Eur. Phys. J. B **49**, 433–439 (2006)
DOI: 10.1140/epjb/e2006-00090-4

THE EUROPEAN PHYSICAL JOURNAL B

Magnetic properties of doped GdI_2

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Received 14 November 2005
Published online 31 March 2006 –

Abstract. Motivated by the recent experimental studies on layered ferromagnetic metallic system GdI_2 and its doped variant GdI_2H_x we develop a model to understand their ground state magnetic phase diagram. Based on first principle electronic structure calculations we write down a phenomenological model and solve it under certain approximations to obtain the ground state energy. In the process we work out the phase diagram of the correlated double exchange model on a triangular lattice for the specific band structure at hand.

PACS. 75.47.Gk Colossal magnetoresistance – 75.30.Et Exchange and superexchange interactions

1 Introduction

Layered magnetic systems with coupled charge and spin degrees of freedom have received considerable attention recently owing to their rich phase diagram and intriguing transport properties. The layered system GdI_2 and its doped variant GdI_2H_x , recently studied by Felser et al. [1] and Ryazanov et al. [2], show significant magnetoresistance [3] of about 60% at room temperature with a ferromagnetic (FM) transition temperature close to 300 K [4]. Unlike the magnetoresistive manganites or their bilayer counterparts, there is no significant Jahn-Teller coupling in these systems and that enables one to study a purely electronic model, coupled to magnetic degrees of freedom, without the involvement of the lattice. In addition, GdI_2 is isostructural to the well-known dichalcogenides like 2H-TaS_2, 2H-$TaSe_2$ with hexagonal layered structure, but do not show any superconducting instability — in fact the resistivity rises at low temperatures.

It has been pointed out recently [5] that the large magnetoresistance in GdI_2 is primarily due to the freezing out of the spin disorder scattering of the conduction electrons in a magnetic field. There is indeed evidence for spin fluctuation coupled to charge degrees of freedom in the ESR experiments [6]. The broad resistivity anomaly at Curie temperature (T_c) shifts towards higher temperatures with magnetic field. From susceptibility measurements [2] a variety of regions with different degree of spin ordering have been proposed. The high-temperature ferromagnetic phase gives way to regions of frozen or short-range correlated spins at lower temperatures. At about 33% hole doping a sliver of spin glass phase appears at low temperatures ($T < 20$ K) changing over to a paramagnetic (PM) phase with doping.

In GdI_2 the rare earth Gd ions have one electron in the d-band coupled to the localised Gd $4f$ electrons through ferromagnetic exchange in the configuration $4f^7 5d^1$. The rare earth ions are arranged in a hexagonally coordinated layer structure, each Gd ion has six nearest-neighbour Gd ions. Each such layer is separated from the next one by two layers of iodine atoms. This results in having the interlayer coupling among the Gd ions considerably weaker than the intra-layer one. LDA band structure results indicate a spin splitting of the conduction band [1] — the splitting is nearly complete in the LDA+U results. The crystal field in the trigonal prismatic layered dichalcogenide is negligible and the $5d$ orbitals are quite strongly mixed. Band structure calculations (see below) indicate that there is one half-filled d-band that crosses the Fermi level. The on-site Coulomb interaction in the rare earth $5d$ level is generally not very strong. But a single, half-filled narrow d-band crossing the Fermi level and low dimensionality of the system make this repulsion quite relevant. The presence of short-range spin fluctuations and spin disordered phases already point to competing magnetic exchange interactions in the system. In the half-filled single d-band, even a small Coulomb repulsion generates AF fluctuations that will compete with the FM interaction mediated by the conduction band via the FM $f - d$ exchange (similar to the Zener double exchange (DE) mechanism). It is also

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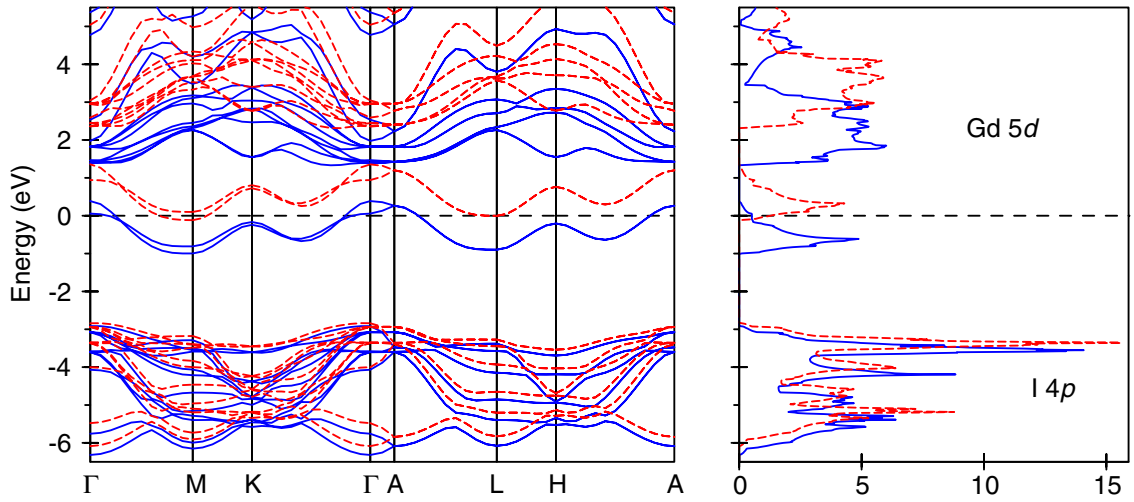

Fig. 1. (Color online) LSDA band structure and the total DOS of GdI_2. Majority and minority spin bands are plotted with solid and dashed lines, respectively.

useful to note that the GdI_2 system never shows full saturation moment, predicted by the LDA calculations. The ordered state has a moment of $7.33\mu_B$, less than the full saturation moment of $8\mu_B$ out of which $7\mu_B$ presumably comes from the $4f$ core spins [1]. Hence the moment coming from the $5d$ electron is considerably less than $1\mu_B$ indicating that correlation effects (beyond the density functional calculations) and coupling of the spin and charge degrees of freedom are very relevant. Also there is almost no literature on the study of a correlated DE model on a non-bipartite lattice. On a triangular lattice, it is known that the nearest-neighbour Ising AF interactions are frustrated leading to a finite ground state entropy. Indeed, the ground state of AF Heisenberg spin model or any correlated electronic model on a triangular lattice is not known. In the few studies that exist on frustrated itinerant systems [7], the geometric frustration of the lattice has often been replaced by a random spin exchange. For a review on these and related issues, see, e.g., reference [8].

2 LSDA band structure

Spin-polarized band structure calculations were performed for the experimental crystal structure of GdI_2 [1] within local spin-density approximation (LSDA) using the LMTO method [9] in the atomic sphere approximation with the combined correction term taken into account. Gd $4f$ electrons were assumed to be completely localized and treated as quasi-core states. All seven majority spin $4f$ states were occupied while the minority spin ones remain empty which models the high-spin state of the Gd $4f$ shell. Ferromagnetic arrangement of Gd magnetic moments was assumed.

The calculated band structure shown in Figure 1 agrees well with the results of previous calculations [1]. I $5p$ states are completely filled and separated from partially occupied Gd $5d$ states by a gap of $\sim$2 eV. The latter are split into majority and minority spin subbands by strong exchange interaction with the completely spin-polarized $4f$ shell, the splitting being of order $\sim$0.9 eV. The total width of $5d$ derived bands is 5 eV. The most striking feature of the band structure is that for each spin direction two lowest Gd $5d$ bands are split off from the others by a gap of 1 eV.

Because of the trigonal local symmetry of a Gd site d orbitals are split into a one-dimensional representation a_1 (d_{z^2}) and two two-dimensional representations e_1 (d_{xz}, d_{yz}) and e_2 (d_{xy}, $d_{x^2-y^2}$). Band plots show the contribution of different Gd $5d$ orbitals to a Bloch wave function represented by the size of a dot (Fig. 2). One can glean that the assumption [1] of two lowest Gd d bands formed predominantly by a d_{z^2} orbital is not confirmed by our calculation. Except for the k space region around the $\Gamma - A$ high symmetry direction, the contributions of d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ orbitals to the bands in question as well as to the two bands above the gap are comparable. Thus, the gap appears as a result of a rather strong hybridization between the above orbitals in the ab plane. Four highest Gd d bands are formed by $d_{xz,yz}$ states which are shifted towards higher energies due to the trigonal component of the ligand field. They do not hybridize with the former three orbitals. The same conclusion on the nature of the gap was drawn by Mattheiss [10] based on a tight binding fit to the calculated band structure of a layered 2H-$TaSe_2$ compound which is isostructural to GdI_2.

3 Effective model

It is clear from the band structure calculations that the band crossing the Fermi level is a mixture of primarily three d-orbitals, namely d_{z^2}, d_{xy} and $d_{x^2-y^2}$. It is therefore not possible to obtain a one-parameter, tight-binding fit of this band with only nearest neighbour hopping [12]. We fit this band using a three parameter (t_0, t_{nn} and $t_{nnn} = -0.514$, 0.070 and 0.073 eV) tight binding one (Fig. 3a). The band width is about 1 eV and we assume the on-site repulsion to be close to or less than this. In any

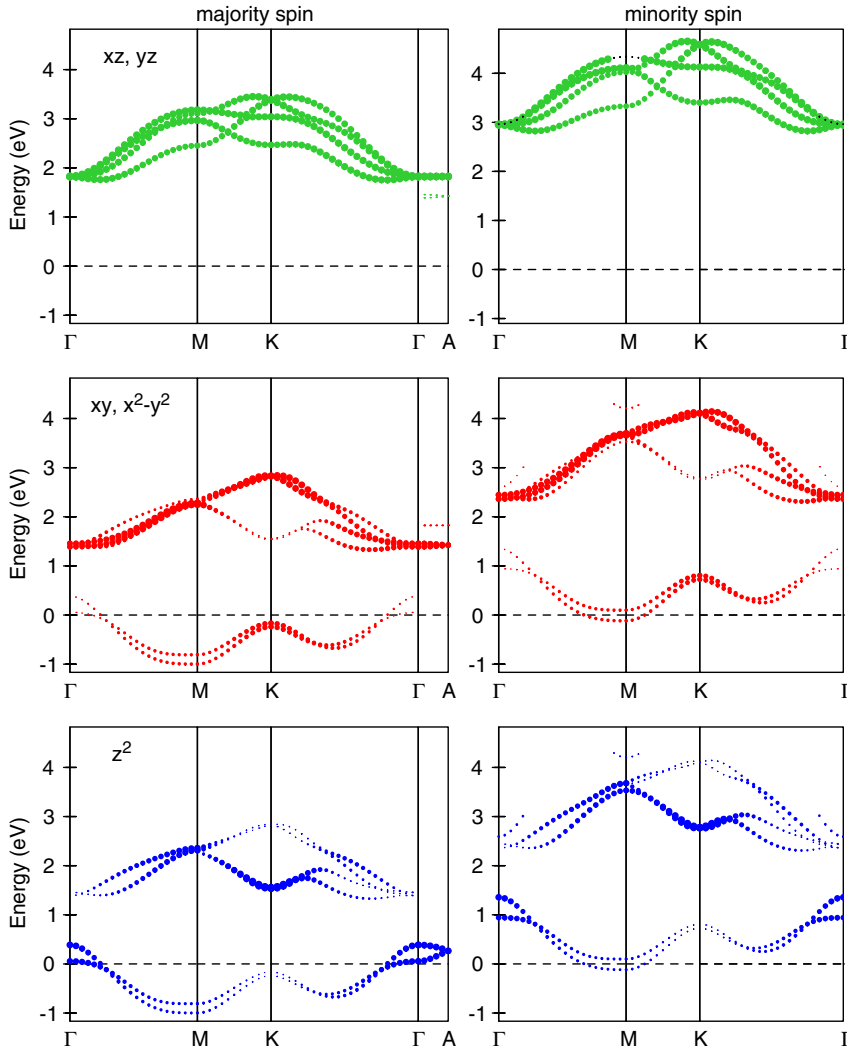

Fig. 2. (Color online) The expanded view of the Gd $5d$ bands. The size of filled circles is proportional to the squared contribution of $5d$ orbitals of different symmetry to the Bloch wave function at a given k point. The coordinates of the high symmetry points are Γ (0, 0, 0), M ($\frac{1}{\sqrt{3}}$, 0, 0), K ($\frac{1}{\sqrt{3}}$, $\frac{1}{3}$, 0), and A (0, 0, 0.136) in $2\pi/a$ units; a being the lattice constant.

case, we treat this as a parameter in our calculation. The corresponding density of states (DOS) is shown in Figure 3b along with the DOS of the one-parameter nearest neighbour DOS used by Hanisch et al. [11] in their study of the Hubbard model on a triangular lattice. The values of $f-d$ exchange have been estimated from the above band structure results assuming a mean-field description for the exchange and a classical description for the core spin. Assuming further that the spin splitting is entirely due to $f-d$ exchange, the value $J_{fd}S = 0.9$ eV then serves as an upper limit for the value of the exchange coupling ($S = 7/2$ is the $4f$ core spin).

Based on the above arguments, a possible Hamiltonian for the effective degrees of freedom can be written as

$$H = -J\sum_{\langle ij\rangle}\mathbf{S_i}.\mathbf{S_j} - J_{fd}\sum_{i}\mathbf{S_i}.\mathbf{s_i} - \sum_{\langle ij\rangle\sigma} t_{ij}c^{\dagger}_{i,\sigma}c_{j,\sigma} + \frac{U}{2}\sum_{i,\sigma}\hat{n}_{i\sigma}\hat{n}_{i-\sigma}. \quad (1)$$

Here J is the exchange interaction between the localised 4f spins $\mathbf{S}_i$ ($S = 7/2$). The second term is the $f-d$ FM exchange coupling ($\mathbf{S}, \mathbf{s}$ are the core and conduction spin, respectively) while the third term represents the hopping of conduction electrons. The last term represents the Hubbard interaction. In second-order perturbation theory, $J \sim -|t_{ij}|^2/(J_{fd}S + U)$ is due to the virtual exchange of conduction electrons between sites i and j. It turns out to be antiferromagnetic (AF). Its magnitude is small for the parameters discussed above. Away from half filling, the DE mechanism favours an FM configuration of the core spins driven by the kinetic energy (KE) of the electrons, while the Coulomb repulsion U favours an antiferromagnetic arrangement. This leads to competing ground states tuned by filling, with additional richness coming from the intrinsic geometric frustration of an AF state defined on a triangular lattice. In the following, we keep $J = 0$ and study the magnetic phase diagram of the model. We treat core spins ($S = 7/2$) semi-classically and use mean-field theory for the Coulomb repulsion U.

The effective $5d$ band at the Fermi surface in the undoped system ($x = 0$) is half-filled i.e., the electron density $n = 1$. Hole (electron) doping, therefore, implies $n < 1$ ($n > 1$). Doping of holes in the GdI_2 is effected by the insertion of hydrogen [2] which localises electrons

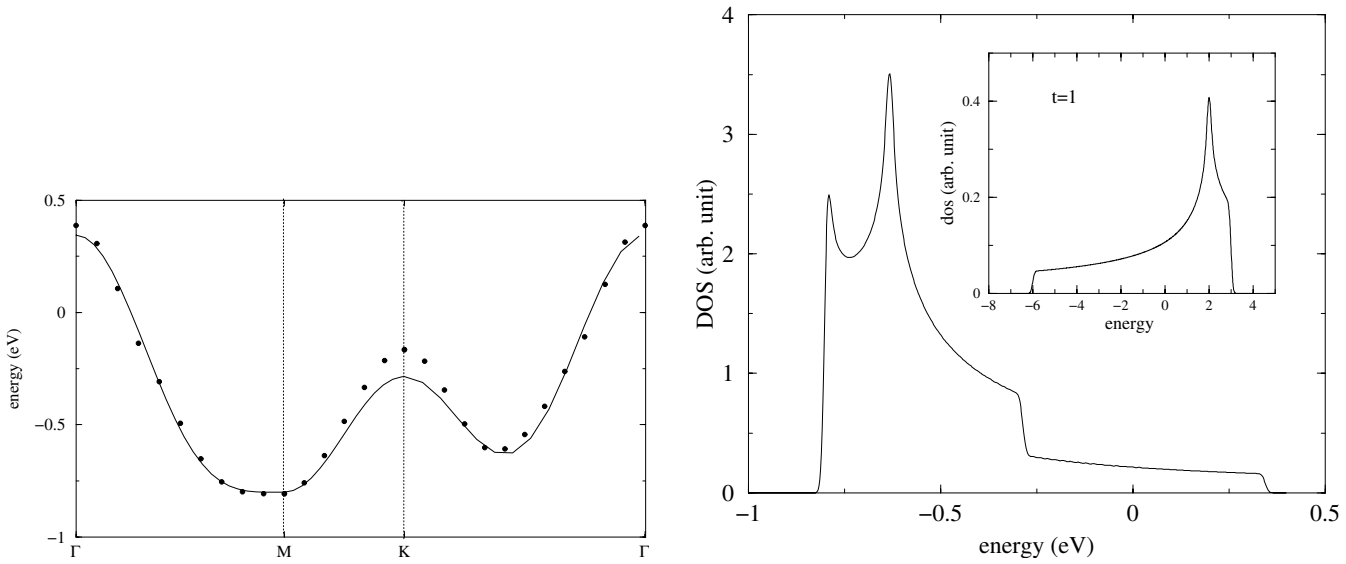

Fig. 3. (a) Tight binding fit (line) for the $5d$ band (dotted line) that crosses the Fermi level in Figure 1, (b) DOS corresponding to the tight binding band in (a) with the inset showing the DOS for the tight binding band considered in the calculations of Hanisch et al. [12] (see text).

away from the band. This is taken care by suitably moving the Fermi energy. In the limit of $J_{fd} = 0$ and with a nearest-neighbour tight-binding band, this model represents the single band Hubbard model on a triangular lattice studied within mean-field theory by several groups [12–17]. These studies find a number of magnetically ordered phases, i.e., the FM state, the Néel state [ferromagnetic rows coupled antiferromagnetically, the ordering wave vector $\mathbf{Q} = (2\pi/\sqrt{3}, 0)$], the AFM state (classical state, angle between spins 120°) and the linear spin-density wave state (LSDW), containing zig-zag FM chains [$\mathbf{Q} = (\pi, 0)$]. For low U there is a region of no long range order (paramagnetic phase) even at half-filling, contrary to the square lattice where the band is particle-hole symmetric.

Disorder in this system plays a significant role in determining the resistivity and short-range order, particularly at low temperatures. In fact, the resistivity is too high — at 100 K the minimum value is about 20 Ω cm, three orders of magnitude larger than the maximum metallic resistivity for this system (about 10 mΩ cm, assuming a cylindrical FS and lattice constants $a, b \simeq 4$ Å along the plane). It cannot be only disorder that is responsible for this high resistivity in the metallic state, the interaction surely plays a major role. At the moment we do not take the disorder into account and look at the clean limit to investigate the possible magnetic orders that the model provides. The effects of disorder will be taken up in a separate calculation [18] later.

It is also useful to note that the $4f$ levels are not very far from the Fermi level and a small hybridisation V_{fd} between $4f$ and $5d$ electrons cannot be ruled out completely on the basis of energetics alone from the band structure results. However, such a term should be very small owing to reasonably large U_{ff} and at most add a small AF coupling between the d and f electrons effectively reducing J_{fd} only slightly.

4 Calculation and results

The physics of the model is controlled by competition between the FM double exchange and the AF correlations coming from the Coulomb repulsion U. The geometric frustration of the AF state on a triangular lattice adds to the number of possible ground states and their closeness in energy. In the limit $J_{fd} \to \infty$, one can project out the direction of conduction electron spins parallel to the local core spin by using the transformation $e^{i\sigma_z\phi_i/2}e^{i\sigma_y\theta_i/2}e^{-i\sigma_z\phi_i/2}$. It operates on a two-component spinor and reduces to a system of spinless fermions (the angles θ_i, ϕ_i refer to the polar and azimuthal angle of the conduction electron spin with respect to $\mathbf{S}_i$). The on-site Coulomb term, in that case, becomes irrelevant. In this situation the AF superexchange term becomes important, though the DE mechanism would lead to an FM state except close to $n = 0$ and $n = 2$.

However, the GdI_2 and GdI_2H_x systems are not really described by this limit and a finite J_{fd} is the relevant limit here. We treat the core spins classically and the Coulomb interaction term in a mean-field approximation. To describe the different magnetic states in this approximation, we choose $\mathbf{S} = \mathbf{S_0}e^{i\mathbf{Q}.\mathbf{r}_i}$, where $\mathbf{Q}$ is the wave vector corresponding to the chosen state described earlier. We choose the spin quantization axis in the xy plane. The second term in the Hamiltonian equation (1) then connects every k point in the Brillouin zone to $\mathbf{k} \pm \mathbf{Q}$ and one has to diagonalise the Hamiltonian on a k-grid in the hexagonal BZ. The order parameter is obtained by minimising the free energy for a particular filling. For the present calculations

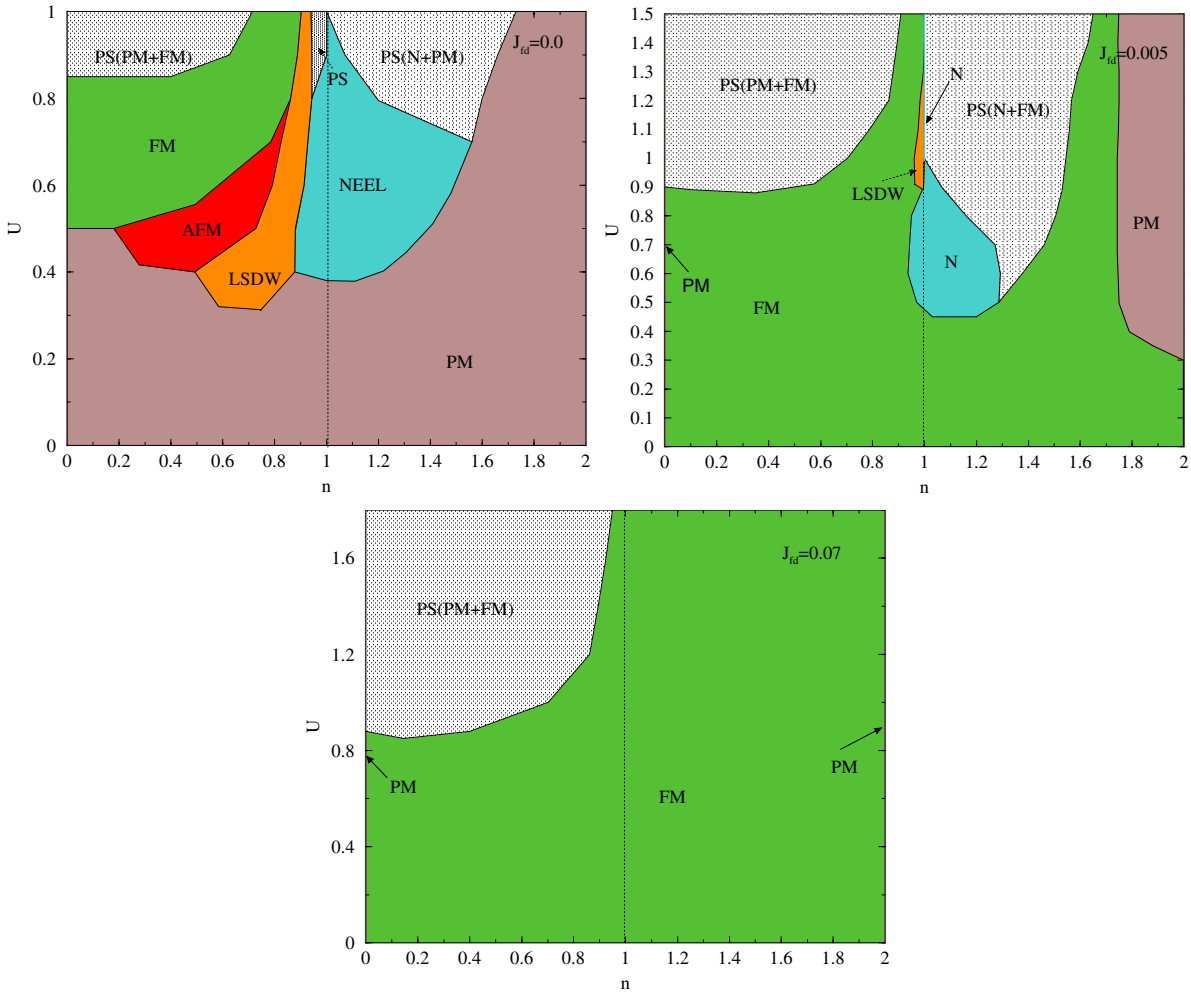

Fig. 4. (Color online) Phase diagram in the $U-n$ plane at $J_{fd} = 0, 0.005, 0.07$.

we have chosen to investigate the following ordered phases known from previous investigations on triangular lattices. The FM phase, the Neèl state, the three-sublattice AFM state and the LSDW state mentioned earlier. We use the three parameter tight-binding fit to the band appropriate for GdI_2 and GdI_2H_x systems for our calculations.

As mentioned above, the Coulomb interactions are generally not very strong in the $5d$ level, though for the narrow band crossing the Fermi level (see Fig. 1) they may still be very important. Since both $f-d$ exchange and U_{dd} contribute to the spin splitting of the conduction band, it is difficult to specify these two parameters. We therefore allow them to vary over a possible range, treat them as free parameters and draw the magnetic phase diagram.

In Figures 4a–4c the phase diagrams for $J_{fd} = 0$, 0.005 and 0.07 eV are shown. The $J_{fd} = 0$ phase diagram can be compared with a similar phase diagram obtained by Hanisch et al. [12] with a nn tight-binding band dispersion $E_k = 4t\cos\frac{\sqrt{3}k_x}{2}\cos\frac{k_y}{2} + 2t\cos k_y$. It is noticed that there are considerable differences between the two calculations. At half-filling, $n = 1$, we observe the Neèl state for U close to 0.4 eV (about 0.36 W, where W is the bandwidth). This continues all the way upto $U = 1$ eV. The region of Neèl state is quite wide in our phase diagram around $n = 1$. For $U < 0.39$ eV, we obtain a paramagnetic phase all the way down. Hanisch et al. report three-sublattice AF phase at half-filling at $U_{red} = \frac{U}{U+Uc} = 0.25$ ($U_c = 15.81t$ for the triangular lattice, so that $U = 0.58\ W$) similar to what has been observed earlier [13]. Away from half-filling we get a small region of phase segregation (PS) followed by LSDW, AFM, FM and finally another region of PS depending on the value of U on the hole-doped side, while for $n > 1$ there is a large region of phase separation from the paramagnetic phase.

The phase diagram changes dramatically with finite values of J_{fd}. As seen in Figure 4b the PM phase reduces to a region close to the empty ($n = 0$) and full ($n = 2$) bands. Due to the asymmetry in the DOS, the regions of stability of the PM phase for $n = 0$ and $n = 2$ are very different, the latter being larger. The rest of the PM region becomes FM for finite $f - d$ exchange as expected. The AFM region completely disappears while the Neèl region

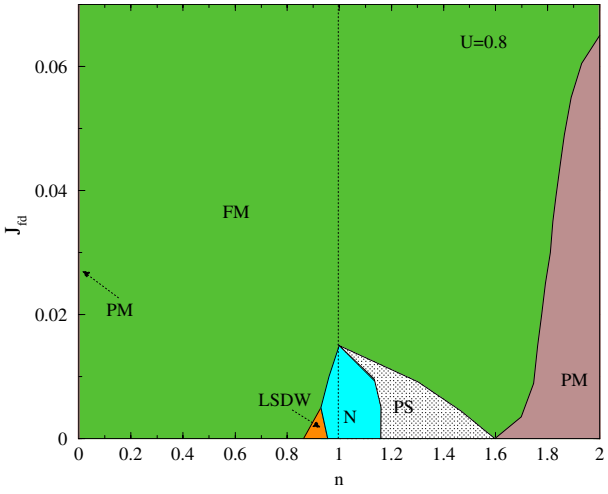

Fig. 5. (Color online) Phase diagram in the $J_{fd} - n$ plane for $U = 0.8$.

becomes narrow beyond $U = 1$ eV. The LSDW phase also shrinks considerably. With increasing J_{fd} the FM region takes over completely (Fig. 4c). Two narrow PM regions survive at the ends owing to negligible KE contributions.

It is obvious from the phase diagrams shown that the value of J_{fd} for GdI_2H_x systems should be very small but finite. In the model without disorder, the phases are extremely sensitive to changes in the $f-d$ exchange. This is suggestive of the fact that indeed in GdI_2H_x several phases appear very close by in energy. Just as in other similar correlated systems with competing interactions, e.g., the manganites [19] and the double perovskites [20], a fine tuning of the model parameters is necessary to specify the phases of the system. Such a situation leads to multiple phases with possible microscopic phase segregation as we observe in Figure 4. The appearance of a multitude of phase segregated regions in the present case also has to do with the underlying frustration of the AF states on a triangular lattice. The large entropy present in the ground state or very close to it make the ground states easily tunable.

In view of such sensitivity of the phases to J_{fd}, we draw the phase diagram also in $n - J_{fd}$ plane for a fixed value of $U = 0.8$ eV. Figure 5 reveals that in order to obtain multiple phases, J_{fd} should be less than about 17.5 meV. There are the phases LSDW, Neèl, FM and PM present in the phase diagram with a region of phase separation coming from the first order transition between the Neèl and FM phases. For bigger values of J_{fd} the entire phase diagram is ferromagnetic. Such a low value for $f-d$ exchange indicates that the spin splitting in the d-band is not due entirely to the $f-d$ exchange. Instead a considerable part must come from correlations in the conduction band.

The phase diagram presented in Ryazanov et al. [2], does not seem to show regions of phase segregation or AF spin order. On the other hand they do indicate the presence of a spin glass region (or a mixture of FM and SG) beyond $n = 0.33$ as can be inferred from the broad susceptibility peak they observe. Doping beyond $n \approx 0.7$ suppresses long range magnetic order completely and leads to a broad paramagnetic region.

The region $n < 0.7$ showed large thermal hysteresis in the susceptibility data. There is a splitting between the field-cooled and zero field-cooled susceptibility at low temperature indicating disordered magnetic behaviour (arising from domain rotations, magnetic clusters or superparamagnetic regions). The ferromagnetic transition temperature is also very sensitive to the method of sample preparation and the measurement techniques. As reported by the authors [21], the data are quite noisy and the system appears to be intrinsically disordered, no matter how carefully prepared. The high value of resistivity in the metallic phase and the unsaturated magnetic moment deep inside the FM phase are suggestive of the presence of disorder as well as correlation. All this indicate a possible competition between different ground states, high degree of magnetic disorder and a possible microscopic phase segregations. As in the observed phase diagram, there is a predominance of the FM region close to half-filling that we also find, but there are other phases close by depending on the value of $f-d$ exchange coupling in the calculated phase diagram. The actual value of hole doping in GdI_2H_x for a given value of x, is difficult to ascertain [2], though increasing x is understood to have the effect of hole doping. It is expected from our calculations that there would be several different phases and microscopic phase segregations in this system too.

The large magnetoresistance in GdI_2 has already been attributed [5] to the quenching of spin disorder scattering of the conduction electrons. In a microscopically phase segregated system, there is likely to be very large magnetic scattering across microscale ordered regions. In an aligning field such scattering is reduced drastically leading to a drop in resistivity. In the model, we had a superexchange interaction to begin with which we have neglected in the calculations that followed. The presence of such a term would increase AF tendencies and thereby allow for a larger value of J_{fd} than we derived above. Besides, the end regions of the phase diagram, $n = 0, 2$ will also become antiferromagnetic owing to the absence of itinerant electrons there.

In conclusion, we have studied a model which, we believe, describes some of the features of the nearly two dimensional, triangular lattice magnetic system GdI_2H_x . The resulting phase diagram has some broad similarity with the experimental one, though it predicts much more structure in the ground state phases than has so far been observed. We hope to motivate more experiments in these directions in order to check on our predictions.

We are indebted to R.K. Kremer and M. Ryazanov for communicating to us some of their results prior to publication and for clarifying some of the experimental points involved.

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