Weak $d^0$ ferromagnetism: Zn vacancy condensation in ZnS nanocrystals

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The possibility to control magnetic properties of semiconductor nanocrystals (NC) at room temperature makes them essential in the growing field of spintronics [1, 2] and biomedicine [3]. Spintronic devices can completely displace their charge based devices because the manipulation of spin is faster and requires less energy. One of the widely discussed possibility of room temperature ferromagnetic ordering can be achieved by introducing vacancy defects in semiconductor nanoparticles [4–13]. Such nanocrystals exhibit $d^0$ ($d$ or $f$ electrons are not involved) ferromagnetism associated with unpaired electron spins. One of the most attractive NC with $d^0$ ferromagnetism is ZnS. A ZnS crystal is found to be in both stable cubic zinc-blende and hexagonal wurzite crystal structures with the bulk band gap of 3.7–3.8 eV [14–16]. Doped by Mn impurities ZnS quantum dots (QDs) can be used as a sensitizer for QD sensitized solar cells [17].

A theoretical description of such materials becomes important in the explanation of the existing experiments and prediction of new properties. The preliminary calculations [9, 10, 13, 18, 19] demonstrate that the value of the magnetic moments per unit cell are three orders of magnitude higher that the experimental values [10, 19]. In the DFT calculations we adopted the model where the Zn vacancies are uniformly distributed inside a nanocrystal including the NC surface. Such a huge discrepancy cannot be explained by the inaccuracy of the DFT calculations and therefore needs a special investigation. As it follows from the preliminary calculations pure ZnS 0% of the Zn vacancy concentration) and S (100% of the Zn vacancy concentration) exhibit the vanishing magnetic moment. Thus, if we suggest that inside a ZnS quantum dot there are large areas of S insurgencies with zero magnetization, this hypothesis could be a possible explanation of the giant discrepancy between the theoretical and experimental magnetizations. A schematic picture of the Zn vacancy cluster inside the nanocrystal is demonstrated in figure 1. In this work we computationally verify this hypothesis and quantitatively prove that the Zn vacancy condensation is the true mechanism, which explains the experimental observations.
Zn vacancy cluster

ZnS nanocrystal

Figure 1. Schematic representation of the quantum dot with the S droplet, which represents the condensed Zn vacancies.

Computational details

The electronic-structure calculations have been performed within the density functional theory (DFT) using the Vienna Ab Initio Simulation Package (VASP) [20–23]. The Pedrew–Burke–Ernzerhof (PBE) exchange-correlation functional [24, 25] within the generalized gradient approximation (GGA) and the projector-augmented plane-wave (PAW) pseudopotential [26, 27] with the cutoff energy of 400 eV are employed for all calculations. The Γ-centered k-point grid has been generated from the Monkhorst–Pack scheme [28]. In this work we conduct the electronic structure calculations of the wurtzite and zinc blende ZnS crystal (see figure 2) and surfaces with Zn vacancies. The conjugate gradient optimization method with \(4 \times 4 \times 4\) and \(4 \times 1 \times 1\) k-point meshes have been employed for the bulk and surface structure relaxation, respectively. The same grids have been used for the magnetic moment calculations. To study the Zn vacancy concentration dependencies of the bulk magnetic moments we keep the same supercell size and change the number of vacancies in the cell. The supercell contains eight Zn atoms as shown in figure 2. Thus eliminating different Zn atoms with proper numbers in the cell we choose a vacancy cluster with different vacancy concentrations of Zn as 100%, 87.5%, 75.0%, 62.5%, 50.0%, 37.5%, and 25.0%. The value of the magnetic moment is very sensitive to how the Zn atoms are withdrawn from the crystal forming a Zn vacancy cluster (figure 2). The numbers in figure 2 are used for specific description of a Zn vacancy cluster, which magnetic moment is calculated. Some numbers are several times repeated because they denote the same atoms due to the translational periodicity of the crystal. We demonstrate below that the magnetization and energy of the unit cell comprised of different configuration for Zn vacancy at large concentrations are sensitive to a specific configuration.

Results

To prove the hypothesis, in which we assume that there are large S-clusters with the zero magnetic moment rather than uniformly distributed Zn vacancies in a quantum dot with finite magnetization. We calculate the total energy of the supercell cut out of the crystal at the same number of vacancies which are (a) uniformly distributed or (b) forming a single cluster. The energy difference \(\Delta E = E_{\text{cluster}} - E_{\text{uniform}}\) is presented in figure 3. In this figure the red and blue curves represent the energy difference, \(\Delta E\), between the supercell with the cluster formation and the uniformly distributed vacancies with the same number of Zn vacancies in the supercell for the wurtzite and zinc blende crystal structures, respectively. From figure 3 we conclude that the structures are in favor of the cluster formation rather than the configuration with the uniformly distributed vacancies. The higher the vacancy concentration, the larger the energy difference.

To facilitate the computations for large clusters in figure 3 we introduce the thermodynamic approximation (TA) the extensive thermodynamic functions. Indeed, as it follows from thermodynamics the energy of a very large system is equal to the sum of the energies of smaller subsystems comprising the system.

\[
E_{\text{system}} = N_{\text{ZnS}} \times E_{\text{ZnS}} + N_{\text{S}} \times E_{\text{S}} + N_{\text{S/ZnS}} \times E_{\text{S/ZnS}}. \tag{1}
\]

where \(N_{\text{ZnS}}, N_{\text{S}}, N_{\text{S/ZnS}},\) and \(E_{\text{ZnS}}, E_{\text{S}}, E_{\text{S/ZnS}}\) denote the number and energy of unit cells, respectively. The system has three subsystems where subsystem 1 contains only ZnS unit cells, subsystem 2 has the area with only S atoms, and subsystem 3 contains Zn vacancies with a specific concentration uniformly distributed inside subsystem 3. The total number of vacancies is determined by the total number of vacancies in subsystems 2 and 3 divided by the total number of unit cells in the whole system. For the thermodynamic limit to be valid, the size of a unit cell has to be large to neglect the interface effects. For the \(\Delta E\) calculations shown in figure 3, \(N_{\text{S/ZnS}} = 0\). We have verified the TA model by the exact DFT calculations. The comparison between the energies calculated within the thermodynamic approximation and exact DFT calculations for the zinc blende crystal structure is presented in table 1. In this table the uniform gas of Zn vacancies has been chosen with the 12.5% Zn vacancy concentration. For the cluster calculations we have considered the S cluster embedded into the ZnS environment. The total number of S unit cells in the S cluster is determined from the requirement of 12.5% of Zn vacancies in the total system, which includes the S cluster and ZnS environment. For the vacancy uniform gas the TA model is valid with the accuracy of 0.06%. For the S cluster calculations the accuracy of the TA model is 0.3%. The S cluster is composed from eight sulfur unit cells with the approximate volume of \(\sim 64 \text{ Å}^3\). We have also calculated the magnetization in the TA limit and compared the results with the ‘exact’ DFT calculations. The total magnetic moment is comprised of the ZnS, S, and ZnS/S interface contributions. From the calculations it follows that each of the contributions provides zero magnetization leading to the vanishing total magnetic moment. We have checked this result from the DFT calculations with the large unit cell composed of 64 elementary unit cells where eight of them are the S unit cells. The DFT calculations have revealed the same zero magnetization. Thus we conclude that the TA model is very accurate for the large system calculations and therefore can be used for the energy computations presented in figure 3.

It is obvious that for an S cluster (100% of Zn vacancy concentration) the total magnetization vanishes. However it is unclear whether the magnetization value vanishes or remains finite for larger Zn vacancy concentrations in the wurtzite and zinc blende crystal structures. In figure 4 we present the Zn
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Vacancy concentration dependence of the magnetization per unit cell for the wurtzite (red) and zinc blende (blue) crystal structures. As shown in figure 4 the magnetization vanishes for Zn vacancy concentrations higher than 37.5% for wurtzite crystal structure. In the case of a zinc blende structure the behavior of the magnetization is more complicated—the magnetization is zero only for 50%, 75.5%, and 100% of the Zn vacancy concentrations. Thus we can draw the conclusion that a cluster with zero magnetization should not be restricted by the condition by 100% of Zn vacancy concentration.

There are different Zn vacancy configurations to comprise a Zn vacancy cluster. It is unclear whether some configurations provide nonzero magnetic moments at large concentrations. We have checked all possible configurations and calculated both magnetic moments and energies for the same supercell and compared the total energies for each configurations. The configuration with the lowest energy provides the true cluster configuration that can be in the experiments. A specific configuration is determined by the withdrawal of Zn atoms with specific numbers from the supercell. We have checked different concentrations of Zn vacancies such as 100%, 87.5%, 75.0%, 62.5%, 50.0%, 37.5%, and 25.0%. As an example we present the two configurations for only 50.0% of the Zn vacancy concentration in table 2.

\[
\Delta E = E_{\text{cluster}} - E_{\text{uniform}}
\]

Figure 2. Wurtzite and zinc blende structures of a ZnS crystal. The Zn atom numbers are used for the description of atoms, which are withdrawn from the crystal to form a Zn vacancy cluster in a particular configuration. (a) Wurtzite. (b) Zinc blende.

Figure 3. The energy difference between the total energies per unit cell for the S vacancy cluster and the configuration with uniformly distributed Zn vacancies. The red and blue curves represent \(\Delta E\) for wurtzite and zinc blende crystal structures, respectively.

Table 1. Comparison between the energies per unit cell found within the TA and exact DFT calculations for the uniform gas and cluster, respectively. The discrepancy is defined \(\Delta = E_{\text{TA}} - E_{\text{DFT}}\).

<table>
<thead>
<tr>
<th></th>
<th>TA energy, eV</th>
<th>Exact DFT energy, eV</th>
<th>Discrepancy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform gas</td>
<td>−6.210</td>
<td>−6.214</td>
<td>0.004</td>
</tr>
<tr>
<td>Cluster</td>
<td>−6.349</td>
<td>−6.330</td>
<td>−0.019</td>
</tr>
</tbody>
</table>

Figure 4. Zn vacancy concentration dependence of the magnetization per unit cell for the wurtzite (red) and zinc blende (blue) crystal structures.
We have studied the effect of condensation of Zn vacancies in a quantum dot in order to explain a giant discrepancy of the three orders of magnitude between the magnetic moments measured experimentally and calculated theoretically. We have found that the cluster configuration is more favorable than the uniformly distributed gas of vacancies inside the quantum dot. Since the sulfur cluster, i.e. 100% of Zn vacancy concentration, carries the zero magnetic moment as well as the ZnS environment, we have suggested that the small magnetic moment could at the interface between the the ZnS crystal and vacancy droplet. The calculations reveal however, that the interface still has the vanishing magnetization for different surface cuts. Thus we draw the conclusion the the experimentally measured weak magnetic moment can be explained by one of the two following pictures: (a) there are two phases where the vacancy cluster with the zero magnetic moment coexists along with the other phase, in which there are uniformly distributed Zn vacancies with low concentrations; and (b) there is only a single vacancy phase—a vacancy droplet being in a metastable state with a weak nonvanishing magnetic moment. In addition the total magnetic moment could be suppressed by the presence of ligands that can change the surface magnetic moment contribution. The other reasons of a magnetization decrease can be the existence of extra charge carriers and existent dopants in a nanocrystal or also temperature fluctuations that can be larger than anisotropy energy to exhibit super-paramagnetic behavior resulting in a small magnetic moment. To include these extra sources of magnetization suppression additional experimental investigations are necessary.

**Acknowledgments**

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**References**


**Table 2.** Magnetic moment and energy per unit cell for different Zn vacancy configurations. The concentration of Zn vacancies is 50%.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Magnetization/unit cell, $\mu_B$</th>
<th>$\Delta E$/unit cell, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wurtzite (1-2-3-4)</td>
<td>0.79</td>
<td>0.289</td>
</tr>
<tr>
<td>(2-3-6-7)</td>
<td>0.00</td>
<td>0.000</td>
</tr>
<tr>
<td>Zinc blende (1-2-3-4)</td>
<td>0.61</td>
<td>0.063</td>
</tr>
<tr>
<td>(1-2-7-8)</td>
<td>0.00</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**Figure 5.** Interface between the ZnS crystal and vacancy cluster with 50% and 100% vacancy concentrations.

As soon as we have proved that the condensation of vacancies into a droplet is energy favorable (see figure 3), the following question may arise whether the transition layers between the sulfur cluster and ZnS environment could carry a nonvanishing magnetic moment. The value of this magnetic moment can result in the total already reduced NC magnetization. Thus we calculate the magnetic moment of the layer system depicted in figure 5 where the two external layers represent the ZnS environment and the two internal layers describe the vacancy droplet interface with some nonzero concentration of Zn vacancies. Then we divide the system of four layers in the two symmetric halves where each of them represents the interface between the vacancy cluster and ZnS environment. In the calculations we have optimized the layer system and obtained that the total magnetic moment is zero again. For the surfaces we have chosen various surface cuts such as (1 0 1 0) for the wurtzite and (1 1 1), (1 1 0) for zinc blende crystal structures. The layer systems with these cuts provide the zero magnetizations. In addition we have also studied different Zn vacancy concentrations in the internals layers, which represent the cluster. For 50% and 100% vacancy concentrations we have found that the magnetic moment of the layer system is zero. Thus we conclude that the interface between the ZnS environment and the vacancy cluster does not carry any magnetic moment. The origin of a nonvanishing very small magnetization can be explained by the coexistence of two vacancy phases where one of them is a vacancy droplet (cluster) and the other is the uniformly distributed vacancy gas at low concentrations.

**Summary**

We have studied the effect of condensation of Zn vacancies in a quantum dot in order to explain a giant discrepancy of