Band structure model of magnetic coupling in semiconductors

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We present a unified band structure model to explain magnetic ordering in Mn-doped semiconductors. This model is based on the p-d and d-d level repulsions between the Mn ions and host elements and can successfully explain magnetic ordering observed in all Mn doped II-VI and III-V semiconductors such as CdTe, GaAs, ZnO, and GaN. This model, therefore, provides a simple guideline for future band structure engineering of magnetic semiconductors.

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Mn-doped II-VI and III-V diluted magnetic semiconductors (DMS) have many unique magneto-optical, magneto-electrical, and magneto-transport properties that are essential for future-generation spintronic device applications [1,2,3,4,5]. These materials also present many interesting behaviors. For example, Mn-doped II-VI semiconductors generally have antiferromagnetic (AFM) ground state, whereas Mn doped III-V semiconductors mostly have ferromagnetic (FM) ground state. Of great interest, some of the systems, such as Mn-doped GaN, can be either FM or AFM, depending on the Mn concentration, carrier density, or pressure [6]. It will be, therefore, rewarding to understand the mechanism of magnetic coupling in these systems in order to design functional spintronic materials.

The mechanism that is responsible for the magnetic coupling in Mn doped III-V semiconductors has been widely discussed over the last few years [1,2,3,4,5]. Several models have been proposed to explain the phenomena, including the Zener/RKKY and super- and double-exchange models. Although these models are quite successful in explaining some of the systems, they often lack universality and transparency, and are difficult to compare directly with ab initio band structure calculations. In this paper, using a band structure approach and level repulsion model, we will describe a unified picture to explain magnetic ordering in Mn-doped II-V and III-V semiconductors and relate them to the previous models. We show that our model can successfully explain magnetic ordering observed in all Mn doped II-VI and III-V semiconductors such as CdTe, GaAs, ZnO, and GaN. Therefore, it provides simple guidelines for future band structure engineering of magnetic semiconductors.

Our model is derived from the coupling and level repulsion between the magnetic ions d and the host element’s p states. When Mn atoms are incorporated into a semiconductor, they will introduce d levels either inside the valence band or above the valence band maximum (VBM) of the semiconductor, depending on the host material. For example, for Mn in GaAs and CdTe, the occupied majority d bands are below the host VBM, which contains mostly anion p states. The unoccupied minority d band is above the VBM. On the other hand, in ZnO and GaN, the d levels are above the VBM. The introduced d orbitals will interact with the host p states forming hybrid pd orbitals. The hybrid orbitals will then also interact with each other. The hybridization occurs because the Mn d states in a tetrahedral crystal field split into t2 and e states, whereas the VBM also has the t2 symme-

![FIG. 1: Schematic model for p-d and d-d couplings. (a) p-d coupling with t2p above t2d. (b) p-d coupling with t2p below t2d. (c) d-d coupling between the t2d states with majority spin level coupled to majority spin level and minority spin level coupled to minority spin level, and (d) d-d coupling between the t2d states with majority spin level coupled to minority spin level. (e) Same as (c), but between the e4d state. (f) Same as (d), but between the e4d state.](cond-mat/0504084v1/cond-mat/0504084v1-1.png)
try, with large anion $p$-character. The two states with the same $t_2$ symmetry can couple strongly with each other. Furthermore, without spin-orbit (SO) coupling, only the states with the same spin configuration can couple to each other \[1\, \text{and} \, 2\]. Figure 1 shows the possible scenarios for the states that may couple to each other. In Fig. 1a, the host $t_{2g}$ state is above the magnetic ion $t_{2g}$ state, and the coupling leads to a level repulsion that pushes up the $t_{2g}$ state by $\Delta_{pd}^1$ and pushes down the $t_{2g}$ state by $\Delta_{pd}^2$. In Fig. 1b, the $t_{2g}$ state is above the $t_{2g}$ state, and they are pushed up and down respectively by $\Delta_{pd}^2$. Figure 1c shows the couplings between the two majority spin $d$ levels and the two minority spin $d$ levels, which lead to splittings $2\Delta_{dd}^1$ and $2\Delta_{dd}^2$, respectively. Figure 1d shows the coupling between the majority spin $d$ state and the minority spin $d$ state, which pushes up the minority spin $t_{2g}$ state by $\Delta_{dd}^2$ and pushes down the majority spin state by the same amount. The coupling between the $e_d$ states is similar to that of between the $t_{2g}$ states, and they are described in Figs. 1e and 1f. In principle, the strength of the interactions in Fig. 1 depends on the distance and orientation of the Mn pair. From these figures, we can see that there will be no energy gain if the two coupled states are fully occupied or fully empty. A magnetic state can be stabilized only if there are both holes and electrons in the coupled states.

In general, the $p$-$d$ coupling is larger than the $d$-$d$ coupling because the host $p$ orbital is more delocalized and Mn $d$ and anion $p$ are nearest neighbors. Within the $d$-$d$ coupling, the coupling between the $e_d$ state is much weaker than the coupling between the $t_{2g}$ state, because the $e_d$ state is very localized, whereas the $t_{2g}$ state is less localized due to the coupling with the host $p$ states. Because the $d$-$d$ coupling between the $e_d$ state is qualitatively similar to that of between the $t_{2g}$ state, they are not discussed explicitly in our model. Furthermore, $\Delta_{dd}^{1,2}$ is smaller than $\Delta_{dd}^1$ when the exchange splitting $\epsilon_d$ is not zero because the level repulsion is larger if the energy separation of the two coupling states is small.

With the understanding above, in the following, we will discuss the mechanism of magnetic ordering observed in Mn doped II-VI and III-V semiconductors. In the discussion, we will use the two-band coupling model described in Fig. 1. First we will discuss the interaction between the $p$ and $d$ levels, and then the interaction between the $d$ levels. We will assume the coupling is additive. The small effect of coupled $p$-$d$ and $d$-$d$ interactions will be discussed briefly for simplicity, but in general, the treatment would not change the results qualitatively.

(i) We discuss first the scenario when the VBM is between the Mn majority and minority spin $d$ states. This is the case for most Mn-substituted II-VI and III-V systems such as CdMnTe and GaMnAs. A schematic plot is shown in Fig. 2, where the level repulsions are arranged in spin-up and spin-down channels in FM and AFM configurations. From (a) to (b) or (a') to (b'), only the $p$-$d$ coupling is turned on. From (b) and (b') to (c), the $d$-$d$ coupling is turned on. We first look at the FM configuration. In the spin-up channel, the $p$-$d$ coupling pushes the $t_{2g}$ state upward by $2\Delta_{pd}^1$, whereas it pushes down the $t_{2g}$ state by the same amount \[1\]. The net energy gain in this process is $-2m_h\Delta_{pd}^1$, where $m_h$ is the number of holes. The $d$-$d$ coupling further splits the $d$ levels by $2\Delta_{dd}^1$. Because all the $t_{2g}$ majority spin levels are fully occupied, there is no energy gain in this process. (The $p$-$p$ coupling is already included in the band structure calculation for the host, and its effect is the same for FM and AFM cases; therefore, it is not discussed here.) In the spin-down channel, the $p$-$d$ coupling lowers the energy of the occupied $t_{2g}$ spin-down state by $2\Delta_{pd}^2$. Because there are six electrons in the two $t_{2g}$ states, the net energy gain in this case is $-12\Delta_{pd}^1$. Therefore, the net energy gain for the FM configuration is $-2m_h\Delta_{pd}^1 - 12\Delta_{pd}^2$. In the AFM configuration, the situation is the same in the spin-up and spin-down channel. When the $p$-$d$ coupling is turned on, the $t_{2g}$ state is pushed up by the occupied majority $t_{2g}$ state by $\Delta_{pd}^1$, but pushed down by the unoccupied minority $t_{2g}$ state by $\Delta_{pd}^2$. The occupied majority $t_{2g}$ state is pushed down by $\Delta_{pd}^1$, and it is further pushed down by the unoccupied minority $t_{2g}$ state by $\Delta_{dd}^{1,2}$. Therefore, the net energy gain in the AFM configuration is $-m_h\Delta_{pd}^1 - (12 - m_h)\Delta_{pd}^2 - 6\Delta_{dd}^{1,2}$. Hence, taking into account the localization of the host $p$ orbitals around the Mn atoms \[1\], the energy difference between the FM and AFM phase is

$$\Delta E_{FM-AFM} = -\alpha m_h (\Delta_{pd}^1 + \Delta_{pd}^2) + 6\Delta_{dd}^{1,2},$$

where $\alpha < 1$ decreases when the hole states become more localized, and when Mn-Mn distance increases. This result suggests that (a) the AFM phase is stabilized by the energy $6\Delta_{dd}^{1,2}$ from coupling between the majority and minority spin $d$ states (often denoted as superex-
change)\(^\text{14}\). (b) The FM phase is stabilized with energy
\[-m_h(\Delta_{pd}^1 + \Delta_{pd}^2)\] which is proportional to the number of
holes and the \(p-d\) exchange splitting \((\Delta_{pd}^1 + \Delta_{pd}^2)\), as
described in the Zener model. Therefore, to enhance FM
coupling, one should increase the hole carrier density and
increase the \(p-d\) exchange splitting. However, large \(p-d\)
coupling also leads to large localization of the hole state,
thus, a balance between \(\alpha\) and \(\Delta_{pd}\) is needed; (c) For
systems where Mn substitution on the cation site does
not introduce holes (e.g., CdMnTe), the system is always
more stable in the AFM phase. (d) For systems where
Mn substitution on the cation site introduces holes (e.g.,
GaMnAs, where each Mn on Ga site introduces one hole),
because the \(p-d\) coupling is larger than the \(d-d\) coupling,
the system in general will have a FM ground state if
enough holes are present in the system. However, when
holes are compensated by donor defects, the system can
revert to the AFM ground state.

(ii) In the second scenario we discuss the case when
the Mn \(d\) state is above the VBM of the host. This is
the case for Mn in ZnO or in GaN. A schematic plot
is shown in Fig. 3. The analysis is similar to that in
the first scenario. In the FM configuration and spin-up
channel, the system not only gains energy through the \(p-d\)
coupling by \(-2m_h\Delta_{pd}^1\), but also through the \(d-d\) coupling
\[^{14}\text{14}\] by \(-m_h\Delta_{dd}^1\) which put holes at a high energy level
and electrons at a low energy level. Here, \(m_h \leq 3\) is the
number of holes at the \(t_{2d}\) level, and for simplicity, we
still use \(\Delta_{pd}\) to describe the coupling between the VBM
and the majority \(t_{2d}\) state. The energy gain in the spin-
down channel is \(-12\Delta_{pd}^2\), thus the total energy gain for
the FM configuration is \(-m_h\Delta_{dd}^1 - 2m_h\Delta_{pd}^1 - 12\Delta_{pd}^2\).
On the other hand, the net energy gain for the AFM
configuration is \(-(6 - m_h)\Delta_{dd}^{1/2} - 2m_h\Delta_{pd}^1 - 12\Delta_{pd}^2\), thus
the energy difference between the FM and AFM phase is

\[
\Delta E_{FM-AM} = -m_h\Delta_{dd}^1 + (6 - m_h)\Delta_{dd}^{1/2}. \quad (2)
\]

These results indicate that when the system has holes
at the \(t_{2d}\)-derived level instead of the \(pd\) orbital, (a) the
stabilization of the FM or AFM phase is not directly related
to the \(p-d\) exchange splitting, but is determined by
the \(d-d\) coupling terms \(\Delta_{dd}^1\) (often denoted as double
exchange) and \(\Delta_{dd}^{1/2}\) terms. (b) When the number of
holes \(m_h\) decreases, the AFM phase is stabilized against
the FM phase. When \(m_h = 0\) (e.g., ZnMnO), the system
is always more stable in the AFM phase. (c) Whether the
system has an FM or AFM ground state depends not only
on hole carrier density, but also on the relative strength
of FM stabilization energy \(\Delta_{dd}^1\), and the AFM stabilization
energy \(\Delta_{dd}^{1/2}\). \(\Delta_{dd}^{1/2}\) increases when the exchange splitting \(\epsilon_{dd}\) decreases.
This can be achieved if the charge is transferred from the majority to minority spin state (e.g.,
from majority \(t_{3d}\) to minority \(\epsilon_{dd}\) state), thus reducing the
magnetic moment and exchange splitting. The majority
\(t_{2d}\) state can be pushed upward through increased \(p-d\)
coupling, which can be realized by increasing Mn con-
centration or applying pressure. Thus, we predict that
for Mn-doped GaN, when the Mn concentration is high
or under pressure, the system will have an AFM ground state.

To test our models, we performed first-principles total-
energy calculations for CdMnTe, GaMnAs, ZnMnO, and
GaMnN. The calculations were performed using an ab
initio plane wave basis code\(^{15}\), based on the local spin

![FIG. 3: Schematic model showing the position of the \(p\) and \(d\) levels and level repulsion between them in FM and AFM configurations. In this case, the Mn \(d\) levels are above the VBM. Note that in (b), (b'), and (c), the states have mixed \(pd\) characters.](image)

![FIG. 4: Total (black) and Mn \(d\) projected (red) density of states for CdMnTe and GaMnAs: (a) ferromagnetic CdMnTe; (b) antiferromagnetic CdMnTe; (c) ferromagnetic GaMnAs; and (d) antiferromagnetic GaMnAs.](image)
density functional theory and using ultrasoft pseudopotentials [10]. For the exchange and correlation potential, we used the generalized gradient approximation of Perdew and Wang [17]. The Brillouin zone integration is performed using the Monkhost-Pack special k points scheme [18] of 4x4x4 for the energy differences and 6x6x6 for the DOS, in a 64 atom supercell with two Mn atoms as first fcc neighbors. Interactions of further neighbors were considered elsewhere [12]. We considered the zinc-blende alloy and assumed that the same results also hold for the alloy in a wurtzite structure.

Figure 4 shows the total (black) and Mn d projected (red) density of states for CdMnTe and GaMnAs in the FM and AFM configurations. We see that these two systems correspond to scenario (i) where the VBM is between the majority and minority Mn d states. For CdMnTe, no holes are present when Mn replaces Cd (Figs. 4a and 4b), therefore, according to our model [Eq. (1)], the system should be AFM. For GaMnAs, holes are present in the VBM-derived states (Figs. 4c and 4d), therefore, our model predicts that it should be FM. Indeed, our directly calculated total energy differences between FM and AFM configurations for these two systems (Table I) agree with those expected from our model.

In summary, we have proposed a model that can successfully explain the stabilization of the ferromagnetic or antiferromagnetic phases in Mn-doped II-VI and III-V semiconductors. This simple model is based on the p-d and d-d level repulsions between the Mn ions and host states and can be directly related to band parameters. Therefore, it should be very useful in understanding and engineering diluted magnetic semiconductors with desired properties. A similar model could also be developed to study other transition metals in semiconductors, as long as the position of the d levels and the number of holes induced by it were known.

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**TABLE I: Energy difference between FM and AFM configurations for Mn-doped semiconductors (x = 6.25%).**

| Material              | ∆E_{(FM-\text{AFM})} (meV) | Ground state |
|-----------------------|-----------------------------|--------------|
| Cd$_{1-x}$Mn$_x$Te    | 35                          | AF           |
| Ga$_{1-x}$Mn$_x$As    | -212                        | F            |
| Zn$_{1-x}$Mn$_x$O     | 110                         | AF           |
| Ga$_{1-x}$Mn$_x$N     | -225                        | F            |

respond to scenario (ii) where the VBM is below the Mn d states. For ZnMnO, no holes are present when Zn is replaced by Mn (Figs. 5a and 5b), therefore, according to our model [Eq. (2)], the system should be AFM. For GaMnN with small Mn concentration (6.25%), holes are created at the Mn 3d-derived level, and the Mn has a high-spin configuration (Figs. 5c and 5d), thus our model predicts that it should have an FM ground state. Again, our direct calculations shown in Table I agree with what is expected from our model.

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[14] Although the coupling is denoted as $d$-$d$ for simplification, due to the strong $p$-$d$ hybridization between the $t_{2d}$ and $t_{2p}$ states, the states in (b), (b'), and (c) in Figs. 2 and 3 have mixed $pd$ characters. Because of this hybridization, the so-called $d$-$d$ coupling is not exactly a short-range interaction.

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