Physics Letters A ••• (••••) •••–•••

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Physics Letters A

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Ferromagnetic ordering inchemically synthesized ZnS:Mn diluted magnetic semiconductor: A density functional theory explanation

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ARTICLE INFO

Article history:
Received 31 July 2017
Received in revised form 10 September 2017
Accepted 12 September 2017
Available online xxxx
Communicated by M. Wu

Keywords:
ZnS nanoparticles
Ferromagnetism
Density functional theory
Density of states

ABSTRACT

We have carried out DFT calculations to investigate the origin of room temperature ferromagnetism in experimentally obtained Mn doped ZnS magnetic semiconductor. For experimental investigations, the formation of the cubic ZnS structure of ~4 nm in size is confirmed by XRD and TEM results. Theoretical calculations reveal that Mn doped ZnS system possesses half metallic characteristics in addition to strong p–d hybridization between the d-states of Mn atom and the p-states of surrounding S atoms, which leads to the strong ferromagnetic coupling and is experimentally realized in the M–H curves of Mn doped ZnS nanoparticles. The ferromagnetic coupling between Mn–Mn atoms are studied by using two dopant model, replacing two Zn atoms by two Mn atoms in ZnS supercell, which depicts that ferromagnetic state is always ground state. In calculating formation energies for single and two Mn dopant ZnS systems, negative values of formation energy are obtained indicating of higher stability of the system.

1. Introduction

The ferromagnetic ordering in semiconducting devices has been actively explored since last two decades by introducing magnetic elements in II–VI semiconductors. Due to the uncertainty in exact confirmation of the origin of ferromagnetism in these materials, it has been a controversial topic of research, for which the same issue is gaining renewed importance. The origin of ferromagnetic coupling in transition metal (Cr, Mn, Fe, Co etc.) doped II–VI (ZnS, CdS, ZnSe etc.) diluted magnetic semiconductors have been receiving much more attention due to their advanced physical, half metallic, magnetic, optical and electrical properties which have prospective applications in spintronic devices like spin-polarized LEDs, memory element, photovoltaics and sensors etc. [1–5]. Several experimental and theoretical reports have disclosed recently that the origin of room temperature ferromagnetism in these materials are results of various phenomena like structural defects, d–d, sp–d, p–d exchange interactions etc. [2,6–8].

Pertaining various theoretical and experimental reports [9,10], in this work, we have investigated the origin of room temperature ferromagnetism in chemically synthesized Mn doped ZnS diluted magnetic semiconductors and correspondingly employed density functional theory calculations to investigate the mechanisms responsible for the origin of ferromagnetic coupling in these semiconductors.

2. Experimental and computational details

For the experimental calculations, we have synthesized Mn doped ZnS nanoparticles using microwave assisted co-precipitation technique [2]. To synthesize Mn doped ZnS nanoparticles, 0.2M (50 ml) Zinc acetate [$Zn(CH_3COO)_3.2H_2O$] solution was mixed with 0.01M (50 ml) Manganese acetate [$Mn(CH_3COO)_3.4H_2O$] solution and 0.2M (50 ml) Sodium sulfide [Na_2S] solution was added drop wise to the above mixer. After stirring for 3 hrs at 80 °C, precipitates were obtained and washed several times using deionized water. Finally, Mn doped ZnS nanoparticles were obtained after heating the precipitates at 80 °C for 8 hrs. XRD and the morphology of the nanoparticles have been carried out by X-ray diffractometer [Rigaku, Ultima-IV] and Transmission Electron Microscope [Model: TECNAI G2 20 S-TWIN (200 KV)] respectively. Magnetic measurements have been carried out by Vibrating Sample Magnetometer [Model: 7410 series].

For theoretical calculations, we have performed spin polarized density functional theory implemented in quantum espresso using generalized gradient approximation (GGA) by Perdew–Burke–Ernzerhof (PBE) functional for exchange–correlation potential [11–13]. Test calculations have been performed using DFT+U method with a cut off energy of 400 eV. Vanderbilt Ultrasoft pseudopotentials has been taken for ion–electron interactions [11]. We

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http://dx.doi.org/10.1016/j.physleta.2017.09.018
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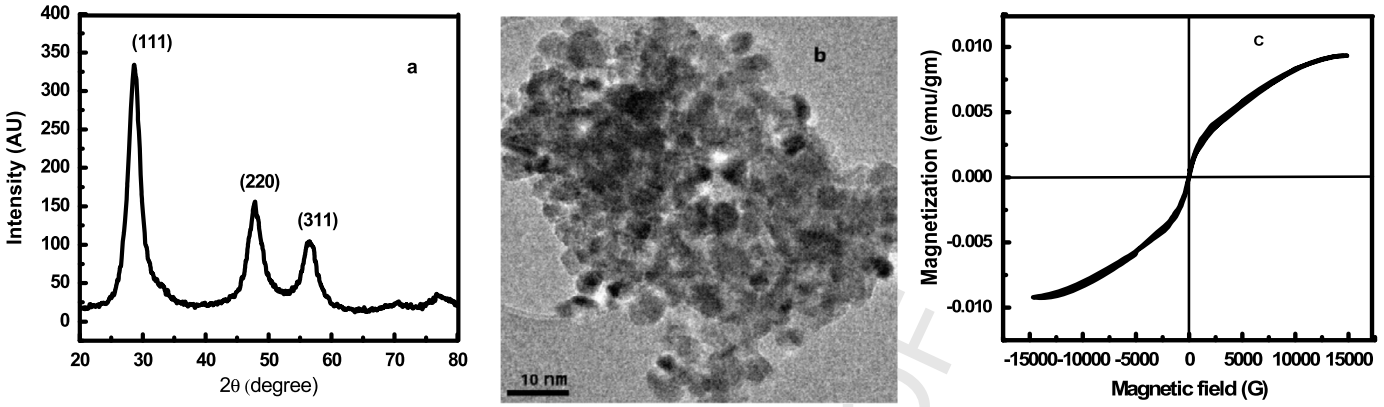

Fig. 1. (a–b) XRD spectrum and TEM image and (c) Room temperature M–H curve of Mn doped ZnS nanoparticles.

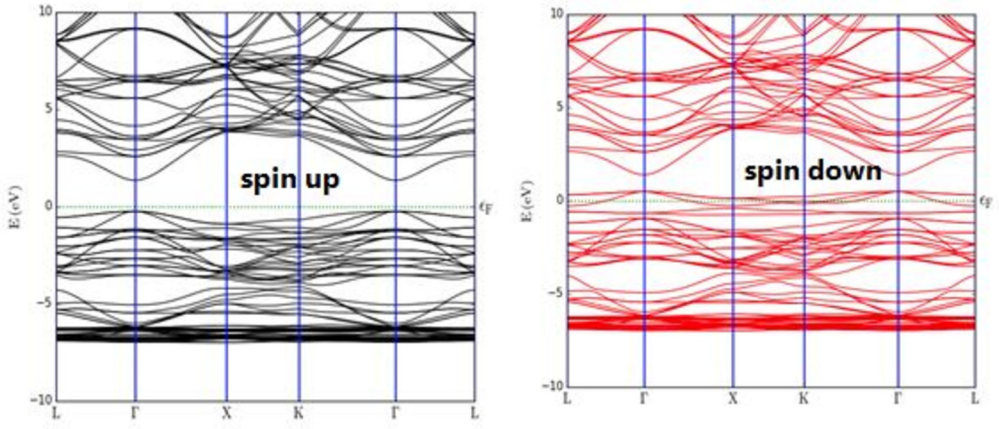

Fig. 2. Spin polarized band structures of Mn doped ZnS system.

use $2 \times 2 \times 2$ cubic ZnS supercell consisting of 64 atoms replacing one Zn atom by one Mn atom. The Brillouin zone is sampled by $4 \times 4 \times 4$ k-points mesh and 300 eV energy cutoff is kept for the calculations.

3. Results and discussion

3.1. Structural and magnetic analysis

Fig. 3 (a–b) shows the XRD spectrum and TEM micrograph of Mn doped ZnS nanoparticle. The XRD spectrum demonstrates the formation of cubic zinc blende structure with an average crystallite size of 4.5 nm which in good agreement with the particle size (5 nm) obtained from TEM result. In transition metal doped ZnS DMSs, the p–d hybridization between the d orbitals of transition metal ion and the p orbitals of four surrounded S atoms play significant role in the origin of ferromagnetic coupling in the system [9]. Dopant occupies partially filled energy levels in the gap of the host material and band broadening occurs which contributes to the ferromagnetic states of the system. Meanwhile, the dopant induces spin polarization to the S atoms and they couple to the dopants ferromagnetically [13,14]. The room temperature M–H curve of the synthesized Mn doped ZnS nanoparticles reflects ferromagnetic behavior with negligible coercivity values (see Fig. 1). The ferromagnetism is observed due to the exchange interactions between Mn^{2+} ions mediated by S^{2-} ions [15,16]. A strong hybridization between the d-states of Mn^{2+} ions and the p-states of S^{2-} ions takes place that causes the ferromagnetism inside the nanoparticles which can be identified in the theoretical calculations [17] (Fig. 2 and 3).

3.2. Band structures and density of states

Firstly, the $2 \times 2 \times 2$ ZnS supercell is optimized using Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [18] which results in a slight decrement in the lattice constant compared to the experimentally quoted value (5.40 Å) due to the difference in ionic radii between Mn^{2+} and Zn^{2+} [19]. While replacing a Zn atom by a Mn atom in the ZnS, the bond length between Mn and S (2.26 Å) reduces compared to that between Zn and S (2.61 Å) and hence the local structure is compressed. The defect formation energy (E_f) for single Mn substituted ZnS system is calculated by using the same formula as in the earlier reports [4,7] and found to be −1.42 eV. The smaller defect formation energy shows that Mn can be incorporated easily in the ZnS host which implies that Mn doped ZnS can be fabricated easily [4].

The spin polarized electronic band structure for single Mn substituted ZnS is shown in Fig. 2, which demonstrates that the majority spin channel is semiconducting with a band gap of 1.79 eV while the minority spin channel is metallic with the overlapping of Mn–d states and S–p states showing half metallic characteristics. Our results are consistence with the results obtained by Hai-Qing Xie et al., [10] in Ni doped ZnS DMSs. Fig. 3 [a–d] shows the total and partial density of states of Mn doped ZnS system which depicts that there is a band gap in the spin up channel conforming the semiconducting nature and the spin-down channel obeys a metallic behavior which confirms the half metallicity of the Mn doped ZnS system. Moreover, from the TDOS and PDOS plots, it is confirmed that, the Fermi level in the spin down channel is partially filled by the d-states of Mn atom and the p-states of S atoms and results in a significant p–d hybridization which employs spin

Please cite this article in press as: D. Saikia, J.P. Borah, Ferromagnetic ordering inchemically synthesized ZnS:Mn diluted magnetic semiconductor: A density functional theory explanation, Phys. Lett. A (2017), http://dx.doi.org/10.1016/j.physleta.2017.09.018