Contents lists available at ScienceDirect

Computational Materials Science

First-principles prediction of magnetic salts: Case study of NaCl bulk and (001) surface doped with light non-metallic 2p-block elements

Yi-Lin Lu [a], Shengjie Dong [b,1], Baozeng Zhou [c], Na Wang [d], Hui Zhao [b], Ping Wu [a,*]

[a] Department of Applied Physics, Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, Faculty of Science, Tianjin University, Tianjin 300072, PR China
[b] Department of Physics, Tianjin Normal University, Tianjin 300387, PR China
[c] Tianjin Key Laboratory of Film Electronic & Communicate Devices, School of Electronics Information Engineering, Tianjin University of Technology, Tianjin 300384, PR China
[d] School of Science, Tianjin Chengjian University, Tianjin 300384, PR China

ARTICLE INFO

ABSTRACT

Based on density functional calculations, we studied the structural, electronic, and magnetic properties of sodium chloride bulk and (001) surface doped with the light non-metallic elements boron, carbon, nitrogen, and oxygen. The results indicated that doping such an isolated foreign atom can produce considerable spin polarization, mainly due to highly localized and partially filled 2p states of the dopants. From simple GGA computation, all these diluted magnetic chlorides exhibit nearly half-metallic characteristic with weak conductivity, and thereby they could be used as spin filter materials for improving spin-specific magnetic tunnel junctions. Especially, substitution onto the surface removes the degeneration of 2p impurity states, leading to anisotropic spin and electron atmosphere with specific orientation. The differences between bulk doping and surface doping were further explained by spin-resolved energy spectrums. In addition, compared with standard GGA approach, applied U_{eff} of 2p orbitals of C, N, and O atoms can correct the error and improve the description of the electronic structures and magnetic properties in some extent. N and O-doped NaCl bulks transform from approximate half metals to magnetic semiconductors, owning to the enhancement of electronic localization and correlation. And the total magnetic moment increases from 1 μ_B to 3 μ_B for C-doped NaCl (001), accompanying with a transformation from intermediate-spin state to high-spin state. In particular, O-substituted system is energetically more favorable than other doped systems, i.e., the negative value of the predicted formation energy, demonstrating that O-doped NaCl should be a candidate material for potential spintronic applications.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Diluted magnetic semiconductors (DMS) have been intensively investigated to fabricate new functional semiconductor-based materials utilizing the spin degree of freedom due to the discovery of the ferromagnetism in so-called DMS [1–5]. The possibility of establishing new semiconductor spintronics based on novel functional solids as a practical technology received a strong boost when both theoretical and experimental results report its feasibility [6–10]. Consequently, designing and developing unknown DMS will be useful and meaningful for spintronic community. It is important not only to explain the already known electrical and

magnetic properties in a given DMS but also to predict what property will be expected for a hypothetical DMS which has not been achieved experimentally.

It is well known that sodium chloride (NaCl), is famous as a prototype for ionic materials and widely used in food, soda ash, medicine, and agricultural industry [11]. For instance, it is the main component of table salt [12]. As an ionic compound, its physical and chemical properties have aroused considerable interest in the literature in the past several years [13–25]. Nevertheless, despite increasing researches on NaCl, reports on the magnetic phenomena related to NaCl within materials science community are rare in the past. Its strong ionic bonding features separate it from the other group II–VI, III–V, and IV–IV semiconducting compounds, showing different possibilities for pure academic and applied electronic communities. Recently, it was found that several investigations about magnetic phenomena related to NaCl were reported. Vlaic et al. showed magnetic tunnel junction in

---

* Corresponding author.
    E-mail address: pingwu@tju.edu.cn (P. Wu).
[1] Present address: Tianjin Key Laboratory for Modern Drug Delivery and High-Efficiency, School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, PR China.

Fe/NaCl/Fe(001) and also analyzed the reason of the enhancement of the interface iron magnetic moment. The interfacial charge transfer is believed to have an important role in stabilizing Fe/NaCl(001) interfaces. Fe induced gap states have been observed in barrier layers on both Na and Cl ions. High magnetoresistance ratios comparable to Fe/MgO/Fe junctions are predicted [26,27]. Tao et al. predicted an interesting and potentially very attractive magnetic tunnel junction FePt/NaCl/FePt(001) for spintronics [28]. Gong et al. proposed a very attractive magnetic tunnel junction Fe(001)/O/NaCl(001)/O/Fe(001) as a two-terminal transport junction. Large tunnel magnetoresistance ratio was predicted [29]. Furthermore, the room temperature ferromagnetism was found in pure NaCl particles with different crystal size synthesized and further explained the origin of ferromagnetism in the nonmagnetic materials [30]. Moreover, single atom and atomic chain on NaCl surface exhibited novel electronic and magnetic properties, demonstrating the possibility of applying the NaCl-based systems on high-density memory devices [31,32].

Nowadays, magnetism without d-block and f-block magnetic elements has been theoretically and experimentally explored within the semiconductors or insulators doped with nonmagnetic elements. Especially, the first-row light non-metallic 2p elements as dopants can produce spin polarization for many nonmagnetic materials. For possible chloride spintronics, it is expected that designing DMSs based on NaCl ionic crystal may be an effective supplement, effectively complementing and strengthening existing studies on magnetic tunnel junction based on NaCl. Despite the possible potential of diluted magnetic chlorides for spintronics, to our knowledge, 2p elements-doping NaCl have rare been investigated so far. Thus, it is meaningful to study that whether these impurities could change the electronic properties and modify the insulating characteristic in NaCl. In this work, we systematically studied the magnetic properties and electronic structures of four light non-metallic elements-doped NaCl bulk and (001) surface by means of ab initio calculations.

2. Computational methods

The first-principles calculation was performed by using the CASTEP module of Materials Studio 5.5 [33–36]. The Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation (GGA) was selected for the exchange-correlation potential [37,38]. Nevertheless, the GGA-PBE approximation is known often to be inadequate to account for the electronic structures and magnetic properties. In particular the energy gap values of semiconductors are predicted to be much smaller than the experimental values. As a result, the location of the defect levels formed in DMS cannot be located correctly relative to the energy gap. This leads to wrong conclusions for underlying physics of the estimated magnetic properties. In the present work, simple GGA-PBE approach would demonstrate the delocalization of the wave function of 2p-electrons among several of C, N, and O sites. To correct this failure affected by the intrinsic lack of accuracy, the improved calculations were carried out by adding the onsite Coulomb repulsion to enhance the electronic correlation and correct the spin polarization of the magnetic ions. Here, we adopted the GGA + U_{eff} scheme for the calculations of refined electronic structures and magnetic properties. The effective Hubbard parameter $U_{eff} = U – J$ (Hubbard U and Hund exchange J) were applied to the 2p states of the C, N, and O elements to account for the onsite Coulomb repulsion. Here, the applied U_{eff} of 2p orbitals of the C, N, and O atoms was set to 3.4 eV (U = 4.6 eV and J = 1.2 eV) [39–41].

The force on each atom is converged to be less than 0.01 eV Å^{-1} and the stress component is less than 0.02 GPa after the optimization. A Monkhorst–Pack k-point mesh of $2 \times 2 \times 2$ and $2 \times 2 \times 1$

were used for the bulk and surface calculations, respectively [42]. The cutoff energies of 370 eV and 410 eV were set for computing all properties of B/C- and N/O-doped bulks and surfaces, respectively. The atomic configurations under considerations of the corresponding isolated atoms were $2s^2 2p^6 3s^1$ for Na, $3s^2 3p^5$ for Cl, $2s^2 2p^1$ for B, $2s^2 2p^2$ for C, $2s^2 2p^3$ for N, and $2s^2 2p^4$ for O, respectively. The optimized lattice parameter for pure NaCl was 5.696 Å, which agree well with that experimental result of 5.640 Å [43], indicating that our methodology is reasonable. The calculated electronic band gap of 5.23 eV is larger than previous theoretical value of 4.55 eV, whereas is still underestimated compared with experimental value of 8.6 eV [15].

3. Results and discussion

To start our theoretical assessments, we built up a $2 \times 2 \times 2$ supercell consisting of 64 atoms. One impurity X (B, C, N, and O) atom was placed in one Cl atom substitutional sites in the supercell, corresponding to the doping concentration of 3.125%. For the $Na_{32}XCl_{31}$, the optimized bond lengths after sufficient geometrical relaxation are summarized in Table 1. The value of optimized C—Na, N—Na, and O—Na bond lengths are shorter than that of optimized Cl—Na bond length of 2.848 Å. The foreign atoms move towards the surrounding Na, which lead to slightly suppressed local structural environments. However, despite the smaller radius of B (82 pm) than Cl (99 pm), the optimal B—Na bond length is longer than that of Cl—Na bond length, suggesting that B-doping weakens the ionic bonds and consequently pushes the neighboring cations around the boron, expanding the local structural environments. Owning to the much smaller electronegativity of B (2.04) compared with that of Cl (3.16), the electrostatic interaction between the Na and the B atoms is much weaker than that between the Na and the Cl atoms.

To learn the stability and the feasibility, the defect formation energy E_{form} was calculated according to the following equations [44–46],

$$E_{form} = E(\text{doped}) - E(\text{pure}) + (\mu_{Cl} - \mu_X) + q(E_F + \varepsilon_{VBM} + \Delta v) \quad (1)$$

where E (doped) is the total energy of the defect NaCl, E (pure) is the total energy of the pure NaCl, μ_{Cl} is the chemical potential for Cl atom, μ_X is the chemical potential for the X atom, E_F is the Fermi energy level with respect to valence band maximum (VBM) in the NaCl bulk, and ε_{VBM} is the energy position of VBM. The correction term Δv is used to align the reference electrostatic potential between the supercell containing the charged defect and the pure supercell without defect. This potential shift is determined by comparing the 1s core level energy of a Cl atom which is located farthest from the defect in the supercell model. The bulk α-B_{12}, graphite, N_2, O_2, and Cl_2 dimmer were used to calculate the chemical potentials for boron, carbon, nitrogen, oxygen, and chlorine, respectively. Here, the chemical potential of the Cl atom depends on the experimental growth condition. Under the Cl-rich condition, μ_{Cl} approaches the value directly achieved from isolated Cl_2 dimmer with gas state. And under the Na-rich condition, the value of μ_{Na} is computed from body-centered cubic Na bulk with solid state. And the values of μ_{Na} and μ_{Cl} are related through the identical equation of $\mu_{Na} + \mu_{Cl} = \mu_{NaCl}^{bulk}$. Here, μ_{NaCl}^{bulk} is the chemical potential of one formula unit of NaCl crystal. As shown in Table 1, the calculated defect formation energies under Na-rich condition are less than that under Cl-rich conditions, suggesting that these anion-site doping are energetically more favorable under Na-rich condition. Under cation-rich condition, the dopants get more opportunities to bind with the cations. Under anion-rich condition, due to the huge competition, the dopants get fewer opportunities to bind with the cations. It is found that E_{form} decreases as the electronegativity of the impurity