Quantum confinement: A route to enhance the Curie temperature of Mn doped GaAs

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The electronic structure of Mn doped GaAs and GaN have been examined within a multiband Hubbard model. By virtue of the positioning of the Mn d states, Mn doped GaAs is found to belong to the p-d metal regime of the Zaanen-Sawatzky-Allen phase diagram and its variants while Mn doping in GaN belongs to the covalent insulator regime. Their location in the phase diagram also determines how they would behave under quantum confinement which would increase the charge transfer energy. The ferromagnetic stability of Mn doped GaAs, we find, increases with confinement therefore providing a route to higher ferromagnetic transition temperatures.

While early research on dilute magnetic semiconductors has focused on II-VI semiconductors, the possibility of using low temperature molecular beam epitaxy for the growth shifted the focus onto III-V semiconductors. Additionally the growth technique allowed the introduction of transition metal atoms far beyond their equilibrium solubility. The quest for higher concentrations of the transition metal in the semiconductor was driven by considerations of increasing the magnetic ordering temperature. However initially various material issues plagued the discovery of new dilute magnetic semiconductors and one was never sure if the magnetism was intrinsic or due to impurity phases. With recent developments in both the growth as well as the characterization of dilute magnetic semiconductors, puzzling observations are emerging which don’t seem to be explainable within the current models used to explain magnetism. Considering the well studied example of GaAs doped with Mn, which is believed to represent a system where the magnetism is intrinsic, the highest Curie temperature has been found to be around 185 K. However, recent photoemission experiments found spin polarized bands even at room temperature and this can’t be reconciled with the existing models for ferromagnetism.

Further the same transition metal atom doped in different semiconductors has led to varying behavior. This was initially explained within the kinetic exchange model in which each transition metal atom was approximated by a spin. This spin interacted with the valence band of the host semiconductor, resulting in a spin polarization of the carriers which mediated the magnetism. Later models questioned this hypothesis and put forth the picture of an impurity band emerging from the interaction of the transition metal with the host semiconductor. However this description has remained at a qualitative level. The picture of the impurity band emerging in GaAs doped with Mn has been supported by recent experiments. There have also been improved approaches to examine the electronic structure, however, there is still no consensus on the mechanism of magnetism.

Bulk transition metal compounds have been studied for a long time and their electronic structure is well established within the framework of the Zaanen-Sawatzky-Allen (ZSA) phase diagram. A similar framework should be possible for dilute magnetic semiconductors which we examine in the present work. We consider a multiband Hubbard model to describe the electronic structure of the dilute magnetic semiconductor with Coulomb interactions included on the transition metal site. Parameters appropriate for Mn doped GaAs place it in the regime of a p-d metal of the ZSA phase diagram, thereby explaining why correlation effects don’t drive it insulating. Quantum confinement effects can be used to tune the charge transfer energy, driving a change in the character of the hole state. We show that this also serves as a parameter to change the Curie temperature, with the largest ferromagnetic stability being in the vicinity of Δ_{eff} equal to zero. Δ_{eff} is the charge transfer energy defined between the Mn d states and the dangling bond states with t_{2} symmetry. Confinement arising from the presence of the surface could lead to the same effect of enhancing the Curie temperature, therefore explaining the experimental observation of spin polarized bands even at room temperature. Mn doped GaN is found to be a covalent insulator within the framework of our calculations, thereby explaining the different behavior found for Mn doping in GaAs and GaN.

In order to discuss various aspects of the electronic structure of Mn doped GaAs, a multiband Hubbard model is set up to solve the electronic structure. In this model, d states are included on the Mn atom, s,p states are included on the Ga atoms while s,p,d states are included on the As atoms. Hopping is allowed between nearest neighbor Mn and As atoms, between Ga and As atoms as well as between nearest neighbor Ga-Ga and As-As atoms. The onsite energies as well as the hopping interaction strengths are determined by fitting the ab-initio band structure of nonmagnetic 25% Mn doped GaAs calculated within VASP to a tight-binding model. Onsite Coulomb interactions between the d orbitals on Mn are parametrised in terms of the Slater-Condon integrals F₀, F² and F⁴. While F² and F⁴ are fixed at 80% of their atomic Hartree-Fock values, F₀ is fixed so that the multiplet averaged U is at a pre-determined value. In the rest of the discussion, we use only the multiplet averaged U. A similar tight binding fitting of the ab-initio band structure for nonmagnetic 25% Mn doped...
GaN is carried out to determine the one electron part of
the multiband Hubbard Hamiltonian for Mn doped GaN
which is then solved. A mean field decoupling scheme has
been used for the four fermion terms in the Hamiltonian
which is solved self-consistently for the order parameters
as discussed earlier21,28 over a 4x4x4 k-points grid for the
64 atoms supercell. In order to explore magnetism, a spin
spiral implementation is considered which uses the gen-
eralised Bloch’s theorem so that the same unit cell could be
used for different magnetic configurations characterised
by the wave vector \( q \).

Early work on transition metal compounds established
the important role that correlations played in driving the
system insulating.\(^2\) As the nature of the ground state
was largely determined by electron-electron interactions
at the transition metal site, it was a surprise when it
was found that on changing the anion in a set of late
3d transition metal compounds, one had large changes in
the bandgaps, with even metallic members being found.\(^3\)
This established that in addition to the onsite Coulomb
interactions (\( U \)), there was another scale in the problem,
which was the cost of charge transfer (\( \Delta \)) between the
anion \( p \) states and the transition metal \( d \) states. This
was brought out by Zaanen, Sawatzky and Allen\(^3\) in
their seminal phase diagram which now forms the basis
for classifying the electronic structure of transition metal
compounds. We now consider examples of two well-
studied semiconductors - GaAs:Mn and GaN:Mn and ex-
amine in which regime they lie in the ZSA phase diagram.

The band dispersions for nonmagnetic 25% Mn doped
GaAs are given in Fig. 1. The ab-initio band dispersions
are given by the dashed blue lines, while the tight-
binding fit are given by the solid red lines. The fitting
procedure involves an optimization of the best fit band
structure along various symmetry directions by a least
square error minimization process.\(^32\). The bare charge
transfer energy between the Mn \( d \) states and the As \( p \)
states estimated from the fitting is found to be 0.53 eV.
Other parameters extracted from the fitting are given in
the Supplementary Information. We then use these pa-
rameters as the tight binding part of a multiband Hub-
bard Hamiltonian and calculate the electronic structure
of Mn doped GaAs at a doping percentage of 3.125% which
is within the range of concentrations probed in
experiments. The calculated partial density of states is
shown in Fig. 2 where the zero of the energy scale is the
Fermi energy. One finds that the up spin states with
dominantly Mn character lie deep inside the valence band
with some weight at the Fermi energy also. The As \( p \)
states which are the nearest neighbors of the Mn atom are found
to contribute primarily to the state at the Fermi level
while those atoms which are far away have a weak con-
tribution. The spin polarization of the states localized
on the nearest neighbors of the Mn atom is large while it
is weaker for the states associated with the farther away
As atoms. This is consistent with the impurity model
description\(^13,15\) introduced by Mahadevan and Zunger
in which the electronic structure of Mn doped GaAs can
be visualised as arising from the interaction of the \( d \) lev-
els on Mn with the states present prior to the introduc-
tion of the Mn atom at a Ga site (i.e the dangling bond
states associated with a Ga-vacancy). The interaction
is primarily between the levels with \( t_2g \) symmetry on Mn
and the levels with the same symmetry on the dangling
bonds. These dangling bond states are dominantly lo-
ralized on the As atoms which are the nearest neighbors
of the Mn atom. Consequently one finds that the states
at the Fermi energy which are the antibonding states of
these interactions are localized on these atoms. A \( U \) of
3 eV is used on Mn, though we have also increased the
value from 3 eV to 4 eV to examine its effect on the elec-
tronic structure. The calculated Mn \( d \) partial density of
states for \( U=4 \) eV is shown in the inset of Fig. 2(a) and
the system is still metallic. Hence considering reason-
able values of \( U \) on Mn does not drive Mn doped GaAs
insulating.

The definition of \( \Delta \) should be with respect to the en-
ergy of the dangling bond states with \( t_2 \) symmetry and is
referred to as \( \Delta_{eff} \) in the subsequent discussion. As this
is difficult to determine precisely, we vary \( \Delta \) and examine
the character of the hole state. When the two interac-
ting levels are degenerate (\( \Delta_{eff}=0 \)) one expects that
the hole has equal weight on Mn as well as the interacting
As \( p \) atoms. In Fig. 3 we have plotted the variation of
the Mn \( d \) partial density of states as a function of \( \Delta \). As
\( \Delta \) is increased, one finds an increase in the Mn \( d \) contri-
bution to the hole state. Tracking the Mn \( d \) char-
acter of this state (\( nd \)) (inset of Fig. 3), one finds that
between \( \Delta \) of 2.6 and 2.7 eV one has a change over with
the hole becoming predominantly Mn \( d \) like. This places
\( \Delta_{eff}=0 \) near a \( \Delta \) of 2.7 eV in contrast to the value of
0.53 eV found from the fitting. Hence Mn doped GaAs
is in the negative \( \Delta \) regime of the ZSA phase diagram.
As it is metallic, we identify it as a \( p-d \) metal. While
the charge transfer energy is usually a fixed quantity for
a system, here, \( \Delta_{eff} \) is referenced with respect to the
dangling bond states. The dangling bond states follow
the valence band maximum of the host semiconductor.
The latter can be tuned in a semiconductor by quantum
confinement.\(^32\). The state corresponding to the bulk case
(\( \Delta=0.53 \) eV) may be described by the configuration \( d^5L \)
where locally Mn is found to be \( d^0 \), and so is Mn\(^{2+} \)-like.
In the regime where \( \Delta_{eff} \geq 0 \), Mn may be represen-
ted by the configuration \( d^4 \) and is therefore in the valence
state Mn\(^{3+} \). Hence one has a valence transition with de-
crease in size of Mn doped GaAs. The valence transition
has been discussed earlier in the literature by Sapra \( et\ al.\)\(^2\)
using a tight binding model. What we show is that a metal-insulator transition accompanies this valence transi-
tion.

The immediate question which follows is how does the
stability of the ferromagnetic state change with quan-
tum confinement. We examine this by considering an
isolated Mn impurity in the 64 atom unit cell (i.e, a dop-
ing percentage of 3.125 %) and comparing the energies of
the ferromagnetic as well as the totally antiferromagnetic
configuration given by \( q = 0.5 \) 0.5 0.5. The Mn atoms are separated by 11.3 Å. The interaction between them is weak and so for small \( \Delta \) values, one finds that the different magnetic solutions have comparable energies (Table I). For larger values we have the system favoring an antiferromagnetic ground state. This is in contrast with experiments which find ferromagnetism\(^{10}\). However Mn atoms show a tendency to cluster\(^{33,34}\) and the high magnetic ordering temperatures observed have been associated with the presence of these clusters\(^{36-38}\). We therefore went on to examine the variations in the ferromagnetic stability by considering pairs of Mn atoms occupying FCC nearest neighbor positions as well as fourth neighbor positions where the separations are 3.995 Å and 7.99 Å respectively. The difference in energy between the ferromagnetic as well as antiferromagnetic configuration are given in Table II. As \( \Delta \) is increased, one finds that the ferromagnetic stability increases till \( \Delta \) of 2.3 eV for pairs of Mn atoms at first neighbor positions and then it begins to decrease. This can be traced to the fact that for a \( \Delta \) of 2.7 eV we had the Mn \( t_{2g} \) and danging bond states almost degenerate for 1 Mn. The presence of the second Mn at the nearest neighbor position changes some details of the \( \Delta \) at which the two interacting levels are degenerate. The result is that the ferromagnetism is stabilized by superexchange between the Mn atoms involving the intervening As atom, explaining the enhanced ferromagnetic stability at \( \Delta_{\text{eff}} = 0 \). The calculated ferromagnetic stability at fourth neighbor also shows a similar trend, being largest at \( \Delta = 2.6 \) eV.

Mn doping in bulk GaAs has a ferromagnetic stability of 73 meV for nearest neighbor atoms. The increase till \( \Delta_{\text{eff}} \sim 0 \) is approached reflects the fact that with quantum confinement one can achieve transition temperatures higher than what is encountered in bulk GaAs. This may be able to explain the experimental observation of spin polarized bands at room temperature found in recent spin resolved photoemission experiments\(^2\).

A similar analysis was carried out for Mn doped GaN to determine the tight binding parameters as well as on-site energies. The extracted parameters\(^{25}\) gave us a \( \Delta \) of 1.27 eV for Mn doping in bulk GaN and the hole has 0.516 Mn \( d \) character \( (n_d) \) (Fig. 4). A small decrease of \( \Delta \) to 1.0 eV reduces the \( n_d \) to 0.487. This places \( \Delta_{\text{eff}} = 0 \) at \( \Delta \sim 1.15 \) eV. Our analysis ignored the width of the Mn \( d \) states and the N \( p \) states and defined \( \Delta_{\text{eff}} \) with respect to the centroid of the Mn \( d \) band. Taking this into account we can place Mn doped GaN in the regime where \( \Delta_{\text{eff}} \) is negative. It is then surprising that we have an insulating ground state. This phase has been called the covalent insulator and has been shown to exist in the ZSA phase diagram by Sarma and co-workers\(^{21,22}\). Strong covalency between the transition metal and the anion are responsible for the insulating state. It is evident from its location in the phase diagram that any increase in \( \Delta \) arising from quantum confinement effects would not be useful in tuning the magnetic transition temperature in Mn doped GaN.

The electronic structure of Mn doped GaAs and GaN have been examined within a multiband Hubbard model. The former may be placed in the \( p-d \) metal regime of the ZSA phase diagram or its variants while the latter belongs to the covalent insulating regime. Quantum confinement allows us to tune the effective charge transfer energy and its effect on the ferromagnetic ordering temperature depends on where they lie within the ZSA phase diagram. This then provides us with a route to higher ordering temperatures in the dilute magnetic semiconductors.

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### TABLE I. Energy difference between $q=(0.5 0.5 0.5)$ and $q=(0 0 0)$ for Mn atoms separated by 11.3 Å for 1 Mn doped in 64 atoms supercell of GaAs

| $\Delta$ (in eV) | $E[q=(0.5 0.5 0.5)] - E[q=(0 0 0)]$ (in eV) |
|------------------|---------------------------------------------|
| 0.53             | -0.002                                       |
| 1.00             | -0.005                                       |
| 1.50             | -0.007                                       |
| 2.00             | -0.009                                       |
| 2.50             | -0.011                                       |
| 2.60             | -0.011                                       |
| 2.80             | -0.044                                       |
| 2.90             | -0.049                                       |
| 3.00             | -0.070                                       |

### TABLE II. Energy difference between the ferromagnetic (FM) and the antiferromagnetic (AFM) configurations for 2 Mn atoms occupying FCC 1st and 4th neighbor positions in a 64 atoms supercell of GaAs

| $\Delta$ (in eV) | $E[\text{AFM-FM}]$ (in eV) | $E[\text{FM-AFM}]$ (in eV) |
|------------------|----------------------------|----------------------------|
| 1.5              | 0.120                       | 0.048                       |
| 1.7              | 0.133                       | 0.056                       |
| 1.8              | 0.140                       | 0.057                       |
| 1.9              | 0.147                       | 0.059                       |
| 2.1              | 0.161                       | 0.067                       |
| 2.2              | 0.167                       | 0.069                       |
| 2.3              | 0.174                       | 0.072                       |
| 2.4              | 0.146                       | 0.080                       |
| 2.5              | 0.116                       | 0.083                       |
| 2.6              | 0.065                       | 0.099                       |
| 2.9              | 0.011                       | 0.074                       |
FIG. 1. Comparison of the ab-initio (dashed blue lines) and best fitted tight-binding (solid red lines) band dispersions for nonmagnetic 25% Mn doped GaAs
FIG. 2. Calculated partial density of states for (a) up spin Mn $d$, up and down spin of (b) As $p$ (nearest neighbor of Mn) and (c) As $p$ (far away from Mn) for a Mn doping concentration of 3.125% in GaAs at $\Delta = 0.53$ eV and $U=3.0$ eV in a multiband Hubbard model. The zero of energy represents the Fermi energy. Inset shows Mn $d$ density of states for up spin at $U=4.0$ eV.
FIG. 3. Up spin Mn d partial density of states for (a) $\Delta = 0.53$ eV, (b) $\Delta = 1.5$ eV and (c) $\Delta = 2.7$ eV calculated for a Mn concentration of 3.125% and a U of 3.0 eV within a multiband Hubbard model. The zero of energy represents the Fermi energy. Inset shows the Mn d component of the hole character as $\Delta$ is varied.
FIG. 4. Up and down spin Mn d partial density of states for (a) $\Delta = 0.53$ eV, (b) $\Delta = 0.75$ eV, (c) $\Delta = 1.0$ eV and (d) $\Delta = 1.27$ eV for a doping concentration of 3.125 % of Mn in GaN calculated within a multiband Hubbard model for $U=3.0$ eV. The zero of energy is the Fermi energy. The Mn d character ($n_d$) of the hole state has been indicated.