

Low-spin to high-spin transition in Mn doped Si nanocrystals

Bhagawan Sahu¹ and Sanjay K. Banerjee¹, Gustavo Dalpian², and James Chelikowsky³

¹*Microelectronics Research Center, University of Texas, Austin, Texas 78758, USA*

²*Universidade Federal do ABC Santo Andre, SP- Brazil*

³*Center for Computational Materials,
University of Texas, Austin, Texas 78712, USA*

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Abstract

Using a real-space electronic structure method with ordinary pseudopotentials, we show that manganese doped silicon nano-crystals with diameters ranging from 1-2.5 nm possess a low-spin or a high-spin magnetic ground state depending upon whether the manganese atom is located at the center or at the sub-surface position of the nano-crystal. The low spin and high spin states co-exist for both doping positions. We discuss the origin of these meta-stable magnetic states. The quantum confinement effects on energy separation are also discussed.

It is known that an isoelectronic impurity or simultaneous doping of n- and p-type impurity (boron or phosphorous) in silicon nanocrystals (Si-NC) can suppress the radiationless Auger recombination of electrons and holes, thereby increasing their quantum photoluminescence yield¹. However, it is an open question what an intentional magnetic doping in Si-NC would do to its electronic structure and whether such doping is useful for studying spin effects relevant to spin-based information processing, if it is possible to insert just one magnetic atom. Doping Si-NC with single Mn has not been achieved experimentally so far but a recent report of insertion of a single Mn into a CdTe quantum dot layer grown epitaxially by molecular-beam epitaxy on (001) ZnSe substrate², optical probing³ of the interaction of injected charge (by electrostatic gating or by resonant optical excitation) with the localized Mn spin, and the direct observation of sp-d exchange interaction in colloidal Mn and Co doped CdSe quantum dots⁴ has opened up such a possibility. Moreover, there are kinetic and thermodynamic reasons for difficulty in doping small II-VI nanocrystals⁵ obtained by colloidal synthesis which two of us (GD and JRC) call it as "self-purification" process. The arguments are general and hold for IV semiconductor nanocrystals too. In this work, we report simultaneous existence of low-spin (LS) and high-spin (HS) magnetic states in Mn doped Si-NC with diameters ranging from 1 to 2.5 nm. Such metastability has been predicted theoretically recently in a bulk tetrahedrally-bonded group III nitride semiconductor⁶. To our knowledge, this is the first study of meta-stable magnetic states in a Mn doped Si-NC. We use a real-space electronic structure method with an ordinary pseudopotential⁷ to probe these magnetic states. To understand the surface effects on the magnetic properties, the sub-surface doping is also considered. One of us (JRC) studied size-dependent spintronics properties of dilutely doped semiconductor nanocrystals⁸ (a Mn atom is doped at the center of Ge, GaAs and ZnSe nanocrystals) and found that Mn-related states lie deep in nano-crystal (NC) energy gap with the decreasing NC size, and Mn states are not affected by the quantum confinement effect unless doped at the sub-surface position. Such an energetic pinning of Mn *d*-states was recently observed experimentally in a Co-doped ZnSe NC⁹.

The spherical nano-crystals studied in this work were carved out of a bulk silicon supercell and the resulting Si dangling bonds were passivated by hydrogen atoms in order to remove surface states from the Si energy gap. We considered four different sizes of Si-NC with diameters between 1-2.5 nm containing 35 (1.1 nm), 87 (1.5 nm), 147 (1.75 nm) and 293 (2.3

nm) Si atoms. In a colloidal synthesis of nano-crystals, organic cappings are used instead of hydrogen and the organic capping may alter the nano-crystal properties in some way but to keep the nano-crystal separate from the capping and in order to reduce the computational effort and complexity, we used hydrogen atoms instead. We replace the central or a sub-surface Si atom in each NC by a Mn atom which corresponds to concentrations of 2.9%, 1.2%, 0.7% and 0.35% Mn, respectively. One of us (JRC) pioneered real-space based electronic structure algorithms, with ordinary pseudopotentials, in the 1990's for low-dimensional systems and it has since been used extensively in the studies of electronic, magnetic and optical properties of NC as well as nano-wires. This algorithm, called PARSEC, is now a public domain software¹⁰.

The self-consistent electronic structures of Mn doped Si-NC were determined using pseudopotentials constructed with local spin density functional approximation¹¹ within density functional theory¹². The Kohn-Sham equations were solved on a real-space grid using a grid spacing of 0.4 au (1 au = 0.529 Å) and higher-order finite difference method⁷. A separation of at least 10 au between outermost passivating atoms and the spherical boundary was used. We first relaxed the Si-NC without Mn impurity and then placed the Mn atom at the center (henceforth called central doping) and near the surface (henceforth called sub-surface doping) of the NC, and the electronic structures were determined without further relaxation. Full relaxation of the nanocrystals with the force convergence criteria of 0.1 eV/Å was also done in order to check the effect of relaxation on the magnetic states of the Si-NC. The results discussed in this report are for fully relaxed structures. In order to probe the possibility of metastable magnetic states, we fixed the occupation of occupied Mn-related energy levels near the NC energy gap. We indeed find such meta-stable states for each size that differ from the ground states by hundred of meV. In NC, such co-existence of HS and LS states in the Kohn-Sham potential landscape is observed, to our knowledge, for the first time. An electrostatic gating can transfer a finite amount of charge from the substrate and therefore can change the occupations of the Si energy levels. This may switch the energetic ordering of LS and HS states, and vice-versa, and therefore, a Si-NC would act as a magnetic switch with potential use in nanoscale data storage. Controlling the charge states by transferring a single electron on and off the dot has been achieved experimentally by electrostatic gating in Mn-doped CdSe nanocrystals wherein the interaction of the spin of the Mn with the excitonic states of the dot was probed by optical means³.

Replacing a tetrahedrally-coordinated silicon by a Mn atom results in an ionic Mn with $3d^3$ configuration. The five degenerate d -orbitals (d_{xy} , d_{yz} , d_{zy} , $d_{x^2-y^2}$ and d_{z^2}), in the presence of the electric field from the neighboring silicons, splits it into a low-lying e doublet and a high-lying t_2 triplet for both spin-channels. A Mn ion with d^3 configuration can have (1) three electrons occupying low-lying e -orbitals (in the up and down spin channels) resulting in a LS magnetic state or (2) two electrons in e spin-up channel and one electron in high-lying t_2 spin-up channel resulting in a HS state. LS or HS magnetic states are determined by the competition between ligand field energy Δ_t (defined as energy difference between t_2 and e levels) and spin-pairing energy Δ_{sp} (defined as energy required to pair-up electrons in the same orbital). If $\Delta_t > \Delta_{sp}$ then the system gains energy by pairing up the electrons in the same orbital and a LS state is realised. Otherwise, a HS state will become energetically favorable.

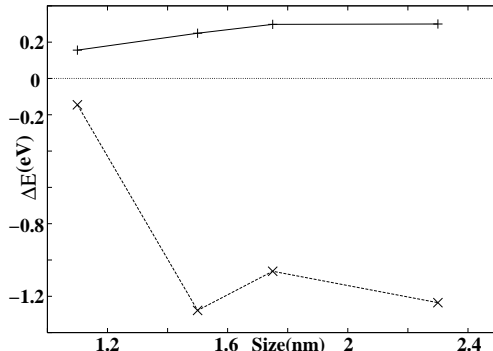


FIG. 1: (Color online) Difference of LS ground state energies from their HS state for two Mn doping positions (upper curve: central doping and lower curve: sub-surface doping) versus NC size.

We note that atomic relaxations around the Mn impurity has a profound effect on the energetic order of the magnetic states. The LS state, which is a ground state in case of central doping, remain LS but the LS state for sub-surface doping changes to a HS state with relaxation. To understand why central doping has LS ground state and sub-surface doping has HS ground state, we compute the difference of Δ_t and Δ_{sp} for each fully relaxed NC and plot them in Figure 1. This difference is positive for LS states and negative for HS states observed for central and sub-surface doping, implying a LS and HS ground state, respectively. In the LS state, two electrons needed to be paired up which cost an energy Δ_{sp} and it costs $-3 \times \frac{3}{5} \Delta_t$ to split five degenerate d -orbitals with occupancy of three electrons in the e orbital. Therefore the LS total stabilization energy is $-1.8 \Delta_t + \Delta_{sp}$. For the HS state,

$\Delta_{sp}=0$ as there are no electrons to pair-up but it costs an energy $(-2 \times \frac{3}{5} + 1 \times \frac{2}{5})\Delta_t$ to split the Mn d -orbital with two e electrons and one t electron. It results in HS total stabilization energy of $-0.8 \Delta_t$. The LS and HS difference is, therefore, $\Delta_{sp} - \Delta_t$ which is then equated to the total energy difference of our computed LS and HS magnetic states.

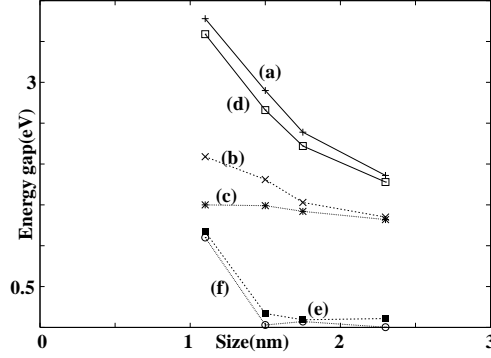


FIG. 2: (Color online) Energy separations for (a) host HOMO-LUMO (b) HOMO- t^\uparrow and (c) $t^\uparrow - e^\uparrow$ for Mn at the center and near the surface ((d), (e) and (f)) of the NC.

We estimate the quantum size effect on the host gap i.e., HOMO-LUMO gap, HOMO(host)- t^\uparrow and $t^\uparrow - e^\uparrow$ for Mn at the center and near the surface in their respective ground states i.e., LS state for central atom and HS state for sub-surface atom. Figure 2 shows the variations in the three gaps versus the NC size for these two cases. Si s and p orbitals are spatially delocalized compared to Mn d -orbitals and therefore the host gap (label (a) in Figure 2) variation is more pronounced than the $t^\uparrow - e^\uparrow$ gap (label (c)) and moderate variations in HOMO(host)- t^\uparrow (label (b)). All the three gaps (label (e), (f) and (g) in Figure 2) show strong variations with size for sub-surface doping which is reasonable as all the orbitals are affected by the confinement.

In conclusion, we find magnetic metastable states in Mn doped Si-NC doped at the center as well as near the surface. The LS state is the ground state for central doping and HS ground state for sub-surface doping. The quantum confinement effect on the energy separation for the sub-surface doping is stronger than the central doping.

Acknowledgments

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