Magnetic Semiconductors are Frustrated Ferromagnets

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Starting from microscopic and symmetry considerations, we derive the Hamiltonian describing the exchange interaction between the localized Mn spins and the valence band holes in Ga$_{1-x}$Mn$_x$As.

Semiconductors resisted for decades the concentrated efforts of a large community of researchers who wished to turn them into magnets. The benefits would be far reaching: spin could eventually be used to carry information in electronic devices. Unfortunately, any conventional method to produce semiconductor-magnet alloys failed repeatedly: magnetic materials were insoluble in most semiconductors. Not long ago, several classes of semiconductor materials finally gave in to a most powerful weapon against insolubility: the molecular-beam epitaxy (MBE) machine. In Ga$_{1-x}$Mn$_x$As, for example, ferromagnetic transition temperatures as high as $T_c \sim 110K$ have been reported. Here we demonstrate, that the victory above the natural tendency of the semiconductor host against magnetic dopants did not simply disappear, but is ever more present in the highly frustrated magnetic correlations that remain in these systems down to the lowest temperatures. We find, that magnetic semiconductors are by no means ordinary ferromagnets, but that the intrinsic frustration pushes these systems into the regime of strongly spin disordered ferromagnets which also exhibit several features reminiscent of spin glasses.

We start our analysis by constructing the Hamiltonian that describes the exchange interaction between a single magnetic ion and the valence band holes. In order to be specific, we will discuss in detail the important case of Ga$_{1-x}$Mn$_x$As. However, our results are rather general, as they qualitatively apply to all those magnetically doped II-VI and III-V compounds (and in general to any material with magnetic impurities) which show strong valence band spin-orbit interaction.

GaAs is a direct gap semiconductor with a valence band maximum at the center of the first Brillouin zone called $\Gamma$ point. The top of the valence band is formed by two two-fold degenerate bands of p-character. These two valence bands become degenerate in $\Gamma$. The orbitals involved in these bands form here a four-dimensional irreducible representation. This four-fold degeneracy is due to the strong spin-orbit interaction that couples the $l = 1$ angular momentum of the p-orbitals to the electron spin ($s = 1/2$), thereby producing an effective total spin $J = l + s = 3/2$ for the valence holes. Since the third p-band with $J = l - s = 1/2$ is separated from the two by a large spin-orbit splitting, $\Delta_{so} \approx 340$ meV, for small hole concentrations it is reasonable to describe the valence band in terms of a two-band model:

$$H_0 = \gamma_1 \frac{p^2}{2m} - \frac{1}{m} \left( \gamma_2 \sum_{\alpha} J_{\alpha\alpha} p_{\alpha\alpha} + \gamma_3 \sum_{\alpha \neq \beta} J_{\alpha\beta} p_{\alpha\beta} \right),$$

where $m$ is the electron mass and the $\gamma_i$’s are the so-called Luttinger parameters. The tensor operators $J_{\alpha\beta}$ and $p_{\alpha\beta}$ ($\alpha, \beta = x, y, z$) are defined as $Q_{\alpha\beta} = \frac{1}{2}(Q_{x\beta} Q_{y\alpha} + Q_{y\beta} Q_{x\alpha}) - \frac{1}{2} \delta_{\alpha\beta} \mathrm{Tr}(Q_{y\beta})$, with $Q = p$ and $J$, referring to the momentum of the electrons and their $J = 3/2$ effective spin. In the above equation the last two terms, proportional to $\gamma_2$ and $\gamma_3$, describe the coupling between the effective spin of the valence hole and its orbital motion due to spin-orbit interaction. These terms will lift the four-fold degeneracy for non-zero momenta.

In Ga$_{1-x}$Mn$_x$As the Mn ion is believed to be in the Mn$^{2+}$ configuration, corresponding to a half-filled d-shell with a total spin $S = 5/2$. The general form of the interaction between the $S = 5/2$ Mn spin and the $J = 3/2$-pseudospin holes depends on the momentum $k$ and $k'$ of the incoming and outgoing holes. However, close to the $\Gamma$ point this momentum dependence is weak and we can approximate the coupling constants by their $k$, $k' \to 0$ value at the $\Gamma$ point. We now proceed to construct a microscopic Anderson-type crystal field model that explicitly takes into account both the local crystal field symmetry around the Mn impurity and the strong Coulomb and Hund couplings. We find that the dominant part of the interaction has the following simple form:

$$H_{\text{int}}(\mathbf{R}) = G \mathbf{S} \cdot \mathbf{J}(\mathbf{R}),$$

with $G$ the exchange coupling, and $\mathbf{J}(\mathbf{R})$ the spin density of the holes at the position $\mathbf{R}$ of the Mn ion. Notice
that \( J \) in Eq. \( \text{(2)} \) denotes the total \( J = 3/2 \) spin of the conduction electrons. The above interaction Hamiltonian can also be established using purely symmetry considerations. In general, more complicated couplings of the from \( \sim G' \sum_{\alpha} J_{\alpha \alpha} S_{\alpha \alpha}, \sim G'' \sum_{\alpha \neq \beta} J_{\alpha \beta} S_{\alpha \beta}, \) etc. are also allowed by the local symmetry \( T_d \) of the Mn ion. However, the magnitude of these couplings turns out to be negligible compared to \( G \), due to the relatively weak spin-orbit interaction on the Mn ion compared to the crystal field splitting of the d-levels.

Equations \( \text{(1)} \) and \( \text{(2)} \) constitute the fundamental equations that describe the intricate interplay between the spin-orbit interaction in the valence band and the local moments. Although the model above can be refined to incorporate the third valence band, it already captures the most important features necessary to understand the properties of the ferromagnetic state and related phenomena in magnetic semiconductors. One of the key differences between this, and earlier models \([10,4]\), consists in that we now take into account the spin 3/2 character of the valence holes. This difference, as we show below, turns out to be crucial for revealing the true ground state of the system.

In order to analyze the physical content of Eqs. \( \text{(3)} \) and \( \text{(4)} \) we first determine the effective interaction between two Mn ions at positions \( \mathbf{R}_1 \) and \( \mathbf{R}_2 \), following the Ruderman-Kittel-Kasuda-Yoshida (RKKY) procedure \([1] \). While the procedure itself is quite straightforward, an explicit evaluation of a more general type of interaction deduced in this way is extremely difficult even numerically. Fortunately, for the case of GaAs host one can make substantial progress by analytical calculations, provided that we rewrite Eq. \( \text{(4)} \) as

\[
H_{0} = \frac{\mu^2}{2m} - \nu \sum_{\alpha, \beta} J_{\alpha \beta} p_{\alpha \beta} + \delta H^{(4)} .
\]  

(3)

The first two parts of the Hamiltonian are rotationally invariant, \( \nu = (6\gamma_3 + 4\gamma_2)/5\gamma_1 \approx 0.77 \), and the octupolar term \( H^{(4)} \) can be shown to represent only a small correction \([2] \). Therefore, in leading order we can set \( \delta = 0 \) and consider only the first two, spherically symmetric terms in Eq. \( \text{(3)} \), which we will denote as \( H_{sp} \).

To diagonalize \( H_{sp} \) we choose the spin quantization axis to be in the \( \hat{z} \)-direction. In this basis the energy of plane waves propagating along the \( \hat{z} \)-direction is \( \epsilon_p(k = k_z) = k^2/2m_\mu \) with \( m_\mu = m_k = m/\gamma_1(1 - \nu) \approx 0.5 \) and \( m_{\mu} = m_l = m/\gamma_1(1 + \nu) \approx 0.07 \) the heavy and light hole masses for \( \mu = \pm 3/2 \) and \( \mu = \pm 1/2 \), respectively. Eigenstates of \( H_{sp} \) propagating in other directions can then be constructed by simple rotations. The eigenstates of \( H_{sp} \) are \textit{chiral} in nature: The spin of the heavy holes is quantized along their propagation direction \( \hat{k} \) and takes the values \( J \cdot \hat{k} = \pm 3/2 \). In this new chiral basis \( H_{sp} \) is given by the following simple form:

\[
H_{sp} = \sum_{k, \mu} \frac{k^2}{2m_\mu} c_{k, \mu}^\dagger c_{k, \mu} ,
\]  

(4)

where \( c_{k, \mu} \) denotes the creation operator of a hole. In this basis the unperturbed ground state \( |0\rangle \) consists of two Fermi spheres. The sphere with the larger radius contains heavy holes and includes about 90% of the valence band holes, while a sphere with the shorter radius is generated by the light holes. The price for diagonalizing \( H_{sp} \) is that the exchange coupling in the new basis becomes strongly momentum dependent:

\[
H_{int}(R) = G \sum_{k, k'} \sum_\alpha S_\alpha c_k^\dagger J^\alpha(\hat{k}, \hat{k}') c_{k'} e^{-(k - k') \cdot R} .
\]  

(5)

Here \( J^\alpha(\hat{k}, \hat{k}') \) denotes the operator \( J^\alpha(\hat{k}, \hat{k}') \equiv D^\dagger(\hat{k}) J^\alpha D(\hat{k}') \), and \( D(\hat{k}) \) is the spin 3/2 rotation matrix, and \( V \) the total volume of the sample. It is precisely this \( \hat{k} \)-dependence that generates the delicate magnetic properties of \( Ga_{1-x}Mn_xAs \). The spherical symmetry of \( H_{sp} \) implies that the interaction between two impurity spins \( S_1 \) and \( S_2 \) at a distance \( R = |R_1 - R_2| \) is given by

\[
K_{par}(R) = -K_{par}(R) S_1^\parallel S_2^\parallel - K_{perp}(R) S_1^\perp S_2^\perp ,
\]  

(6)

where \( S_1^\parallel \) and \( S_2^\parallel \) denote the spin components parallel and perpendicular to \( R_1 - R_2 \). The form of \( H_{eff} \) is somewhat similar to that of dipolar interactions as it shows explicit dependence on the relative position of the Mn impurities. Indeed, the interaction between two Mn ions far away from each other is in large part mediated by holes propagating along the axis \( R \) that connects them. Since the majority of the holes are heavy and their spin is quantized along the propagation direction, it immediately follows that the interaction must be different for spin components parallel and perpendicular to \( R \).

It turns out that the structure of the effective interaction Eq. \( \text{(3)} \) can be calculated analytically, although the details are rather technical and will be reported elsewhere \([3] \). The dominant part of the interaction comes from the heavy hole sector, since this has a much larger density of states at the Fermi level than the light hole band. The heavy hole contribution to \( K_{par} \) and \( K_{perp} \) can be expressed as

\[
K_{par/\perp}(R) = 2\pi \epsilon_F g_{hh}^2 C_{par/\perp}(k_{F,h} R) ,
\]  

(7)

where \( g_{hh} = Gg_h \) is the dimensionless heavy hole exchange coupling, \( g_h \) is the heavy hole density of states at the Fermi energy \( \epsilon_F \), and \( k_{F,h} \) denotes the heavy hole Fermi momentum. The dimensionless functions \( C_{par/\perp}(y) \) are clearly different (see Fig. \( \text{[1]} \), and in the \( y \rightarrow 0 \) limit are approximately given by \( C_{par}(y) \approx 1/y \) and \( C_{par}(y) \approx 1/2y \).

In \( Ga_{1-x}Mn_xAs \) only a small fraction \( f \) of the Mn ions gives a hole into the valence band. Although the exact
value of this fraction is not precisely known, latest experiments suggest [3], that for x=0.05 Mn concentration (corresponding to the highest Tc) this fraction is about f = 0.2 – 0.3 (or kF,h ≈ 0.141/Å) and a typical Mn-Mn distance is approximately dMn–Mn ≈ 12 Å. Thus, for typical nearest-neighbor Mn ions Kperp is larger than Kpar and ferromagnetic. However, this ferromagnetic interaction is strongly anisotropic as it tries to align nearby pair of Mn spins parallel to the axis connecting them (see the illustration in Fig. 1). Since f is clearly impossible to simultaneously satisfy each pair of spins, this effect induces orientational frustration and influences the magnetic properties of Ga1–xMnxAs in a fundamental way.

We investigated the implications of the anisotropy [19] on the magnetic properties of Ga1–xMnxAs by performing classical Monte Carlo (MC) simulations using the effective interaction of Eq. (1). In the simulations the Mn spins were replaced by classical angular variables, \( S \rightarrow S \Omega \). The Mn ions were randomly distributed on a \( N \times N \times N \) face-centered cubic lattice with a probability \( x = 0.05 \). \( N = L/a \) is the linear extension of the lattice in units of the conventional lattice constant \( a = 5.65\,\text{Å} \), where \( a \) is the lattice constant [18]. To take into account the finite mean free path \( l \approx 7\,\text{Å} \), we used an exponential cutoff for the RKKY interaction [14]:

\[
K_{\text{par/perp}}(R) \rightarrow K_{\text{par/perp}}(R) e^{-R/l}.
\]

In the inset of Fig. 1, we show the magnetization \( M \equiv |\langle \Omega \rangle| \) as a function of temperature. We find that a spontaneous magnetization develops at low temperatures [18]. The transition between the paramagnetic and magnetic phase takes place rather smoothly, and then increases approximately linearly with decreasing temperature. Both properties agree qualitatively with the experiments [15], and are characteristic to strongly disordered magnets [14]. The spontaneous magnetization, however, tends to a value at \( T = 0 \) that is much smaller than that of a fully polarized ferromagnet. This reduction is clearly due to orientational disorder originating in the anisotropy of the interaction, and has nothing to do with possible antiferromagnetic couplings due to the RKKY oscillations of the Mn-Mn interaction. To demonstrate this, we repeated the simulations by replacing the interaction in Eq. (1) by its angular average. As shown in Fig. 2, the magnetization in this case saturates to its maximal value (normalized to unity), and all the Mn spins are fully polarized.

More information can be obtained about the ground state properties by measuring the distribution of the product \( \cos \theta = \Omega \cdot n \), where \( n \) is the a unit vector parallel to the ground state magnetization. Without the spatial anisotropy structure discussed here, \( P(\cos \theta) = \delta(\cos \theta - 1) \), since the spins are fully aligned. As shown in Fig. 2 in the system with the correct exchange interaction, the quantity \( \cos \theta \) has a very broad but asymmetric distribution. Depending on the actual value of \( f \) the distribution has more or less weight in the vicinity of \( \cos \theta = 1 \): For \( f = 0.1 \) the Mn spins tend to point approximately into the direction of the global magnetization, however, they deviate at the average by an angle \( \theta \approx 30 \) degrees and the magnetization is reduced considerably by \( \approx 20\% \). The ground state becomes more spin disordered for larger carrier fractions: The distribution has less weight at \( \cos \theta = 1 \) and many of the spins are
aligned antiferromagnetically with respect to the global magnetization, thus reducing the magnetization by about \sim 50\%.

The large reduction in the magnetization we find here has been observed experimentally. The measured in-plane saturation magnetization of GaMnAs is about 50% less than the value that would correspond to the known Mn concentration. Also, cooling down the sample in a relatively weak (B \lesssim 4 T) external field results in a 20-40% increase in the T = 0 magnetization. Also, the broad linewidth of ferromagnetic resonance data is consistent with the substantial intrinsic spin-disorder reported here.

The results of our simulations are consistent with a highly spin disordered ferromagnetic ground state with spin glass-like behavior. Indeed, we found many metastable, macroscopically different local energy minima of the Hamiltonian, extremely close to the ground state, a characteristic property of spin glass systems. The precise nature of the ground state can be determined experimentally. One of the typical experimental signatures of a spin glass state would be the history dependence of the high field magnetization in fields parallel to the film, or the difference between field cooled and zero field cooled susceptibilities. This is a straightforward experiment, which can be performed with already existing samples and apparatus. However, the outcome would provide a highly valuable insight into the true order present in these magnetically ordered semiconducting systems.

The intrinsic spin disorder we described above could be the reason for various resistance anomalies. Since this intrinsic spin disorder produces a large spin scattering contribution to the resistivity, it may provide an explanation to the anomalous magnetoresistance of GaMnAs alloys with smaller Tc at temperatures T \ll Tc. It can also possibly explain why these materials exhibit a resistance peak precisely at the ferromagnetic phase transition: Due to the spin disorder present in the ground state, the magnetic order parameter which appears at Tc also involves 'disordered' fluctuations corresponding to finite momenta. These finite momentum components of the soft modes may result in a maximum of the resistance at Tc. This should be contrasted to any conventional ferromagnet, which exhibits predominantly long wavelength soft modes and, therefore shows no peak in the resistivity at Tc.

In conclusion, we have computed the effective exchange interaction strong spin-orbit interaction in its valence band. We found that the resulting exchange interaction inevitably shows a highly anisotropic structure, which in turn generates a strongly spin disordered ground state. We have shown that the qualitative features of the experimentally measured magnetization can be reproduced by a straightforward simulation of a spin system governed by the effective exchange interaction we derived. Our results suggest that the actual experimental systems are disordered ferromagnets with features reminiscent of spin glasses, and proposed an experimental test of such glassy behavior.

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[1] J.K. Furdyyna, J. Appl. Phys. 64 R29 (1988).
[2] H. Ohno, Science 281 951 (1998).
[3] T. Dietl, et al., Science 287 1019-1022 (2000).
[4] J. König, H.H. Lin, A.H. MacDonald, Phys. Rev. Lett. 84 5628 (2000).
[5] W. Kohn and J.M. Luttinger, Phys. Rev. 98, 915 (1955).
[6] J.S. Blakemore, J. Appl. Phys. 53 R123 (1982).
[7] J.M. Luttinger and W. Kohn, Phys. Rev. 97 869 (1955).
[8] M. Linnarson, Phys. Rev. B 55, 6938 (1997); J. Szczypko, et al., Phys. Rev. B 60, 8304 (1999); J. Okabayashi, et al., Phys. Rev. B 58, R4211 (1998).
[9] See D.L. Cox, and A. Zawadowski, Adv. Phys. 47, 599 (1998)
[10] R.N. Bhatt, X. Wan, Int. J. Mod. Phys. C 10 1459 (1999).
[11] K. Yosida, Theory of Magnetism, Springer-Verlag, Berlin, New York, 1996.
[12] A. Baldereschi, and N.O. Lipari, Phys. Rev. B 8, 2697 (1973).
[13] G. Zarnand and B. Jankó (unpublished).
[14] H. Ohno, et al., Phys. Rev. Lett. 68, 2664 (1992).
[15] A. VanEsch et al., Phys. Rev B 56 13103 (1997).
[16] H. Ohno, and F. Matsukura, Sol. State Commun. 117, 179 (2001).
[17] P. Majumdar P. and P.B. Littlewood, Nature 395, 479 (1998). This work also suggested spin polaronic contributions as the explanation of the resistance maximum. This interesting scenario somewhat less probable since it predicts a maximum above Tc (in contrast to the experimentally observed maximum at Tc). Also, according to M.J. Calderon, L. Brey, and P. B. Littlewood, Phys. Rev. B 62, 3368 (2000), the temperature range where these polaronic excitation exist in Ga1-xMnxAs is probably rather limited.
[18] Well below Tc, the valence bands become partially spin-polarized. While the polarization of the carriers could influence the quantitative value of the magnetization, all the qualitative aspects of the ordered state are already captured by the simulation described above.
[19] We neglected the effect of global anisotropy energy terms, which determine the actual orientation of the macroscopic magnetization in the symmetry broken phase. They are about 1% of the average exchange interaction energy between neighboring spins, and therefore do not influence the microscopic structure discussed here.
[20] J.K. Furdyyna et al. (unpublished).