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Magnetic properties of 3d impurities substituted in GaAs

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Abstract

We have calculated the magnetic properties of substituted 3d impurities (Cr–Ni) in a GaAs host by means of first-principles electronic structure calculations. We provide a novel model explaining the ferromagnetic long-range order of III–V dilute magnetic semiconductors. The origin of the ferromagnetism is shown to be delocalized spin-uncompensated As dangling-bond electrons. Besides the quantitative prediction of the magnetic moments, our model provides an understanding of the half-metallicity, and the rise of the critical temperature with the impurity concentration.

As electronic device sizes continue to shrink, physicists are asked to provide new device concepts—devices that work not despite quantum mechanics but because of quantum mechanics. One active area is that of magnetoelectronics, where one tries to exploit, in addition to the charge of the electron, its spin degree of freedom [1]. A central problem here is the spin injection into the semiconductor [2]. The idea of using a ferromagnetic semiconductor, i.e. a diluted magnetic semiconductor (DMS), for the spin injection is now being worked on worldwide [3]. So far, the mechanism of the ferromagnetic long-range order in DMSs has been a matter of dispute. Akai [4] and more recently Dietl *et al* [5] proposed a double-exchange mechanism to explain the ferromagnetic order.

In this paper, we propose a novel mechanism for the ferromagnetism of DMSs. We show that the ferromagnetic order is caused by itinerant spin-uncompensated As dangling-bond (DB) states: the 3d impurity atom interacts with the As DBs. Because of the spin polarization of the 3d atom, the hybridization with the spin-up As DBs is larger than with the spin-down ones. This has two consequences: (i) since the DB states are delocalized, the hybridization leads to an itinerant magnetic moment; (ii) the filling of the As DBs remains incomplete. The eventual filling of these holes destroys the ferromagnetic order in agreement with experiment [6].

To support our analysis, we perform *ab initio* calculations of Ga-substituted impurities (Cr, Mn, Fe, Co, and Ni) in a GaAs host. The magnetic properties were calculated using a

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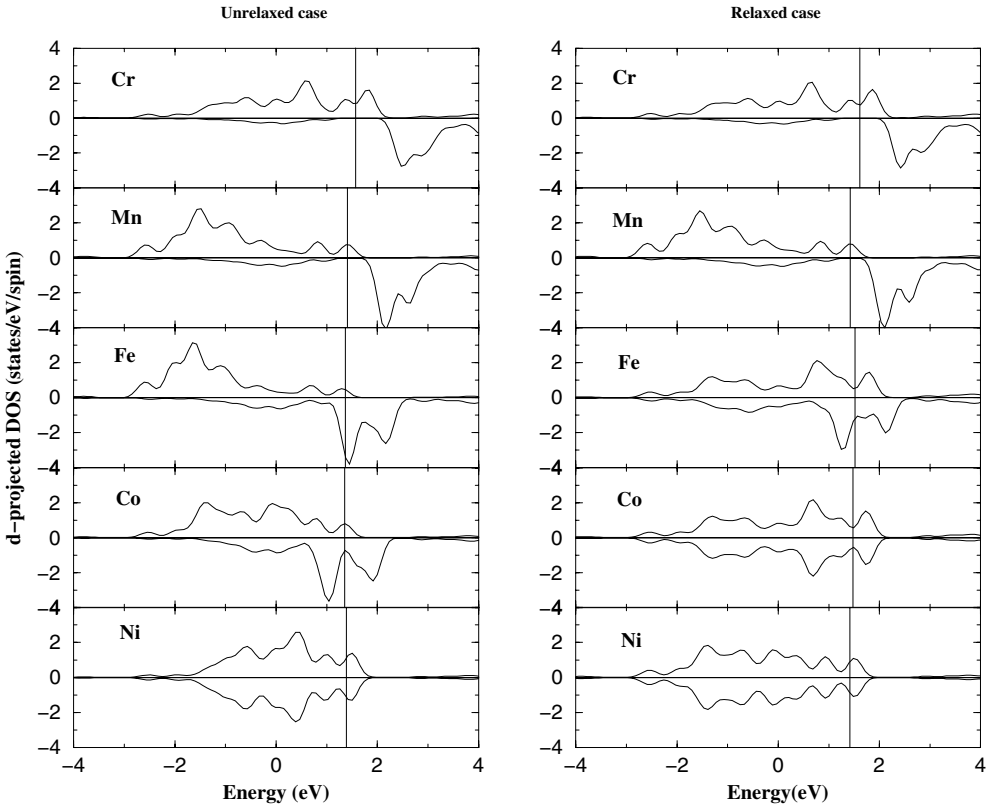

Figure 1. The calculated d DOS projected onto the 3d impurity site. The left (right) column shows the DOS for the unrelaxed (relaxed) case. The vertical lines indicate the position of the Fermi energy.

plane-wave pseudopotential code (VASP [7, 8]) within the local spin-density approximation (LSDA) [9]. The atoms are described by ultrasoft Vanderbilt-type pseudopotentials [10] as supplied by Kresse and Hafner [11]. The wavefunctions are expanded in plane waves with an energy cut-off of 295 eV. The electron density was calculated using special $\boldsymbol{k}$-point sets [12] corresponding to a $2 \times 2 \times 2$ folding. The resulting number of $\boldsymbol{k}$-points was shown to be sufficient for the properties studied here. The calculations are performed within a 64-atom supercell, where the 3d atom is put on a Ga site in the centre of the cell.

In figure 1 we show the spin-resolved d-projected density of states (DOS) at the impurity site. For the unrelaxed case (left column), i.e. where all atoms are sitting on ideal high-symmetry positions, the GaAs containing Cr, Mn, or Co (Fe or Ni) impurities has become a half-metal (metal). In the right column of figure 1 we show the results for the position-, volume-, and shape-relaxed case. For Cr or Mn impurities in GaAs, the effect of the relaxation is negligible, whereas for Fe, Co, and Ni, the relaxation almost suppresses the ferromagnetism. Co or Ni impurities in GaAs are non-magnetic; for Fe in GaAs the magnetic moment has drastically decreased (figure 2).

In order to understand these *ab initio* results, we apply an 'impurity molecule model' [13, 14] which we develop in three steps.

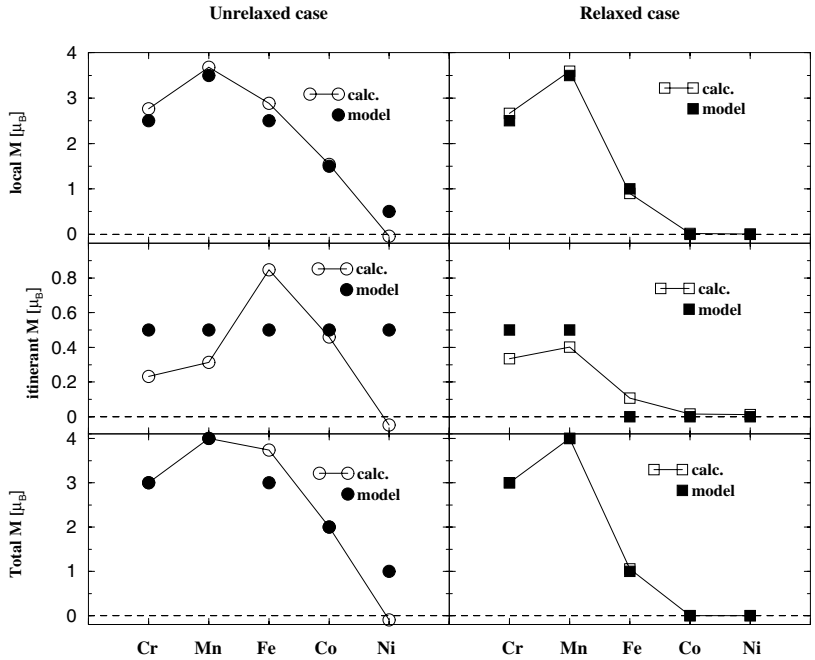

Figure 2. Comparison of the calculated magnetic moments and the model predictions. The left (right) column shows the unrelaxed (relaxed) case. In the first row we show the local magnetic moment, in the second row we show the itinerant magnetic moment, and in the last row we show the total magnetic moment.

(i) We consider the ideal, i.e. unrelaxed, GaAs host with a Ga vacancy. At the vacancy site the four surrounding As neighbours contribute five electrons to the four DBs. We calculate the Ga vacancy to be non-magnetic. The site-projected vacancy DOS is shown in figure 3. Close to the Fermi energy (E_F) a split peak appears in the DOS of the Ga vacancy (bottom panel of figure 3). The two peaks have the following origin: three As DBs give rise to the peak at E_F (top three panels), whereas one As DB gives rise to the peak below E_F (panel four of figure 3). We conclude that the occupation of the As DBs is as follows: one DB is completely occupied (the peak below E_F) and three DBs are only half-occupied (the peak at E_F). In total the vacancy has three holes, i.e. there are 1.5 holes per spin. In a tetrahedral crystal field the sp^3 orbitals split into 's'-like a_1 orbitals and 'p'-like t_2 orbitals [14]. At the vacancy site the a_1 state is completely filled and the t_2 states have three holes. The t_2 state of the Ga vacancy is located 0.06 eV above the valence band edge and is thus almost degenerate with the continuum of extended states [15]. The Ga vacancy t_2 state can thus be treated as a delocalized state. Only then is the non-magnetic state of the vacancy understandable.

(ii) Next the vacancy is filled with the 3d impurity. In a tetrahedral crystal field the d states are split into e and t_2 states, where the e states lie lower in energy than the t_2 states [16]. For all 3d impurities (with the exception of Ni), only the spin-up t_2 ($t_2^{\uparrow}$) states are occupied, i.e. the $t_2^{\downarrow}$ states are completely empty. We assume that the impurity retains its atomic character, i.e. the occupation of the e and t_2 levels follows Hund's rules.

(iii) Finally, we consider the interaction of the 3d impurity with the four As DBs. It is well known that a substitutional impurity in a semiconductor is ionized with the result that the

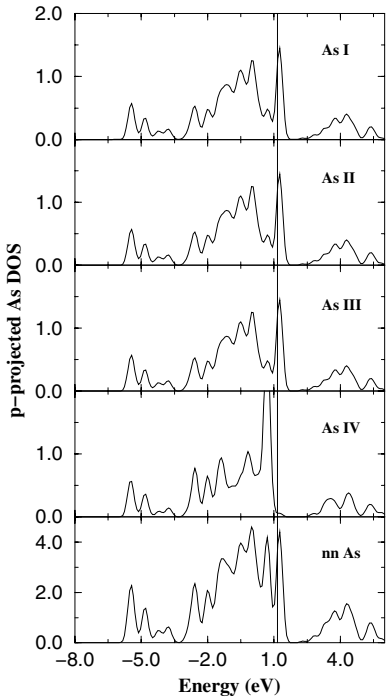

Figure 3. The calculated DOS for the unrelaxed vacancy: the top four panels show the p DOS projected onto the four nearest As neighbours (As I, As II, As III, As IV) of the vacancy. The bottom panel shows the sum of the p DOSs of the four As neighbours.

semiconductor holes become filled. One would thus expect the 3d atom to contribute three electrons to the hole filling, i.e. a 3+ state of the 3d impurity. However, for a spin-polarized impurity there are two possibilities: (1) if the exchange energy is larger than the energy gain (bonding energy) due to the complete hole filling of the As DBs, only the spin-up channel will interact with the As DBs, i.e. a spin flip on the 3d impurity site is prohibited; (2) if, in contrast to the first possibility, the bonding energy exceeds the exchange energy, three electrons will be transferred to the As DBs, i.e. a spin flip on the 3d impurity site is allowed. In the following, we will discuss the two cases separately.

First we assume case (1), i.e. that the exchange energy exceeds the bonding energy. This case agrees with the results for the unrelaxed first-principles calculation. Due to their like symmetry and large overlap, only the $t_2^{\uparrow}$ states of the impurity and the As DB hybridize. Therefore the 3d impurity contributes only 1.5 spin-up electrons to the hole filling of the As DBs. Because the 3d impurity states are localized, not 1.5 but an integer number of two electrons are promoted to the Fermi energy, of which 0.5 electrons have a high probability of being found on the impurity site itself. Thus one electron is shared between the impurity and the delocalized As DBs. The occupation of the impurity atom $t_2^{\uparrow}$ level is therefore reduced by two electrons (states), i.e. the 3d atom assumes a 2+ state. In the following we discuss this charge transfer in more detail.

The As DBs receive 1.5 $t_2^{\uparrow}$ electrons. In order to minimize the energy (especially the kinetic energy of the host), it seems at first sight that the optimal situation would be to equally distribute the 1.5 electrons over both spin channels of the host, i.e. 0.75 electrons have to spin flip. But this apparently optimal situation is not allowed, because of the following. On

the impurity site only spin-up states are available at the Fermi energy (due to the exchange splitting of the d states). Since, as mentioned above, one promoted electron is shared between the impurity atom and the delocalized As DBs, the spin of one of the two promoted electrons is restricted to being spin up. In order to minimize the energy, only one electron of the 1.5 transferred $t_2^{\uparrow}$ electrons is allowed to be equally distributed among the two spin channels, i.e. only 0.5 electrons are allowed to spin flip. In total then, the spin-up (spin-down) channel of the host has received 1.0 (0.5) electrons.

An alternative approach to the charge transfer is the following: let us start from the vacancy DBs. As mentioned earlier, three orbitals of the four delocalized As DBs are half-occupied (0.5 electrons/spin) and one orbital is completely occupied (1 electron/spin), because five electrons have to be redistributed on four DBs. Assume now that we add one electron to the vacancy and distribute it equally among the two spin channels. Adding 0.5 electrons to each spin channel of the As DBs gives rise to the following occupation of the As DBs: three orbitals are completely occupied (1 electron/spin) and one orbital is completely empty (0 electrons/spin), because six (five plus one) electrons have to be redistributed on four DBs. This is an energetically very favourable situation, because the DOS at the Fermi energy is drastically reduced to zero, i.e. a band gap exists. The 3d impurity donates to the As DBs 1.5 $t_2^{\uparrow}$ electrons, of which one is used to create the band gap as described above. Now, because not just one electron but 1.5 $t_2^{\uparrow}$ electrons are transferred from the impurity to the As DBs, the spin-up channel of the As DBs receives an additional 0.5 electrons. Therefore the spin-down channel has a band gap, whereas the spin-up channel has one partly occupied orbital, i.e. a state at the Fermi energy (figure 1). This additional 0.5 electrons corresponds to one half of the shared electron. This discussion also shows that any other distribution of the 1.5 $t_2^{\uparrow}$ electrons within the As DBs will increase the total energy, because the band gap in the spin-down channel would have to disappear.

In total the impurity has lost 1.5 spin-up electrons and the As DBs have gained 0.5 spin-down electrons and 1.0 spin-up electrons. Hence the occupation of the spin-up As DBs exceeds the occupation of the spin-down As DBs by 0.5 electrons and this spin imbalance is accompanied by an *itinerant* magnetic moment, $M_{itinerant} = 0.5\ \mu_B$. Note that, although this amounts to a relatively small moment per formula unit, it constitutes the origin of the long-range order, i.e. the ferromagnetism of the DMS. Our model also gives a natural explanation for the observation of so-called 'hole-mediated ferromagnetism' [6]. That is, any spin imbalance (ferromagnetism) will be quenched if the remaining 1.5 holes of the As DBs are filled (disappear), for instance by additional donor dopants.

We can now express the (local) magnetic moment at the impurity site simply as follows:

$$M_{local} = \mathrm{d}^{\uparrow} - \mathrm{d}^{\downarrow} - N, \tag{1}$$

where N is equal to 1.5 (unrelaxed case), and $\mathrm{d}^{\uparrow}$, $\mathrm{d}^{\downarrow}$ correspond to the d occupation of the impurity atom.

The total magnetic moment per impurity atom, M_{total}, is the sum of the local and itinerant moment:

$$M_{total} = M_{local} + M_{itinerant} = \mathrm{d}^{\uparrow} - \mathrm{d}^{\downarrow} - 1. \tag{2}$$

In the case of, for example, (Ga, Mn)As, the local Mn magnetic moment amounts to $M_{local} = 5 - 0 - 1.5 = 3.5\ \mu_B$ and M_{total} amounts to 4 μ_B. In figure 2 we summarize our results for Cr, Mn, Fe, Co, and Ni impurities in a GaAs host. We compare our model (equations (1), (2)) with the self-consistently calculated magnetic moments. For the unrelaxed case (left column) discussed above, one notices an overall agreement with some deviations, which however can be explained easily. For Cr and Mn the total magnetic moment

agrees perfectly, whereas the itinerant magnetic moment is smaller by about 0.2 μ_B and the local magnetic moment is larger by the same amount as predicted by our model. In our model, we assumed one electron to be shared equally between As and the 3d impurity. Appreciating that due to the difference in electronegativity, more than half of the shared electron is located on the impurity site, the deviations are obvious and follow the expected chemical trend.

The other deviation we find for Ni and Fe. This can also be easily understood from the calculated d- and site-projected densities of states (figure 1). For Fe and Ni we do find spin-down states at the Fermi energy: in the case of Fe these are $e^{\downarrow}$ states and in the case of Ni they are $t_2^{\downarrow}$ states. These additional states contribute to the minimization of the total energy and are for simplicity neglected in our model, though it is straightforward to expand the model.

Now we compare our model with the calculated DOS (figure 1). In agreement with our model, we find two important features in the spin-up channel: (1) one deep-lying broad feature originating from the localized t_2 and e states on the impurity site ($E \sim 1.7$ eV). For Cr this broad feature does not exist, because the Cr atom only has two t_2 electrons. Thus for Cr there is an additional empty t_2 peak above the Fermi energy. (2) One double t_2 peak close to the Fermi energy originating from the electron shared between the Ga vacancy and the impurity.

So far we have not considered any relaxations that increase the overlap between the As DBs and the impurity t_2 states. With increased overlap, the gain in bonding energy, E_{bo}, might become larger than the energy gain due to the exchange splitting, E_x. Then three electrons of the 3d impurity hybridize with the As DBs, because the cost of spin flipping 1.5 d electrons (of the impurity) is compensated by the gain in bonding energy. Therefore the impurity will undergo a transition from a high-spin state to a low-spin state. A similar discussion on 3d transition metal ions in Si was given earlier by Beeler *et al* [17]. For Cr and Mn the exchange energy is large and there are no spin-down states at the Fermi level into which a t_2 spin-up electron could flip. The system therefore would lose energy when increasing the overlap between As and Cr (Mn). That is why the As–Cr and As–Mn bond length is more or less maintained.

For Fe, Co, and Ni, on the other hand, the system gains energy when 1.5 t_2 electrons spin flip to fill all As DB holes, and consequently the bond length is decreased by about 7%. (Co, Ga)As and (Ni, Ga)As are non-magnetic, whereas M_{total} amounts to 1 μ_B for (Fe, Ga)As. Our model ($N = 3$ in equation (1)) predicts for Fe a local magnetic moment of 1 μ_B, but a zero itinerant magnetic moment. With our first-principles calculations we find an itinerant moment of 0.2 μ_B and a local moment of 0.8 μ_B. This difference is explained as follows: due to the difference in electronegativity between Fe and As, some of the delocalized electrons become localized on the Fe site. Since the $e^{\uparrow}$ states at the Fermi energy are completely filled, only spin-down electrons can become localized at the Fe site. It follows that the local magnetic moment is reduced by the amount, A, of localized spin-down electrons. From figure 2 one would expect an A-value between -0.1 and -0.2 μ_B. This in turn leaves an itinerant magnetic moment of A μ_B, in agreement with our first-principles calculations. We thus find the ferromagnetism of (Fe, Ga)As to be independent of the number of holes in the DMS.

In order to understand the increase of the critical temperature, T_c, with the increase of the Mn impurity concentration [6], consider the following: the itinerant magnetic moment per host atom increases with Mn concentration, whereas the total magnetic moment per impurity atom is independent of the Mn concentration. Because in our model just the itinerant magnetic moment is responsible for the long-range order, we assume T_c to be proportional to the itinerant magnetic moment. Accordingly, T_c increases with the Mn concentration.

Recent theoretical calculations on (Ga, Mn)As report the As nearest-neighbour (nn) local magnetic moment to be antiparallel to Mn [18–21]. But this does not contradict our model, as we will illustrate in the following.

First, notice that the spin-down channel of the As DBs is more localized than the spin-up channel, for the following reason: the 0.5 additional electrons in the spin-up channel shift the spin-up DB states deeper into the valence band, and hence increase its resonance with the valence band, and in effect the spin-up DB states become more delocalized.

Second, it thus follows that on the As nn sites, the local As moment might be determined by the spin-down channel and accordingly the local As moment may be antiparallel to the impurity moment. The sign of the local As moment depends thus on the chosen local sphere radius. The smaller the chosen sphere radius, the more negative (and also in our calculations) the local As moment becomes. However, most important, these recent calculations confirm the existence of an integer total magnetic moment and a non-integer local moment at the impurity site.

Experimentally, often a magnetic moment of 5.0 μ_B is measured for (Ga, Mn)As. We did a calculation where we add one electron to the unit cell which becomes charge compensated by a jellium background. In this way we simulate the electronic effect of additional dopants in the unit cell, whose defect level(s) determine the Fermi level to lie above the pure (Ga, Mn)As Fermi energy. We find a total moment of 5.0 μ_B and a local moment of 4.0 μ_B. Within our model this is understandable in the following way: on adding one electron, the vacancy has, instead of three, only two holes, i.e. one hole per spin. The energetically most stable situation is with three fully occupied orbitals and one empty orbital. Out of the five spin-up d electrons now only one electron is transferred to the As DBs. This electron will maintain the spin, because the system would lose energy if both (spin-up and spin-down) empty orbitals became filled by half an electron. Moreover, this transferred spin-up electron is delocalized, i.e. the itinerant moment is 1.0 μ_B. Therefore, the Curie temperature of the negatively charged Mn impurity should be higher than that of the neutral Mn impurity.

In summary, the present model explains the ferromagnetic long-range order as being caused by itinerant spin-uncompensated t_2 orbitals. The simultaneous occurrence of an itinerant and local magnetic moment is explained. Our model quite naturally explains the half-metallicity of (Ga, Mn)As. Moreover, because the itinerant moment per host atom increases with the impurity concentration, our model explains the dependence of T_c on the impurity concentration.

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