Computational Materials Science 142 (2018) 338–345

Contents lists available at ScienceDirect

Computational Materials Science

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

Room-temperature ferromagnetism in alkaline-earth-metal doped AlP: First-principle calculations

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ARTICLE INFO

Article history:
Received 4 June 2017
Received in revised form 8 October 2017
Accepted 23 October 2017

Keywords:
Room-temperature ferromagnetism
Alkaline-earth-metal doped
Half-metallic
AlP

ABSTRACT

Substituting alkaline-metal (AM) or alkaline-earth-metal (AEM) atom for IIIA cations in III-V semiconductor is a very common method for modulating the physical properties of host compound. Herein, we investigated the electronic and magnetic properties of AEM doped AlP using first-principle calculations. Our calculation results indicate that the Ca, Sr, and Ba doped AlP exhibit intriguing half-metal feature as well as room-temperature ferromagnetism. Moreover, the ferromagnetism in AEM doped AlP is long-ranged, which is attributed to the hole-mediated double exchange through the p-p interaction. Further, the Ca, Sr, and Ba doped AlP are possibly fabricated under P-rich condition. Therefore, we suggest that the AEM doped AlP compounds are very promising material for novel spintronic devices.

1. Introduction

During past twenty years, dilute magnetic semiconductors (DMSs) have been paid for extensive attentions because of their massive potential in spintronic devices [1–3]. By utilizing charge and spin degree of freedom of electron, DMSs are very promising material for spintronic devices, such as spin valves [4], spin light emitting diodes [5], magnetic sensors [6], and anomalous Hall organic lattice [7]. In most cases, DMSs are produced by doping magnetic transition-metal (TM) atoms into nonmagnetic semiconductors, but TM atoms would form clusters or secondary phases, which may be detrimental to applications [8,9]. On the other hand, alkaline-metal (AM), alkaline-earth-metal (AEM) and 2p light elements such as C, N and O can induce ferromagnetism in host according to previous experimental and theoretical studies [10–12]. In contrast to TM atoms, these atoms do not have partial filled 3d or 4f orbital electrons, so the induced ferromagnetism of DMSs is called as d^0 ferromagnetism [13].

The AE and AEM atoms are typical p-type dopants for III-V compounds. When group-III atoms are substituted by above atoms, holes will be generated into valence band. The holes induce the Stoner instability and produce d^0 ferromagnetism in III-V semiconductors. In Zhang et al.'s study, the holes access into valence band and provide d^0 ferromagnetism in InN when the In atoms are substituted with AEM atoms, such as Mg, Ca, Sr and Ba [14].

Similar to the crystal structure of InN, AlP is also crystallized in zinc-blende (ZB) phase with an indirect band gap of about 2.5 eV between the Γ and X points [15]. The AlP compound had been extensively used in electronics, optoelectronics and spintronics. Recent calculations have shown that the TM-doped AlP, such as Cr, Mn and V can exhibit room-temperature ferromagnetism with Curie temperature beyond 600 K [16–18]. On the other hand, Yang et al. [19] found that the C-doping doses not induce ferromagnetism into AlP. Later, Ca doped AlP, $Al_{1-x}Ca_xP$ compound ($x = 0.0313$, 0.0625), was calculated by Zhang [20]. His result shows that the total magnetic moment of $Al_{1-x}Ca_xP$ is 1.0 μB per supercell. The magnetic moments are attributes to the 3p state of four nearest-neighboring P atoms around Ca atom. But, according to his investigation, the spin polarized state of Ca-doped AlP is not enough stable at room-temperature since its polarized energy is smaller than the thermal fluctuation (<26 meV). Recently, d^0 ferromagnetism in alkaline metal (AE) doped AlP was reported by Zheng et al. [21]. The total magnetic moment of Na and K doped AlP are 2.0 μB per supercell. The magnetic moments are also contributed by the 3p orbital of four nearest-neighboring P atoms around the AE atom. But, the polarized state of Na-doped AlP is not stable energetically and the anti-ferromagnetic coupling dominates the collective magnetic behavior in K-doped AlP. These results demonstrate that Na- and K-doped AlPs are unlikely to be d^0 ferromagnetism DMSs for spintronic devices.

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https://doi.org/10.1016/j.commatsci.2017.10.041

In this work, we systematically investigated AlP supercell by doping with AEM elements using first-principle calculations. Our calculation results suggest that the doping of Ca, Sr, and Ba atoms can induce robust d^0 ferromagnetism in AlP supercell. Also, the AEM-doped AlPs are long-ranged ferromagnetic coupling with half-metal character. Further, the calculated Curie temperature of Ca, Sr and Ba doped AlP are all about 600 K. The AEM-doped AlP compounds with robust half-metal ferromagnetism and high Curie temperature are beneficial to application for spintronic devices.

2. Computational details

The first-principle calculations were performed by adopting the Density Functional Theory (DFT) methods implemented in the Vienna ab initio simulation package (VASP) [22]. The projector augmented wave (PAW) pseudopotentials were employed to describe the interactions between valence electrons and ionic cores [23]. A plane wave basis set with a cutoff energy of 500 eV was used to expand the wave functions. The Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was adopted to describe electron exchange and correlation [24]. A gamma centered $5 \times 5 \times 5$ k-point mesh was employed to sample the irreducible Brillouin zone [25]. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [26], which reduces the self-interaction error by incorporating a fraction of exact exchange, was also employed to study the electronic and magnetic properties for doped systems. Both lattice constants and atomic positions of doped system were fully optimized by using conjugate gradient algorithm until the maximum force on a single atom was less than 0.02 eV/Å.

3. Results and discussion

Our calculation results show the lattice constant of AlP is 5.507 Å and the bond length of Al-P is 2.384 Å. It is found that AlP is non-magnetic semiconductor with 2.13 eV and 1.65 eV band gap at HSE06 and PBE functional, respectively. Our results agree with the previous studies [27,28]. Fig. 1 shows the optimized crystal structure of AlP supercell with $2 \times 2 \times 2$ dimension, which contains 32 Al and 32 P atoms. This $2 \times 2 \times 2$ supercell is referred therein as $Al_{32}P_{32}$. The five positions of Al atoms (1, 2, 3, 4, and 5) and two positions of P atoms (j and k) are denoted in Fig. 1.

We investigated the alkaline-earth-metal (AEM) atom doped AlP at low doping concentration. The Al atom at site 1 is substituted by one AEM in $Al_{32}P_{32}$, which give us systems of $Al_{31}XP_{32}$ (X = Be, Mg, Ca, Sr and Ba). The doping concentration is 3.125%. The optimized lattice constants of $Al_{31}XP_{32}$ and the bond lengths of X-P are listed in Table 1. Compared with Al-P bond length, the X-P bond length increases by 0.12 Å, 0.32 Å, 0.44 Å and 0.55 Å for X = Mg, Ca, Sr and Ba, respectively. That's to say, four nearest-neighboring P atoms around these doped atom move away from the X atom in $Al_{31}XP_{32}$. This outward relaxing is induced by the Coulomb repulsion and the larger atomic radius of the doped X atom (1.60 Å for Mg, 1.97 Å for Ca, 2.15 Å for Sr and 2.17 Å for Ba) in contrast with the replaced Al atom (1.43 Å).

The spin polarized energy E_{pol} is the energy difference between the non-polarized and polarized state, defined as $E_{pol} = E_{non-polarized}$ - $E_{polarized}$. In Table 1, we found that the total energy of polarized states equal to that of the non-polarized states for X = Be and Mg. However, for X = Ca, Sr, and Ba, the polarized states are lower than the non-polarized state by 14 meV, 32 meV, and 32 meV, respectively. In particular, for $Al_{31}SrP_{32}$ and $Al_{31}BaP_{32}$, the spin polarized energies are higher than thermal fluctuation (26 meV), demonstrating that the spin polarized $Al_{31}SrP_{32}$ and $Al_{31}BaP_{32}$ are favorable at room-temperature condition.

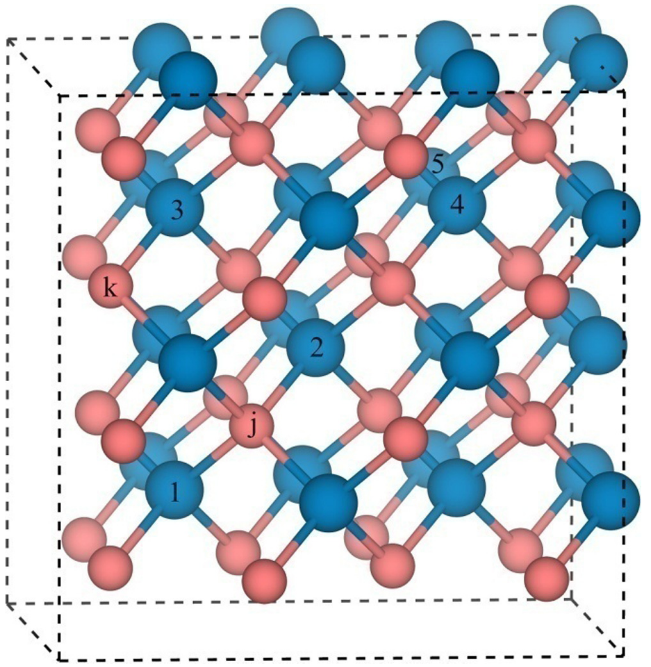

Fig. 1. The crystal structure of AlP supercell ($2 \times 2 \times 2$). The navy blue balls are Al atoms and the pink balls are P atoms. The positions of Al substituted by alkaline-earth-metal atom are denoted by 1, 2, 3, 4, and 5. The positions of P-defect are denoted by j and k. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
For $Al_{31}XP_{32}$ system, a (in Å) is optimized lattice constants, d (in Å) is bond length of X-P, E_{pol} (in meV) is spin polarized energy. M_T (in μB) is total magnetic moment. M_X (in μB) is the magnetic moment projected on X atom. M_{NN} and M_{2ND} are the averaged magnetic moment projected on nearest-neighbor P and second nearest-neighbor P respected to X. (X = Be, Mg, Ca, Sr and Ba).

	a	d	E_{pol}	M_T	M_X	M_{NN}	M_{2ND}
$Al_{31}BeP_{32}$	10.979	2.225	0.0	0.0	0.0	0.0	0.0
$Al_{31}MgP_{32}$	11.019	2.499	0.0	0.0	0.0	0.0	0.0
$Al_{31}CaP_{32}$	11.054	2.702	13.86	1.0	0.04	0.12	0.03
$Al_{31}SrP_{32}$	11.072	2.822	31.84	1.0	0.05	0.14	0.03
$Al_{31}BaP_{32}$	11.089	2.938	31.87	1.0	0.08	0.15	0.03

Since $Al_{31}BeP_{32}$ and $Al_{31}MgP_{32}$ are non-magnetic, we only focused on the results of $Al_{31}CaP_{32}$, $Al_{31}SrP_{32}$ and $Al_{31}BaP_{32}$ in the following studies. According to Table 1, the corresponding magnetic moments of $Al_{31}CaP_{32}$, $Al_{31}SrP_{32}$, and $Al_{31}BaP_{32}$ are 1.0 μB. By projecting the spin density onto atomic orbitals and integrating over the PAW sphere, we obtained the magnetic moment on a nearest-neighboring P atom are 0.12 μB, 0.14 μB, and 0.15 μB for X = Ca, Sr and Ba, respectively. The magnetic moment projected on the four nearest-neighboring P atoms is one order magnitude larger than that on the doped X atom and the farther P atoms. The magnetic moments projected on the doped X atoms are 0.04 μB, 0.05 μB, and 0.08 μB for X = Ca, Sr, and Ba, respectively. The magnetic moment projected on a second nearest-neighboring P atom is 0.03 μB per atom, as shown in Table 1.

Further, we plotted the spin density distribution of Sr-doped AlP at low doping concentration of 3.13% in Fig. 2(a). (The spin density distributions of Ca- and Ba-doped AlP are similar to that of Sr-doped AlP). We noted that the magnetic moments of Sr-doped AlP mainly focus on the four nearest-neighboring P atoms around the doped Sr atom. The magnetic moments projected on Sr atom and farther P atoms are not shown due to the smaller values of magnetic moments. In Fig. 2(b), two Al atoms