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Ab initio investigation of local magnetic structures around substitutional 3*d* transition metal impurities at cation sites in III–V and II–VI semiconductors

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ABSTRACT

The local magnetic structures around substitutional 3*d* transition metal impurities at cation sites in zinc blende structures of III–V (GaN, GaAs) and II–VI (ZnTe) semiconductors are investigated by using a spin-polarized density functional theory. We find that Cr-, Co-, Cu-doped GaN, Cr-, Mn-doped GaAs and Cr-, Fe-, Ni-doped ZnTe are half metallic with 100% spin polarization. The magnetic moments due to these 3*d* transition metal (TM) ions are delocalized quite significantly on the surrounding ions of host semiconductors. These doped TM ions have long range interactions mediated through the induced magnetic moments in anions and cations of host semiconductors. For low impurity concentrations Mn in GaAs also has zero magnetic moment state due to Jahn–Teller structural distortions. Based upon half metallic character and delocalization of magnetic moments in the anions and cations of host semiconductors these above mentioned 3*d* TM-doped GaN, GaAs and ZnTe seem to be good candidates for spintronic applications.

1. Introduction

The diluted magnetic semiconductors (DMSs), which have both ferromagnetic and semiconducting properties, are a unique type of promising materials for the fast emerging field of spintronics. The DMSs are created by doping the magnetic ions like Cr, Mn, Fe, Ni, or Co (having net spin) into a semiconducting host such as GaAs, GaN, ZnO and ZnTe [1–8]. The 3*d* TM-doped III–V (GaAs, GaN, etc.) and II–VI (ZnTe, ZnO, etc.) compound semiconductors have attracted a lot of attention as the promising DMSs for spintronic applications. While the conventional semiconductor devices use the *s* and *p* electrons and the conventional magnetic devices use *d* electrons to perform their functions, the DMS materials-based spintronic devices are proposed to use both *s* and *p* electrons of host semiconductors and *d* electrons of transition metal impurities to perform their semiconducting and magnetic functions [9,10].

DMSs have opened a way for the manipulation of spin degree of freedom of electrons through interaction between the local magnetic moments of doped magnetic ions and the spins of charge carriers in the host semiconductors. Thus, DMSs are key materials for spintronics which have been intended to manipulate both spin and charge of electrons. The ferromagnetism in DMSs due to interactions between local magnetic moments of doped magnetic ions and the spins of charge carriers in host semiconductors is known as carrier-induced ferromagnetism [9]. The interaction among the doped magnetic ions (mediated through holes or electrons) leads to ferromagnetic order at relatively low temperatures [11–13]. The pair exchange interactions exhibit a strong directional dependence and exponentially damped with increasing distance between doped magnetic atoms [14]. The room temperature magnetism in TM-doped GaN, ZnO and ZnTe semiconductors has also been reported in the literature [4,15–17]. However, the origin of observed ferromagnetism in DMSs is still a subject of debate. This is due to the fact that the dopants themselves are intrinsically magnetic. Thus, their precipitates or secondary phases may also contribute to the observed ferromagnetism in DMSs. Such precipitates as well as secondary phases have actually been observed in some DMSs [18–21].

For practical applications DMSs require long range interactions between TM impurities mediated by delocalized spin-polarized charge carriers of host semiconductors. Thus, along with ferromagnetism, the more important aspect in DMSs is to create delocalized spin-polarized charge carriers that are injected and manipulated in spintronic devices. TM impurities doped in DMSs showing localized magnetic character are not useful for practical applications. In the predicted GaN- and ZnTe-based room

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temperature DMSs the local magnetic character of doped TM impurities is not completely known. The knowledge of local spatial distributions and local magnetic structures around TM impurities is prerequisite to understand the delocalization of doped magnetic impurities and mechanism of magnetism in DMS materials. The GaAs-based DMSs have been studied quite extensively both theoretically and experimentally [9,22–24]. However, extensive study of GaN- and ZnTe-based DMSs is still lacking. Here, we investigated local structures around different substitutional 3*d* TM impurities doped at cation sites in zinc blende (ZB) structures of III–V (GaN, GaAs) and II–VI (ZnTe) semiconductors using spin-polarized density functional approach. The main focus of computational work presented in this paper is on the local atomic structures and local magnetic structures around 3*d* TM impurities doped at cation sites in ZB structures of GaN, GaAs and ZnTe semiconductors.

The linear spin density approximation (LSDA) gives usually incorrect occupation of the 3*d* TM impurity induced levels and misrepresent host conduction bands. However, generalized gradient approximation (GGA), which is a quite good correction to LSDA, gives quite reasonable results. GGA has been extensively used in the literature for the study of GaAs-, GaN- and ZnTe-based DMS materials [25–28]. Recently, a number of other corrections, like supercell size effect correction, band gap correction via LDA+U, nonlocal external potentials, and on-site Coulomb energy corrections for TM impurities in semiconductors are also being discussed in the literature [29–32]. However, our main focus in this manuscript is to understand the delocalization of magnetic moments of magnetic impurities in dilute magnetic semiconductors. The inclusion of these above mentioned corrections may improve the results quantitatively but the overall qualitative picture of delocalization of magnetic impurities will not change. LDA+U does not affect the coupling type (ferromagnetic or antiferromagnetic) between the vacancies, although it affect the magnitude of magnetic moments in the system [33]. Therefore, in this computational work we used generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) [34] to investigate the local structures around different substitutional 3*d* TM impurities doped at cation sites in ZB structures of III–V (GaN, GaAs) and II–VI (ZnTe) semiconductors.

2. Computational details

We employed spin-polarized density functional theory as implemented in Vienna ab initio simulation package (VASP) [35,36] to study the local magnetic structures around substitutional TM (V, Cr, Mn, Fe, Co, Ni and Cu) impurities doped at cation sites in ZB structures of GaN, ZnTe and GaAs semiconductors. The standard projector augmented wave (PAW) pseudopotentials [37,38] are used to describe the core electrons and valance electrons [s^2p^3 for N, d^4s^1 for V, d^5s^1 for Cr, d^6s^1 for Mn, d^7s^1 for Fe, d^8s^1 for Co, d^9s^1 for Ni, $d^{10}p^1$ for Cu, $d^{10}p^2$ for Zn, s^2p^1 for Ga, s^2p^3 for As and s^2p^4 for Te atoms]. The exchange-correlation energy of the electrons is treated within the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) [34]. An energy cutoff of 400 eV was used for the expansion of wave function into a plane wave basis set. For the Brillouin zone integration, we used $5\times5\times5$ Monkhorst–Pack grid of k-space. The atoms were relaxed until the change in forces on each atom upon ionic displacements is below 0.01 eV/Å. Reference calculations using our choice of pseudopotentials indeed give correct ground state structures for the bulk phases of TM and conventional semiconductors (ZB for GaAs and ZnTe, wurtzite for GaN). However, here we investigated local magnetic structures of substitutional TM impurities doped at cation sites only in ZB structures of GaN, ZnTe and GaAs semiconductors. The calculations on 3*d* TM-doped GaN-, ZnTe- and GaAs-based DMSs were performed by using 64 atom $2\times2\times2$ supercell. We consider $Ga_{32-x}(TM_x)N_{32}$ supercells with $x=1, 2$ and TM = V, Cr, Mn, Fe, Co, Ni, Cu for ZB GaN, and similarly for ZB ZnTe and GaAs. For $x=2$ the TM atoms are substituted for cations of host semiconductor at origin and center of supercell.

3. Results and discussion

The TM atom substituted for a cation site in III–V semiconductors contributes three electrons to the anion dangling bonds, while that substituted for a cation site in II–VI semiconductors contributes two electrons to the anion dangling bonds. The remaining d electrons are localized on the doped TM atom site and are responsible for its magnetic state. According to crystal field theory the tetrahedral crystal field of surrounding anions splits the five-fold degenerate d states of a free TM ion into high-lying t_{2g} (d_{xy}, d_{yz} and d_{zx}) and low-lying e_g (d_{z^2} and $d_{x^2-y^2}$) symmetry states [27]. The energies of e_g states are lower than t_{2g} states due to less Coulomb interactions. In Fig. 1 we showed schematically the t_{2g} and e_g states of TM ions doped in ZB structures of III–V and II–VI DMSs. The Jahn–Teller structural distortions for some TM impurities affect the splitting between t_{2g} and e_g states. This results into the change in electronic configuration of TM ions and consequently their magnetic states. The magnetic state of a doped TM ion is the result of competition between crystal field splitting energy (the energy difference between t_{2g} and e_g states) and mean spin pairing energy (the energy required to pair up electrons in the state) [27]. A critical distinguishing characteristic of a DMS is the presence of $sp-d$ interactions between s, p band carriers of host semiconductor and d electrons of doped TM ion [23]. The interactions between cation-substituted TM ion and host semiconductor lattice mainly depend upon the hybridization between d electrons of doped TM ion and p orbitals of host anions around TM ion [27,39]. If the dopant introduces partially occupied d-bands into the gap of a host semiconductor, then the ferromagnetic state is favored by energy gain from band broadening [40,41]. The strong hybridization between doped TM ion and its neighboring anions of the host semiconductor induces spin polarization with significant magnetization in its neighboring anions. Consequently, neighboring anions couple ferromagnetically or antiferromagnetically to the dopant. Other dopants in turn couple to the spin polarized anions in the same way for an energy gain and resulting into a ferromagnetic coupling between the dopants. We investigated magnetic coupling and local magnetic structures around 3*d* TM impurities doped at cation sites in ZB structures of III–V (GaN, GaAs) and II–VI (ZnTe) semiconductors using 64 atom $2\times2\times2$ supercells. The local atomic bond lengths and magnetic structures around different 3*d* TM impurities doped at cation sites in these DMSs are discussed in detail in the following.

3.1. GaN-based DMSs

GaN normally crystallize in the hexagonal (wurtzite) structure with a direct band gap of 3.4 eV [42]. The unique feature of wurtzite group III-nitrides, in comparison with conventional III–V semiconductors, is the existence of very strong electric fields inside the crystal structure. The interest in ZB nitrides is rapidly increasing due to various reasons such as: (1) the absence of electric fields in cubic (1 0 0) nitrides [43] and (2) the enhanced mobility of charge carriers [44]. The ZB GaN can be grown by epitaxial growth technique [45] and plasma-assisted molecular beam epitaxy [46]. Here we performed calculations on ZB