Unusual Directional Dependence of Exchange Energies in GaAs Diluted with Mn: Is the RKKY Description Relevant?

Priya Mahadevan,[1,2] Alex Zunger,[1] and D. D. Sarma[3]
[1]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*
[2]*Department of Physics, Indian Institute of Technology, Chennai 600036, India*
[3]*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*
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Ferromagnetism in Mn-doped GaAs, the prototypical dilute magnetic semiconductor (DMS), 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 for Mn pairs, a dependence that cannot be explained within RKKY. In the limit of a hostlike hole engineered here where the RKKY model is applicable, 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 Mn pairs and minimal for ⟨100⟩-oriented Mn 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. 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 exact nature of the hole-TM interaction is still under debate. In a model Hamiltonian approach [3–5] one selects *a priori* a favored mechanism and works out its physical consequences and manifestations. 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 between TM pairs has either a vanishing or a weak dependence [5] on the direction of the vector joining the TM ions inspite of host fermi surface anisotropies.

As 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 $J_{\mathrm{RKKY}}(\mathbf{R})$ [7], taking the Fermi surface of hole doped GaAs explicitly into account. We find that $J_{\mathrm{RKKY}}(\mathbf{R})$ 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 [8]. To see if this can affect our conclusion we use a simplified self-interaction correction scheme in the form of generalized gradient approximation + Hubbard U (GGA + U) [9]. 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 within the pseudopotential plane-wave total energy method [12], using ultrasoft 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 GGA PW91 [16] optimized value for GaAs, but the atomic positions were allowed to relax. GGA + U calculations were performed with a U on Mn. While the intra-atomic exchange strength was fixed at values used earlier [17], U was varied.

Figures 1(a) and 1(b) show the TM *d* projected partial density of states (PDOS) for V and Fe which introduce no states at the Fermi level, 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 2(b). The unperturbed exchange-split 3*d* levels on the isolated atoms TM1 and TM2 are shown on the left and right side of Figs. 2(a) and 2(b) for FM (ferromagnetic) and

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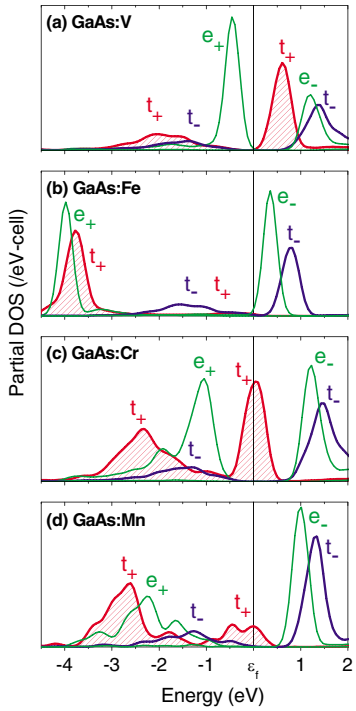

FIG. 1 (color online). The broadened up (+), down (−) spin TM d PDOS in spheres of radius 1.2 Å with t_2, e symmetry for different TMs.

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 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 [Figs. 3(a) and 3(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 1(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.

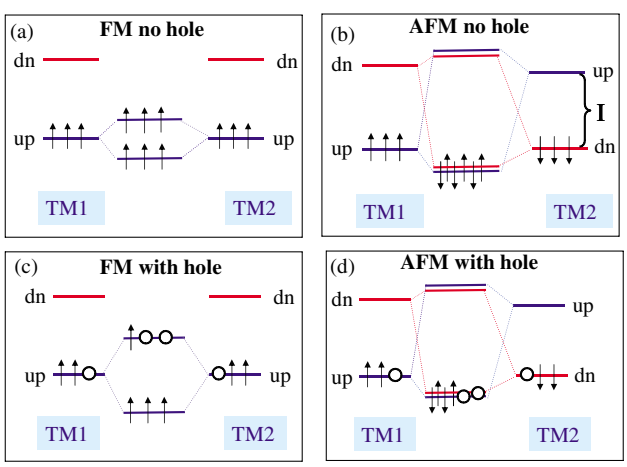

FIG. 2 (color online). Schematic energy levels for two interacting TM with their spins FM [(a),(c)] and AFM [(b),(d)] aligned and highest occupied level fully [(a),(b)], partially [(c),(d)] filled.

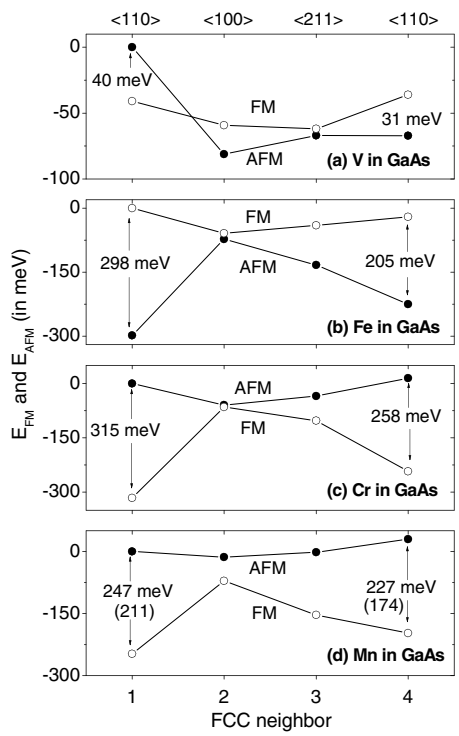

FIG. 3. Distance/orientation dependence of $E_{\mathrm{FM}}/E_{\mathrm{AFM}}$ for two (a) V, (b) Fe, (c) Cr , (d) Mn in 64 atom GaAs cell using USP potentials [using PAW in (d) in parentheses]. The upper x axis gives the direction of the vector joining the two TM atoms.

The expectations of the simple model are verified by our *ab initio* calculations [Figs. 3(c) and 3(d)]. Ferromagnetism is favored at all separations for Cr and Mn pairs.

Focusing on Mn-doped GaAs, we extract J_{ij} [18] 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 4(b) is the pronounced domination of orientation over distance dependence. In Fig. 4(a) the three pairs oriented along the $\langle 110\rangle$ 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., $\langle 100\rangle$ 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 $\langle 110\rangle$ and $\langle 411\rangle$. One Mn is placed at the origin and the other either at (1.5a 1.5a 0) for $\langle 110\rangle$ or at (2a 0.5a 0.5a) for $\langle 411\rangle$. 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 nonspherical 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 nonspherical 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 $6\times 6\times 6$ k points. The eigenvalues were interpolated over a finer grid of $10\times 10\times 10$ and the generalized susceptibility $\chi(q)$ was computed using the method of Ref. [7]. The Fourier transform of $\chi(q)$ was used to calculate J_{RKKY}. 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 $\langle 100\rangle$ and largest along $\langle 110\rangle$ as seen in Fig. 4, whereas J_{RKKY} is almost maximal for $\langle 100\rangle$. Obviously, any RKKY-type model in spite of extending it to account for real band structure effects is inadequate.

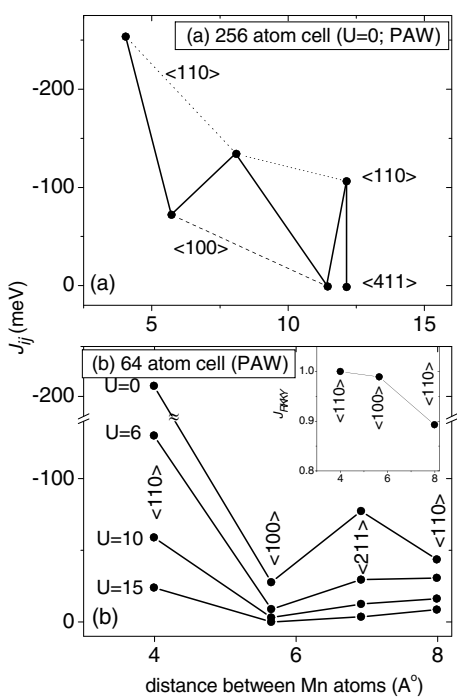

FIG. 4. The distance/orientation dependence of J_{ij} for Mn pairs in (a) 256, (b) 64 atom GaAs cell using PAW potentials. The expected dependence of J_{RKKY} for a hole in GaAs is given in the inset.

The above mentioned failure of RKKY model for DMS 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), $E_{\mathrm{exch}} \ll E_F$. 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 $\mathbf{R}$ dependence of J_{RKKY} in the inset to Fig. 4(b) is entirely inadequate to describe the $J_{ij}(\mathbf{R})$ observed. Next we point out that the $\mathbf{R}$ 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 2(d). They interact via hopping and lower the total energy of the FM arrangement. The dependence of the exchange integral on lattice

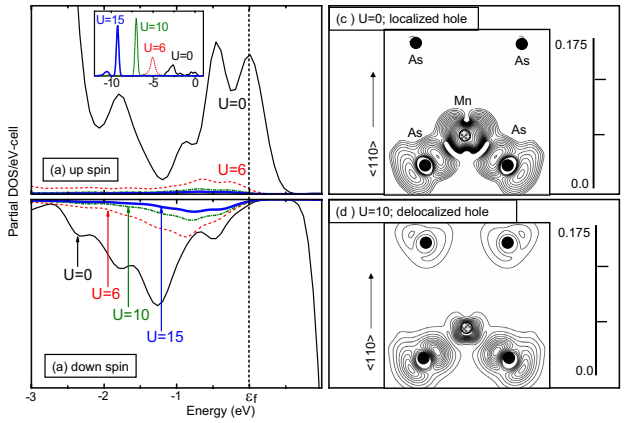

FIG. 5 (color online). The up [(a) and inset] and down (b) spin Mn t_2 PDOS for $U = 0$ (thin solid line), $U = 6$ (dashed line), $U = 10$ (dash-dotted line), and $U = 15$ (thick solid line) eV. Hole wave function squared in the $\langle 110 \rangle$ plane are shown for $U = 0$, and $U = 10$ in parts (c) and (d), respectively.

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 nonspherical 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_2FeMoO_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 hostlike and delocalized. Figures 5(a) and 5(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 [10] 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 antibonding t_+ states at E_F decreases as U increases [Figs. 5(a) and 5(b)]. This decrease in Mn content is clearer from the hole wave function squared plotted in the $\langle 110 \rangle$ plane for $U = 0$ and 10 eV in Figs. 5(c) and 5(d): At $U = 0$, a considerable portion of the hole wave function 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, hostlike 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 $3d$ 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 hostlike. The dominant contribution to FM stabilization is found to be from p-d hopping.

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