Noncollinear Ferromagnetism in (III,Mn)V Semiconductors

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(Received 27 July 2001; published 14 March 2002)

We investigate the stability of the collinear ferromagnetic state in kinetic exchange models for (III,Mn)V semiconductors with randomly distributed Mn ions. Our results suggest that *noncollinear ferromagnetism* is common to these semiconductor systems. The instability of the collinear state is due to long-range fluctuations involving a large fraction of the localized magnetic moments. We address conditions that favor the occurrence of noncollinear ground states and discuss unusual behavior that we predict for the temperature and field dependence of its saturation magnetization.

DOI: 10.1103/PhysRevLett.88.137201 PACS numbers: 75.50.Pp, 75.30.Ds, 75.50.Lk

In systems with local moments, interactions that favor parallel spin alignment (*ferromagnetic* interactions) yield ferromagnetic ground states. Interactions that favor antiparallel spin alignment (*antiferromagnetic* interactions), on the other hand, yield antiferromagnetism only in the special case of short-range interactions on bipartite lattices. More generally, longer range antiferromagnetic interactions often lead to complex order or, when spatial disorder is also present, to spin-glass ground states [1].

In this context, the occurrence of ferromagnetism [2] in III-V semiconductors with Mn substituted on a relatively small fraction of the cation sites is unusual, since Mn provides $S = 5/2$ local moments in this system and the distribution of Mn ions among the cation sites is thought to be random. A ground state with parallel alignment can be understood in a system with randomly located local moments only if interactions are dominantly ferromagnetic, a property not normally associated with the carrier-mediated interactions thought [3] to be responsible for ferromagnetism in these systems. Indeed there is ample evidence that randomness can play an important role in these ferromagnets, since transport and magnetic properties depend strongly on the molecular-beam epitaxy growth conditions used for material synthesis, with reproducible results achieved only if growth protocols are followed carefully [2].

An important step toward the systematic analysis of such effects was taken very recently by Potashnik *et al.* [4] who studied the effect of annealing procedures on magnetic and transport properties for samples with a Mn fraction close to that at which the maximum Curie temperature (T_c) occurs, $x \sim 0.05$. They find that T_c, the ground state saturation magnetization $M(T = 0)$, and the shape of the $M(T)$ curve all depend on the temperature and duration of annealing. Since the Mn content of the system is not believed to be changed by annealing, changes in the $T = 0$ magnetization can be explained only if Mn moments are not always, or perhaps never, completely aligned in the ground state. Moreover, drastic changes in the shape of the $M(T)$ curve are evidence of changes in the magnetic excitation spectrum. Both changes most likely reflect the sensitivity of carrier-mediated interactions between the Mn local moments to the defect distribution that is varied by annealing.

In this Letter we study the stability of states with parallel Mn local moments using the kinetic-exchange model of carrier-induced ferromagnetism. We find that fully aligned ferromagnetic ground states do not occur when the band electron wave functions are strongly concentrated around Mn ion locations, and propose that this circumstance must be avoided to achieve high ferromagnetic transition temperatures. On the other hand, we find, consistent with the observations of Potashnik *et al.,* that noncollinear ferromagnetism is common in (III,Mn)V semiconductors. On the basis of calculations of external-field-dependent magnetic excitation spectra, we discuss unusual temperature and field dependence of the magnetization that we predict will be characteristic of noncollinear states in these ferromagnets.

Ferromagnetism in (III,Mn)V semiconductors has been addressed using first-principles local spin-density approximation calculations [5], phenomenological impurity-band models [6], and, most commonly [3,7–9], using a semiphenomenological approach that sidesteps atomic scale physics by using an envelope function description of the bands. The last approach is strongly supported by the large literature on the closely related (II,Mn)VI semiconductors [10] and we follow it here. The model Hamiltonian we study,

$$\mathcal{H} = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \sum_I \int d^3r\, J(\vec{r} - \vec{R}_I)\vec{s}(\vec{r}) \cdot \vec{S}_I\,, \quad (1)$$

describes noninteracting carriers in a parabolic band characterized by an effective mass m, whose spin density $\vec{s}(\vec{r})$ is coupled to ionized Mn acceptor spins $\vec{S}_I$ at locations $\vec{R}_I$ by a spatially extended antiferromagnetic exchange coupling $J(\vec{r})$, which we take to be of the form

$$J(\vec{r}) = \frac{J_{pd}}{(2\pi a_0^2)^{3/2}}\, e^{-r^2/2a_0^2}, \quad (2)$$

where J_{pd} parametrizes the strength and a_0 the range of the interaction. Similar models were studied some time

ago [11] in connection with classical spin-glass systems; in that case, however, the density of magnetic impurities N is taken to be much smaller than the density of charge carriers n, $n/N \gg 1$ [11]. (III,Mn)V semiconductors are opposite, $n/N \ll 1$, because of strong compensation of Mn acceptors by antisite defects N. The model (1) is unrealistic in its use of a single parabolic band to represent the semiconductor valence bands, in its neglect of Coulomb interactions between holes in the valence band and other holes and Mn acceptors, and in the absence of any representation of the defects (other than the Mn ions) whose distributions presumably vary during the annealing process. We return to these limitations of the model later. In addition, the range of the exchange interaction in this model accounts [12] for the atomic scale physics only crudely. We believe, nevertheless, that this relatively simple model captures much of the physics associated with the approach of and the occurrence of reduced saturation magnetization states for nonoptimal defect configurations.

Recently a theory of magnetic fluctuations around a fully aligned state of magnetic ions was developed using the *virtual crystal* approximation [7]. In contrast to that work we do not adopt this simplifying approximation in which the Mn magnetic distribution is replaced by a continuum, retaining instead individual spins of length $S = 5/2$ placed at arbitrary locations. The virtual *crystal approximation,* which has a long and successful history in analyzing the properties of (II,Mn)VI ferromagnets, completely eliminates disorder and, as we discuss further below, noncollinear ferromagnetism.

We first address the stability of the collinear state in which all Mn moments have parallel orientation taken to be in the $\hat{z}$ direction, parametrizing changes in the orientation of spin I by a complex number, $z_I = (S_I^x + iS_I^y)/\sqrt{2S}$. The zeroth-order band-electron Hamiltonian is given by Eq. (1) with $\vec{S}_I = S\hat{z}$. For small changes in spin orientation the change in the band-electron Hamiltonian is

$$\mathcal{H}_1 = \frac{1}{2}\sum_I \left[J(\vec{r} - \vec{R}_I) \begin{pmatrix} -z_I\bar{z}_I & \sqrt{2S}\,\bar{z}_I \\ \sqrt{2S}\,z_I & z_I\bar{z}_I \end{pmatrix} \right]. \quad (3)$$

The contribution to the carrier ground state energy of first order in the z_I vanishes. At second order, one obtains

$$E^{(2)} = \sum_{I,J} \bar{z}_I M_{IJ} z_J\,, \quad (4)$$

where $M_{IJ} = L_{IJ} + K_{IJ}$ and

$$L_{IJ} = -\delta_{IJ} \int d^3r\, J(\vec{r} - \vec{R}_I)\langle s^z(\vec{r})\rangle\,, \quad (5)$$

$$K_{IJ} = \frac{S}{2}\sum_{\alpha,\beta} \left[\frac{n_F(\xi_\alpha) - n_F(\xi_\beta)}{\xi_\alpha - \xi_\beta} F_I^{\alpha\downarrow,\beta\uparrow} F_J^{\beta\uparrow,\alpha\downarrow} \right]. \quad (6)$$

Here $\langle \vec{s}(\vec{r})\rangle$ is the band-electron spin density in the collinear state, and n_F is the Fermi function at zero temperature. In these equations we have defined

$$F_I^{\alpha\sigma,\beta\mu} = \int d^3r\, J(\vec{r} - \vec{R}_I)\bar{\psi}_{\alpha\sigma}(\vec{r})\psi_{\beta\mu}(\vec{r})\,, \quad (7)$$

with $\psi_{\alpha\sigma}(\vec{r})$ being the spin σ component of the carrier wave function with energy $\varepsilon_\alpha = \xi_\alpha + \mu$, where μ is the Fermi energy. All eigenvalues of M must be positive for the collinear state to be stable. The diagonal contribution to M from the positive definite matrix (5) gives the energy change associated with reorienting each localized spin in the mean-field created by the polarized band electrons, while the contributions from the matrix (6) represent the energy reduction due to the response of band electrons to reorientation of the localized spins. When the Mn spins are treated quantum mechanically using a Holstein-Primakoff boson representation [13] and coherent state path integrals, the z_I are boson coherent state labels, equivalent to replacing z_I and $\bar{z}_I$ by bosonic creation and annihilation operators a_I and a_I^+. Then Eq. (3) is the spin-wave Hamiltonian, and the eigenvalues [14] of M_{IJ} are the system's spin-wave energies.

We have evaluated the matrix M_{IJ} and its spectrum by solving for the band-electron mean-field eigenstates, applying periodic boundary conditions to cubic simulation cells. The single-particle wave functions $\psi_{\alpha\sigma}(\vec{r})$ are computed in a plane-wave basis taking into account wave vectors $\vec{q}$ with length up to an appropriate cutoff q_c. The upper panel of Fig. 1 shows typical results for the eigenvalue distribution of L_{IJ} averaged over a large number of randomly chosen Mn distributions. We have established

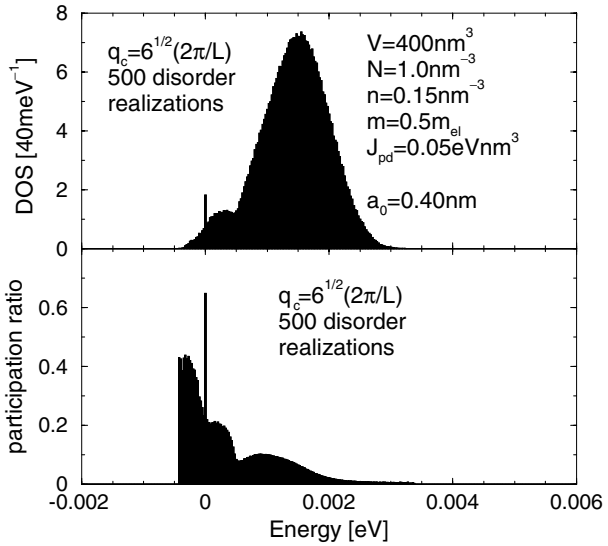

FIG. 1. Upper panel: disorder-averaged density of states for spin-wave excitations. These results were obtained with a simulation cube of volume $V = L^3 = 400$ nm^3 with a Mn density of $N = 1.0$ nm^{-3}, a carrier density $n = 0.15$ nm^{-3}, and $m = 0.5m_{el}$. The strength of the exchange interaction between ions and carriers is $J_{pd} = 0.05$ eV nm^3 with a spatial range of $a_0 = 0.40$ nm. Lower panel: disorder-averaged participation ratios for the same system. In both graphs the value at zero energy is enhanced due to the contribution of the uniform-rotation mode which occurs for any disorder realization.

by further calculations that the effects of the wave vector cutoff on the low-lying excitations have already saturated for the value of q_c used here. We note that for any arrangement of the Mn positions $\vec{R}_I$ the matrix M_{IJ} contains a zero eigenvalue corresponding to a uniform rotation of all spins where all components z_I are the same. This implies that summing over all columns of M gives the zero vector, a sum rule that is perfectly fulfilled in our numerics independently of q_c since this plane-wave cutoff does not influence the rotational invariance in spin space.

In the above calculations the Mn positions were chosen completely at random with a uniform distribution, while in a real (III,Mn)V semiconductor the Mn ions are located on the fcc lattice of cation sites. Our disorder-averaged data for the two cases are indistinguishability, however, establishing that atomic scale correlations in Mn locations do not alter our results. Our most important finding, illustrated in Fig. 1 and discussed at length below, is that for a wide range of parameter values *there are always a few negative eigenvalues, i.e., the collinear ferromagnetic state is not stable.*

To analyze the nature of this instability we have evaluated the participation ratios for these elementary excitations which we define by

$$p_j = \left[NV \sum_I |\alpha_I^j|^4 \right]^{-1}, \tag{8}$$

where α_I^j is the Ith component of the jth normalized eigenvector of M_{IJ}. p_j is an estimate for the fraction of Mn sites which have important involvement in the jth spin wave. For instance, if a vector contains exactly a fraction of p nonzero components of equal modulus and all others being zero, its participation ratio is p. The largest participation ratio of unity is achieved for the zero-energy uniform-rotation mode, where all components of the corresponding eigenvector are equal.

The lower panel of Fig. 1 shows the disorder-averaged participation ratio as a function of spin-wave energy for the same situation as in the top panel. The property that negative energy excitations have large participation ratios shows that the instabilities of the collinear state involve correlated reorientations of many spins, rather than lone loosely coupled moments. It is the high-energy excitations, for which the mean-field term dominates, that are single ion in character with participation ratios comparable to $1/400$, where 400 is the number of Mn ions in these simulations cells. The shape of the spin-wave density of states is, in the model we have studied, sensitive to the Mn density N, the carrier density n, and the Hamiltonian parameters m, J_{pd}, and a_0. Situations in which the collinear ferromagnetic state is, for certain disorder realizations, stable can be approached most simply (for technical reasons) by letting a_0 be larger, but also we believe for larger n/N. For the value of n/N illustrated in Fig. 1, which corresponds to a carrier density somewhat smaller than that measured in the highest T_c samples, negative eigenvalues occur for nearly any Mn ion distribution. We note that negative eigenvalues increase in number as the wave vector cutoff is increased toward its converged value. These results suggest that noncollinear ferromagnetic states are common, and that they are sensitive to the distribution of Mn ions and defects, especially those that trap carriers. We find that the collinear ferromagnetic state tends to become unstable as mean-field band eigenfunctions become more strongly localized around Mn ion sites.

The effect of a weak external magnetic field on the eigenvalue spectrum of M_{IJ} is particularly simple. The field couples to the local moment through its Landé g factor, adding $2\mu_B H$ to the energy of a spin-wave excitation for $S = 5/2$, and to the spin and orbital degrees of freedom of the band electrons. The orbital coupling leads to Landau levels that do not play an important role at weak fields in these highly disordered samples. Zeeman coupling is also unimportant, because it gives a contribution to the spin splitting that is negligible compared to the mean-field exchange splitting $\Delta = J_{pd}NS \sim 0.1$ eV.

Thus, provided that the modulus of the smallest eigenvalue (i.e., the onset of the eigenvalue distribution of M_{IJ} at negative energies) is small compared to Δ (as is the case in data shown above), this modulus is the value of $g_L\mu_B H$ necessary to force full spin alignment of a noncollinear state. The experiments of Potashnik *et al.* [4] demonstrate that the maximum value of $M(T = 0)$ is achieved over a certain range of annealing histories. We associate this maximum value with the fully aligned collinear Mn configuration state; indeed the maximum moment per Mn is consistent with full alignment partially compensated by band electrons. In this circumstance, the *virtual crystal approximation* used in earlier spin-wave calculations which neglected disorder [7] can be accurate. For other annealing histories, $M(T = 0)$ is reduced corresponding, we propose, to the noncollinear order of the Mn spins. Calculations such as those described above show that these spins gradually align as an external field is added to the Hamiltonian. Since full alignment is achieved at a finite external field, we expect full alignment to be indicated experimentally by a kink in the $M(T = 0, H)$ curve. At this point, we predict that the system will still have gapless excitations and power-law temperature dependence of the magnetization, in sharp contrast to the gapful excitations and exponentially suppressed temperature dependence of conventional ferromagnets in an external magnetic field. At the same time, spin-resonance experiments will see a gapped spin-wave spectrum since they couple only to the uniform-rotation mode which has finite energy $g_L\mu_B B$ over the noncollinear ground state.

To address the noncollinear state, we generalize our formalism by expanding around and defining Holstein-Primakoff bosons [13] with respect to a general noncollinear orientation configuration, of each Mn spin, $\vec{S}_I = S\hat{\Omega}_I = S(\sin\vartheta_I\cos\varphi_I, \sin\vartheta_I\sin\varphi_I, \cos\vartheta_I)$. If this configuration is not an extremum, there will be an energy

correction that is *linear* in the Holstein-Primakoff variables:

$$E^{(1)} = \frac{1}{2}\sum_I [\bar{g}_I z_I + g_I \bar{z}_I], \tag{9}$$

with $g_I = g_I^1 + i g_I^2$, and

$$g_I^1 = \sqrt{2S}\,(\vec{e}_{\varphi_I} \times \vec{e}_z) \cdot \int d^3r \{J(\vec{r} - \vec{R}_I)[(\langle \vec{s}(\vec{r})\rangle \cdot \vec{e}_{\varphi_I})\vec{e}_{\varphi_I} + (\langle \vec{s}(\vec{r})\rangle \cdot \vec{e}_z)\vec{e}_z] \times \vec{\Omega}_I\}, \tag{10}$$

$$g_I^2 = \sqrt{2S}\,\vec{e}_z \cdot \left(\vec{e}_{\varphi_I} \times \int d^3r\, J(\vec{r} - \vec{R}_I)\langle \vec{s}(\vec{r})\rangle\right), \tag{11}$$

where $\vec{e}_{\varphi_I} = (\cos\varphi_I, \sin\varphi_I, 0)$ and $\vec{e}_z = (0,0,1)$. The contributions to the carrier ground state energy quadratic in the Holstein-Primakoff variables can also be obtained via perturbative calculations similar to those for the collinear case. The components g_I represent the gradient of the energy with respect to deviations, parametrized by the z_I, from the reference orientations. A given orientation of Mn spins is stationary with respect to fluctuations if all complex coefficients g_I vanish. This is the case if and only if $\int d^3r\, J(\vec{r} - \vec{R}_I)\langle \vec{s}(\vec{r})\rangle$ is parallel with the direction $\hat{\Omega}_I$ of the local ion spin. (The collinear ferromagnetic state is always stationary but not necessarily stable.)

We have employed the energy gradient expression (9) in a numerical steepest descent procedure to search for true energy minima. Briefly, our results are as follows. In cases where the energy minimum found by this method is close to that of the collinear state [with $M(T = 0)$ about 90% or more of the maximum value], this minimum appears to be unique for each disorder realization. We can therefore be confident that we have located the absolute ground state of our model. In situations where the magnetization is reduced more substantially, however, by about 20% or more typically, we converge to different energy minima from different starting points. In these cases the model has substantial spin-glass character with a complex energy landscape. For the system shown in Fig. 1, for instance, magnetization values at local energy minima are typically 30% to 40% of the collinear state value.

We thank T. Dietl, J. König, B. Lee, F. von Oppen, N. Samarth, P. Schiffer, C. Timm, and S.-R. E. Yang for useful discussions. This work was supported by the Deutsche Forschungsgemeinschaft, the Indiana 21st Century Fund, DARPA/ONR Award No. N00014-00-1-0951, and the Welch Foundation.

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[14] Strictly speaking K_{IJ} is frequency dependent in a quantum formulation, reflecting the retarded nature of the carrier-mediated interaction between local moments. The frequency dependence is weak, however, because of the small ratio between spin-wave excitation energies and the mean-field spin splitting of the itinerant electron bands. It can be shown that, for high-participation ratio and low-frequency excitations, the only role of the frequency dependence is to incorporate the band electron contribution to the magnetization and to rescale the collective mode energies by a factor of $1/(1 - n/2SN)$. Terms at second and higher order in the low-frequency expansion of K_{IJ} reflect correlated fluctuations between local moment and itinerant electron spins that suppress the total magnetization by a further small factor.