Unusual direction dependence of exchange energies in GaAs:Mn - Is the RKKY description relevant

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Ferromagnetism in Mn-doped GaAs, the prototypical dilute magnetic semiconductor, has so far been attributed to hole mediated RKKY-type interactions. First-principles calculations reveal a strong direction dependence of the ferromagnetic (FM) stabilization energy of two magnetic ions, a dependence that cannot be explained within RKKY. In the limit of host-like hole (engineered here by an GGA+U approach with large $U$) where the RKKY model is applicable, we find that the exchange energies are strongly reduced, suggesting that this limit cannot explain the observed ferromagnetism. The dominant contribution stabilizing the FM state is found to be maximal for $<110>$-oriented pairs and minimal for $<100>$-oriented pairs, providing an alternate explanation for magnetism in such materials in terms of energy lowering due to $p$-$d$ hopping interactions, and offering a new design degree of freedom to enhance FM.

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The discovery of ferromagnetism in Mn doped GaAs [1] has spurred considerable attention in this important class of materials. Experimentally it is known that the introduction of Mn in GaAs gives rise to an acceptor [2]. The hole produced by the acceptor is believed to interact with the localized orbitals of the TM impurity and mediate ferromagnetism. The question is what type of mechanism explains the FM resulting from the interaction between the hole and the magnetic ion. In a model Hamiltonian approach [3, 4, 5] one selects a priori a favored mechanism and works out its physical consequences and manifestations. For example, in the limit where the magnetic electrons can be treated as a localized entity, and the quantum oscillations of the electron spin polarization around the localized impurity can be neglected, the exchange interaction between the TM impurity and the hole can be RKKY-like. It has been argued [4] that this limit is indeed reached for TM impurities in semiconductors. A consequence is that the exchange interaction has either a vanishing dependence on the direction of the hole $d$-oriented pairs and minimal for $<100>$-oriented pairs, providing an alternate explanation for magnetism in such materials in terms of energy lowering due to $p$-$d$ hopping interactions [11].

An alternative one can use ab-initio total energy calculations for magnetic ions in a host crystal [6] to distill a mechanism a posteriori. We consider TM (V-Fe) pairs in GaAs, at various separations and calculate the exchange interaction strength, $J_{ij}(\mathbf{R})$. For all cases $J_{ij}(\mathbf{R})$ are found to exhibit a strong dependence on the specific lattice orientation of the TM pairs, in sharp contrast to the simplest realization of the RKKY model with a system-independent spherical Fermi surface. To test if an extended RKKY model does better, we have calculated the anisotropic $J_{\text{RKKY}}(\mathbf{R})$ [7], taking the Fermi surface of hole doped GaAs explicitly into account. We find that $J_{\text{RKKY}}(\mathbf{R})$ is qualitatively different from $J_{ij}(\mathbf{R})$ determined from ab-initio calculations, thereby establishing that the magnetic interactions in these systems cannot be described even within a realistic RKKY-type model. The ab-initio results are subject to specific uncertainties in the energy position of the $d$ levels [3]. To see if this can affect our conclusion we use a simplified self-interaction correction scheme in the form of GGA+U [3]. We tune $U$ so as to fit the incorrect GGA value of the energy position of the primarily Mn $d$ states in the valence band of GaAs ($E_v$ -2.6 eV) to experimental photoemission ($E_v$ -4 eV) [10]. The strong non-RKKY anisotropy is still present for $U \sim 3$-4 eV, proving that the GGA error is qualitatively inconsequential. Finally we show that this directional dependence can be explained within a model of ferromagnetism arising from energy gain coming from $p$-$d$ hopping interactions [11].

We have carried out first-principle electronic structure calculations using density functional theory, within the pseudopotential plane-wave total energy method [12], using ultra-soft pseudopotentials (USP) [13] and projected augmented wave (PAW) [14] potentials as implemented in VASP code [15]. The equilibrium lattice constant of the TM containing GaAs supercells was fixed at the value obtained for zincblende GaAs (5.728 Å) using the PW91 GGA exchange functional [16], but the atomic positions were allowed to relax. The basis sets had a cutoff energy for plane waves equal to 13.3 Ry. K-point grids of 4x4x4 including Γ and 2x1x1 were used for the 64 and 256 atom calculations. GGA+U calculations were performed with a $U$ on Mn, keeping the intra-atomic exchange interaction fixed at values used earlier [17], while $U$ was varied.

In order to understand the role played by the hole, we consider the cases of V and Fe in GaAs, both of which do not introduce holes into the system. Fig. 1(a), (b) show...
the TM d projected partial density of states (PDOS) resolved into $t_2$ and $e$ symmetries for up (+) and down (-) spin channels. In each spin channel we have a pair of states (bonding and antibonding) with $t_2$ symmetry. The magnetic ground state that would be favored can be readily understood with a schematic two level model shown in Figs. 2(a) and (b). The unperturbed exchange-split 3d levels on the isolated atoms TM1 and TM2 are shown on the left and right side of Fig. 2(a) and Fig. 2(b) for FM and AFM (antiferromagnetic) arrangement of TM spins, respectively. The up and down spin states on the TM atoms interact via spin-conserving hopping interactions of strength $v$ and form a set of bonding-antibonding states for each spin channel, as shown in the central part of each panel. In a FM arrangement (Fig. 2(a)), both bonding and antibonding levels of one spin channel are completely filled, so to a first order, there is no gain in energy in this magnetic coupling. For the AFM arrangement (Fig. 2(b)), however, the bonding states with $t_2$ symmetry are completely filled for both spin channels, while the antibonding states are empty. Consequently, the resulting AFM energy gain is $\sim v^2/I$, where $I$ is the energy separation of the same spin levels on TM1 and TM2. Hence, the AFM arrangement of the TM spins is favored in the absence of a hole. The expectations of the simple model of Fig. 2 are verified by the results from our ab-initio calculations (Fig 3(a) and (b)). The AFM configuration is favored at all separations, with the exception of V at first neighbor. Interestingly the largest AFM stabilization energy is only 31 meV for V, while it is 298 meV for Fe. This difference can be understood in terms of the hopping interaction strength, $v$, entering the $v^2/I$ stabilization of the AFM states. When the highest occupied states have $t_2$ symmetry as in GaAs:Fe (Fig. 1(b)), the relevant hopping matrix element is between the Fe $t_2$ states. These are much larger than those between e states as in GaAs:V (Fig. 1(a)) because $e(t_{2g})$ orbitals point in-between (towards) the nearest-neighbors.

Turning next to GaAs:Mn and GaAs:Cr, it is evident from the PDOS (Figs. 1 (c) and (d)) that both these impurities introduce holes in the system. In the presence of partially occupied orbitals, the simple model of Fig. 2 predicts ferromagnetism as the energy gain for a FM arrangement is large because the interacting levels are degenerate in the case of FM arrangement, while these are separated by a large energy in the AFM case. The expectations of the simple model are verified by our ab-initio calculations (Figs. 3(c) and (d)). Ferromagnetism is favored at all separations for Cr and Mn pairs.

Focusing on Mn-doped GaAs, we extract $J_{ij}$ from $E_{FM}-E_{AFM}$ of Fig. 3(d) for different orientations of Mn atoms in the 64-atom cell, as well as for the 256 atom cell. The significant feature of $J_{ij}$ shown in Figs. 4(a) and (b) is the pronounced domination of orientation over distance dependence. In Fig. 4(a) the three pairs oriented along the <110> direction (connected by a dotted line) show a monotonic decay with $R$, while remaining higher in strength compared to the pairs oriented along other directions (e.g. <100> direction, connected by a dashed line), even when such pairs have a smaller separation. This is further established by our results for two Mn atoms at the same distance, but oriented in different directions, namely <110> and <411>. One Mn is placed at the origin and the other either at (1.5a 1.5a 0) for <110> or at (2a 0.5a 0.5a) for <411>. The calculated $J_{ij}$’s for these two pairs at the same separation are vastly different (Fig. 4(a)). Such an observation is obviously incompatible with the usual RKKY model based on an isotropic Fermi surface. It is however, possible that such orientation dependencies arise from the non-spherical Fermi surface of the specific system. We have calculated the orientation dependent exchange interaction strengths, $J_{RKKY}$ based on the RKKY model including the realistic band structure effects such as the non-spherical Fermi surface of the host GaAs. The 64 atom supercell of GaAs with one hole was taken and the eigenvalues were computed over a grid of 6x6x6 k-points. The eigenvalues were interpolated over a finer grid of 10x10x10 and the generalized susceptibility $\chi(q)$ was computed using the method of Ref. 4. The Fourier transform of $\chi(q)$ was used to calculate $J_{RKKY}$. We checked the stability of our calculation by increasing the number of k-points to 20x20x20. The changes were found to be less than 5%. This $J_{RKKY}$ is plotted for comparison as an inset to Fig. 4(b). Evidently, the behaviors of $J_{ij}$ and $J_{RKKY}$ are qualitatively different; for example, the first principles calculated $J_{ij}$ is smallest along <100> and largest along <110> as seen in Fig. 4, whereas $J_{RKKY}$ is almost maximal for <100>. Obviously, any RKKY-type model in spite of extending it to account for real band structure effects is inadequate to describe the underlying magnetic interactions of these systems.

The above mentioned failure of RKKY model is in fact easy to understand, as GaAs:Mn clearly violates the fundamental assumptions needed for the validity of the RKKY model. The RKKY theory involves a perturbative treatment in which the exchange splitting ($E_{exch}$) of the host band is small in comparison with the Fermi energy ($E_F$). $E_{exch}<<E_F$. However, the DMS’s, in particular Mn doped GaAs, are half-metallic ferromagnets, with complete spin-polarization which arises from $E_{exch}$ being larger than $E_F$. Thus, a perturbation in $E_{exch}/E_F$ is bound to fail, making the inapplicability of RKKY mechanism obvious for these systems. Another interesting consequence of the half-metallicity is the complete suppression of spin flip scattering between up and down spin states of the conduction electrons essential in the RKKY exchange coupling, thereby distinguishing the present system from those dominated by RKKY interactions. It should be noted that total $J_{RKKY}$ is a product of two terms. The first term is proportional to the square of the strength of the spin-coupling between the
local (Mn) moment and the conduction electrons explicitly accounted for in the Kondo-lattice Hamiltonian; the second term includes all the band structure information concerning the host lattice. All RKKY-type approaches assume the first term to be a constant, representing the strength of the spin-coupling between the local moments; thus, all the dependencies on the distance and orientation within RKKY approach arise exclusively from the second term. We have already shown that the $R$ dependence of $J_{RKKY}$ in the inset to Fig. 4(b) is entirely inadequate to describe the $J_{ij}(R)$ observed. Next we point out that the $R$ dependence of $J_{ij}$ is in fact controlled almost entirely by the distance and the orientation dependencies of the spin-coupling in the Kondo-lattice model, which itself arises from the anisotropic hopping for example in a Periodic Anderson Hamiltonian.

A single Mn in GaAs introduces fully occupied $t_+, e_+$ states inside the valence band, and partially occupied $t_+$ state at $E_F$ made of TM $d$ and anion $p$ orbitals. These partially occupied levels are represented in the left and right panels of Figs. 2(c) and (d). They interact via hopping and lower the total energy of the FM arrangement. The dependence of the exchange integral on lattice orientation comes from the dependence of the hopping matrix element entering the FM energy stabilization. This is different from any dependencies within the RKKY mechanism that arise from non-spherical Fermi surface [19]. The mechanism discussed here based on $p$-$d$ hopping is not unique to dilute magnetic semiconductors, but is common to a wide class of materials. It was first introduced to explain the robust ferromagnetic state of Sr$_2$FeMoO$_6$ [11]. In the present work, we have pointed out another novel aspect of this mechanism in terms of its specific and characteristic orientation dependence.

It is interesting to examine whether the orientation dependence changes with the localization of the hole-carrying $t_+$ orbital. We achieve this using the GGA+U approach [9] with a finite $U$, that pushes the bonding $t_+$ levels at $E_V$=2.6 eV (Fig. 1(d)) deeper in the GaAs valence band, making them more Mn-localized, while the hole-carrying $t_+$ state at $E_F$ becomes more host-like and delocalized. Figs. 5(a) and (b) show the Mn $d$ PDOS with $t_2$ symmetry for $U = 0, 6, 10$ and 15 eV. As is evident from the inset of Fig. 5(a), the introduction of $U$ pushes the location of the Mn feature from $E_v$=-2.6 eV at $U$=0 to $E_v$=-5, $E_v$=-7 and $E_v$=-9.3 eV for $U$=6, 10 and 15 eV, respectively. Agreement with the photoemission determined position [14] of $E_v$ = 4 eV requires a $U$ of around 3-4 eV. Most features of the $U=0$ calculations are preserved at this value of $U$, including the strong anisotropy in $J_{ij}$ (see Fig. 4(b)). Thus the GGA error does not affect our results much.

We can use GGA+U to simulate the conditions under which RKKY is supposed to work: The amplitude of the Mn $d$ PDOS of the anti-bonding $t_+$ states at $E_F$ decreases as $U$ increases (Fig. 5 (a),(b)). This decrease in Mn content is clearer from the hole wavefunction squared plotted in the $<110>$ plane for $U = 0$ and 10 eV in Figs. 5 (c) and (d): At $U = 0$, a considerable portion of the hole wavefunction at $E_F$ is localized on Mn and its nearest neighbor As atoms, while at $U = 10$ eV, the states at $E_F$ become more delocalized, host-like as in the case for GaAs:Zn. At this limit ($U=10-15$ eV) of ”host-like-hole” the conventional RKKY approach is supposed to be valid. Our calculations show that at this limit the FM stabilization $J$ is already quite small, and the $J_{ij}$’s become more short-ranged with only nearest-neighbor pairs contributing (Fig. 4(b)). Thus, the observed FM is unexplained by a model simulating ”host-like-hole” RKKY conditions.

In summary, we have examined the microscopic mechanism giving rise to ferromagnetism in 3$d$ impurities in GaAs. A strong deviation is found from current carrier-mediated ferromagnetism based models [3, 4], which we find are not appropriate even when the hole is more host-like. The dominant contribution to FM stabilization is found to be from $p$-$d$ hopping.

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FIG. 1: (Color online) The broadened up(+) and down(-) spin TM $d$ PDOS in spheres of radius 1.2 Å with $t_2$, $e$ symmetry for different TMs.

FIG. 2: (Color online) Schematic energy levels for two interacting TM with their spins FM [(a),(c)] and AFM [(b),(d)] aligned and highest occupied level fully [(a),(b)], partially [(c),(d)] filled.

FIG. 3: Distance/Orientation dependence of $E_{FM}/E_{AFM}$ for two (a) V, (b) Fe, (c) Cr, (d) Mn in 64 atom GaAs cell using USP potentials (using PAW in (d) in parentheses). The upper $x$-axis gives the direction of the vector joining the two TM atoms.

FIG. 4: The distance/orientation dependence of $J_{ij}$ for Mn pairs in (a) 256, (b) 64 atom GaAs cell using PAW potentials. The expected dependence of $J_{RKKY}$ for a hole in GaAs is given in the insert.

FIG. 5: (Color) The up [(a) and inset] and down (b) spin Mn $t_2$ PDOS for $U=0$ (black line), $U=6$ (red line), $U=10$ (green line) and $U=15$ (blue line) eV. Hole wavefunction squared in the $<110>$ plane are shown for $U=0$, and $U=10$ in parts (c) and (d) respectively.
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Fig. 2
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Fig. 3

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(a) 256 atom cell (U=0; PAW)

(b) 64 atom cell (PAW)

\[ J_{ij} \text{ (meV)} \]

distance between Mn atoms (Å)

modified Fig. 4
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