The computational materials design of (Ga, Cr)N: effects of co-doping on exchange interactions

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Abstract
We investigate the effect of O or Be co-doping on the exchange interaction between Cr spins in (Ga, Cr)N by means of first-principles calculations based on the density-functional theory. The ferromagnetic exchange interactions are reduced by doping Be around Cr. On the other hand, O doping reduces the ferromagnetic interaction remarkably only for the case of Cr–O–Cr complex formation. The enhancement of the ferromagnetic exchange interaction cannot be achieved by doping O or Be impurities. However, the O and Be impurities can help the clustering of Cr atoms due to the enhancement of the attractive interaction between Cr atoms.

1. Introduction

Diluted magnetic semiconductors (DMSs) are formed by doping magnetic impurities into non-magnetic semiconductors such as InAs, GaAs, and so on [1, 2]. They need to have high Curie temperature (T_c) for room-temperature operation of spintronics devices. It has been predicted that the use of wide band-gap semiconductors as the host material for DMSs leads to high T_c [3]. Furthermore, the stability of the ferromagnetic state of the wide band-gap semiconductor based DMSs has been investigated by means of *ab initio* calculation [4, 5], and several DMSs based on wide band-gap materials have shown ferromagnetic properties above room temperature in experiments [6–8]. On the other hand, magnetic circular dichroism (MCD) spectra of (Ga, Mn)N and also (Ga, Cr)N have shown paramagnetic behaviour [9, 10]. These magneto-optical studies have suggested that the origin of ferromagnetism of these DMSs is not intrinsic but unidentified ferromagnetic materials, clusters of magnetic impurities, and so on.

Recently, the calculated Curie temperature of the wide band-gap DMS, (Ga, Mn)N, has been found to be much lower than room temperature, since percolation of ferromagnetic coupling is difficult to achieve for small concentrations due to short-ranged interaction [11]. On the other hand, it has been suggested by Monte Carlo simulation that the spinodal decomposition in DMSs offers the possibility to have high T_c even if the magnetic exchange interaction is short-ranged [12]. The simulation of the spinodal decomposition has also been
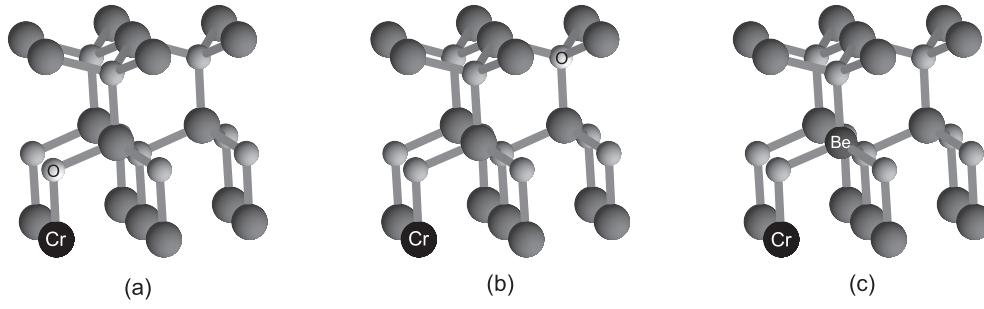
Figure 1. Typical location of an O or Be atom in (Ga, Cr)N; (a) an O atom is substituted for a N atom that is a nearest neighbour of a Cr atom, (b) an O atom is substituted for a N atom at a distance from a Cr atom, (c) a Be atom is substituted for a Ga atom around a Cr atom. The Cr, Be and O atoms are denoted by the symbol of each element and Ga and N atoms are represented by large and small spheres, respectively, without a symbol.

carried out under layer by layer crystal growth condition. Consequently, it has been proposed that the delta-doping method can be an effective approach to realize high T_c [13]. Indeed, (Ga, Mn)N/GaN digital ferromagnetic heterostructures have led to the enhancement of the saturation magnetic moment and a coercive field at low temperature in experiments [14]. The enhancement of magnetization has been achieved by doping O [15] or Be [16] into (Ga, Mn)N similar to in the study of the (Ga, Mn)N/GaN digital ferromagnetic heterostructures. In this paper, we investigate the effect of O or Be co-doping in (Ga, Cr)N on the exchange interaction between Cr spins by first-principles calculations based on the density-functional theory.

2. Method

We have carried out first-principles calculations by using the ultrasoft pseudo-potential method as implemented in the Vienna *ab initio* simulation package (VASP) [17], and have adopted a generalized gradient approximation (GGA) for the exchange correlation potential. We have used the cut-off energy of 36.75 Ryd for plane waves. The sampling of k-points in the Brillouin zone has been performed by using the Monkhorst–Pack scheme, including in total $5 \times 5 \times 5$ points with the Γ point. We consider wurtzite (Ga, Cr)N supercells including 32 atoms, where all atomic positions are optimized so as to minimize the total energy. The optimization is achieved once the energy difference for the relaxation process converges within 10^{-5} eV. The lattice constants of the supercell are fixed as $a = 3.249$ Å and $c = 5.282$ Å (the axial ratio $c/a = 1.626$), which are achieved theoretically for undoped GaN after the optimization. These values are larger by about 1.9% than the experimental values, $a = 3.189$ Å and $c = 5.185$ Å ($c/a = 1.626$) [18]. We assume that O and Be atoms are substituted for N and Ga atoms, respectively. Some typical cases on the arrangement of dopants are depicted in figures 1(a)–(c).

3. Results and discussion

3.1. Binding energy

The binding energy E_B between a Cr atom and a co-dopant X (= O or Be) is defined by

$$E_B[\text{Cr–X}] = E_f[\text{Cr}] + E_f[\text{X}] - E_f[\text{Cr; X}], \tag{1}$$

$$E_f[\text{Y}] = E_{\text{total}}[\text{GaN:Y}] - N_{\text{Ga}}\mu_{\text{Ga}} - N_{\text{N}}\mu_{\text{N}} - N_{\text{Y}}\mu_{\text{Y}}, \tag{2}$$

$$E_f[\text{Cr; X}] = E_{\text{total}}[\text{GaN:Cr, X}] - N_{\text{Ga}}\mu_{\text{Ga}} - N_{\text{N}}\mu_{\text{N}} - N_{\text{Cr}}\mu_{\text{Cr}} - N_{\text{X}}\mu_{\text{X}}, \tag{3}$$
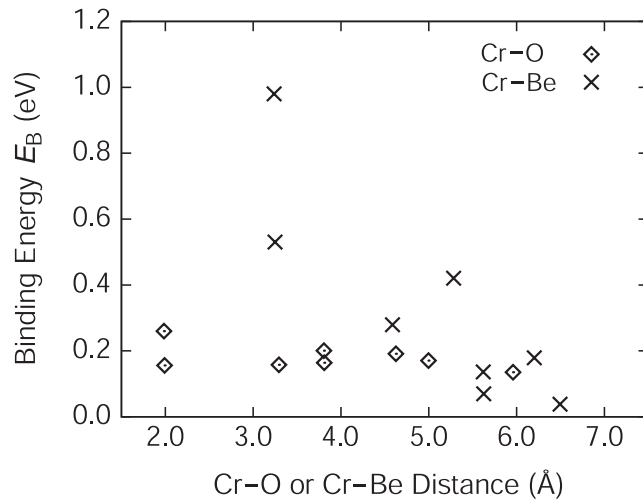
Figure 2. The binding energy E_B of Cr–O ($\diamond$) and Cr–Be ($\times$) as a function of their interatomic distance.

where $E_f[Y]$ (Y = Cr, O, and Be) represents the formation energy of an isolated impurity Y in GaN and $E_f[Cr; X]$ the formation energy of a Cr atom co-doped with a non-magnetic impurity X in GaN. Note that $E_B[Cr–X]$ and $E_f[Cr; X]$ depend on the interatomic distance between Cr and X. Here, $E_{total}[GaN:Y]$ is the total energy calculated for the supercell containing an impurity Y, and $E_{total}[GaN:Cr, X]$ that for the supercell containing a Cr atom and an X atom. We assume the neutral charge state for each impurity. The number of constituent atoms in the supercell is represented by N_Z (Z = Ga, N, Cr, O, Be). We assume Ga- and Cr-rich growth conditions, i.e. the chemical potentials are $\mu_{Ga} = \mu_{Ga[bulk]}$ and $\mu_{Cr} = \mu_{Cr[bulk]}$. The chemical potential μ_N is determined by the condition that the system is in equilibrium with bulk GaN: $\mu_{Ga} + \mu_N = \mu_{GaN[bulk]}$. The chemical potentials of O and Be are determined by the equilibrium condition with Ga_2O_3 [19] and Be_3N_2 [20], respectively.

Figure 2 shows the calculated binding energies $E_B[Cr–O]$ and $E_B[Cr–Be]$ as a function of their interatomic distance. The origin of E_B corresponds to the sum of formation energies of isolated Cr and O (or Be) atoms, i.e. $E_f[Cr] + E_f[O(or Be)]$. The binding energy E_B is positive for attractive coupling between Cr and O (or Be) atoms. In the case of O co-doping, the binding energies of Cr and O atoms are about 0.2 eV for every Cr–O distance, as shown in figure 2. This implies that O impurities can be substituted equally for any N site independent of the position of Cr atoms. On the other hand, the binding energies of Cr and Be atoms become remarkably larger when decreasing the Cr–Be distance, implying that doped Be impurities are easily bound around Cr atoms, as depicted in figure 1(c). Next, we investigate the effect of co-doping on interatomic interactions between Cr atoms, considering a supercell containing two Cr atoms together with an additional co-dopant. We assume that the doped O or Be atom occupies a near-neighbouring N or Ga site of one Cr atom in the supercell. Figure 3 shows the calculated binding energies as a function of the distance between Cr atoms. The binding energy between Cr atoms becomes larger by co-doping O for almost all the distances, namely the coupling between Cr atoms becomes more attractive due to the O impurity compared with that between Cr atoms without O. The Be doping enhances the attractive interaction between Cr atoms, similar to the O impurity.
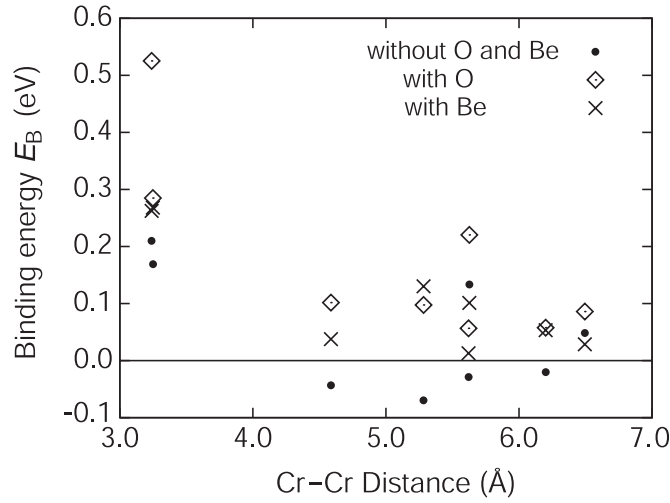
Figure 3. Binding energies of Cr atoms in (Ga, Cr)N with O or Be as a function of the distance between Cr atoms. Filled circles represent the binding energies of Cr atoms in (Ga, Cr)N without O and Be. Diamonds and crosses denote the binding energies of Cr atoms with O and with Be, respectively.

It has been suggested by Monte Carlo simulation that the effective interatomic interactions between Mn are attractive in (Ga, Mn)N and that they lead to the spinodal decomposition [12]. We found that the O and Be impurities could help the clustering of Cr atoms due to the enhancement of the attractive interaction between Cr atoms. Indeed, about a 10 nm cluster in (Ga, Cr)N has been confirmed experimentally [21].

3.2. Exchange interaction

The exchange coupling constants J_{ij} between Cr spins at the sites i and j have been estimated by mapping the total-energy difference $\Delta E (= E_{ap} - E_p)$ between parallel and anti-parallel spin alignments onto a simple Heisenberg model:

$$\Delta E = 2 \sum_{i>j} J_{ij} S_i S_j. \tag{4}$$

Here, we assume the quantum number of Cr spins as $S_i = S_j = 3/2$, i.e. the nominal valence of Cr to be $+3$. Figure 4 shows the exchange interaction J_{ij} between Cr spins as a function of the interatomic distance in (Ga, Cr)N. Note that the interaction is ferromagnetic for $J_{ij} > 0$, whereas it is antiferromagnetic for $J_{ij} < 0$.

Without O and Be impurities, the magnitude of J_{ij} decreases rapidly with the Cr–Cr distance and almost all of the interactions are ferromagnetic. The behaviour is characteristic for wide band-gap DMSs and is in agreement with the previous theoretical result [11]. The wave function of the impurity state in the gap is well localized due to the wide band-gap, leading to the strong and short-ranged exchange interaction. The magnitude of the ferromagnetic interaction between Cr spins is larger than that between Mn spins [22]. The interaction is reduced from 0.046 eV to 0.012 eV due to a Cr–O–Cr complex formation as indicated by the vertical arrow in figure 4. The magnetic moment per Cr atom is enhanced from 2.6 μ_B/Cr to 2.8 μ_B/Cr due to the formation of the Cr–O–Cr complex [23]. The enhancement is originated from the electron transfer from the O impurity to majority-spin Cr 3d orbitals.
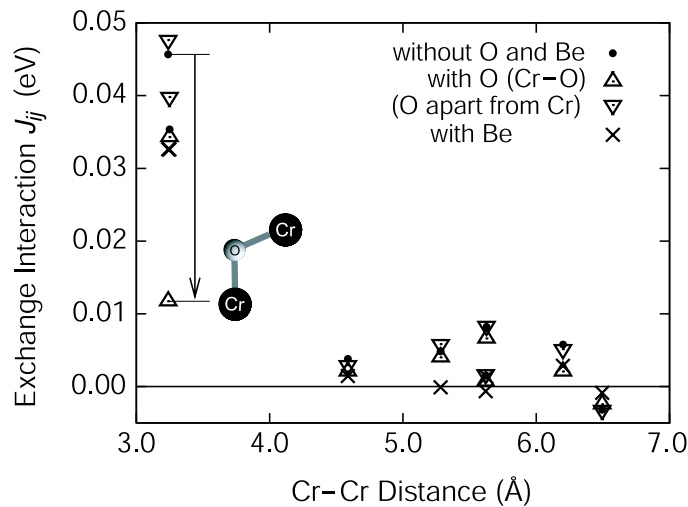
Figure 4. Exchange interaction between Cr spins as a function of the interatomic distance in (Ga, Cr)N. Filled circles represent the exchange interactions without O and Be impurities. Triangles denote that an O atom is substituted for a N atom that is a nearest neighbour of a Cr atom. Inverted triangles indicate that an O atom is separated from a Cr atom in (Ga, Cr)N. On the other hand, crosses indicate that a Be atom is substituted for Ga around a Cr atom. The inset shows a Cr–O–Cr complex.

(This figure is in colour only in the electronic version)

In the case that a N vacancy (V_N) is formed as an n-type dopant in (Ga, Cr)N [24], the Cr–V_N complex is energetically favorable to form, and it weakens the ferromagnetic interactions. Moreover, the interaction is reduced considerably by the formation of the Cr–V_N–Cr complex similar to the Cr–O–Cr complex. As for the Be doping, the ferromagnetic interactions are reduced by the Be dopant around Cr. Hence, it follows that the enhancement of the ferromagnetic exchange interaction cannot be achieved by doping O or Be impurities, contrary to the preceding prediction [25]. For increasing the Curie temperature of wide band-gap DMSs, it is necessary to create the region that contains magnetic ions densely in the sample by using appropriate methods such as delta-doping [13].

4. Summary

We have studied the effect of O or Be co-doping on the exchange interaction between Cr spins in (Ga, Cr)N by means of first-principles calculations based on the density-functional theory. In the case of O doping, the binding energies between Cr and O atoms are attractive and almost the same for every Cr–O distance. This means that O impurities can be substituted equally for any N site independent of the position of Cr atoms. The binding energy between Cr atoms becomes larger by co-doping O for almost all the distances, namely the coupling between Cr atoms becomes more attractive due to the O impurity compared with that between Cr atoms without O. The exchange interactions between Cr spins are not affected by the doping, except for the formation of the Cr–O–Cr complex. The magnitude of the ferromagnetic exchange interaction becomes smaller by 0.034 eV due to the Cr–O–Cr complex formation.

As regards Be doping, doped Be impurities are easily substituted for Ga in the vicinity of Cr atoms due to the attractive interaction between Cr and Be atoms, and enhance the attractive interaction between Cr atoms. The ferromagnetic interactions are reduced by the Be dopant

around Cr. In conclusion, the enhancement of the ferromagnetic exchange interaction cannot be achieved by doping O or Be impurities, contrary to the preceding prediction. However, doping of O or Be impurities could help the clustering of Cr atoms due to the enhancement of the attractive interaction between Cr atoms. It is expected to increase the Curie temperature of (Ga, Cr)N by cluster formation, although the magnetic interaction between Cr spins is short-ranged. The dynamics of Cr and other dopants migrating in GaN should be investigated in order to understand the process of cluster formation.

Acknowledgments

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