Z = \pm S$ is the localized spin also known as Ising spin and H_{imp} is the molecular field approximation as $S_i^Z S_j^Z = \square S_i^Z\rangle S_j^Z + \square S_j^Z\rangle S_i^Z - \square S_i^Z\rangle\langle S_j^Z\rangle$ Within this mean approximation, the Hamiltonian (3) become

$$H_{imp}^{MF} = NxJ\gamma m^2 - \sum_{i} S_i^z (h + 2J\gamma m)$$

where N is the number of lattice sites, x is Mn density, $m = \langle S_i^z \rangle$ refers to the average magnetization per lattice site, γ is the effective number of surrounding impurities a given impurity interacts with.

We apply CPA to the Hamiltonian (4). In CPA the carriers are described as independent particles moving in an effective medium of spin-dependent coherent potentials. The coherent potential $\sum_\sigma (\sigma = \uparrow, \downarrow)$ is determined by demanding the scattering matrix for a carrier at an arbitrarily chosen site embedded in the effective medium vanished on average. By using a bare semicircular non-interacting density of states (DOS) with half bandwidth W:

$$\rho_o(z) = \frac{2}{\pi W^2}\sqrt{W^2 - z^2}$$

we obtain a quadratic equation for $G_\sigma(\omega)$ and it is solved analytically by using Farrari method [7][11]. Throughout this work, we assume that the carriers are degenerate. Then the carrier energy can be expressed as

$$E_{carr}(m) = \int_{-\infty}^{\mu} \omega\left(\rho_\uparrow(\omega) + \rho_\downarrow(\omega)\right)d\omega$$

where μ is the chemical potential and $\rho_\sigma(\omega) = -\frac{1}{\pi}\tilde{S}G_\sigma(\omega)$ is the DOS with spin σ. The free energy per site of the system (1) at temperature T is given as

$$F(m) = E_{carr}(m) + hmx + xJ\gamma m^2 - xk_BT\ln\left(\sum_{S^z=\pm S} e^{\beta(h+2J\gamma m)S^z}\right) \quad (3)$$

By minimizing F with respect to m we obtain the following equation for h

$$h = -\frac{1}{x}\frac{dE_{carr}(m)}{dm}$$

By using the Weiss molecular field theory, each impurity spin feels an effective field $\bar{h} = h + 2J\gamma m$ and the local magnetization is then calculated by

$$m = SB_S\left(\frac{\bar{h}S}{k_BT}\right)$$

where

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

is the conventional Brillouin function and for Ising spin $S = \frac{1}{2}$

The Curie temperature is determined by differentiating both sides of Eq. (9) with respect to m at m = 0. This leads to the formula

$$k_BT_C = \frac{S(S+1)}{3}\left(-\frac{1}{x}\frac{d^2E_{carr}(m)}{dm^2}\bigg|_{m=0} + 2J\gamma\right)$$

So, we have

$$T_c = T_{c0} - T_{AF}$$

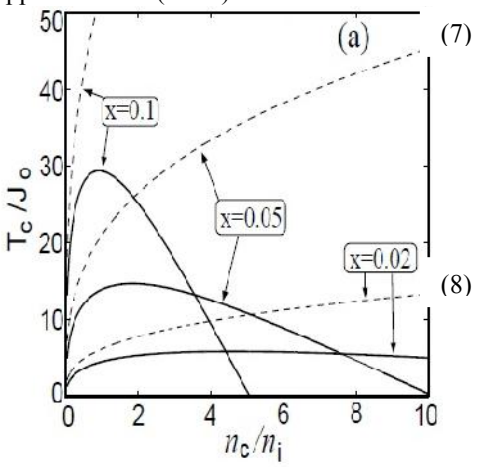
Where

$$T_{c0} = -\frac{S(S+1)}{3xk_B}\frac{d^2E_{carr}(m)}{dm^2}\bigg|_{m=0}$$

is the Curie temperature of the system in the absence of antiferromagnetic interaction between magnetic impurities; and $T_{AF} = \frac{2S(S+1)}{3k_B}J\gamma$ describes the contribution of the antiferromagnetic interaction to the Curie temperature. Above equation has been derived in some early studies within the Weiss mean field theory, implies that the Curie temperature is determined by competition between the ferromagnetic and antiferromagnetic interactions.[6] (6)

Curie temperature is complicated function of carrier density, magnetic impurity density, carrier mean free path etc.

Curie temperature has been plotted against different carrier concentrations for different values of magnetic dopant (Mn) concentration and mean free path using equation (10) and compared against predictions from standard Virtual Crystal Approximation (VCA) method.



(7)

(8)

Figure 1 : Calculated Curie temperature as function of normalized carrier density (n_c/n_i) for different values of x & fix MFP. VCA computations have been **shown** in dashed line.

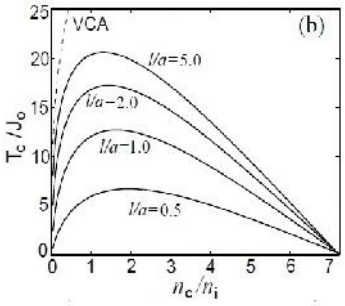


Figure 2 :Calculated Curie temperature as a function of normalized carrier density (n_c/n_i) for different values of MFP & fix x. VCA computations has been shown in dashed line.

Upon analyzing the above results from theoretical calculations it is apparent that maximum Curie temperature is obtained for optimum carrier density n_c/n_i ~ 0.5 - 2 and also T_c first increases with concentrations for very low values of x after attaining it's maximum values it starts decreasing. T_c cannot be increased by just increasing magnetic impurity concentration for optimum carrier density (n_c/n_i) actually we have to maximize mean free path for obtaining maximum curie temperature. Also curie temperature depends upon type of magnetic impurity being doped however it affects amount of magnetization below curie temperature also. The elements with large number of unpaired valence electrons shows lager magnetization as well as curie temperature as compared to those which have less unpaired valence electrons as shown in the figure below

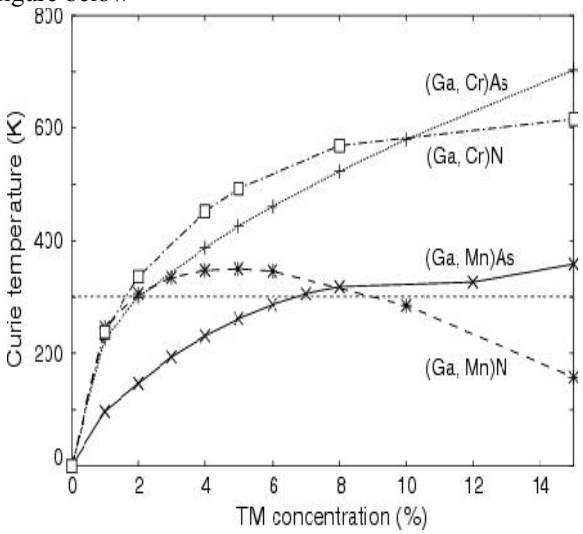


Figure 3 : Curie temperature as function of Magnetic imurity doping concentrations for Mn & Cr doped in GaAs & GaN

From figure 3 it is apparent that curie temperature of Cr doped GaAs/GaN is more as compared to Mn doped GaAs/GaN because Cr has one more unpaired valence electron as compared to Mn which contribute to higher net spin of Cr ions in the lattice which give rise to large amount of magnetization and also contribute to higher ferromagnetic interactions as compared to Mn in the host semiconductor lattice.

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