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Electronic structure and magnetic moment formation in Mn–Ga–As alloys

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Abstract

We present calculations of the electronic and magnetic structure of the cubic phases of Mn–Ga–As. We find that for high coordination numbers, as for a bcc and fcc environment, the Ga/As atoms form broad metallic-like sp bands which interact with Mn. For most of these systems antiferromagnetic structures are the most stable configurations. For AsMn in the ZnS structure we find a half metallicity both in the ferromagnetic and the [001] anti ferromagnetic modification. Calculations of Mn–GaAs supercells allow us to formulate a possible mechanism to enhance the magnetic ordering temperature. Since T_c is found to depend strongly on the number of excess electrons in the system, alloying with constituents with fewer electrons than As could help to stabilize the FM state and thus might increase the magnetic ordering temperature.

1. Introduction

The discovery of ferromagnetic order in diluted magnetic semiconductors made of heavily Mn-doped InAs [1] and GaAs [2–4] paved the way for many semiconductor spin devices [5]. In particular the ferromagnetism of $Ga_{1-x}Mn_xAs$ adds the spin degree of freedom to the GaAs/(Al, Ga)As system which has been argued to have tremendous scientific and technological importance [3].

Substitution of Mn for Ga in GaAs has been shown to result in a particularly promising material and the observation of ferromagnetism at temperatures up to 100 K [4] has spurred intense experimental [3, 4, 6] and theoretical [7–11] activity. Typically, these materials are produced by thin film growth since Mn has limited solubility in bulk GaAs. The long spin lifetime [12] and the spin coherence [13] of GaAs have already been demonstrated. Recently, the feasibility of spin injection into GaAs using $Ga_{1-x}Mn_xAs$ contacts was proved [14]

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to overcome the intrinsic difficulty of injecting spins into semiconductors from magnetic metals [15].

Experimental and theoretical work agree so far upon the conclusion that for $(Ga_{1-x}Mn_x)As$ the critical temperature depends on the hole concentration and that the hole concentration correlates to the concentration of Mn atoms that have substituted Ga [6–8]. The latter is expected if Mn is assumed to be divalent in GaAs, bearing in mind that it replaces trivalent Ga. However, the correlation between the Mn and the hole concentration is not one to one [6], suggesting that Mn substitution is accompanied by lattice defects such as As antisites [16].

Calculations employing the disordered local moment formalism confirmed such a behaviour [17] upon introduction of As_{Ga} antisites. Performing frozen magnon calculations for supercells of (Ga, Mn)As [18] and for (Ga, Cr)As and (Ga, Fe)As [19] the influence of the Mn and the hole/electron concentration on the Curie temperature has been studied.

2. Scope and method of calculation

Experimentally, there do not exist too many stable phases between As, Ga, and Mn on the Ga or As rich side of the phase diagram. *Pearson's Handbook* gives only MnAs in the zincblende (ZnS), the wurtzite (NiAs) and the orthorhombic MnP structure. For Ga–Mn one finds a hexagonal disordered modification of the Mg-type structure and further, highly complex, Ga rich phases like Ga_3Mn (Hg_4Pt-structure) and Ga_5Mn (Al_6Mn-structure). Since the main interest of our work is the properties of Mn in an essentially cubic environment of Ga and As we restricted our investigation to these partly hypothetical cubic phases, which, however, should provide the systematics for how the formation of a semiconducting gap of a half-metallic ferromagnetic phase depends on the number and type of atomic coordination. To this end we have performed calculations of the electronic and magnetic structures of the hypothetical alloys of Mn–Ga and Mn–As in a bcc and fcc environment. We have thus studied the bcc phases CsCl and ABX_2 (Heusler alloy) and the fcc phases CuAu and Cu_3Au. For Mn–As we also studied the realistic ZnS structure. Finally, we performed calculations for for a Ga_8As_8 supercell (ZnS structure), where one Ga has been replaced by Mn in order to model the Mn doped Ga–As semiconductor for a nominal composition of $MnGa_7As_8$. Within the supercell approach the problem of antisites (i.e. As atoms on Ga positions) will also be investigated. To simulate small concentrations of antisite atoms within the supercell we use the virtual crystal approximation, which allows us to study the stability of the magnetic order as a function of the excess electron/hole concentration. All calculations were carried out employing the augmented spherical wave (ASW) method as devised by Williams *et al* [21], which includes the possibility of calculating non-collinear magnetic order [22]. For all calculations a minimum number of 514 **k**-points in the irreducible wedge of the Brillouin zone was used. With this choice, the self-consistency cycle was carried out until a charge self-consistency related to an interband charge transfer smaller than 10^{-6} was ensured. Within these assumptions a stability of the total energy better than 0.1 mRyd was achieved. Effects of exchange and correlation are treated within the density functional theory (DFT) [23, 24] using the LSDA (local spin density approximation) within the parametrization given by von Barth and Hedin [25].

3. Results

3.1. Body centred structures

The most simple representation of a binary alloy in a bcc structure is the CsCl phase. In this modification each Mn atom is coordinated by eight Ga/As neighbours and vice versa. It is

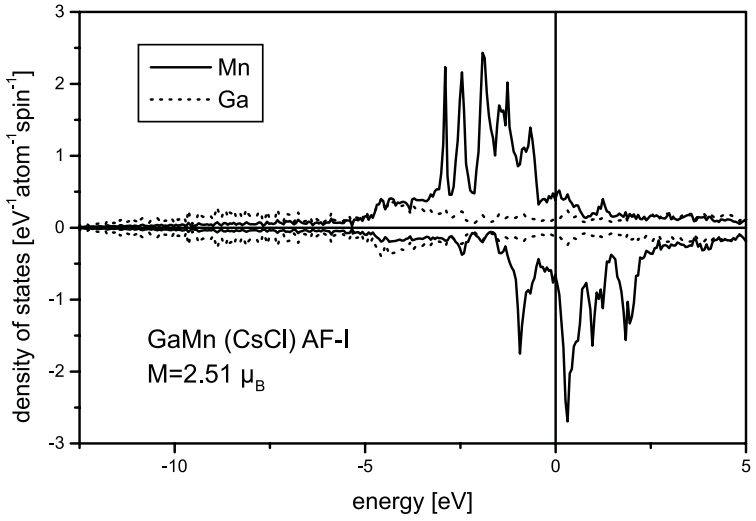

Figure 1. Density of states of AF-I GaMn.

known that for the CsCl structure the second neighbour shell also has a non-vanishing influence which leads to a large crystal field splitting of the transition metal d states as in FeAl [26, 27].

In the CsCl structure, GaMn (AsMn) has an equilibrium lattice constant of 5.542 (5.715) bohr, respectively. In GaMn the Mn magnetic moment is 1.88 μ_B. Increasing the lattice constant one observes an almost discontinuous increase of the moment to a saturation value of about 3.5 μ_B, a behaviour which is found for both GaMn and AsMn and which is also known from FeAl [26]. In terms of symmetry decompositions this means that the Mn 3d band is split into e_g and t_{2g} orbitals where the e_g orbitals mediate the interaction between neighbouring Mn atoms. These states become strongly split and form the lower (bonding) and upper (antibonding) peaks of the Mn 3d band. The peaks in the centre of the Mn 3d band have mainly t_{2g} symmetry. In the CsCl structure these t_{2g} states would normally describe the interaction with the eight nearest neighbours. In the case of Ga and As the corresponding sp states are, however, too low in energy to allow for a sizeable overlap. As a result the t_{2g} states remain fairly localized and the bonding between the Mn and the Ga sublattice is rather weak.

Allowing non-collinear spin alignment for both GaMn and AsMn gives a ground state with magnetic order according to the AF-I structure (figure 1). This splitting destroys the low spin state, which was found for the FM phase, so that the magnetic moment in the AF-I modification becomes 2.51 μ_B.

Increasing the Ga/As content and keeping the bcc environment leads to an alloy of the nominal form ABX_2, the Heusler-type structure. Although this structure type contains three different constituents it allows us to study a Ga_3Mn compound, namely $Ga^{I}Ga^{II}_2Mn$, where Ga^{I} and Ga^{II} occupy different crystallographic sites. Ga^{I} has eight Ga neighbours; Ga^{II} has four Ga and four Mn neighbours; Mn has eight Ga neighbours. Since the interaction between Ga and Mn is weak Ga^{II} has effectively only four Ga neighbours, a situation which should be favourable for the stability of this structure because the sp elements prefer low coordination numbers following the $8 - N$ rule. Mn forms a rather localized d band with a saturated ferromagnetic moment of about 3.7 μ_B. Varying the magnetic order along the [111] and the [001] direction shows that the ground state is again antiferromagnetic with a moment of 3.66 μ_B as expected in the metallic state.

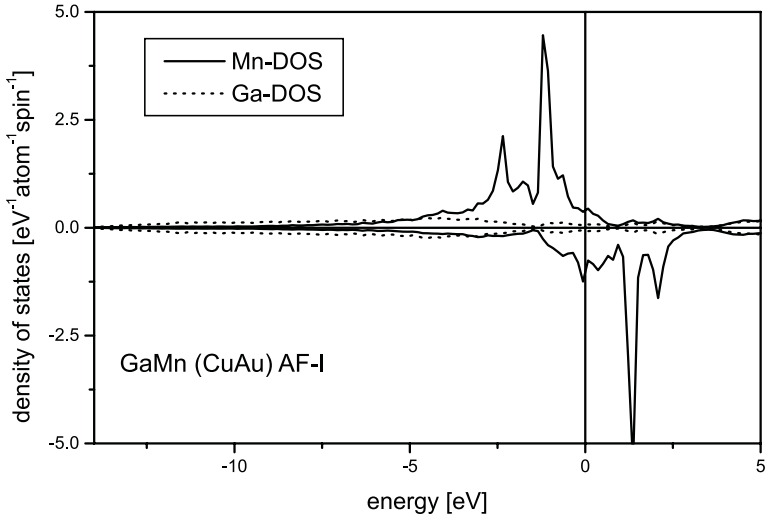

Figure 2. Density of states of GaMn (CuAu structure) for [001] magnetic order.

3.2. Face centred structures

The most simple fcc alloy of nominal composition GaMn is the CuAu structure. In this structure Mn and Ga/As atoms occupy adjacent planes which are stacked along the [001] direction so that actually a layered crystal structure is realized. This also has an effect on the 'chemical bonding' since each atom has four neighbours of its own kind and eight of the other. One would thus expect that, given that the interaction between Mn and Ga/As is relatively weak, the $8-N$ rule would become fulfilled locally. However, since this fourfold coordination is planar, an sp^3-hybridization cannot be expected. The ground state of GaMn in the CuAu structure turns out to be again antiferromagnetic along the [001] direction. The coupling between the Mn planes is mediated by the Ga/As planes and thus relatively weak. This results in a characteristically structured DOS where the in-plane Mn d orbitals overlap and form two bonding/antibonding broad peaks at the lower/upper band edge, whereas the out-of-plane orbitals remain as a non-bonding localized peak in the centre of the d band (figure 2), a scenario which somewhat resembles the CsCl case. The equilibrium lattice constant is 6.572 bohr and the equilibrium moment in the AFI state is again 3.6 μ_B as in the other cases where Mn is in a metallic state.

Reducing the concentration of Mn and retaining the fcc environment leads to the Cu_3Au structure. In this structure Ga/As occupy the face centres and Mn the corners in a fcc cell, so that Mn has 12 Ga/As neighbours and is thus in a rather isolated position. At an equilibrium lattice constant of 6.862 bohr Ga_3Mn is found to be ferromagnetic with a moment of 3.6 μ_B. A variation of the spin spiral q-vector shows a metastable minimum for [111] antiferromagnetic order, which becomes the ground state at lower volume.

3.3. ZnS structure

Although the ground state of MnAs is the hexagonal NiAs-type structure, a study of the ZnS structure is justified by the fact that for the diluted semiconductors $Ga_{1-x}Mn_xAs$ Mn finds itself in a local ZnS-type environment when substituted for Ga. Due to the tetrahedral coordination the As sp band separates into a 4s state (at about -11 eV) and p states which interact with the Mn d orbitals. The different symmetry of the As 4p and the Mn 3d states makes the interaction

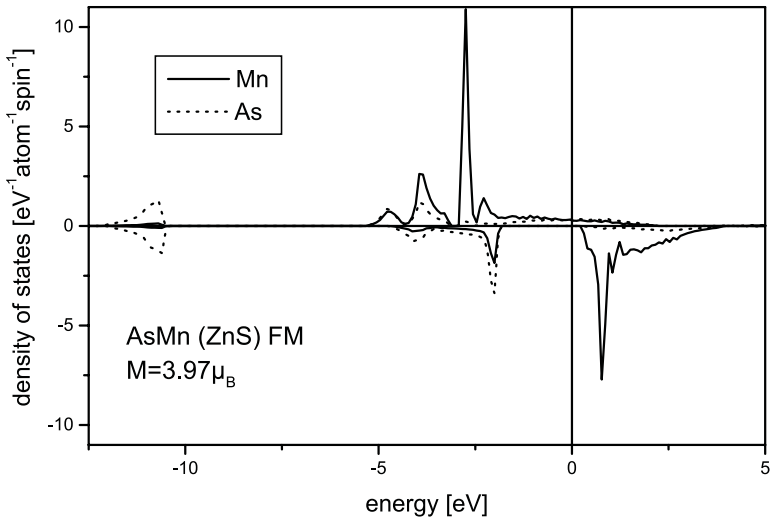

Figure 3. Density of states of AsMn (ZnS structure) in the ground state (half metallic ferromagnet).

weak so that the Mn 3d states become very narrow and look almost 'atomic-like'. The As has three p electrons so that another three electrons have to be provided by Mn to fill the As 4p state with six electrons. Assuming an atomic picture, Mn therefore supplies two 4s electrons and one 3d electron to fill this covalent state. Because Mn is now left with four 3d electrons, these have to fill the spin up band and consequently the magnetic moment becomes very large ($\sim 4\ \mu_B$). The interaction with the much less polarizable As 4p states shifts the bonding Mn 3d states to an energy of about -2.5 eV (for the spin down band) so that in the spin down band a wide gap opens. This causes AsMn to form a so called 'half metallic ferromagnet'. The density of states for the FM ground state at an equilibrium lattice constant of 10.685 bohr is shown in figure 3. This half metallic state makes AsMn technologically highly important since it would allow us to inject only spin-up electrons into a MnGaAs bulk. A stability study of AsMn for both the ZnS and the NiAs modification has been performed in [20]. If one allows for antiferromagnetic order one finds that the [111] AF structure is almost degenerate in energy and is also half metallic with the same magnetic moment.

3.4. Mn–Ga–As supercell calulations

In order to simulate Mn diluted in a Ga–As host we performed calculations for a Ga_8As_8 supercell. Experimentally, it is claimed that in the dilute limit Mn occupies Ga positions so that the effective composition of our supercell reads $MnGa_7As_8$. Adding small amounts of Mn to the GaAs system, for low concentrations the usual dilute alloy mechanism can be observed. The electronic structure is of course dominated by the strong covalent GaAs orbitals, so that any impurity atom has to place its states right at the Fermi energy. Normally this leads to a small, undispersed impurity peak (localized limit). In the present case, the situation is slightly different, because Mn occupies a Ga site and interacts with its four As neighbours in a way similar to MnAs (ZnS) described above. The density of states for the ferromagnetic ground state is shown in figure 4.

Since the magnetic coupling is mediated by the GaAs holes the As concentration (As antisites) must thus have an influence on the coupling constant. In lowest order that just

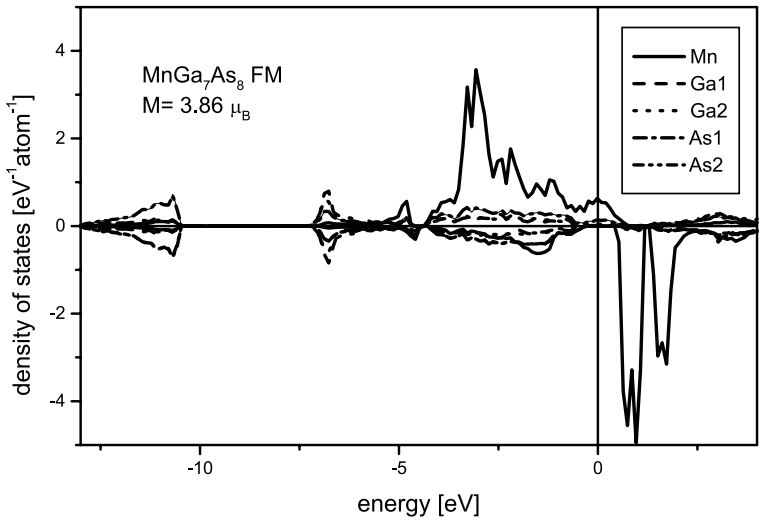

Figure 4. DOS of $MnGa_7As_8$.

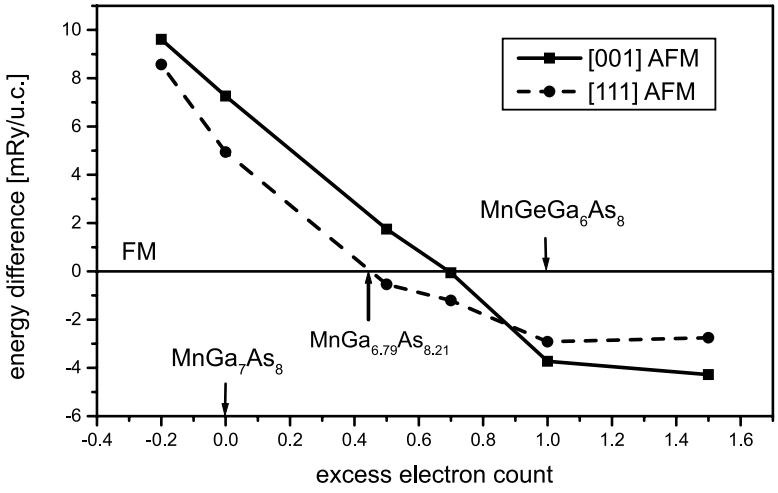

Figure 5. Energy difference between the ferromagnetic (FM) state and [001] and [111] spin ordering. Energies are plotted with respect to the FM energy (horizontal line for energy difference zero). The lowest curve is always the most stable one.

means that there are additional sp electrons coming from As antisites present in the system. We thus tried to simulate these excess As by adopting the 'virtual crystal' (VC) approximation varying the number of electrons in the appropriate way.

Plotting the energy difference between the FM modification and the respective [001] and [111] spin ordering as a function of the number of excess electrons shows that for a nominal composition of $MnGa_{6.79}As_{8.21}$ the FM state becomes unstable with respect to [001] magnetic order (figure 5).

These results allow us to suggest a possible solution to the problem that the ordering temperature in these diluted semiconductors is until now well below ambient temperature. Since the FM order is destabilized by adding electrons and stabilized by removing electrons

(see figure 5) adding excess Ga upon producing the host material could lead to an increase of T_c. Also adding materials like Zn could help to reduce the electron count and could increase the FM ordering temperature. A full account of our work will be published elsewhere [28].

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