Influence of Quantum Confinement on the Electronic and Magnetic Properties of (Ga,Mn)As Diluted Magnetic Semiconductor

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ABSTRACT

We investigate the effect of quantum confinement on the electronic structure of diluted magnetic semiconductor $Ga_{1-x}Mn_xAs$ using a combination of tight-binding and density functional methods. We observe half metallic behavior in the clusters as well as a strong majority-spin Mn d−As p hybridization down to sizes as small as 20 Å in diameter. Below this size, the doped holes are significantly self-trapped by the Mn sites, signaling both valence and electronic transitions. Our results imply that magnetically doped III−V nanoparticles will provide a medium for manipulating the electronic structure of dilute magnetic semiconductors while conserving the magnetic properties and even enhancing them in certain size regimes.

Over the past few years, there has been an explosively rapid increase of activity in two frontier areas of semiconductor research: diluted magnetic semiconductors (DMSs) and semiconductor quantum dots. The renewed interest in diluted magnetic semiconductors[1,2] was motivated by the discovery of ferromagnetism in $In_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$.[3,4] Such ferromagnetic semiconductors are enabling materials for the emerging technology of "spintronics"[5] where, in addition to the charge degree of freedom of conventional electronics, the spin degree of freedom is also exploited. One immediate application is that storage (traditionally achieved in magnetic metals) and processing (traditionally semiconductor-based) can be performed simultaneously on the same device component.[1] In addition, DMSs have been used to inject spin into normal semiconductors,[6,7] where enormous spin lifetime and coherence[8] have been demonstrated. These are two key ingredients for the physical realization of solid-state quantum computing based on the spin degree of freedom.[9]

The second frontier area, the study of semiconductor quantum dots, exploits the fact that by reducing the size of a semiconducting material, typically below the Bohr exciton radius, it is possible to tune its electronic and optical

properties.[10] The changes result from the confinement of the electron and hole wave functions by the potential of the finite-sized semiconductor nanoparticle, thereby increasing the energy as the particle size is decreased. This quantum size effect can have spectacular and desirable effects on the material properties and has already been utilized for various device purposes. The most obvious applications are in tailoring the band gap for specific applications, such as the tuning of the absorption or emission energy in electronic, electrooptical, optoelectronic, or purely optical devices.

In this paper we explore the integration of the fields of diluted magnetic semiconductors and semiconductor quantum dots in a theoretical study of nanoparticles made from the DMS material (Ga,Mn)As. Various experimental groups are actively pursuing the synthesis of magnetic semiconducting nanoparticles, and the production of magnetically doped II−VI, including CdS,[11] ZnS,[12] CdSe,[13] and ZnSe[14] has already been achieved. The chemistry of III−V nanocrystal growth makes the synthesis of (Ga,Mn)As nanoparticles more challenging; therefore, a preliminary theoretical investigation is sensible before launching a large synthetic effort. The main question that we answer in this work is whether the conditions that lead to ferromagnetism in bulk (Ga,Mn)As, namely the combination of strong Mn d−As p hybridization in the majority spin band and a half-metallic band structure allowing hole-doping of the majority spin channel, persist

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as the size of the system is reduced. Our results suggest that quantum confinement will not have a detrimental effect on the magnetic properties of (Ga,Mn)As nanoparticles down to very small sizes. As a consequence, it is possible to exploit the quantum confinement effect to tune the electronic properties of (Ga,Mn)As nanocrystals over a very wide size range while retaining the desirable properties or even enhancing them. Additionally, we see drastic changes in the electronic and magnetic properties at very small (<20 Å diameter) sizes, arising from competition between different subparts of the electronic degrees of freedom. In ultrasmall nanoparticles, these changes eventually lead to the destruction of the essential electronic structural features required for ferromagnetism.

There is, in fact, no a priori reason that the magnetic properties of magnetically doped semiconductor nanoparticles should be the same as those of the corresponding bulk system. Bulk (Ga,Mn)As is a half-metallic ferromagnet[15] (HMFM) with 100% spin polarization of the states at the Fermi energy, E_F. Half-metallic ferromagnetism requires a very specific arrangement of the various bands (in this case majority and minority spin Mn 3d with respect to the Ga and As s, p states) such that a gap opens for one spin channel only. However the energy levels of these states shift in nanoparticles due to the quantum size effect, and the extent of the shift depends on both the size of the nanoparticle and the effective masses of the electrons and holes. In particular, the transition metal 3d bands in a doped semiconductor are rather flat compared to the s and p valence and conduction bands of the host. This results in a rapid shift in the s and p derived bands and a relative insensitivity of the d band energy position as the nanoparticle size is reduced. Thus the underlying electronic structure of the doped nanoparticle will change rapidly and may become incompatible with the HMFM state. Such a loss of half-metallicity would in turn destabilize the ferromagnetism, limiting the tunability of the electronic properties with size if the magnetic properties need to be retained intact. In the present work we concentrate on understanding such changes in the electronic structure, and their influence on the magnetic interactions, as a function of the size of (Ga,Mn)As nanoparticles. We emphasize, however, that there are additional factors, beyond the changes in the electronic structure discussed here, that can affect the magnetism in nanoparticles. For example ferromagnetism in the strictest sense requires a long range order, persisting over long times. This can be disrupted in very small particles when thermal energy causes the direction of the magnetization to fluctuate rapidly (the super-paramagnetic effect).

We calculate the electronic structure of Mn-doped GaAs nanoparticles as a function of size using a second nearest neighbor, one-particle tight-binding (TB) method.[16] We obtain the TB parameters by fitting to our density functional band structure calculations of the corresponding bulk systems and assume that they are transferable to the nanometer size regime. Such an approach has been shown to correctly predict the band gap variation with size for semiconductors[17] and is far less computationally intensive than more rigorous ab initio approaches. Our numerical DFT implementation uses a

pseudoatomic orbital basis set and pseudopotentials, within the local spin density approximation (LSDA). Details of the method and its optimization can be found in reference 15. We have made no attempt in this paper to correct for the well-known underestimation of the band gap within the LSDA. As a result, the absolute values of our calculated band gaps are all too small, but the shifts with size, which are dominated by occupied valence band states, should be reproduced quite accurately. The first step in the TB parameterization is to fix the Ga and As on-site energies and the Ga−Ga, As−As, and Ga−As hopping integrals by fitting to the GaAs band structure along several directions in k-space. In this fit we use 35 k-points and we consider all the eigenvalues up to the conduction band. Then we repeat the fitting procedure for both the spin bands of MnAs. In this case we do not change the As−As hopping integrals and we allow the As on-site energies to be only rigidly shifted with respect to their values in GaAs. We do not allow spin-splitting of the Mn s and Mn p orbitals, since only the d orbitals are magnetically active. Finally, we fix the remaining Ga−Mn parameters by fitting to the calculated band structure of a monolayer GaAs/MnAs superlattice.

$Ga_{1−x}Mn_xAs$ nanoparticles are generated by starting with a central Ga atom surrounded by four As atoms, then progressively adding successive shells of Ga and As atoms in the bulk GaAs zinc blende structure. Mn atoms are randomly substituted at the Ga sites, keeping the composition close to $x = 0.05$ in every case. We use an additional outermost shell of passivating atoms bonded to the outer layer of (Ga,Mn)As cluster in order to passivate the dangling bonds. In absence of the passivating layer, these dangling bonds give rise to energy states within the band-gap of the corresponding passivated nanocluster without any other substantial influence on the electronic structure in other energy regions. We have investigated particles ranging in size from 9.0 Å diameter to 71.0 Å diameter (containing 9527 atoms). We use exact diagonalization of the TB Hamiltonian for the small clusters (up to 31.6 Å containing 981 atoms) and the Lanczos method for larger clusters.

In Figure 1a, we show our calculated DFT majority and minority spin densities of states (DOSs) of bulk $Ga_{1−x}Mn_xAs$ with $x = 0.0625$, along with the partial Ga s, p, As p, and Mn d DOS. As previously reported,[15] the material is a half metallic ferromagnet, with a gap in the minority spin DOS at E_F, but no gap in the majority channel. The metallic majority spin DOS at E_F is composed largely of As p states, suggesting that hole doping at the top of the valence band by the Mn^{2+} $3d^5$ ions, and subsequent polarization of the mobile charge carriers by interaction with the exchange-split energy levels of Mn d^5 is responsible for the HMFM state.[18] The orbital resolved DOS for the Mn 3d states is qualitatively different for majority and minority spins. The majority channel has extensively mixed states over the −1 to −4 eV energy range due to the strong hybridization between the Mn 3d and the As p states. In contrast, the DOS of the Mn 3d states for the minority spin shows a sharp feature at ∼1.5 eV above E_F with minimal admixture from other states. This difference is due to the fact that in the majority spin the Mn
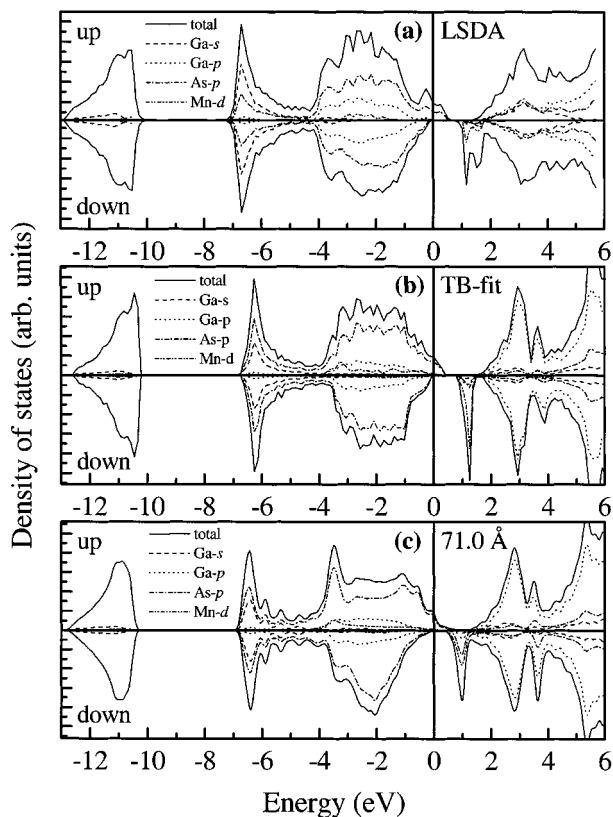
Figure 1. Density of states for $Ga_{1-x}Mn_xAs$ with $x = 0.0625$ calculated with different methods: (a) LSDA calculation for the bulk, (b) tight-binding calculation for the bulk, (c) tight-binding calculation for a 71.0 Å cluster containing 9527 atoms (the cluster DOS has been broadened by a Gaussian with 0.3 eV fwhm).

3d states are in the middle of the valence band of GaAs, thereby mixing extensively with the As p. In contrast, the minority spin Mn 3d states fall in the GaAs gap, thereby remaining relatively unmixed. The DOS for the extended solid obtained from the tight binding Hamiltonian is shown in Figure 1b. All the features of the DOS, including the HMFM behavior, are reproduced extremely well by the TB calculation, confirming the accuracy of our parameterization.

In the limit of large size, the electronic properties of semiconductor nanoparticles must approach asymptotically those of the corresponding bulk semiconductor. The calculated DOS for a 71.0 Å diameter cluster, shown in Figure 1c, is indeed similar to that of the infinite solid. Clearly smaller particles are required to see any strong effect of quantum confinement. Our calculations of the electronic structures of progressively smaller-sized nanoparticles (not shown here) indicate that qualitatively similar electronic properties persist down to a very small size (∼25 Å diameter) although the band gap increases monotonically with decreasing size as expected. In Figure 2a we show the calculated majority and minority spin DOS for a 25.0 Å diameter nanoparticle. We see that even such a small particle is both half-metallic and has strong Mn 3d−As p hybridization, therefore has all the indications for being ferromagnetic. This is remarkable, since it implies that it is possible to exploit the tunability of nanoparticles to tailor-make materials with specific electronic properties, without sacrificing the ferromagnetism. For example, the gap (1.4 eV) in the down-spin
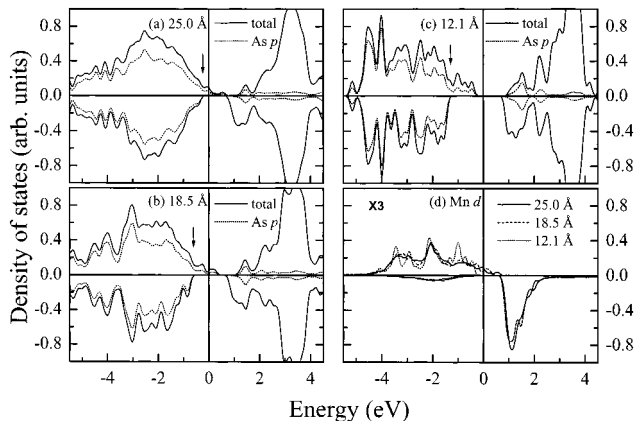

Figure 2. Density of states and partial As p density of states for three (Ga,Mn)As finite clusters: (a) 9 shells and 25.0 Å diameter, (b) 7 shells and 18.5 Å diameter, (c) 5 shells and 12.1 Å diameter, and (d) partial Mn d density of states for these three clusters (the Mn d partial DOS has been multiplied by 3 for clarity). In all the panels, the zero of energy corresponds to the E_F of bulk $Ga_{1-x}Mn_xAs$ with $x = 0.0625$; the individual E_F is marked with an arrow in each panel. DOS have been broadened by a Gaussian with 0.3 eV fwhm.

channel in this cluster is substantially larger than that in the larger 71.0 Å diameter particle (0.55 eV) or in the bulk (0.4 eV). So, for example, such nanoparticles could be used as a source of polarized light over a broad range of wavelengths.

However, the 25.0 Å diameter (Ga,Mn)As nanoparticle is close to the size limit below which the essential properties of the bulk magnetic semiconductor are no longer retained. At smaller sizes, we see remarkably rapid changes in the electronic structures with decreasing size, signaling a complete change of electronic and magnetic properties. In fact, we observe a crossover behavior, akin to a valence as well as a metal−insulator transition, that is driven by the quantum size effect. We illustrate this in Figure 2 where we also plot our calculated DOSs of 18.5 and 12.1 Å diameter nanoparticles. Compared to the 25.0 Å nanoparticle, the DOS of the 18.5 Å particle (Figure 2b) shows a substantial increase of the energy gap in the down-spin channel, as a consequence of the enhanced confinement, and a significant reorganization of the orbital contributions to the DOS near E_F, particularly in the majority spin channel. We find that the states close to E_F develop a significant amount of Mn d character, whereas the larger particles (Figure 1c) and the infinite solid (Figures 1a and 1b) have almost negligible contribution from the Mn d states at E_F. Simultaneously, the Mn d states in the majority channel are reduced in bandwidth compared to the larger clusters. For example, the majority spin Mn d bandwidth in 12.1 Å diameter nanoparticles (shown in Figure 2d) is ∼1 eV narrower than that in the bulk solid. These results are easily understood in terms of quantum confinement effects: the GaAs s and p states, with low effective masses, shift very rapidly compared to the higher effective mass Mn d states. As the GaAs valence and conduction bands shift away from each other, majority spin Mn d states begin to appear at the top of the valence band. There is a decrease of the As p bandwidth upon size reduction which is also primarily responsible for the reduced bandwidth of the Mn d band in the majority channel, through the strong hybridization
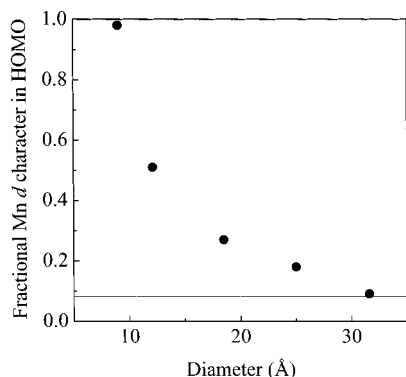
Figure 3. Mn d character of the HOMO as a function of the cluster size.

between the Mn d and the As p orbitals. In contrast, the Mn d minority spin states continue to form a narrow peaked structure a couple of eV above the Fermi energy, even for the smallest nanoparticles.

There are interesting consequences of these movements of the energy levels, via changes in the Mn d character in the highest occupied molecular orbital (HOMO) with the size of the clusters (Figure 3). The percentage of Mn d character at E_F is ~8% in the extended solid as well as in the large clusters, indicated by the horizontal dotted line in Figure 3. The Mn d character begins to increase appreciably below about 32 Å due to the downward shift of the valence band. As the shift of the top of the valence band continues beyond the Mn d majority state, the holes that were originally doped at the top of the valence band are increasingly trapped by the Mn sites, driving a change in Mn valency. This is signaled by the sharp rise in the Mn character in the HOMO (Figure 3) below ~20 Å cluster size with as much as 98% Mn d contribution for the 9.0 Å clusters. This is also clearly shown by the change in the average Mn d occupancy, $\langle n_d \rangle$. Note that this quantity cannot be used to determine directly a formal oxidation state of the Mn sites, due to the presence of substantial covalent admixture of Mn states with the GaAs states. We calculate $\langle n_d \rangle$ of about 5.1 and 4.9 in the 25.0 and 18.5 Å nanoparticles, respectively, corresponding to the formally divalent Mn^{2+} state. However, $\langle n_d \rangle$ changes very rapidly with further decrease in the size to become 4.0 for the smallest sized 9.0 Å cluster. This change of almost unity in $\langle n_d \rangle$ between 25.0 and 9.0 Å clusters indicates a valence transition with the Mn^{2+} ions self-trapping the doped holes, resulting in Mn^{3+} and the removal of the doped holes from the top of the valence band of GaAs.

The initial approach of the Fermi energy toward the Mn d majority state will in fact enhance the effective exchange coupling between the localized Mn d^5 spins and the conduction band[18] and thereby enhance the magnetic interactions between the localized spins at various Mn sites with decreasing cluster size. However, in particles smaller than ~20 Å diameter, the placement of the valence band below the Mn majority spin state will reduce kinetic stabilization via the strong antiferromagnetic exchange splitting of the conduction states,[18] thereby undermining the stability of the magnetic state. Moreover, the valence transition at the small cluster limit will most probably lead to an insulating state due to Coulomb interactions within the Mn d states.

In conclusion, we have studied the effect of quantum size confinement on the electronic properties of (Ga,Mn)As nanoparticles, using an LSDA-derived TB parameterization. We find that the nanoparticles retain the desirable half-metallic properties observed in bulk (Ga,Mn)As down to diameters as small as ~20 Å with a polarized essentially As p hole at the Fermi energy. Smaller clusters show a large contribution of the Mn d state at E_F. These results suggest that the magnetic properties observed in bulk (Ga,Mn)As will persist down to very small sizes. In addition, it should be possible to manipulate effectively the electronic properties (in particular the band gap and also possibly T_c) of diluted magnetic semiconductor nanoparticles by controlling the cluster size.

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