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Calculating the Curie temperature reliably in diluted III-V ferromagnetic semiconductors

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Abstract. – We present a semi-analytic theory for the Curie temperature in diluted magnetic semiconductors that treats disorder effects exactly in the effective Heisenberg Hamiltonian, and spin fluctuations within a local RPA. The exchange couplings are taken from concentration-dependent *ab initio* estimates. The theory gives very good agreement with published data for well-annealed samples of $Mn_xGa_{1-x}As$. We predict that critical temperatures for strongly p-type $Mn_xGa_{1-x}N$ would be lower than in doped GaAs, despite the stronger nearest-neighbour ferromagnetic coupling. We also predict the dependence on the hole concentration.

Search for diluted magnetic semiconductors with ferromagnetism stable to high temperatures has been hampered by the many physical parameters that may determine magnetic properties. These include the choice of host semiconductor, that of the doping magnetic impurity, the degree of compensation, and methods of preparation and treatment of the sample [1]. The underlying mechanism of interaction between dopant spins has without doubt been correctly identified: Ruderman-Kittel-Kasuya-Yosida(RKKY)–like effective interactions mediated by both the host [2, 3] and the doping band [4–6]. Despite this, the theory has not led to reliable quantitative predictions. Comparison of calculations has been complicated by difficulties of fully characterizing the samples. In samples of GaAs doped with Mn, extensive experimental studies [1] have now allowed for greater control over sample parameters and there is now apparently convergence to reliable experimental values of the critical temperature of different groups [7–10]. An important factor was that the carrier densities were measured simultaneously by magneto-transport. There is now the possibility of testing calculations against experiments and determining the origin of past discrepancies.

Ab initio calculations using the Local Density Approximation and the magnetic force theorem can be used [5] to derive realistic values of magnetic exchange interactions between

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classical impurity spins. These calculations also take into account the effect on the effective exchange of disorder of the carriers, within a Coherent Potential Approximation (CPA). Similar calculations based on supercells [11,12] lead to comparable results at low concentration. It has become apparent that the difficulty is not in deriving the effective magnetic Hamiltonian correctly but in treating its thermodynamics accurately. As we will demonstrate explicitly here, treating the magnetic correlations by oversimplified mean-field theories [13,14] has led to overstatement, by a wide margin, of the critical temperature $T_{\rm c}$. The disorder in the effective magnetic model also plays an important role that cannot be simply treated by an effective medium theory of the style of the Virtual Crystal Approximation (VCA) [15]. This suggests that the discrepancy with experiment is largely due to approximations made to the effective Hamiltonian, not the values of the couplings themselves. Thus by improving the treatment of the effective Hamiltonian we can hope to find good agreement with experiments.

In this paper we shall argue that the effective random Heisenberg model may be treated by an accurate semi-analytic method separating the treatment of disorder, which will be treated without approximation, and an analytic approach, a form of the Random Phase Approximation (RPA) for spin fluctuations. Thus, the calculation starting from first principles is in three stages: first, the *ab initio* calculation of the Heisenberg couplings with pairs of magnetic dopants at different relative displacements. In the second stage, we generate a sequence of different configurations on the fcc lattice by sampling techniques. For each configuration the random Heisenberg model is treated analytically within RPA. This approximation is an extension of standard RPA of the Heisenberg model to a disordered system. It is equivalent to that used in ref. [15], except that in that case the disorder was treated in a CPA-type manner. As the lattice configuration is random, the equations must be solved numerically. The full derivation of the equations will be given elsewhere [16]: here we shall simply summarize the determination of the critical temperature: The Green's functions $G_{ij}(E)$ for spins on impurity sites i and j, satisfy

$$EG_{ij}(E) = 2\lambda_i\delta_{ij} + \left(\sum_l J_{lj}\lambda_l\right) G_{ij}(E) - \epsilon\left[\lambda_i \sum_l J_{il}G_{lj}(E)\right], \tag{1}$$

where the variables $\lambda_i = \frac{m_i}{m}$ are the average magnetization m_i on individual sites, normalized with respect to the magnetization m averaged over all impurities. For an RPA treatment of Heisenberg spins, $\epsilon = 1$. In order to compare to approximations that we shall term "Ising-like", this term can be taken to be zero, *i.e.* $\epsilon = 0$. For a given temperature the Green's functions for impurity spins are determined following a self-consistent procedure for the $G_{ij}(E)$ and $\lambda_i(T)$ similar to that of Callen [15,17,18]. In the limit of $T \to T_{\rm c}$ and a total of N_0 classical spins, we can write

$$F_i = -\frac{1}{2\pi\lambda_i}\int_{-\infty}^{\infty} \frac{{\rm Im}G_{ii}(E)}{E}{\rm d}E\,, \tag{2}$$

$$k_{\rm B}T_{\rm c} = \frac{2}{3N_0}\sum_i \frac{1}{F_i}\,. \tag{3}$$

$T_{\rm c}$ is now determined by the self-consistency of these equations, which are solved exactly for a given configuration. The critical temperatures are averaged over different samples (typically 10^5 host sites averaged over 50 configurations). We remark that the results are close to recent results obtained by Monte Carlo simulations [19,20], which also take into account fluctuations in the positions of the magnetic impurities. Semi-analytical calculations are intrinsically much faster and essentially no finite-size extrapolation is needed. For a given configuration,

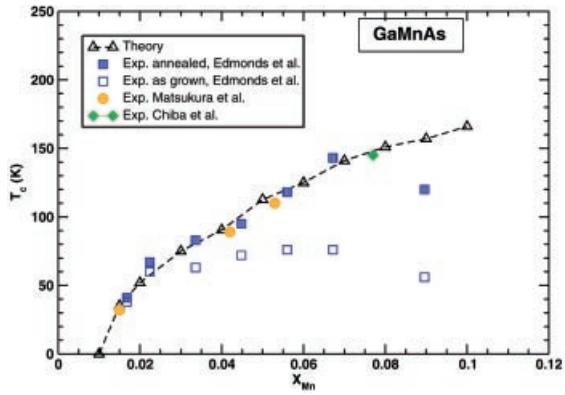

Fig. 1 – T_c as a function of doping for $Mn_xGa_{1-x}As$: theory for uncompensated samples and experiment.

eqs. (2) and (3) give an explicit form of T_c. The greatly improved accuracy over previous mean-field methods is due essentially to the fact that the RPA approximation includes the low-temperature modes that destroy long-range order as the temperature increases, and that the geometric disorder is fully included.

In fig. 1 we show the calculation of T_c as a function of x for $Mn_xGa_{1-x}As$. The values of the exchange constants are as in ref. [5] (as shown explicitly in figs. 3, 4 and 5 of that paper). We show also the experimental results of Edmonds *et al.* [7,8], Matsukura [9], and Chiba *et al.* [10] for different concentrations of Mn in $Mn_xGa_{1-x}As$. We note that the agreement with the results of Edmonds *et al.* is for the case of *fully* annealed samples. This is consistent with the fact that we use the couplings calculated for uncompensated samples. The annealing changes the compensation via the density of Mn interstitials and As antisites. This also increases the density of carriers, as shown by transport studies. The agreement with experiment is excellent, except for the single highest concentration (9%): our theory suggests that at this concentration annealing is not complete. For uncompensated samples, we do expect a maximum in T_C, as increasing carrier density induces frustration, but for higher concentrations than those currently attained. Monte Carlo calculations with the same effective couplings [19], gave, for example, 137 K [19] and 103 K [20] at 5% agreeing well with our value of 125 K for the same concentrations. Note also that the theory correctly predicts a threshold (about 1.5%), below which there is no ferromagnetism.

In fig. 2 we show the calculations of T_c as a function of x for $Mn_xGa_{1-x}As$ within different theoretical approaches: "Ising"-like Mean-Field theory (*i.e.* $\epsilon = 0$ in eq. (1), but fully including disorder), Mean Field-Virtual Crystal Approximation (MF-VCA), in which the disorder is treated as a simple effective medium: $T_c^{\text{MF-VCA}} = \frac{2}{3}x\sum_i J_{0i}$, RPA-disorder (*i.e.* ϵ =1, full disorder and transverse fluctuations, the present approach). One can see the large overestimate of the critical temperatures for the "Ising-like" mean-field approximations (essentially the same as in ref. [14]) which includes the disorder correctly but does not treat transverse fluctuations. In such simple mean-field theories, the critical temperature is overly influenced by sites in large local effective fields due to strong short-range ferromagnetic interactions. For low dilution long-range order cannot propagate simply by nearest-neighbour interactions. The RPA form, in contrast, gives more weight to the low-frequency excitations and this is the reason for its success. The MF-VCA results reproduce in essence those of Sato *et al.* [13], showing that the difference with our final theory is in the treatment of the effective Hamiltonian, not in

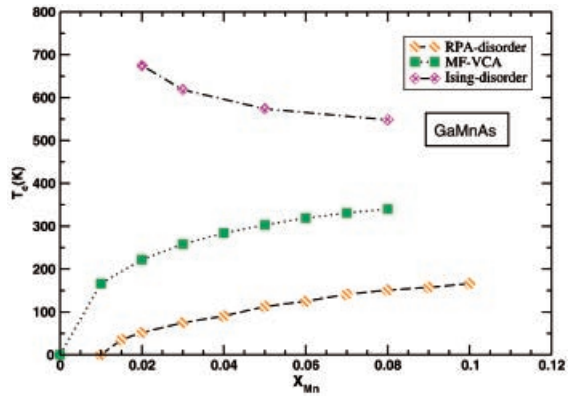

Fig. 2 – T_c for $Mn_xGa_{1-x}As$: comparison of different theories, as defined in the text.

the couplings estimated *ab initio*. The current theory and Monte Carlo simulations [19, 20] show the threshold effect for ferromagnetism: this is an example of the failure of the simplest RKKY-like theories.

The flexibility and accuracy of our calculation allows us to make more precise the question of the dependence of the Curie temperature on the density of carriers. In fig. 3 we present the estimated critical temperature as a function of the number of carriers for the dopant concentration 5%. For direct experimental comparison, annealing may also change the number of magnetically active impurities through the variation of the density of Mn interstitials. For simplicity, we analyse the effect of carrier density assuming a constant magnetic impurity density. The exchange integrals are calculated (see fig. 5 of ref. [5]) by introducing compensation via a concentration y of As antisites, giving a carrier density $n_h = x - 2y$. It is seen that the temperature is rather insensitive to the hole density, provided that it is above a value of about $\sim 60\%$ of the number of dopant atoms. Below this value, it diminishes rapidly and ferromagnetism disappears between 50 and 60%. From the dependence of the coupling constants on concentration x (see fig. 5a of ref. [5]), we expect the threshold value of γ to decrease further as x increases. This transition is associated with suppression of the ferromagnetism presumably in favour of a spin-glass phase, owing to dominance of antiferromagnetic superexchange. For comparison, we show the results if the disorder is treated by a Virtual Crystal Approximation (MF-VCA). While that approximation gave a threshold level of carrier density at rather lower values, it increasingly overestimates the critical temperature as γ increases, *i.e.* the compensation decreases.

It would be interesting to verify this curve experimentally in different samples. Reference [7] estimates that in as-grown samples γ is about 0.5 for 5% Mn. Annealing increased T_C substantially: this is consistent with our estimates of the transition region. We note that older, possibly less precise, measurements of carrier concentrations [9] gave lower values ($\gamma \approx 0.2$) where we would predict that ferromagnetism is unstable. This lower value has been used in RKKY-type models which failed to predict the spin-glass instability. This was due to the neglect of superexchange contributions important especially at low carrier concentration [21], in contrast to *ab initio* calculations where they are fully included. The relative insensitivity to the degree of compensation indicates that our previous calculations (fig. 1) should remain accurate in the presence of a small number of antisite substitutions. We remark that figs. 1 to 3 indicate the qualitative and quantitative failures of simplified RKKY approaches in which $T_c \propto x^{\frac{4}{3}}\gamma^{\frac{1}{3}}$. While this has already been noted experimentally [8], we can see from a theoretical

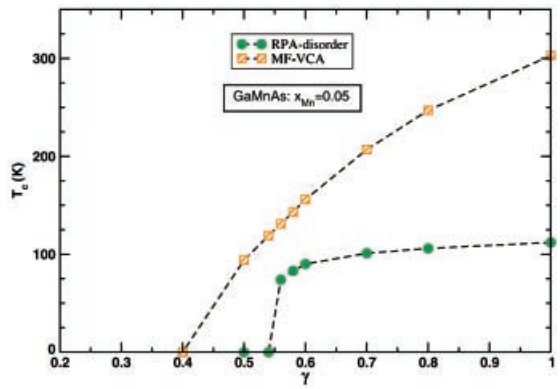

Fig. 3 – T_c for $Mn_xGa_{1-x}As$ for fixed concentration as a function of carrier density. The parameter γ is the ratio of carrier concentration n_h to the doping density x.

point of view while this must be so: each magnetic exchange is renormalized by the impurities, disorder in the effective Hamiltonian is significant, and transverse spin fluctuations are crucial.

We now turn to the calculations made by the same procedure for the case of (Ga,Mn)N which has attracted great interest [22]. Application of simple RKKY models predicted a T_c as high as 700 K for moderately low concentrations (6% Mn) [23]. The experimental situation is somewhat controversial: there have been reports of ferromagnetism at high temperatures [24] as well as reports of paramagnetism down to low temperatures [25]. Here we shall content ourselves with estimating the critical temperatures with the assumption that, as for well-annealed samples in (Ga,Mn)As, it should be possible to obtain p-type samples with hole concentrations as large as the Mn concentration, *i.e.* $\gamma = 1$ in our notation. In fact this is far from being the case experimentally, where for reasons that are not fully understood, only very small positive values of γ have been obtained. The purpose of our calculations is to show that *even if* one could obtain strongly p-type samples, the estimates of simplified mean-field theory must be questioned. In fig. 4 we show predicted Curie temperatures for $Mn_xGa_{1-x}N$, with $\gamma = 1$, showing, for comparison, the same calculations for $Mn_xGa_{1-x}As$. It is seen that the critical temperature of the doped GaN is always lower than for the same concentration of doped GaAs. This is despite the fact that the nearest-neighbour ferromagnetic coupling at $\gamma = 1$ is substantially stronger: propagation of long-range magnetic order naturally depends crucially on the further-neighbour couplings which are much weaker [5]. The reason why they fall off more rapidly is that the impurity band of Mn is near mid-gap, in contrast to the case of (Mn,Ga)As, where it is close to the valence band edge of GaAs. As in GaAs, the estimates by Sato *et al.* [13] are qualitatively different because of the mean-field treatment, with maximum critical temperatures for GaN at 350 K, much higher than the current results. We emphasise that this is not due to the differences in the couplings, but to the treatment of the Heisenberg model. For the carrier concentrations currently obtained in real samples the value of γ is, as we have mentioned, much smaller than 1, and as in fig. 3 for Ga(Mn)As, the predicted Curie temperature would be zero.

In conclusion, we present a novel approach allowing for reliable calculation, starting from *ab initio* methods, of the critical temperatures in diluted magnetic semiconductors. This shows that apparent discrepancies in the past between predictions from *ab initio* methods and observed material properties have been due to the incomplete treatment of the effective Hamiltonian rather than inaccuracy in the couplings, especially with the need to include dis-

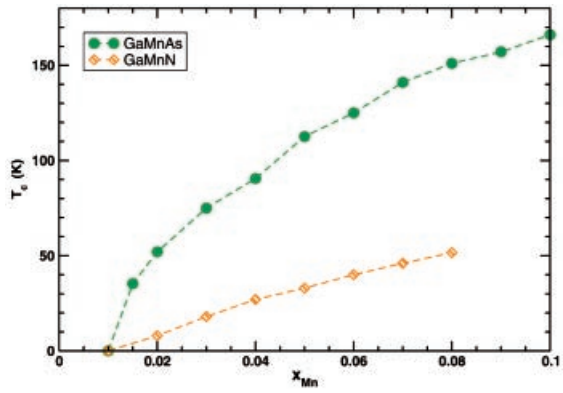

Fig. 4 – Predicted T_c for (Ga,Mn)N compared to (Ga,Mn)As.

order properly. The speed, orders of magnitude faster than Monte Carlo methods [19, 20], and flexibility of the method allow us to consider parameters that may be useful in designing useful materials in a variety of non-translationally invariant situations. Good agreement is found with experimental data on well-annealed samples of $Mn_xGa_{1-x}As$. The apparent strong increase of T_c due to proper treatment of disorder, as observed in previous "Ising-like" mean-field theories, is shown to be due to the neglect of transverse fluctuations. These in fact *reduce* the critical temperatures significantly compared to simple MF-VCA. We also predict the dependence on the carrier concentration, corresponding to samples with different concentrations of antisites. For the average dopant concentrations chosen, this predicts weak dependence on antisite concentration when this is small but eventually the critical temperature falls rapidly. For uncompensated samples of GaN our theory predicts consistently *lower* critical temperatures than for GaAs, despite the larger short-range ferromagnetic coupling. Our estimates differ by an order of magnitude from previous estimates in the concentration range 0–10%. Thus we conclude that *even if* such strongly p-type samples of (Ga,Mn)N are prepared over the concentration range, room temperature ferromagnetism is highly unlikely. These results call for explicit experimental verification and also show the oversimplification of previous theories.

Additional Remark. – The present paper appeared in its original manuscript form as ref. cond-mat/0405332/ in the electronic archive `http://www.arxiv.org`. More than half a year later, the manuscript cond-mat/0501143/ by Hilbert and Nolting appeared, which although referring to our work concerning the method we applied, fails to acknowledge that the same method is applied to identical systems, namely to uncompensated Ga(Mn)As and Ga(Mn)N obtaining very similar results. The work of Hilbert and Nolting must then be considered as a copy of parts of our work. Furthermore, the suggestion of Hilbert and Nolting raised at the end of their manuscript to extend the study to the full local self-consistency was already presented in ref. cond-mat/0405332/, and is also implemented in the present paper. A full discussion in particular of this last point, which has significant consequences, will be published elsewhere.

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