Journal of Magnetism and Magnetic Materials 352 (2014) 61–65

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Ferromagnetic half-metallic characteristic and phase transition in rare-earth Yb doped SiC: A GGA+U study

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ARTICLE INFO

Article history:
Received 9 January 2012
Received in revised form
5 July 2012
Available online 18 October 2013

Keywords:
Half-metallic
Diluted magnetic semiconductor
Magnetic phase transition
GGA+U

ABSTRACT

The electronic, magnetic and structural properties of rare earth Yb doped on SiC are investigated theoretically based on the density functional theory (DFT). Both zincblende (ZB) and rocksalt (RS) structures of SiC have been calculated. We found that Si_3YbC_4 with ZB exhibits a complete half-metallic characteristic with a wide gap more than 1.8 eV using GGA and GGA+U methods. However, the half-metallicity is destroyed with RS. The sensitivity of magnetic moments of Si_3YbC_4 as a function of pressure is also discussed, there are two magnetic phase transition points with increased pressure. The exchange interaction between local Yb-4f electrons and conduction electrons plays an important role in their heavy fermion characters. The exchange splitting of the conduction band is confirmed to be much larger than that of the valence band in Si_3YbC_4, which makes the holes-mediated ferromagnetism in this material.

1. Introduction

Spintronics, as potential materials for second-generation electronics, focused on the transmission of charge and spin of electrons. It has more extensive application prospects than microelectronics as the first-generation electronics that only studies charges of electrons [1]. In recent years, there has been increasing interest in the spintronic materials, especially the half-metallic ferromagnets (HMFs) which has a 100% spin-polarization at the Fermi level. The concept of a HMF was introduced by de Groot et al. [2]. HMFs possibly have a higher magnetoresistance effect than ordinary magnetic materials due to their much higher spin-polarization at the Fermi level. On account of these advantages, HMFs have attracted much more attention and become one of the hottest topics in the past years. Especially dilute magnetic semiconductors (DMSs), such as Cu-doped GdN, V-doped ZnSe, and Mn-doped CdTe [3–5], which have a few fractions of host elements, are usually replaced by transition-metal (TM) ions. Some groups also have reported the intrinsic nonmagnetic elements, such as Mg, Ca, C and N [6–9], as dopants can order ferromagnetism (FM) in some semiconductors hosts. However, there is few theoretical work on FM order realized in the rare-earth-doping compound. Among all HMFs compounds, the rare earth (RE) containing semiconductors have a special role, which is a class of compounds with a large structural variety [10] and different interesting properties such as heavy-fermion systems [11], heavy electron behavior, half-metallic behavior in some Ce compounds [12], mixed-valent behavior in Eu, Yb and Ce compounds [13–15] and superconductivity [16,17]. Some groups reported that the rare-earth elements, such as Yb [18], are treated as dopants favoring spin polarization and ferromagnetic coupling in semiconductors recently. An accurate description of the electronic structure of the RE doped compound is a very challenging problem because of their partially filled 4f shells [19], which leads to the magnetic behavior and the magnetic moments of the rare-earth containing semiconductor. These localized 4f electrons are responsible for many of the interesting properties in these compounds.

SiC is the only IV–IV compound that forms stable long-ordered structures [20]. The technological interest in SiC is driven by its outstanding mechanical and electronic properties, which makes it possible for electronic and optical device applications [21]. In some previous work, first-principles and experiments predict that SiC has many polytypes like 4H, 6H, zincblende (ZB), and rocksalt (RS) [22]. The phase transition from ZB to RS is very common for SiC under high pressure [23]. However, the possible phase transitions in SiC doped systems are still scarce. Meanwhile, the density functional theory (DFT) has predicted the ferromagnetism in the tetrahedrally coordinated semiconductor SiC doped with heavier elements [24,25], and also demonstrates that many TM or intrinsic nonmagnetic elements-doping SiC exhibit a complete half-metallic characteristic with a wide gap [26,27]. Thus, SiC doped systems are preferred to other III–V and II–VI based HMFs. However, there are a few works that focus on the RE-doped SiC system.

The aim of the present work is to investigate the magnetic, electronic and structural properties of SiC in zincblende and rocksalt structures with the simultaneous presence of a low concentration of rare earth atoms such as Yb. In order to achieve the realistic dopant concentration, we used a periodic supercell Si_3YbC_4 by substituting a Si atom with a Yb atom, which resulting in each rare-earth atom connects with four adjacent C atoms and

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http://dx.doi.org/10.1016/j.jmmm.2013.10.016

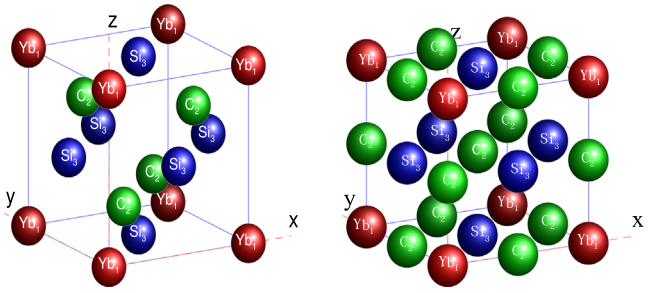

Fig. 1. Crystal structure of Si_3YbC_4, the Yb atoms at (0,0,0) in both phases. (a) is the zincblende and (b) is the rocksalt structure.

three second nearest neighboring Si atoms in both ZB and RS supercells, then the rare-earth dopant concentration is 12.5%. The bulk modulus and its pressure derivative have been fitted using the Murnaghan [28] form of the equation of states. At the constant optimal Si^{4+} doping level, substitution of Yb^{2+} ions with larger-sized rare-earth ions would decrease the tolerance factor, and result in the suppression of double-exchange interaction and the increase in the magnetoresistance ratio [29,30]. However, the substitution would not only induce the lattice distortion but also introduce extra magnetic coupling, due to the magnetic moments of rare earth ions. Our results indicate that Yb-doped SiC is a very interesting functional material which might be widely used in spintronic in future.

2. Computational methods

The electronic structure and magnetic calculations were performed in the framework of density functional theory [31]. The calculations were done using the full-potential local-orbital minimum-basis band structure scheme (FPLO) [32]. Exchange–correlation potential was treated using generalized gradient approximation (GGA) according to Perdew–Burke–Ernzerhof (PBE) [33] and the strong correlation effects were introduced by the DFT+U model developed by Dudarev et al. [34], in which an effective $U_{eff} = U - J$ incorporated the on-site Coulomb (U) and the exchange interaction (J). We used U=4.5, 5.5, 6.5, 7.5 for all 4f states in Yb atoms. The site-centered potentials and densities were expanded in spherical harmonic contributions up to $l_{max} = 12$. Accurate Brillouin zone integrations were performed using the standard special k point technique of the cubic method. We found that $10 \times 10 \times 10$ k points were sufficient in all cases. For self-consistent field iteration, the charge density was converged to 1×10^{-6}, which corresponded to a total energy convergence of 0.001 meV.

HMF calculations were executed by taking $1 \times 1 \times 1$ standard eight atoms per supercell of zincblende and rocksalt phase for Si_3YbC_4 with cubic symmetry. For zincblende, whose space group is $F\bar{4}3m$, substitution of one silicon at (0,0,0) of the supercell by one Yb-ion. For rocksalt, we also replaced the Yb atoms at the corner with Si. In this approach, we get a cubic structure of space group $Fm3m$. Both phases keep the other three Si and four C atoms untouched. The Yb-doped supercells are shown in Fig. 1.

To extract a value of the bulk modulus and optimize the equilibrium lattice constant from the calculated total energy data, the safest procedure is a three-parameter fit to the data using the Murnaghan equation of state (EOS). The optimization is essential in order to reveal the half-metallic ferromagnetism of doping systems.

3. Results and discussions

Total energy calculations are performed for binary host SiC from which the equilibrium lattice constants are calculated. $a_z = 4.34$ Å for zincblende and $a_r = 4.00$ Å for rocksalt. The calculated lattice constants are slightly underestimated as compared with experimental values, $a_z' = 4.36$ Å and $a_r' = 4.03$ Å [35]. Both atomic position and lattice size have strong effects on magnetic and electronic properties. So before doing the electronic and magnetic calculations, full atomic position and volume optimization were performed for Si_3YbC_4. In order to determine the total energy difference ΔE between AFM and FM states of the supercell, we double the standard supercell in one direction for taking $2 \times 1 \times 1$ supercell to distinguish Yb atoms, which have the same Wyckoff coordinates in space group $F\bar{4}3m$ and $Fm3m$, to configurate opposite initial spin magnetic both in ZB and RS phases. The total energy difference ΔE ($\Delta E = E_{AFM} - E_{FM}$) is established in Table 1. It is observed that FM states of ZB-Si_3YbC_4 are more stable than AFM, however, RS-Si_3YbC_4 exhibits nonmagnetic (NM). The relaxed lattice constants of Si_3YbC_4 with zincblende and rocksalt phase have been calculated and shown in Fig. 2, which is 4.68 Å and 4.33 Å for ZB and RS, respectively. It is clear that the ZB phase is more favorable than the RS phase. The calculated equilibrium lattice constant a, bulk modulus B, derivative of bulk modulus B' and total energy difference ΔE_{AFM-FM} per Yb atom are listed in Table 1.

As an indication of the stability of the Yb dopant, the formation energy (E_f) is estimated from

$$E_f = E(\mathrm{SiC:Yb}) - E(\mathrm{SiC}) + n[E(\mathrm{Yb}) - E(\mathrm{Si})] \quad (1)$$

where E(SiC:Yb) is the total energy of the supercell with n Si atoms replaced by Yb atoms and E(SiC) is the corresponding energy in the bulk structure. E(Yb) and E(Si) are energies of bulk Ytterbium and Silicon. The calculated formation energies for Si_3YbC_4 with zincblende and rocksalt are 1.3 eV and 0.35 eV, respectively.

So far, calculations are only based on the scalar relativistic formulation that means the influence of spin–orbit interaction is not taken into account. We also calculated the orbit magnetic moment by using a full relativistic approach in order to see the effects of spin–orbit coupling explicitly. It is expected from Table 1

Table 1
Optimized lattice constant a, bulk modulus B, derivative of bulk modulus B', ΔE_{AFM-FM} for Si_3YbC_4 and orbit magnetic moment M_l.

Structure	a (Å)	B (GPa)	B'	ΔE_{AFM-FM} (meV)	M_l (μ_B)
Zincblende	4.68	122.4	3.75	1.69	0.006
Rocksalt	4.36	222.1	3.09	–	0.012

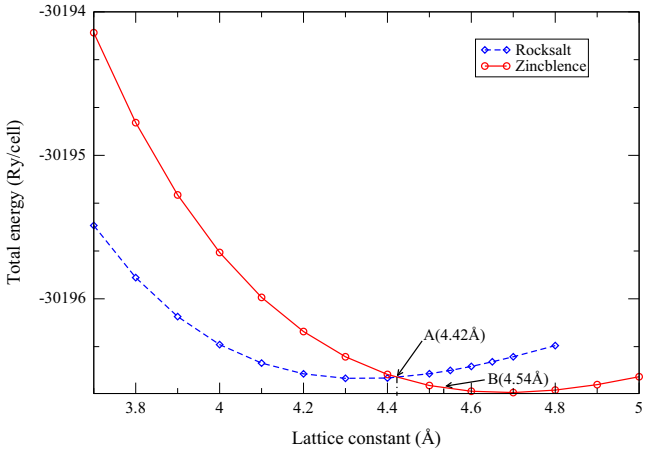

Fig. 2. The total energy versus unit lattice constants for Si_3YbC_4. Point A reveals the phase transition point and Point B reveals the magnetic transition point that integer magnetic moment to non-integer magnetic moment.