Electronic States and Magnetism of Mn Impurities and Dimers in Narrow-Gap and Wide-Gap III-V Semiconductors

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Abstract

Electronic states and magnetic properties of single Mn impurity and dimer doped in narrow-gap and wide-gap III-V semiconductors have been studied systematically. It has been found that in the ground state for single Mn impurity, Mn-As(N) complex is antiferromagnetic (AFM) coupling when $p$-$d$ hybridization $V_{pd}$ is large and both the hole level $E_v$ and the impurity level $E_d$ are close to the midgap; or very weak ferromagnetic (FM) when $V_{pd}$ is small and both $E_v$ and $E_d$ are deep in the valence band. In Mn dimer situation, the Mn spins are AFM coupling for half-filled or full-filled $p$ orbits; on the contrast, the Mn spins are double-exchange-like FM coupling for any $p$-orbits away from half-filling. We propose the strong $p$-$d$ hybridized double exchange mechanism is responsible for the FM order in diluted III-V semiconductors.

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Diluted magnetic semiconductors (DMS), such as $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xN$, with ferromagnetic (FM) Curie temperature ($T_c$) as high as 110K in $Ga_{1-x}Mn_xAs$, or even as room temperature in $Ga_{1-x}Mn_xN$ have attracted much attention, since these properties provide perspective applications in the fabrication of spintronics devices as well as in quantum computers [1-5]. The unusual FM order in Mn- or Cr-doped III-V semiconductors with such low concentrated magnetic ions and the interesting magnetotransport properties have also raised many fundamental problems, e.g. the electronic states of 3$d$ impurities and the origin of the FM long-range order (LRO) [2-4]. Many experiments have established the fact that local magnetic moments $S$ and hole states are simultaneously introduced in DMS as Ga atoms are substituted by Mn ions. An elaborated relation between doped concentration and $T_c$ in Ref.[1] demonstrated the important role of mobile hole carriers in the formation of FM LRO in DMS, leading to the hypothesis that the FM coupling between Mn spins are mediated through these delocalized holes.

Several microscopic mechanisms have been proposed to explain the origin of the carrier-induced FM LRO in DMS. In the presence of local magnetic ions and mobile carriers, the RKKY interaction seems to be a natural candidate [6]. Magnetic properties of $Ga_{1-x}Mn_xAs$ were interpreted in the RKKY scenario in the mean field (MF) approximation. Although the theory successfully explained the dependence of Curie temperature $T_c$ and spontaneous magnetization on doping concentration measured in experiments in some doping range [7], there are still some important issues to be taken into account. The RKKY model validates only when isolated local spins merge in the sea of free carriers and the carrier bandwidth $D$ is much greater than the spin-hole exchange constant $J$. However in DMS, the hole concentration $n_h$ is much less than local spins concentration $N_s$, and the $Mn-As(N)$ spin-hole exchange constant, $J\sim1eV$, is much larger than the Fermi energy $E_F$ of the hole carriers, about 0.3 eV [8]. Furthermore, the Mn concentration is so small that the nearest neighbour number $z$ is less than that of the conventional 3-dimensional systems, thus it is expected that there will be a large discrepancy between the MF result and realistic situation. Therefore the MF RKKY theory might be not accurate for describing the FM ordering in DMS.

The double exchange model which is responsible for the FM order in doped perovskite manganites was also suggested for the FM coupling of the distant Mn spins in DMS [8, 9]. However, the spatial separation of Mn spins in DMS is much further than dense Mn spins in manganites, and the hole wavefunction extends over tens of lattice sites in doped GaAs
and the valence fluctuation in Mn 3d orbits is small, dissimilar to the mixed valence of 3d³ and 3d⁴ in doped manganites. At present, whether or not the conventional double exchange mechanism works for the nature of FM in DMS does not get strong support experimentally and theoretically. The polaronic mediated FM mechanism [10] and some other theories are also proposed to interpret the origin of FM LRO, which shows that more efforts are needed for the microscopic origin of the FM order in DMS.

One of the central problems in the debate on the microscopic origin of FM LRO in DMS is that the single impurity electronic states and the spin interaction of two magnetic ions, especially its evolution with various parameters of DMS, are not well understood. Single Mn impurity in III-V and IV semiconductors had been studied by Zunger et al. [11, 12] based on local density approximation and unconstrained MF approximation, substitutional impurity state properties of different transition-metal atoms in III-V semiconductors had also been studied in Ref.[13], the dependence of the impurity energy level on the nuclei charge of the transition metal atom had been known. The FM ground state (GS) in Mn doped DMS has also been confirmed by a lot of authors based on the first-principle electronic structure calculation, for example, see Ref.[14] and [15]. However these numerical studies are hard to clarify the microscopic processes of interacting Mn spins and the evolution of electronic states and magnetic properties of the Mn atoms and the host atoms in DMS with the doping concentration, the p-d hybridization strength, the energy gap of the host III-V semiconductors, the energy levels of the 3d impurities and the 4p holes, etc.. How these factors affect the FM ordering is crucial for our understanding of the unusual magnetism and transport in DMS.

The aim of this Communication is to elucidate the electronic states, the magnetic properties of single Mn-As(N) complex, and the spin coupling between Mn spins for various parameters. In the rest of this Communication, after describing the model Hamiltonian, we first study the GS of single Mn-As(N) for various electron configurations, determining the parameter range of the antiferromagnetic (AFM) coupling in the Mn-As(N) complex; then we study the Mn-Mn spin couplings in the GS of two Mn-As(N) complexes,i.e. the Mn dimer, and show that the double-exchange-like mechanism is responsible for the FM order when the p-orbits of As(N) is away from the half-filling, suggesting the intrinsic compensation of antisite defect or the inhomogeneity of hole distribution plays crucial roles.

For Mn doped III-V semiconductors with zinc-blende structure, such as In, Ga, or Al
for $III$ group elements and $As$ or $N$ for $V$ group elements, the five valence electrons of $As(N)$ occupies the four $sp^3$ dangling bonds with symmetry $A_1$ and $T_2$, the two $4s$ electrons of $Mn$ ion covalently couple to the $A_1$ orbit of the $As$ or $N$ dangling bonds. When the divalent $Mn$ impurity substitutes the trivalent $In, Ga$ or $Al$ as an effective mass acceptor, we now have a basic interaction scenario in DMS from various early experimental and theoretical studies: $Mn$ ion contributes a spin and a hole, the spin localizes in $Mn$ site, while the hole is bound to $As$ or $N$ site with an extension radius of $r_s$ much larger than the lattice constant; the $3d$ electrons in $Mn$ impurity interacts with the holes in the $p$ orbits of surrounding $As$ or $N$ sites through hybridization $V_{pd}$, forming the $Mn$-$As(N)$ complex. Under $T_d$ symmetry environment of the zinc-blende $III$-$V$ semiconductors, the hole has equi-possibility to occupy the $T_2$ orbit in one of the four nearest-neighbour $As$ or $N$ sites around $Mn$ ion, the hole is 4-fold degenerate; and in the $T_d$ crystalline field, the $3d$ orbits of $Mn$ ions split into lower energy $E_g$-like $d$ orbits with pure atomic character and not coupling to $As$ or $N$, and higher energy $T_{2g}$-like orbits coupling to the $T_2$ $p$ orbit of $As$ or $N$ [13]. The $Mn$ $T_{2g}$ electron which hybridizes with the $As$ or $N$ hole is thus 3-fold degenerate. Due to the strong Hund’s rule coupling, the hybridized $3d$ electron still couple with the local spin $S$ ($S = 2$) of $Mn$ $3d^4$ configuration via Hund’s rule coupling $J_H$. The on-site Coulomb interactions between $3d$ electrons and between holes, $U_d$, and $U_v$, are also taken into account.

With the increase of doped $Mn$ concentration, the wavefunctions of the holes centered at $As$ or $N$ atom with large radius $r_s$ start to overlap with each other, the hopping integral between holes, $V_h$, crucially depends on the extension radius $r_s$ and the hole density $n_h$. The Hamiltonian modeling the preceding physics in DMS thus reads:

$$\hat{H} = \sum_i \hat{H}_0(i) + \hat{H}_1$$

$$\hat{H}_0(i) = \sum_\sigma (E_d \hat{d}_{i\sigma}^\dagger \hat{d}_{i\sigma} + E_v \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} + \frac{U_d}{2} n_{i\sigma} n_{i\sigma}^d + \frac{U_v}{2} n_{i\sigma} n_{i\sigma}^c)$$

$$-\frac{J_H}{2} \sum_{\mu\nu} S_i \cdot \hat{d}_{i\mu} \sigma_{i\mu\nu} \hat{d}_{i\nu} + \sum_\sigma V_{pd}(\hat{d}_{i\sigma}^\dagger \hat{c}_{i\sigma} + \hat{c}_{i\sigma}^\dagger \hat{d}_{i\sigma})$$

$$\hat{H}_1 = \sum_{<ij>\sigma} V_h(\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})$$

where $\hat{H}_0(i)$ and $\hat{H}_1$ represent the interactions in the $i$th $Mn$-$As(N)$ complex and the intercomplexes hopping, respectively; $E_d$ and $E_v$ are the bare $d$-electron and $p$-orbit energy levels,
FIG. 1: Hybridization dependence of magnetic moment $m_1, m_2$ of the $d, p$ electrons and spin polarization $P$ of $p$ electrons in the GS of $Mn - As(N)$ complex for (a) $GaAs: Mn$, $E_v = -0.95$ eV, $E_d = -1.2$ eV; (b) $GaN: Mn$, $E_v = -1.8$ eV, $E_d = -0.5$ eV. The other parameters: $U_d = 4.0$ eV, $U_v = 0.35$ eV, $J_H = 1.0$ eV.

respectively; $\hat{d}_i^\dagger$ and $\hat{c}_i^\dagger$ denote the creation operators of the $d$ electron and $p$ electrons with spin $\sigma$ in the $i$th $Mn - As(N)$ complex; we separate $Mn 3d$ electrons into an inert local spin $S_i$ of $3d^4$ configuration and a $3d$ electron which hybridizes with $4p$ orbit, the $3d$ electron couples with the local spin via strong Hund coupling; $n_{i\sigma}^d$ and $n_{i\sigma}^c$ denotes the electron occupation number of $d$ state and $p$ state with spin $\sigma$, and $n = \sum_\sigma n_{\sigma}^c + n_{\sigma}^d$ the total electron number; here $U_v$ is usually much smaller than $U_d$ [13]; unlike many other authors, we do not write our Hamiltonian as the simple Kondo lattice model, since we recognize that there exists strong $pd$ hybridization between $Mn 3d$ orbits and As or $N p$ orbits, the $3d$ electron occupation varies with the $pd$ hybridization, and the hole in the $p$ orbit extends over a few of lattice constants, thus the Kondo lattice model is not proper to describe the physics in DMS. In this paper, we take the chemical potential $\mu$ located at the middle of the band gap, and the $p$- and $d$-levels $E_v$ and $E_d$ are taken with respect to $\mu$. For clarity we neglect the degeneracy of $Mn 3d$ electrons and $p$ holes in the present study.

In the following we first present the electronic states and the evolution of single $Mn$ impurity with the interaction parameters, and then the effective coupling between $Mn$ spins of two $Mn$-As complexes in the DMS background.
A. Single Mn Impurity

We first study the electronic states of Mn and its ligand As or N atoms in the diluted limit, which describes the case that the distance of Mn ions is so far that the interaction between Mn impurities can be neglected, and no summation over lattice is needed in the Eq.(1)-(3). The local spin $S$ is assumed to be aligned in the z axis, the electronic states and the magnetic properties of Mn-As complex are easily obtained by the exact diagonalization of $H_0$ for various physical parameter and electron configurations. As a contrast to the local moments formation in the Anderson impurity model, the $p$-electron is AFM polarized as the $p$-$d$ hybridization $V_{pd}$ is stronger than a critical value $V_c$, as seen in Fig. 1. When $V_{pd}$ is small, $V_{pd} < V_c$, we find that in the GS the $p$ orbit is almost full filled and the electrons in each $p$ orbit are positive polarized weakly. The $p$ and $d$ electron occupations are almost fixed for $V_{pd} < V_c$. The maximized polarized moment of each As or $N$ are about $0.026 \mu_B$ for $GaAs:Mn$ and $0.042 \mu_B$ for $GaN:Mn$ as $V_{pd} \rightarrow V_c$. A small fraction of spin-down $p$ electron transfers to $3d$ orbit, which leads to the weak positive polarization of the $p$ orbit and $S \approx \frac{5}{2}$ at Mn site. As $V_{pd}$ increases to $V_c \approx 0.88eV$ for $GaAs:Mn$ or $\approx 1.33eV$ for $GaN:Mn$, the holes strongly hybridize with the $3d$ electron, a large fraction of $d$ electron transfers to the $p$ orbit, leading to the AFM alignment of the $p$ electron in respect to the $d$ electron. This result is in agreement with the magnetic circular dichroism experiment [16]. The corresponding polarization of the As or $N$ atoms around Mn impurity, is also shown in Fig.1. The maximum polarized magnetic moment of each As($N$) is about $-0.58 \mu_B$ for $GaAs:Mn$ and $-0.32 \mu_B$ for $GaN:Mn$. Our result for $GaN:Mn$ is in good agreement with that obtained by the first-principles electronic structure calculation in Ref. [17] for Mn-N cluster, but considerable larger than that in periodic systems [18]. While, considering the four equivalent As or $N$ atoms around the Mn ion, we expect the polarized moment of each As or $N$ atom is smaller than this value.

The dependence of the magnetic moment and the polarization of the $p$ orbit on the $3d$ energy level $E_d$ is very similar to that on the hybridization $V_{pd}$ in Fig.1. For deep $3d$ energy level $E_d$, the $p$ electrons in $p$ orbits are positively polarized and very weak; there also exists a critical value $E_d^c$ that when $E_d$ is shallower than $E_d^c$, the electrons in the $p$ orbits are AFM polarized, the polarization of the $p$ orbit is about $-40\%$ for $GaAs:Mn$ or $-20\%$ for $GaN:Mn$. Since the hole is located around the top of valence band, the closer
the $E_d$ is to $E_v$, the larger the $p$-$d$ hybridization is, hence more strong polarization of the $p$ electron. Too deep or too shallow $E_d$ level is not favorable of the formation of the AFM Mn-As(N) complex. In the GS for $V_{pd} = 1.0\, \text{eV}$, the energy difference between FM and AFM configurations of Mn-As(N) complex is $-0.93\, \text{eV}$ for GaAs:Mn and $-1.26\, \text{eV}$ for GaN:Mn. The former agrees with the photoemission data obtained by J. Okabayashi et al. [19].

The magnetic phase diagrams of single Mn-As(N) complex on $V_{pd}$ vs $E_d$ and vs $E_v$ are shown in Fig.2a and Fig.2b. The common character of the phase diagrams is there exist very weak FM and AFM polarized regions. We find when both $E_d$ and $E_v$ are very deep, the electrons in the $p$ orbits are not polarized, i.e. the paramagnetic region, this region is not shown in Fig.3; as $E_d$ and $E_v$ are lifted, the $p$ electrons become weak FM polarization to the Mn spin; and for large enough $V_{pd}$ and shallow $E_d$ or $E_v$, the $p$ electrons in As or N site are AFM polarized. In fact, the physical parameters in realistic DMS GaAs:Mn and GaN:Mn fall into the AFM region, this provides such a possibility that the Mn spins interact through AFM polarized As or N ligands to form FM correlation. As we showed in the following, the Mn spins establish double-exchange-like FM correlation via the polarized $p$-$d$ hybridized band.

**B. Mn Dimers**
FIG. 3: The ground state energy difference between $Mn-Mn$ FM coupling and AFM coupling vs. $V_h$ in ($Mn-As$) dimer for (a) $GaAs: Mn$ and (b) $GaN: Mn$, $V_{pd} = 1.0eV$. The other parameters are the same in Fig.1.

Next we consider two $Mn-As(N)$ complexes, and study the GS magnetic configuration and the spin coupling between $Mn$ ions. With the increasing of $Mn$ doping density and hole concentration, the separation between holes becomes smaller and smaller, the wavefunctions of these holes begin to overlap. The hopping integral between two overlapped holes at sites $R_i$ and $R_j$ is depicted by $V_h(i, j) = \langle \psi_h(R_i)|h_0|\psi_h(R_j) \rangle$, here $\psi_h(R_i)$ is the hole wavefunction and $h_0$ is the Hamiltonian of single particles. We approximate $\psi_h$ with the hydrogen-like wave function with radius $r_s$ and effective mass $m^*$. In this situation, the summation of lattice in Eq.(1)-(3) runs over indices 1 and 2. For simplify, the core spins of two $Mn$ ions are assumed semiclassical and the spin $S_2$ deviates an angle of $\theta$ with respect to $S_1$.

In the GS of $Mn$ dimer, the $Mn$ core spins are either strong FM or weak AFM coupling, depending on the electron filling the $p$-orbits, as shown in Fig.3. Comparing the GS energy of the $Mn$ dimer of FM configuration with that of AFM configuration, we find that $Mn-Mn$ AFM configuration is stable for the half- or full-filled $p$-orbits in the two $As$ or $N$ sites, however, FM is more stable when the electron filling in the $As$ or $N$ $p$-orbit deviates from half- or full- filling; and the more the hole number is, the stronger the $Mn-Mn$ FM coupling is. The magnetic coupling strength of the $Mn$ dimer monotonically increases with
the hopping integral $V_h$ and the AFM coupling strength is much less than the FM coupling strength, which can be clearly seen in Fig.3.

With the substitution doping of $Mn$ to $Ga$, core spins and holes are introduced simultaneously in the semiconductor host. Formally the density of $Mn$ spins equals to the hole concentration. It seems that the active $p$ orbits is always half-filled. For the half-filled $Mn$ dimer, the opposite spin alignment of the different $p$ orbits, the AFM coupled $p$-$d$ hybridization, the strong Hund’s coupling between the 3$d$ electron and the local spin lead to AFM coupling of the $Mn$ local spins. However, considering the existence of numerous antisite $As$ and the intersite $Mn$ defects, a significant fraction of holes are compensated by the electrons from these defects. Thus the hole concentration is considerable less than the $Mn$ density, the $n = 5$ electron configuration in the $(Mn-As)$ dimer is the most probable in realistic DMS. In the GS with electron configuration away from half-filling, the hopping of holes and their AFM hybridization with 3$d$ electrons lead to the FM coupling between $Mn$ 3$d$ electrons, hence the FM coupling of $Mn$-$Mn$ spins, just as our prediction for $GaAs$:Mn and $GaN$:Mn.

To further understand the nature of FM LRO in DMS, we study the GS total energy on the azimuthal angle $\theta$ between two local spins for various electron filling, and the result is shown in Fig.4. The total energies $E(\theta)$ are measured relative to the $Mn$-$Mn$ AFM configuration. We notice that for the half-filling case, the energy difference exhibits $\cos \theta$ behavior, indicating that the $Mn$-$Mn$ coupling is Heisenberg-like AFM. In contrast, in the case deviating from half-filling, the GS energy difference can be well fitted by $|\cos \frac{\theta}{2}|$, and this character is very similar to doped manganites, which implies that the $Mn$-$Mn$ FM coupling is double-exchange-like. This outstanding behavior seems to conflict with what we fore-mentioned. In fact, in the present scenario of strong hybridization with $p$ orbit and strong Hund’s coupling with core spin in the DMS, the $d$-electron form a narrow itinerant band, so the physical interaction of $Mn$ spins in proper doping DMS quite resembles double exchange interaction in mixed-valence manganites. The FM coupling energy of two $Mn$ spins in $GaAs$:Mn is about 11 meV, comparable with experimental Curie temperature $T_c$. In $GaN$:Mn the FM coupling energy is about 75 meV, it seems plausible to explain the origin of extremely high Curie temperature $T_c \approx 600 – 900K$ in wide-gap $GaN$:Mn.

We find in AFM polarized $Mn$-$As$ and $Mn$-$N$, the polarized magnetic moment at $As$ site is larger than that at $N$ site, this occurs both for single complexes and for dimers; on
the contrary, the FM coupling energy of the Mn spins in GaAs:Mn is smaller than that in GaN:Mn. This arises from that the charge transfer of the spin-up 3d electron to the p-orbit in Mn-As is less than that in Mn-N; however, the hopping integral of the holes in the latter is larger than the former, leading to more wider hybridized d-band in the latter and contributing more strong double-exchange FM coupling strength. From Fig.3 and Fig.4, one find that the more the hole number is, the stronger the Mn-Mn magnetic coupling is, implying that the presence of more holes favors the FM in DMS. The observation of FM ordering in DMS suggests that antisite As or intersite Mn atoms may compensate a significant fraction of holes, leading to the observed double-exchange-like FM coupling strength. Also, the possible inhomogeneous distribution of the hole density could lead to the FM phase, since even in the molecular-beam epitaxy grown DMS thin films inhomogeneous strain was found to widely exist in most of DMS samples, this favors the inhomogeneous distribution of the holes. With the coexistence of both the $n=3$ and the $n=5$ electron configurations, lower magnetic energy and inhomogeneous distribution of FM coupling are expected in the GS.

As we mentioned in the preceding, the Mn local spins in DMS is so distant in comparison with dense spins in doped manganites that one may question the role of the double exchange
mechanism in DMS. The microscopic mechanism for the double exchange FM in Mn-doped DMS is depicted as follows: due to the strong hybridization of the As(N) p orbits with the 3d electrons, the system forms two hybridized narrow bands; the hybridized band with dominant d orbital character couples to the Mn core spins via strong Hund’s rule coupling, thus the hopping of the mobile electrons between localized Mn spins gives rise to the double-exchange-like FM coupling and leads to the FM order in DMS, similar to that in doped manganites.

Compare the present double-exchange-like FM with the conventional double exchange FM in manganites, we find the valence fluctuation in the FM ordered DMS is significantly less than that in doped manganites. Due to the strong p-d hybridization and the extended wavefunctions of the p holes, the lifetimes of the mobile electrons staying around two local spins are nearly equal, therefore one would not expect strong valence fluctuation in Mn 3d orbits. Meanwhile, the Curie temperature in DMS seems to be too high in comparison with the FM critical temperature in manganites, this may attribute to that the strong Jahn-Teller e-ph coupling and polaronic effect weaken the FM phase transition point in manganites.

In summary, we have shown that in doped III-V semiconductors, Mn-As(N) is AFM polarized only for strong p-d hybridization; the Mn-Mn spin interaction is double-exchange-like ferromagnetic coupling, addressing the strong ferromagnetism in diluted magnetic III-V semiconductors. The consideration of the p-orbital degeneracy will lead to more reasonable polarized magnetic moment and polarization at As or N site.

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