Journal of Magnetism and Magnetic Materials 413 (2016) 19–24

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Critical analysis of the vacancy induced magnetism in Scandium Nitride (ScN): An *ab-initio* study

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ARTICLE INFO

Article history:
Received 8 November 2015
Received in revised form
9 March 2016
Accepted 8 April 2016
Available online 9 April 2016

Keywords:
Vacancy
Magnetic moment
Strain
Magnetic interactions
Formation energy
Percolation threshold

ABSTRACT

We have studied the origin of the magnetism induced by a neutral cation vacancy in rocksalt ScN using *ab-initio* calculations based on spin density functional theory. Our results showed that Sc vacancy induces a total local magnetic moment of $0.50\mu_B$. The main contributors to this induced magnetism are the 2*p* orbitals of nearest nitrogen atoms surrounding the vacancy. The spin polarization energy (defined as the energy difference between the spin polarized and non-polarized states) is well above the room-temperature energy. Furthermore, we have investigated the effect of an external strain on the induced magnetism. Our calculations showed that applying an external strain leads to a decrease of the stability of the magnetic state. Moreover, calculations of the magnetic interactions showed that the most stable configuration corresponds to the fifth nearest neighbor distance with a ferromagnetic state. Finally, using thermodynamic considerations, we demonstrated that the minimum defect concentration to achieve magnetic percolation cannot be reached at equilibrium conditions. However, we found that by applying an external strain, we could reduce the formation energy of the defect, achieving therefore the magnetic percolation.

1. Introduction

Diluted magnetic semiconductors (DMSs) have been the subject of extensive research and become a very attractive material system for spin based electronic applications (spintronic devices) [1]. Several DMS research have focused upon nitride and oxide materials. One of the classic way of synthesizing DMS materials is to dope III-V or II-VI semiconductors with a transition metal (TM) atom. Initial work began with H. Munekata et al. who studied the magnetism of the Mn doped InAs [2]. Subsequent theoretical and experimental progress have been made to investigate the magnetism of TM-doped semiconductors and to grow DMS with room-temperature ferromagnetic ordering [3–12]. Since TM atoms are intrinsically magnetic, the origin of magnetism in DMS is difficult to identify when these atoms are used as dopants. Moreover, several works exhibited a ferromagnetic (FM) behavior in DMS doped with non-magnetic elements [7,13–16]. A ferromagnetic ordering was also reported by doping with a non-metallic element [17–19]. Recently, *ab-initio* calculations have reported a FM phase in undoped materials by introducing a native defect (vacancy). Typical undoped semiconductors with a native defect such as ZnO [20–22], MgO [23,**?**], CaO [25], GaN [26–28], BN [26,28] and AlN [28] have been predicted to display FM ordering. These works provided a novel way of producing DMS materials. Although several studies were performed to understand the magnetism induced by defects in nitride semiconductors, few studies were carried out on ScN. For example, Herwadkar and Lambrecht [4] have theoretically investigated the case of Mn doped ScN. Moreover, using *ab-initio* calculations, Kerdsongpanya et al. [29] have studied the localized magnetism induced by native vacancies (Sc and N) in ScN. Interestingly, their calculations lead to a vanishing total magnetic moment for both cation and anion vacancies with a 3.125% at. concentration. However, for 1.562% at. concentration of nitrogen vacancy they found a total magnetic moment of $0.9\mu_B$.

The aim of this article is to thoroughly investigate in the framework of *ab-initio* methods, the origin of the magnetism induced by a cation vacancy (V_{Sc}) and the vacancy concentration dependence of total localized magnetic moment in Rocksalt ScN. In the first part, we have studied the defect localized magnetic moments

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http://dx.doi.org/10.1016/j.jmmm.2016.04.026
0304-8853/

by calculating the density of states (DOS), the projected density of states (PDOS), the electronic charge density redistribution and the electronic spin polarization density. Furthermore, we have studied the possibility of enhancing the stability of the localized magnetism by strain engineering. In the second part, we have investigated the long range behavior of the induced magnetism (magnetic interactions) by calculating the relative magnetic energy, i.e, the energy difference between the antiferromagnetic (AFM) and the ferromagnetic (FM) states. Moreover, we have used the Heisenberg model to calculate the exchange coupling parameters. Finally, in the third part, following Osorio-Guillen et al. [30] and using the distance dependence of the exchange coupling parameters we have determined the percolation threshold (the minimal defect concentration needed to achieve magnetic percolation) and have discussed the thermodynamic realization of magnetic percolation by strain engineering.

Our paper is organized as follows. In Section 2, we briefly reviewed the underlying theory and the computational methods used in the calculation. In Section 3, our calculations are presented and discussed in comparison with available *ab-initio* calculations. Finally, in Section 4, we have summarized our main results and conclusions.

2. Theory and computational methods

Our calculations are performed based on spin density functional theory [31,32] using a plane wave basis set and ultrasoft pseudopotential (USPP) [33] as implemented in Quantum Espresso-package [34]. Generalized gradient approximation (GGA) [35,36] is used to treat the exchange correlation potential using the PW91 functional of Perdew and Wang [36]. For comparison purposes, we also used a norm conserving pseudopotential with the hybrid functional of Heyd, Scuseria, and Emzerhof (HSE06) [37] (the HSE06 exchange-correlation functional is known to correct the band gap problem). However, if the pseudopotential type is not mentioned explicitly in the text, the calculations are assumed to be carried out with USPP and GGA. The cutoff energies for the plane wave (40 Ry) and for the compensating charge density (320 Ry) are carefully tested to ensure the convergence of the calculations. For the hybrid functional calculations, we use a cutoff energy of 45 Ry. A $2\times2\times2(4\times2\times2)$ ScN supercells containing 64 (128) atoms were found to be sufficient for the calculations of the localized magnetism (extended magnetism). To study the cation vacancy concentration dependence of the magnetic properties, we have also used a $3\times3\times3$ (216 atoms) supercell. The Brillouin zone integrations generated by Monkhorst-Pack scheme [38] were performed using a $4\times4\times4$, $2\times4\times4$ and $4\times4\times4$ k-point grids for the 64, 128 and 216 atoms supercells, respectively. These grids were chosen to achieve a convergence in energy of 0.1 meV/atom. The valence configurations were $3s^23p^64s^23d^1$ and $2s^22p^3$ for Sc and N respectively. Atomic positions were fully relaxed for all calculations (the relaxation threshold for the Hellman-Feynman [39] forces was set to 5×10^{-4} Ry/a. u.).

In order to calculate the formation energy of a V_{Sc}, we have used [40]:

$$E_{form} = E_{tot}(V_{Sc}) - E_{tot}(\text{bulk}) + \mu_{Sc}, \quad (1)$$

where $E_{tot}(V_{Sc})$ and $E_{tot}(\text{bulk})$ are the total energies of V_{Sc} contained ScN and the pure ScN cells respectively. μ_{Sc} is the chemical potential of the scandium atom. μ_{Sc} depends on the experimental growth conditions, which can vary between the limit of Sc-rich (N-poor) and the limit of N-rich (Sc-poor). In thermodynamic equilibrium, the stability conditions for ScN set the following relation:

$$\mu_{Sc} + \mu_N = \Delta H_f(\text{ScN}). \quad (2)$$

Where μ_N is the chemical potential of the nitrogen atom and $\Delta H_f(\text{ScN})$ is the formation enthalpy of ScN. Under extreme Sc-rich (N-poor) condition, the chemical potential μ_{Sc} is:

$$\mu_{Sc} = \mu_{Sc}(\text{bulk}), \quad (3)$$

and under extreme Sc-poor (N-rich) condition is:

$$\mu_{Sc} = \mu_{Sc}(\text{bulk}) + \Delta H_f(\text{ScN}). \quad (4)$$

3. Results and discussion

3.1. Perfect ScN structure

ScN crystallizes in the rocksalt (RS) structure, i.e, a face centered cubic (FCC) compound with each Sc cation surrounded by six N with filled valence p bands. The arrangement of the atoms is a regular octahedron. Our structural calculation of the lattice constant leads to a value of 4.502 Å, in agreement with the experimental value (4.503 Å) of Al-Brithen et al. [41] Fig. 1(a) represents the spin density of states (DOS) of the perfect ScN.

This figure shows that the up and down spin densities are totally symmetric, indicating a non-magnetic state of the system ($\mu_t = 0$) in good agreement with previous studies [4]. However as expected [29,42,43], one observes that the band gap is underestimated using the USPP and GGA exchange-correlation functional. This discrepancy can be corrected using the HSE06 hybrid functional [37] as shown in Fig. 2 where the calculated bang gap energy is about ~0.8 eV in good agreement with the experimental value of ~0.9 eV measured by Al-Brithen et al. [44].

3.2. Localized magnetic moments

In order to study the magnetic properties induced by a neutral Sc vacancy (V_{Sc}^0) in ScN, we removed a single Sc atom from the $2\times2\times2$ supercell ($Sc_{1-x}N$ with $x = 0.03125$). After a full ionic relaxation, the six N atoms surrounding the vacancy (V_{Sc}) move outward by about 0.125 Å, and the bonding in the first shell around V_{Sc} shrinks by the same value. In the unrelaxed $Sc_{1-x}N$, the spin polarization energy (ΔE_{sp}) defined as the difference between the spin unpolarized and the spin polarized energies, is found to be 41 meV well above the room-temperature energy (RT = 25.9 meV). In the following, $Sc_{1-x}N$, refers to the relaxed structure with a cation vacancy. Our total energy calculation of $Sc_{1-x}N$ leads to a ground state with a total magnetic moment $\mu_t = 0.50\mu_B$. Moreover, the calculation performed by the norm-conserving pseudopotential and the hybrid functional (NCPP-HSE06) leads to the same value of μ_t. This result shows that the band gap correction obtained by the hybrid functional does not change the value of μ_t. Our results are in disagreement with the first principles calculations performed (in a 64-atoms supercell with $x = 3.125\%$) by Kerdsongpanya et al. [29]. Indeed, their calculated values of μ_t vanish for both a cation and anion vacancies and lead to a non polarized state. However, they found a non vanishing value of μ_t at lower concentration (a 216-atoms supercell) for the anion vacancy (ScN_{1-x}) where $x = 1.562\%$. Then, it was also interesting to calculate μ_t for our case with the same concentration. These (USPP-GGA) calculations lead to a value of $0.77\mu_B$ which indicates a vacancy concentration dependence of the localized magnetic moment. As the size of the magnetic moment is independent of the band gap underestimation, we choose to continue all the following calculations in the USPP-GGA framework.

The origin of the induced localized magnetism can be understood using the molecular orbital theory (MOT). Indeed, the decomposition of the reducible representation for the six equivalent