Magnetism of Transition Metal Doped Semiconductors

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Abstract: Substitution of magnetic ions into a semiconductor creates the material for future electronic. Transition metal impurities introduce deep levels in the gap region of semiconductors. Transition metal impurities do not behave like the usual donor and acceptor impurities and introduce extra d-like orbitals which can accommodate electrons. Transition metal impurities produce structures similar to those of free ions. In the present discussion a spin Hamiltonian formalism has been used to understand the localized electronic states of a substitutional metal having two electrons. Spin Hamiltonian has been used to calculate the parameters required to understand the Zeeman photo-luminescence experiments.

Key Words: Magnetic Semiconductors, Magnetism, Transition metal, Doped Semiconductors, Exchange Interactions.

INTRODUCTION

Newly developed non equilibrium growing techniques have made possible the growth of semiconductors doped with transition metal ions. Today's semiconductors work by exploiting the electric charge attached to electrons. But electrons in solids have another fundamental property known as "spin," which makes them act like small magnets. The possibility of using electrons' spins in addition to their charge in information technology has created much enthusiasm for a new field of electronics popularly known as "spintronics" [1]. An intensely studied approach to obtaining spin-polarized carriers for data-storage devices is the use of diluted magnetic semiconductors created by doping transition metal ions. Transition metal impurities can exist in several charge states in a semiconductor [2]. These impurities introduce deep levels in the gap region of semiconductors and constitute a distinct class of defects that has been extensively investigated from the theoretical as well as experimental point of view [3-5]. Deep impurities are normally dominated by the short range forces while the shallow donors and acceptors are dominated by the coulomb interactions.

BASIC CONCEPTS

Compounds formed by elements of the third and fifth columns of the periodic table crystallize as $A^{(III)}B^{(V)}$, while elements of the group II and VI form compounds of the form $A^{(II)}B^{(VI)}$. This structure is derived from the diamond structure by replacing alternate carbon atoms leading to a decrease in symmetry. Since each atom of group III is surrounded tetrahedrally by group V atoms, it is assumed that each atom has four valence electrons. The major technical importance of these compounds is that they provide a wider selection of forbidden energy gaps, mobilities compared with those of the limited number of elemental semiconductors.

In a pure semiconductor, inner shell electrons screen the nuclear charges and the important electrons are those which reside in the outer shell and delocalized into Bloch functions or bands. At absolute zero all the electrons occupy the valence band. An increase in temperature excites some electrons from valence to conduction band, leaving holes behind. These electrons and holes move like free particles or in combination like excitons. These free motions of charged particles give rise to electrical conduction.

When one or more of the host atoms is replaced by an impurity atom next to it in the periodic table with one extra positive nuclear charge and one extra electron, then it is expected that this extra electron would be found in the lowest conduction band state. It minimizes the electron's kinetic energy, but not the coulomb energy in the field of extra nuclear charge. In fact this extra electron goes into linear combinations of conduction band states which minimize the total energy. The resulting orbital is hydrogenic in nature. It can be noticed that the hole at the impurity due to excitation of the electron remains bound and do not contribute to the conduction. Similar discussion can be written for an impurity which has one less electron. In this case an electron from the valence band can be excited onto the impurity leaving behind a hole in the valence band. Transition metal impurities usually do not behave like the above described donor or acceptor impurities and it requires a special description.

$A^{(III)}B^{(V)}$ [or $A^{(II)}B^{(VI)}$] type compounds can be considered as prototype hosts for the transition metal ions. Considering Gallium Phosphide, Gallium has one less electron than the normal elemental semiconductor having 4 valence electrons and Phosphorus has one more. Each Gallium site is surrounded by a regular tetrahedron of Phosphorus sites and vice versa. As each Phosphorus atom provides one electron to Gallium, all sites become isoelectronic. It is expected that initial orbitals give different

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weights to the two atoms which are joined together. Since there is no operation which interchange A and b atoms, it will be difficult to label the linear combinations of atomic orbitals as symmetric or antisymmetric. Transfer of an electron from Phosphorus to gallium generates the sp^3 hybridized orbitals.

Transition metal impurities in III-V and II-VI semiconductors occupy the substitutional sited, replacing the cation. Therefore, the impurity neutral charge state should correspond to oxidation state 3+ in the III-V hosts and 2+ in the II-VI hosts. In fact, Va^{3+} (with 2 d electrons) and Cu^{3+} (with 8 d electrons) or 2 holes in the d shell) can be substituted in III-V hosts, while Ti^{2+} (with 2 d electrons) and Ni^{2+} (with 8 d electrons or 2 holes in the d shell) can replace a cat ion in the II-VI compounds.

STATES OF d^2 (d^8) CENTRES

When a transition metal, such as Va^{3+}/ Cu^{3+} (or Ti^{2+}/ Ni^{2+}) replaces a Gallium atom, it tries to simulate its electronic configuration. The initial configurations of Vanadium and Nickel are ($1s2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) $3d^3\ 4s^2$ and ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) $3d^9 4s$. Vanadium has 23 electrons by receiving one electron from atom B (Phosphorus/Arsenic) and promoting one of its 4s and 3d electrons to the vacant 4p orbitals, it acquires the configuration [Ar] $3d^2\ 4s^1\ 4p^3$, thus forming sp^3 hybridized orbitals similar to those of the atom A (Gallium). The 3d orbitals are partially filled since that contains just two electrons which are localized around the Vanadium nucleus. It forms a deep level because very high energy is required to remove another electron from the Vanadium atom.

Vanadium looks electrically neutral, but spectroscopically speaking; it has lost three electrons and is described by four atoms of the type B forming a regular tetrahedron in the absence of strains. It seems natural that Vanadium experiences a tetrahedral crystal field. If crystal field is stronger than the coulomb repulsion between electrons at the Vanadium centre, then 3d orbitals should split into e type and t_2 type orbitals. At this stage Vanadium has two electrons in the (e, t_2) orbitals. On symmetry arguments, one can assume that energy of the e orbitals will be lower than those of three t_2 orbitals. It is expected that the ground crystal field configuration will be e^2, with et_2 and t_2^2 as the possible excited states. The ground configuration e^2 is six fold degenerate and by taking suitable orthogonal linear combinations of e orbitals, it will produce terms of the type $^3A_2$, $^1A_1$, ^1E. There will be several excited terms arising from configurations et_2 ($^3T_1$, $^3T_2$, $^1T_1$, $^1T_2$) and t_2^2 ($^3T_1$, $^1T_2$, ^1E, $^1A_1$). The ground terms $^3A_2$ is orbitally non degenerate and it does not couple to any vibrational mode to produce Jahn Teller effect.

If the crystal field is weaker in comparison with the coulomb repulsion within the Vanadium/ Nickel centre, then the possible multiplets of two d electrons (or holes) are ^3F, ^1D, ^3P, ^1G and ^1S. tetrahedral crystal field split these multiplets into many states. $^3F \rightarrow {}^3T_1 + {}^3T_2 + {}^3A_2$, $^1D \rightarrow {}^1T_2 + {}^1E$, $^3P \rightarrow {}^3T_1$, $^1G \rightarrow {}^1T_1 + {}^1T_2 + {}^1E + {}^1A_1$, $^1S \rightarrow {}^1A_1$.

The ground state $^3T_1$ is nine fold degenerate. This state is three fold spin degenerate, but it does not have well defined angular momenta. At this stage, one can think of a pseudo three dimensional space with T = 1, where T_x, T_y and Tz are components of T obeying the angular momentum quantum relations. With T =1 and S = 1, nine states are available, $| T_Z = 1, 0, -1, M_S = 1, 0, -1 \rangle$, and any 9x9 matrix can be written as an operator in the $T \otimes S$ space. Therefore an effective Hamiltonian can be defined to get the states of the system.

EFFECTIVE HAMILTONIAN

The Hamiltonian of a many electrons, many nuclei system normally contain kinetic energies of the electron, their mutual coulomb repulsion and their energies in the field of nuclei. These are the main energy terms, but in addition there will be many smaller perturbations, such as spin orbit, strain effects, Zeeman interactions if a magnetic field is present or interactions with incident radiation, and so on. It has been assumed that Vanadium has replaced Gallium. These two atoms are different is sizes, so Vanadium is unlikely to be at a true tetrahedral site and it implies that lattice will have some internal strains. V^{3+} is a non Kramer ion and it is sensitive to strains and show Jahn Teller effect. In fact, when the ground state is degenerate, the terms linear in Q's (linear displacements of the lattice) become invariant sums of products of tensor angular momentum operators and transform according to irreducible representations of the symmetry group of the crystal. In the present example, the ground triplet state T_1 will couple to ($E \oplus T_2$), so the Jahn Teller coupling is of an orthorhombic $T_1 \otimes (E \oplus T_2)$ type. The effective Hamiltonian for the $^3T_1$ ground state can be written as

$$H = H_{S\text{-}O} + H_{2,S\text{-}O} + H_{Strain} + H_{Zeeman}$$

Where

$$H_{S\text{-}O} = a\,[\,L_Z S_Z + \tfrac{1}{2}(L_+ S_- + L_- S_+)\,]$$

$$H_{2,S\text{-}O} = \lambda\,[\,\{\,b\,(L_Z^2 S_Z^2) + 1/2\,(L_Z S_Z L_+ S_- + L_Z S_Z L_- S_- + L_+ S_- L_Z S_Z + L_- S_+ L_Z S_Z) + 1/4\,(L_+^2 S_-^2 + L_-^2 S_+^2 + L_+ S_- L_- S_+ + L_- S_+ L_+ S_-)\,\} + c/4\,\{\,3 L_Z^2 - L(L+1)\,\}\,\{\,3 S_Z^2 - S(S+1)\,\} + 3c/16\,\{\,(L_Z^2 + L_-^2)(S_+^2 + S_-^2)\,\}\,]$$

$$H_{strain} = V\,[\,3/2\,L_Z^2 - 1/2\,L\,(L+1) \pm i\tilde{E}/8\,(-\sqrt{3}\,L_+^4 + \sqrt{3}\,L_+^2 L_-^2 + 4\,L_-^2 L_+^2 - 4\,L_-^4)\,]$$

$$H_{Zeeman} = [\,a\,(L_x B_x + L_y B_y + L_z B_z) + 2\,(S_x B_x + S_y B_y + S_z B_z)]\,\mu_B + [\,2c\,(S_x B_x + S_y B_y + S_z B_z) + \{\,3 L_z^2 - L(L+1)\,\}\,\{\,3 S_z^2 - S(S+1)\,\} + 3/16\,(L_+^2 + L_-^2)(S_+^2 + S_-^2\}\,\mu_B + b\,\{\,(L_x^2 S_x + L_y L_x S_y + L_z L_x S_z + L_x^2 S_x + L_x L_y S_y + L_x L_z S_z)\,B_x + (L_x L_y S_x + Ly^2 S_y + L_z L_y S_z + L_y L_x S_x + L_y^2 S_y + L_y L_z S_z)\,B_y + (L_x L_z S_x + L_y L_z S_y + L_z^2 S_z + L_z L_x S_x + L_z L_y S_y + L_z^2 S_z)\,B_z\,]$$

Here, $H_{2,S\text{-}O}$ describes the second order spin orbit effects.

The expectation values of the Hamiltonian within $(T \otimes S)$ space is 9×9 matrix. On diagonalization, it generates a quartet, a doublet and a triplet, where quartet with the lowest energy is the ground state. It suggests at least two transitions in absorption.

RESULTS AND DISCUSSIONS

The d^2 and d^8 transition metal impurity centres can be found in three different charged states. In GaAs, Vanadium can be found in neutral, $V^{3+}(d^2)$, and in the singly negative $V^{2+}(d^3)$, charged state. It indicates that the vanadium can act as an acceptor in GaAs. Photoluminescence spectra of Kaufman *et al*. [6] confirm the theoretical analysis.

Nickel can be found in three charged states, namely the neutral $Ni^{3+}(d^7)$ as well as $Ni^{2+}(d^9)$ and $Ni^{+}(d^9)$ states. Photo induction generates the recharging process and it appears difficult to isolate the centres.

The present interest is in the trivalent copper (d^8) centres, which exhibits two different spin states, S = 1 and S = 0, stems from the idea that these centres play an important role in the mechanisms of high temperature superconductivity [7] and the degenerate magnetic and non magnetic states. All these systems prefer to order magnetically and it helps to understand the behaviour of nano materials.

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