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## Exchange interactions in diluted magnetic semiconductors

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### Abstract

On the basis of *ab initio* calculations for Mn-doped GaN, GaP, GaAs and GaSb, we discuss the origin of ferromagnetism in diluted magnetic semiconductors. The calculations use the Korringa–Kohn–Rostoker method in connection with the coherent potential approximation to describe the substitutional and moment disorder. By mapping the total energy results onto a Heisenberg model, the Curie temperature  $T_C$  is estimated in the mean field approximation (MFA). If impurity bands are formed in the gap, as is the case for (Ga, Mn)N, double exchange dominates leading to a characteristic  $\sqrt{c}$  dependence of  $T_C^{\text{MFA}}$  as a function of the Mn concentration  $c$ . On the other hand, if the d states are localized, as in (Ga, Mn)Sb, Zener's p–d exchange prevails, resulting in a linear  $c$  dependence of  $T_C^{\text{MFA}}$ . (Ga, Mn)As is an intermediate case, showing a  $\sqrt{c}$ -like behaviour in the local density approximation (LDA), but a nearly linear  $c$  dependence, if the more accurate LDA +  $U$  method with  $U = 4$  eV is used.

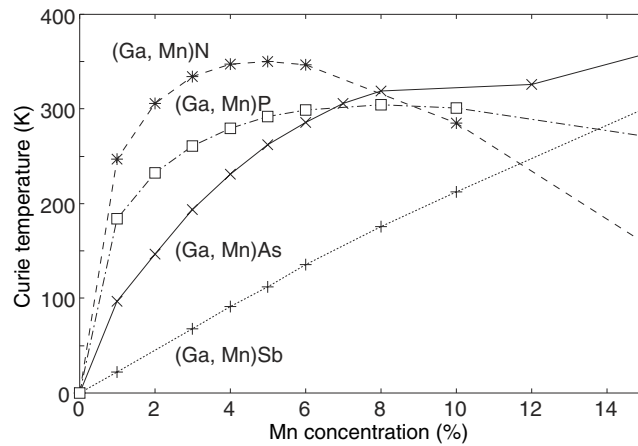
Ferromagnetic diluted magnetic semiconductors (DMS), such as (In, Mn)As and (Ga, Mn)As, were discovered by Ohno *et al* [1], and are regarded as promising materials for spintronics use. However, their Curie temperatures  $T_C$ , e.g., 150 K for (Ga, Mn)As [2], are not high enough for real applications. Therefore, many experiments have been performed to search for DMS with room temperature ferromagnetism and recently high  $T_C$ -values were reported for several systems ((Ga, Mn)N [3], (Ga, Cr)N [4] and (Zn, Cr)Te [5]).

The ferromagnetism in DMS has been investigated theoretically either by a model Hamiltonian [6–8] or by *ab initio* methods [9–14]. Despite their basic differences, the two methods gave similar predictions for the ferromagnetism. Nevertheless, no consensus has been reached about the origin of the ferromagnetism. In fact, Dietl *et al* proposed Zener's p–d

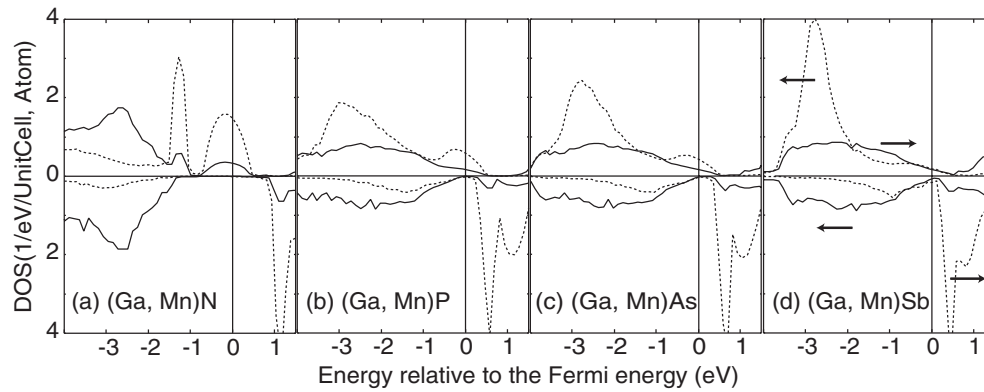
exchange interaction to describe the magnetism [6, 7]. This model predicts room temperature ferromagnetism in (Ga, Mn)N [6, 7] and explained many physical properties of (Ga, Mn)As successfully, as is shown by MacDonald *et al* [8]. On the other hand, Akai pointed out from first-principles calculations that Zener's double-exchange mechanism is responsible for the ferromagnetism in (In, Mn)As [9]. Similar arguments were also given by Sato *et al* [10, 11], who predicted high  $T_C$ -values for (Ga, Mn)N, (Ga, Cr)N and (Ga, Cr)As. Thus, despite the fact that ferromagnetism of DMS is one of the most important topics in spin-electronics, this is still a controversial issue. In this paper, we show that both mechanisms are present in these systems, can be easily understood on the basis of hybridization effects and can be described by density functional theory. We calculate the electronic structure of (Ga, Mn)X, where X refers to N, P, As or Sb, and estimate their  $T_C$  s from first principles within the mean field approximation (MFA). We discuss the relation between the electronic structure and the dominant exchange mechanism and show that the two mechanisms lead to very different concentration dependences of  $T_C^{\text{MFA}}$  and naturally divide the DMS into two classes. Since our emphasis lies on understanding the exchange mechanism, we will not discuss the important problems arising in real materials due to dopants and self-compensation effects. For the same reason we will also not discuss the validity of the MFA.

Our calculations are based on the local density approximation (LDA) and use the Korringa–Kohn–Rostoker method in connection with the coherent potential approximation (CPA) [9] to describe the substitutional and moment disorder. Two magnetic states are considered, i.e., the ferromagnetic (FM) state and the disordered local moment (DLM) or spin-glass state. In the FM state, Mn impurities with parallel aligned magnetic moments distribute randomly at Ga sites in the host semiconductor. Therefore, the FM DMS is described as  $(\text{Ga}_{1-c}, \text{Mn}_c^\uparrow)\text{X}$ , where the up arrow indicates the direction of the Mn local moment and  $c$  is the Mn concentration. On the other hand, the DLM state with vanishing total magnetic moment is described by considering three components of  $\text{Mn}^\uparrow$ ,  $\text{Mn}^\downarrow$  and Ga on the Ga site, i.e.,  $(\text{Ga}_{1-c}, \text{Mn}_{c/2}^\uparrow, \text{Mn}_{c/2}^\downarrow)\text{X}$  [9]. As shown in [11, 12], in MFA the Curie temperature  $T_C$  can be estimated from the total energy difference  $\Delta E = E(\text{DLM}) - E(\text{FM})$  between the DLM and the FM state as calculated in the CPA. Using a mapping onto the Heisenberg model, the evaluation of  $T_C$  in the mean field approximation yields  $k_B T_C^{\text{MFA}} = \frac{2}{3} c \sum_{j \neq i} J_{ij} = \frac{2}{3} \Delta E / c = \frac{2}{3} \Delta \epsilon$ , where  $\Delta \epsilon$  is the energy difference per Mn atom between the DLM and the FM configuration and  $J_{ij}$  are the exchange coupling constants for two Mn atoms at positions  $i$  and  $j$ . Therefore  $T_C$  in the MFA is also a direct measure of the stability of the FM state with respect to the DLA state as given by the energy difference  $\Delta E$ . Note that in the present approach we use two MFAs: the MFA in the form of the CPA for the effect of the substitutional disorder on the electronic structure and the MFA to the Heisenberg model for the statistical problem of the moment orientations. Since for small Mn concentration the calculated  $J_{ij}$  are usually long ranged (except for (Ga, Mn)N), our double MFA procedure seems to give quite reasonable values for the Curie temperatures [15]. For the present KKR–CPA calculations, we use the package MACHIKANEYAMA2000 coded by Akai [16]. We assume muffin-tin potentials and use the experimental lattice constants of the semiconductors [17]. The angular momenta are cut off at  $l = 2$  in each muffin-tin sphere. GaN is calculated in wurtzite structure and GaP, GaAs and GaSb in zinc-blende structure. All calculations are performed for the neutral charge state of Mn.

Figure 1 shows the Curie temperatures of (Ga, Mn)N, (Ga, Mn)P, (Ga, Mn)As and (Ga, Mn)Sb as calculated in the above mean field approximation from the total CPA energies for the FM and DLM states. For low concentrations, the  $T_C^{\text{MFA}}$  s of (Ga, Mn)N, (Ga, Mn)P and (Ga, Mn)As scale roughly proportionally to the square root of the Mn concentration. This behaviour has already been observed in our previous work [11]. In contrast to this, the  $T_C^{\text{MFA}}$  of (Ga, Mn)Sb shows an almost linear concentration dependence. As a whole, we find clear



**Figure 1.** Curie temperatures of (Ga, Mn)N, (Ga, Mn)P, (Ga, Mn)As and (Ga, Mn)Sb calculated from first principles in the mean field approximation.



**Figure 2.** The total density of states per unit cell (solid curves) and local density of d states at the Mn site (dotted curves) in (a) (Ga, Mn)N, (b) (Ga, Mn)P, (c) (Ga, Mn)As and (d) (Ga, Mn)Sb in the ferromagnetic state for 5% Mn. In (d), the arrows indicate the relative shifts of the p and d states due to hybridization.

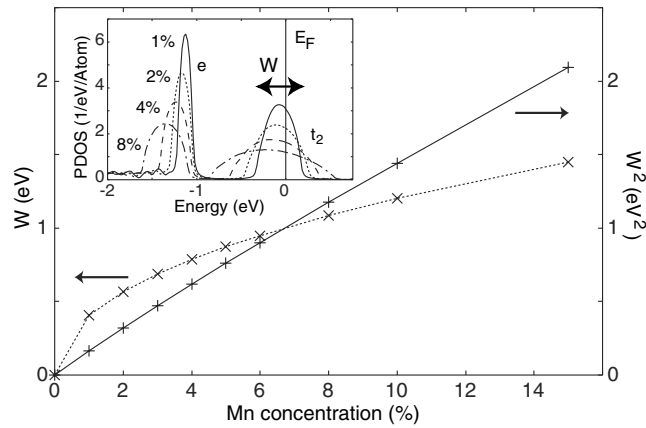
chemical trends in the concentration dependences. For (Ga, Mn)N,  $T_C$  goes up very sharply and reaches a maximum value of 350 K at approximately 5% of Mn, then goes down. For (Ga, Mn)P,  $T_C$  increases sharply up to a saturated value of about 300 K. For (Ga, Mn)As,  $T_C$  shows a similar dependence to that for (Ga, Mn)P, but  $T_C$  increases more moderately for low concentrations and still increases for high concentrations. Finally,  $T_C$  for (Ga, Mn)Sb shows a linear dependence with nearly no curvature. As a result, the concentration dependence shows in the sequence (Ga, Mn)N  $\rightarrow$  (Ga, Mn)Sb a dramatic transition from a  $\sqrt{c}$  dependence to a linear  $c$  behaviour.

In order to discuss the origin of the different concentration dependences, we show in figure 2 the total density of states (DOS) and local density of d states at a Mn site in the FM state. In III–V compounds, the host valence band originates from anion p states. Therefore, the DOS reflects the increase of the atomic p level in the series N, P, As, Sb, resulting in the gradual change of relative position of Mn d states with respect to the host valence bands.

Due to the large relative changes of d and p levels the calculated results are representative for a large variety of DMS systems. In the case of (Ga, Mn)N, the p valence band is lower in energy than the Mn d states and clear impurity bands appear in the band gap. The Fermi level ( $E_F$ ) is located in the  $t_2$  impurity band, being induced by the majority d states of Mn. Since the minority d states are much higher in energy, (Ga, Mn)N shows a half-metallic behaviour. In the other extreme case, i.e., for (Ga, Mn)Sb, the majority d states of Mn are located deep in the host valence band and the local DOS at  $E_F$  agrees well with the host DOS. Thus in (Ga, Mn)Sb the majority d states are localized representing a  $d^5$  configuration, and the hole states above  $E_F$  consist of host valence states. The DOS is no longer half-metallic, which is presumably an LDA error since in the LDA the band gap of GaSb vanishes. (Ga, Mn)P and (Ga, Mn)As are apparently intermediate cases. Their local DOS still show small peaks around the  $E_F$ , slightly larger in GaP than in GaAs. However, the gap states are almost merged into valence bands showing rather broad resonances (figures 2(b) and (c)). Both systems are half-metallic and the total magnetic moment per Mn atom is just  $4 \mu_B$  as in (Ga, Mn)N.

The chemical trends seen in the DOS allow us to explain the drastic differences in concentration dependence of  $T_C^{\text{MFA}}$  and the stabilization energy  $\Delta E$  of the FM state. Here we will concentrate on the extreme cases, (Ga, Mn)N and (Ga, Mn)Sb. The electronic structure of (Ga, Mn)N is characterized by the sharp e impurity band and the broader  $t_2$  impurity band. Of the seven valence electrons of Mn, three are accommodated in the valence band, two in the majority e band and the remaining two in the threefold-degenerate  $t_2$  band, so the Fermi energy falls in the upper part of this band, leaving one state per Mn empty. With increasing concentration the impurity bands broaden, and it is just the broadening of the partially filled  $t_2$  band which stabilizes the ferromagnetism. This is the double-exchange interaction in DMS [9, 18]. The energy gain due to double exchange is proportional to the bandwidth ( $W$ ), being defined as the deviations of the energy eigenvalues  $E$  from the mean value  $\bar{E}$ , i.e.,  $W^2 = \langle (E - \bar{E})^2 \rangle = \sum_{m \neq 0} |H_{0m}|^2$ . The last step follows from a tight-binding description and  $H_{0m}$  is the integral of hopping between the sites 0 and  $m$ . The impurity band is formed due to the hopping of electrons between Mn atoms. Suppose that a certain configuration of Mn atoms in GaN has one of them at site 0. In this configuration,  $H_{0m}$  has a finite value, say  $t_{0m}$ , if another Mn atom sits at site  $m$ ; otherwise,  $H_{0m} = 0$ . In the CPA, we make a configurational average over all sites  $m \neq 0$ . The probability for finding a Mn atom at site  $m$  is given by  $c$ , the atomic concentration of Mn. Thus the configurational average gives:  $\langle W^2 \rangle_{\text{conf.}} = c \sum_{m \neq 0} |t_{0m}|^2$ . Therefore the effective bandwidth  $W$  is proportional to  $\sqrt{c}$  [19]. This is in fact found in our KKR-CPA calculations, as is shown in figure 3. Here the effective quantities  $W$  and  $W^2$  of the  $t_2$  impurity band of (Ga, Mn)N are plotted as a function of the Mn concentration. The linear behaviour of  $W^2$  proves the  $\sqrt{c}$  scaling of  $W$ , in agreement with the above arguments.

Now we discuss the stability of the FM state with respect to the DLM state. In the CPA description of the DLM state, half of the Mn neighbours have moments parallel to the Mn moment at site 0. Therefore the energy gain due to double exchange is always smaller by a factor of  $1/\sqrt{2} \sim 0.71$  than that of the FM state. The other half of the Mn neighbours, being anti-parallel aligned, gain energy by super-exchange interaction [9, 18]. For each spin direction, the majority d states of the one Mn and the minority d states of the other one hybridize covalently. This super-exchange interaction is expected to scale with the concentration  $c/2$  of anti-aligned Mn pairs. Therefore for small concentrations, the double-exchange interaction always wins due to the  $\sqrt{c}$  behaviour and stabilizes the ferromagnetism. This explains the behaviour of  $T_C$  for (Ga, Mn)N shown in figure 1. However, if the  $t_2$  impurity band is full or completely empty, as is e.g. the case for (Ga, Fe)N or (Zn, Mn)Te, the double-exchange interaction vanishes and the super-exchange interaction stabilizes the DLM state.

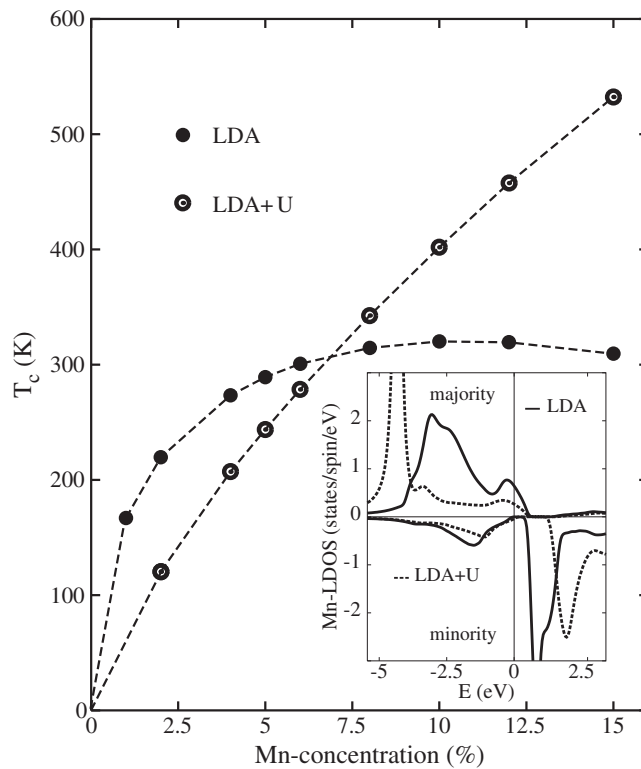


**Figure 3.** The width ( $W$ ) and its square ( $W^2$ ) for the impurity  $t_2$  band of (Ga, Mn)N as a function of Mn concentration. The inset shows the local density of Mn gap states.

For (Ga, Mn)Sb, the other extreme case, the majority d states can be regarded as localized and holes exist in the majority valence band of GaSb. This behaviour is well described by Zener's p–d exchange model used by Dietl *et al* [6, 7] and MacDonald *et al* [8]. As in the discussion of Kanamori [18], in the FM state the hybridization between the Mn d levels and the As p states pushes the lower levels down and the higher levels up, as is indicated for both spin directions by the arrows in figure 2(d). As a result, holes appear in the majority host band, while the minority band is almost fully occupied, so the GaSb host becomes polarized with a moment anti-parallel to the local Mn moment. This moment is close to  $1 \mu_B$ , since the system is nearly half-metallic. By configurational averaging, a homogeneous host polarization of  $c\mu_B$  is obtained, which favours the ferromagnetic coupling of the Mn moments, by an energy proportional to the host polarization, scaling linearly with  $c$ . In the DLM state the average host polarization vanishes, so this state is unfavourable. In conclusion, ferromagnetism is stabilized and  $T_C$  increases linearly with  $c$ .

In (Ga, Mn)P and (Ga, Mn)As, the impurity bands fuse in the concentration range considered with the host valence bands and the lower Mn d states are not yet fully localized. In this sense, these systems are intermediate cases being influenced by both mechanisms, so one might expect a superposition of  $\sqrt{c}$  and a linear  $c$  dependence. This is in line with figure 1, indicating that (Ga, Mn)As shows a weaker  $\sqrt{c}$  and a somewhat stronger  $c$  dependence than (Ga, Mn)P.

According to the previous discussion, the more the impurity states are localized, the more important the p–d exchange mechanism is. It is well known that the LDA underestimates the electron correlation effects and that occupied d states are systematically predicted at too high energies. Thus the LDA underestimates the localization of d states and also the importance of the p–d exchange interaction. One way to improve the LDA is the LDA +  $U$  method [20] which treats the Coulomb repulsion between electrons in localized orbitals in a Hubbard-like procedure. For these reasons we have performed LDA +  $U$  calculations for (Ga, Mn)As with a  $U$  parameter of 4 eV. The calculations are performed using the linear muffin-tin orbital (LMTO) Green function method [21]. In figure 4, the  $T_C$  calculated within LDA +  $U$  is compared to the one calculated within the LDA. Obviously, the LDA +  $U$  gives a more linear  $c$  dependence as compared to LDA. In the inset in figure 4, the local DOS calculated by the LDA +  $U$  method is compared to the local DOS of the LDA. It is found that the Mn d states become more localized in the LDA +  $U$  method. Therefore, the p–d exchange mechanism becomes more



**Figure 4.** The mean field value of the Curie temperature evaluated as a function of the Mn concentration for the LDA and the LDA +  $U$  approach. The inset shows the corresponding spin-resolved local density of states of the Mn atom.

dominant leading to the nearly linear concentration dependence of  $T_C$ . The calculated position of the d peak at 4.3 eV is in good agreement with photoemission measurements [22, 23] which supports our choice of  $U = 4$  eV and at the same time the use of the p–d Hamiltonian for (Ga, Mn)As.

In this paper, we have discussed the origin of the ferromagnetism in DMS based on *ab initio* calculations for Mn-doped III–V compounds. We find that double exchange dominates if impurity bands in the gap are formed and that then  $T_C$  in the MFA increases proportionally to  $\sqrt{c}$ , where  $c$  is the Mn concentration. A typical example showing this is (Ga, Mn)N. On the other hand, the p–d exchange mechanism dominates if the d states of the impurity are nearly localized, as is the case for (Ga, Mn)Sb, and then a linear  $c$  dependence of  $T_C$  is obtained. (Ga, Mn)P and in particular (Ga, Mn)As are intermediate cases. Actually, (Ga, Mn)As is on the border between the two mechanisms, and the results depend sensitively on the position of Mn d states. In the LDA,  $T_C^{\text{MFA}}$  of (Ga, Mn)As still shows a square root behaviour. However, in the more accurate LDA +  $U$  calculation,  $T_C^{\text{MFA}}$  versus  $c$  becomes linear, showing that correlation effects lead to a dominating p–d exchange mechanism.

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