First-principles calculations of spin-polarized cation vacancies in wide-gap semiconductors

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Abstract

First-Principles Calculations of Spin-Polarized Cation Vacancies in Wide-gap Semiconductors

ワイドギャップ半導体中のスピン分極陽イオン空孔に関する第一原理計算

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Abstract

Vacancy-induced spin-polarization in wide-gap semiconductors has attracted scientific interest over the recent years. By using first-principles calculations, we systematically study the spin-polarized cation vacancies in wurtzite structures of wide-gap semiconductors, i.e, II-VI (Beo, ZnO, ZnS, and CdS) and III-V (BN, AlN, GaN, and GaP) semiconductors. A single vacancy is introduced in 128-atoms of supercell wurtzite structures and it is found that the most stable structures are spin-polarized C_{3v} symmetry. We find that the magnetic moment is 2 (3) μB in the cases of II-VI (III-V) semiconductors due to two (three) majority spin electrons occupying the defect E (E and A_1) levels. The spin densities are localized at the near four-anions sites and the semiconductors consist of first-row anions (oxygen and nitrogen) have substantial spin-polarization energies because the atomic radii of oxygen and nitrogen are small. We examine the opportunity of symmetry lowering distortions from C_{3v} to C_s symmetries and find that the pairing or depairing distortions occur. This effect leads to splits of E level and lowers the spin multiciply. We find that the effect of symmetry lowering is small and thus the spin polarized C_{3v} symmetry is the most stable state.

Introduction

1.1 Research background and motivation

Dilute magnetic semiconductors (DMS) materials have attracted scientific interest due to the multifunctionality. The integration of the two fundamental properties (magnetism and semiconducting) can be improved overall device performance. Hence, one primary goal in the research DMS materials is to develop magnetic semiconductor above room temperature.

DMS materials have two main classes: (1) impurity-DMS and (2) vacancy-DMS. In the case of impurity-DMS, the materials are doped with magnetic atoms that includes *d* or *f* atomic orbitals. In general, the impurity atoms are located on substitutional and/or intersitial sites of the semiconductor host [1-4]. DMS based on impurity of atoms are one of the promising candidate for the implementation in spintronics devices. However, these materials are found have below room temperature.

Recently, the most attention of vacancy-induced spin-polarization of DMS materials has been focused on wide-gaps semiconductors. The discovery vacancy-induced spin-polarization in thin film of HfO_2 have attracted attention. These materials are observed at high-temperature of magnetism (400 K) [5]. This phenomenon leads to the new technology of spin-polarization without localized *d* or *f* atomic orbitals. Spontaneous spin-polarization is also found in various undoped of wide-gap semiconductors, i.e, nitrides (GaN [13], AlN [11], BN [12]), oxides (MgO [10], ZnO [8,9], SnO_2 [7], TiO_2 [6]) and sulfides (ZnS [14] and CdS [13,15]). The experimental study was observed that the spin-polarizations are caused by intrinsic defect such as Ga vacancies in GaN case [13]. By spin-polarized positron annihilation spectroscopy (SP-PAS) [20], spin-polarization occurs at 300 K in GaN film due to Ga vacancies and vanish at low-temperature (30 K). In the case of phosphide, it leads to spin S=3/2 at 20 K[16]. This spontaneous spin-polarization indicates that this effect appears at room temperature. Therefore, study the mechanism of spontaneous spin-polarization in III-V semiconductors is necessary.

In oxides semiconductors, the spontaneous spin-polarization is also observed in oxides (ZnO). Zn vacancies are suggested to induce the magnetism in bulk [19]. The magnetism increases in high-temperature and decreases when reach 100 K. It is indicated that the Curie temperature is higher than room temperature. The unpaired atoms near vacancies are proposed to induce spontaneous spin-polarization. These vacancies formations are also detected by using electron microscopy, X-ray absorption spectroscopy and positron annihilation spectroscopy [17-20]. Hence, it is required to study vacancy-induced spin-polarization in II-VI semiconductors.

Theoretical study based on density functional theory (DFT) has been increased to study the mechanism of vacancy-induced spin-poalrization in semiconductors [21-26]. The DFT study is clarified that atomic spin-polarization is strong and localized in the first-row anions like N or O. The spin-polarization was observed in bulk CaO due to the strong interactions in oxygen-oxygen near vacancies [26]. It is theoretically predicted that isolated cation vacancies induce the formation of the high-spin state as the ground state in TiO_2 and HfO_2 [5,6]. These vacancies form *sp*-hybridized electronic state and hence the spin-polarization leads to d^0 systems. Therefore, it is important to study the mechanism of vacancy-induced spin-polarization in wide-gap (II-VI and III-V) semiconductors.

1.2 Research objectives

Theoretical study based on DFT calculations are reliable to study the mechanism of spin-polarized in cation vacancy of semiconductors. It has been recognized that the atoms near vacancies lead to robust spin-polarization inducing the formation of high-spin states. In this paper, we sytematically study the spin-polarized cation vacancies in wige-gap of wurzite structure semiconductors, i.e, BeO, ZnO, ZnS, CdS, BN, AlN, GaN, and GaP. The first goal is to understand the spin-polarization mechanism by investigating the stable structures and the ground state. We choose various semiconductors because our purpose is to study the chemical trend for the anions. We find that the spin density is localized at the four near vacancies and the first-row anions (oxygen and nitrogen) lead to large spin-polarization. Two (three) majority spin electrons occupy the defect E (E and A_1) levels inducing the magnetic moment become 2 μB (3 μB).

We next examine the possibility of the occurence of symmetry lowering which reduces the spin multiplicity. This effect decreasing the symmetry from C_{3v} to C_s symmtery and two types of symmetry lowering occurs (pairing and depairing distortions). We find that the energy gain induced by the symmetry lowering is small. Hence, the most stable structure is spin-polarized C_{3v} state.

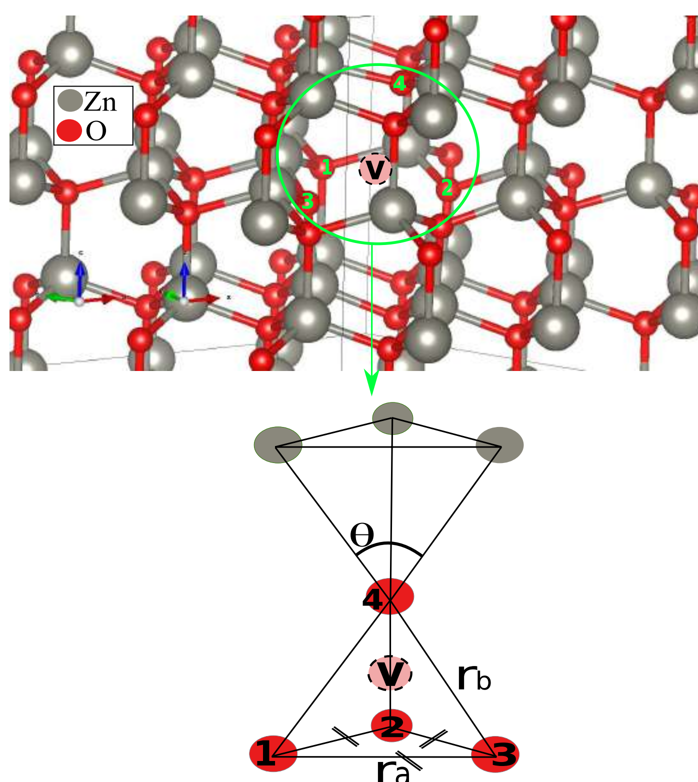

Figure 1. Atomic structure of a single cation vacancy in the 128-atoms of wurtzite supercell (upper part). The atomic distance of anion-anion near vacancies, r_a and r_b, and bond angle, θ, are defined and these value are Tabulated in Table I (down part).

2. Computational method

By using PHASE/0 code [28], we carry out first-principles calculations based on spin-polarized density functional theory (DFT). We use general gradient approximation [27] and ultrasoft preudopotential. The optimization geomerties are under the condition that the atomic force are less than than 5×10^{-3} eV $Å^{-1}$. We optimize lattice constant for pristine wurtzite of BN, AlN, GaN, GaP, BeO, ZnO, ZnS, and CdS (Table I). We introduce a single cation vacancy in 128-atoms of wurtzite supercell and run with 3×3×3 of *k*-points mesh (Figure 1.). We evaluate the stability of geometry with increasing of *k*-points mesh until 7×7×7 and find that the bond angles and bond lengths are well convergence. The wavefunctions are analyzed at Γ point of first Brillouin zone and are identified by analyzing the irreducible representation of defect levels [29,30].

Table 1. Lattice constants of wurtzite structures.

Systems	a(Å)	c(Å)
BN	2.559	4.239
AlN	3.145	5.029
GaN	3.144	5.119
GaP	3.842	6.335
BeO	2.718	4.389
ZnO	3.305	5.285
ZnS	3.909	6.349
CdS	4.332	6.745

3. Result and Discussions

3.1 Cation vacancy in II-VI semiconductors

We first study cation vacancy in II-VI (oxide and sulfide) semiconductors. We find that the stable structures are spin-polarized C_{3v} symmetries. We find that two majority spin electrons occupy the defect E level and thus the magnetic moment is found to be 2 μB; the defect A_1 level is occupied by majority and minority spin electrons. In the BeO case, the occupy minority spin electrons of defect A_1 level is located below the Fermi level (Fig. 1a). In above Fermi level, the defect E level is unoccupied of the minority spin electrons. The magnetic moment is 2.00 μB due to two majority spin electrons occupy the defect E level. The calculate magnetic moment in ZnO is 1.71 μB and the origin of the non-interger value due to finite dispersion of the defect E an A_1 levels (Fig. 1b). We expect that the defect level become narrow when use large supercell. Non-interger value of mangetic moment were also obtained in previous studies [31-35].

We find the atomic distances (r_a and r_b) are larger than the ideal crystals in the BeO and ZnO cases. This is due to the outward relaxation of the atoms near vacancies. The calculate of atomic distances, r_a and r_b, are 10.3% and 10.1% (11.2% and 10.1%) for ZnO (BeO), as Table II shows. The bond angles of four atoms near vacancies become larger than sp^3 bond angle. We find that the spin densities are localized at the oxygen-oxygen atoms near vacancies in the case of oxides.

Because the bond angles are larger than the sp^3 bond, the spin densities mainly consist of the oxygen *p*-orbitals and small *s*-component (Fig. 2a). The small *s*-component is observed in defect E level of the minority spin electrons as in the PDOS (Fig 1a and 1b). In the case of sulfides (ZnS and CdS), the bond angles near vacancies are found to be close to sp^3 bond angle and the outward relaxation is small (Tabel II). The r_a and r_b are 1.1% and 1.0% (5.3% and 2.3%) larger than the ideal crystal of ZnS (CdS). We find that the spin densities are localized at four sulfur near vacancies contain more *s*-components than that in the case of oxides (Fig. 1a and 1b). The *s*-component is large at the defect E level of minority spin electrons. This is originated from the fact that the bond angle is closed to sp^3 bond and the *s*-component become large. We evaluate the spin-polarization energies and find that this energy is found to be larger in the case of oxides; the very small spin-polarization energy is found in ZnS and CdS. We expect that the large spin-polarization energies is due to the fact that the atomic radii of oxygen is smaller than that in the sulfur [33,34]. We conclude that spin-polarized state are the most stable in nitrides and oxides case. This conditions are consistent with the experimental results that high-temperature ferromagnetism are found in cation vacancy of oxides and nitrides [8,9,13,20,21].

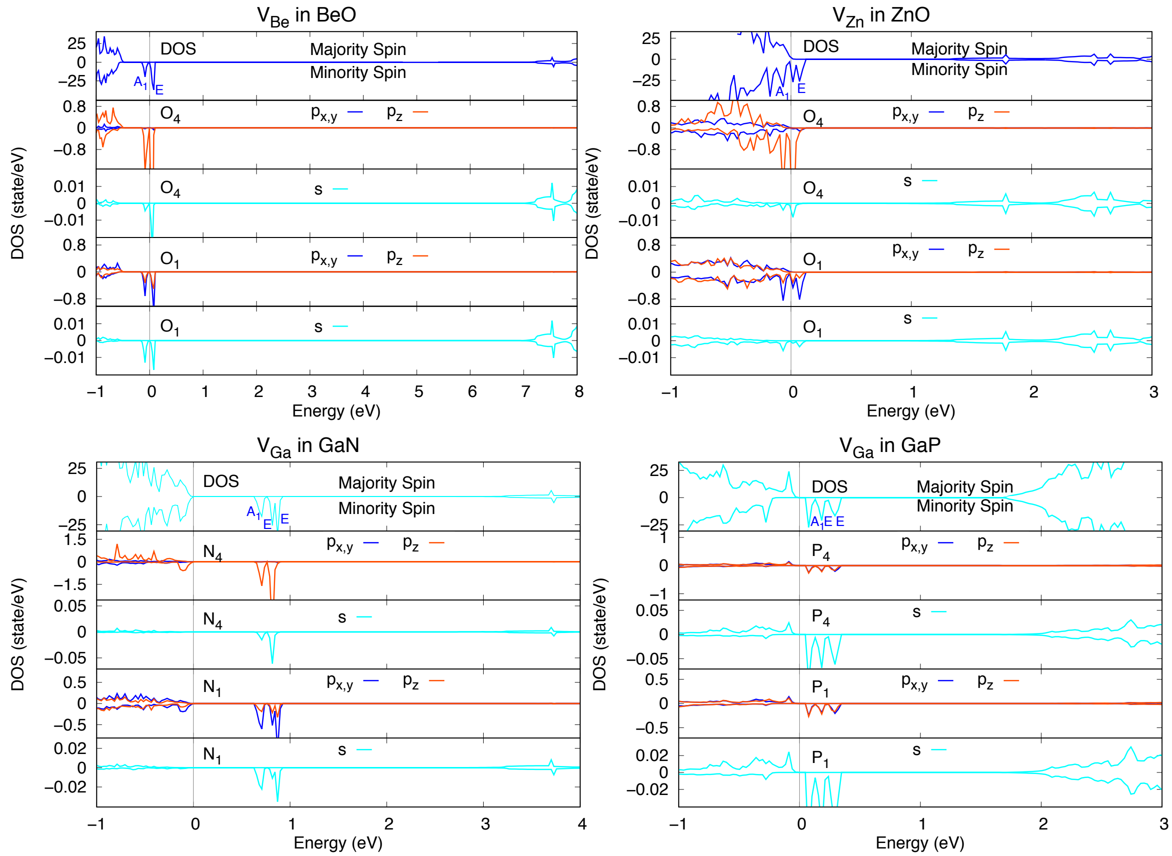

Figure 1. Density of state (DOS) and Partial DOS (PDOS) of cation vacancy in (a) BeO, (b) ZnO (c) GaN, and (d) GaP.

3.2 Cation vacancy in III-V semiconductors

We next study the cation vacancies in nitride (BN, AlN, and GaN). We find that the spin-polarized C_{3v} is the most stable structures. The magnetic moments are found to be 3 μB because three majority (minority) spin electrons are occupied (unoccupied) in the defect E and A_1 levels. The outward relaxation occurs at the four nitrogen near vacancies. As result, the atomic distance between nitrogen-nitrogen r_a (r_b) is found to be 9.4% (9.2%), 11.6% (11.1%), and 9.2% (9.4%) larger than than that the ideal crystal of BN, AlN, and GaN, respectively (Table II). The large outward relaxation of anions near vacancies cause the bond angles are close to the sp^2 bond angle. We find the localized spin densities at the four nitrogen near vacancies and these spin densities mainly consist of *p*-orbitals and small *s*-component (Fig. 2c). This is due to large *p*-orbitals and small *s*-components detect in defect E and A_1 levels, as seen in PDOS (Fig. 1c). The small *s*-component because the bond angle are large than that sp^3 bond angle.

Table II. Optimized geometries of a single cation vacancy in wide-gap semiconductors. The bond angles and the atomic distances are defined θ and r_a and r_b. The spin polarization energy ΔE_p (eV) and the moment magnetic m (μB) are also presented.

Systems	θ	$\bar{\theta}$	r_a (Å)	r_b (Å)	ΔE_p (eV)	m (μB)
V_{Be} in BeO	115.2	116.6	3.022	2.971	0.35	2.00
V_{Zn} in ZnO	116.0	116.7	3.647	3.588	0.04	1.71
V_{Zn} in ZnS	109.5	110.5	3.944	3.890	< 0.01	1.66
V_{Cd} in CdS	112.4	113.1	4.560	4.293	< 0.01	1.95
V_B in BN	114.1	114.1	2.798	2.822	0.19	3.00
V_{Al} in AlN	116.1	117.4	3.509	3.444	0.83	3.00
V_{Ga} in GaN	115.0	115.0	3.434	3.431	0.48	3.00
V_{Ga} in GaP	107.6	10.74	3.595	3.653	< 0.01	3.00

We mention that the GaP forms zinc blende [16] and wurtzite structure achieve in the nanowires [36]. Since our focus study is the chemical trends of anions, we observe GaP bulk. In fact, the phosphide has stable geometry and magnetic moment as the same as nitrides. The defect E and A_1 levels occupy by three majority spin electrons. However, the outward relaxation is small and thus the bond angle is close to sp^3 bond angle (109.5°). We find that the spin density is mainly composed large *s*-component than *p*-orbitals and thus the defect E and A_1 levels contain more *s*-component (Figs. 1d and 2d). We study the spin-polarization energy and analyze that the energy is found to be larger in the case of nitrides. In contrast, spin-polarization energy is very small in the case of phosphide. Since the spin densities are localized at atoms near vacancies of nitrides and phosphide, the difference of spin-polarization energy is due to the fact that the atomic radii of nitrogen is smaller than that phosphorus. We conlude that the spin-polarized is the most stable state.

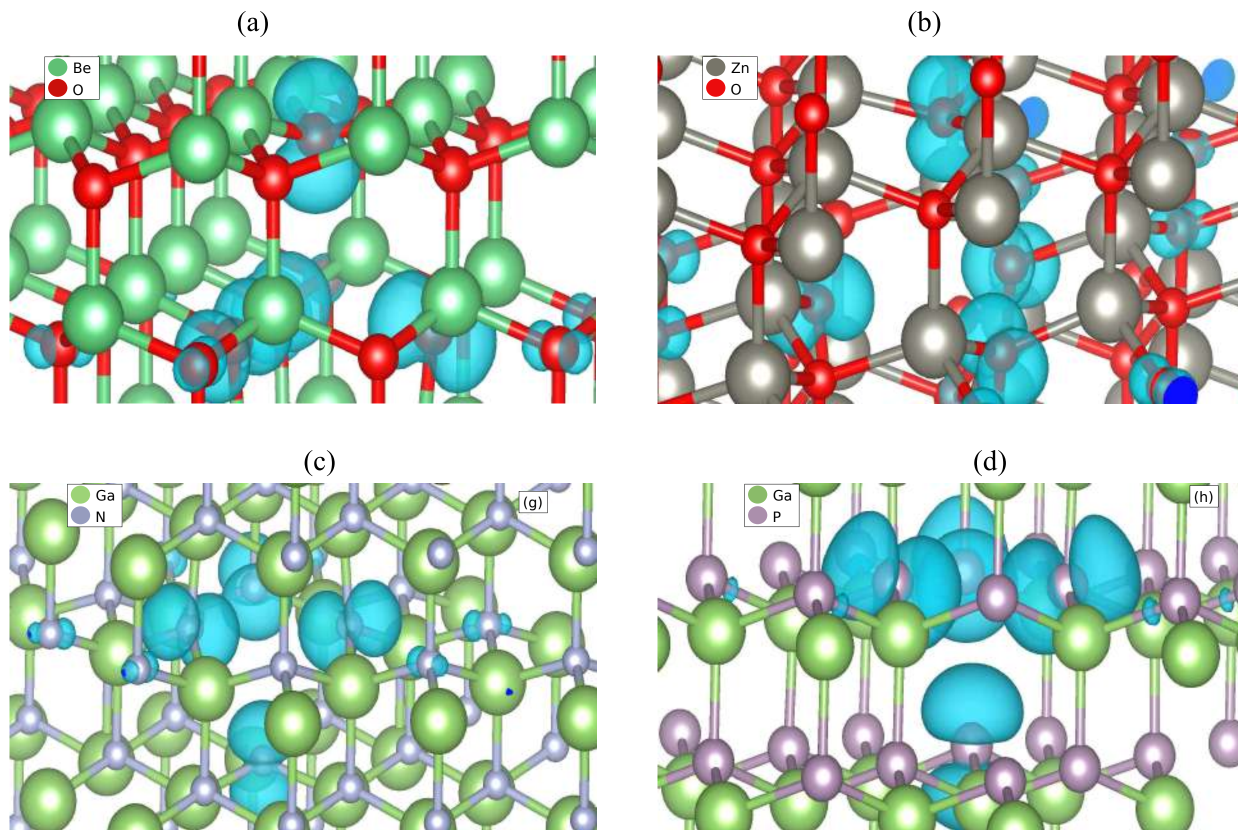

Figure 2. Spin densities: (a) V_{Be} in BeO (b) V_{Zn} in ZnO, (c) V_{Ga} in GaN, and (d) V_{Ga} in GaP. We set the isovalues to be 1×10^{-3} electron $Å^{-3}$ and set its with cyan colors.

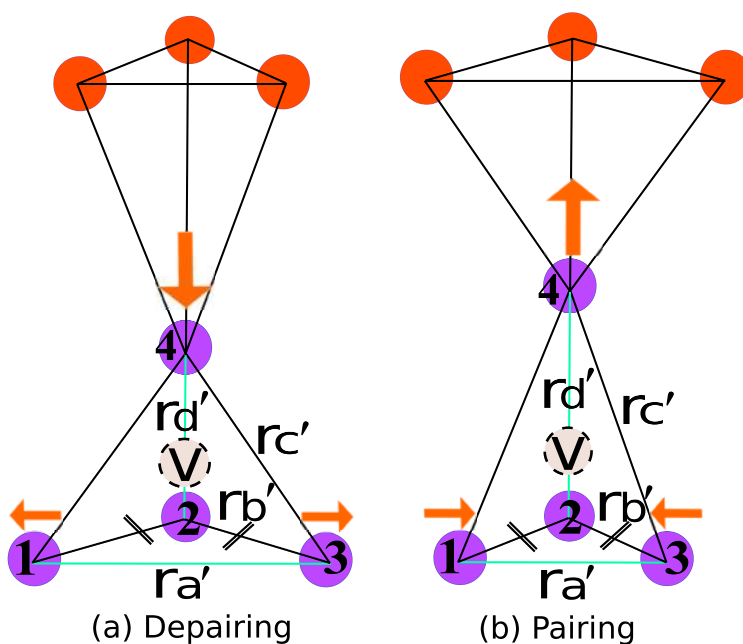

Figure 3. Two types of symmetry lowering effect: (a) depairing and (b) pairing distortions.

3.3 Lowering symmetry effect

We examine the possibility of the occurence of the lowering symmetry in II-VI and III-V semiconductors. We first study lowering symmetry in ZnO case. Since two majority spin electrons occupy the defect E levels, the spin state is triplet (S=1). The Jahn-Teller (JT) effect occurs and the symmetry become lower from C_{3v} to C_s and the E level splits become A'(ψ_1) and A"(ψ_2). This condition leads to decreasing magnetic moment and become spin singlet (S=0); two electrons occupy the lower level. We find that lowering symmetry in ZnO is pairing distortion case; the atomic distance between 1st and 3rd atoms become close (Fig. 3). We calculate the energy of symmetry lowering: by measuring the energy low spin (spin singlet) C_{3v} symmetry to the energy of low spin (spin singlet) C_s symmetry. We find that the JT energy in ZnO is small ($\Delta E_1 = 0.01$ eV). Therefore, the spin triplet state of the C_{3v} symmetry has 0.03 eV lower energy than the spin singlet C_s symmetry (As Table III shows, $\Delta E_2 = \Delta E_p - \Delta E_1 = 0.03$ eV). On the contrary, the lowering symmetry in BeO is depairing distortion case; the atomic distance between 1st and 3rd atoms become far. We calculate that the energy of symmetry lowering in BeO case is very small and thus the spin triplet state of the C_{3v} symmetry is the most stable.

Based on a simplified model, we here construct the wavefunctions to understand the mechanism of lowering symmetry. The wavefunctions consider by including the dangling bond orbitals, φ_i, of the four near anions (i=1-4) forming the tetrahedron; on the basal plane the three (i=1-3) anions dangling bond orbitals are located and 4th anion is located at the top of the tetrahedron (Fig. 3). The E representation in the C_{3v} symmetry belong the two wavefunctions: $\psi_1 = \frac{1}{\sqrt{6}}(2\varphi_2 - \varphi_1 - \varphi_3)$ and $\psi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3)$. Due to the lowering symmetry to C_s, ψ_1 and ψ_2 belong to A' and A", respectively (Since φ_4 belongs to A', it can be mixed with ψ_1 but the mixing is found to be very small as Fig. 4 shows). Since the lowering symmetry in ZnO case is pairing distortions, we find that the A' level is lower than the A" level because the small distance between 1st and 3rd atoms (Fig. 3).

On the other hand, the depairing distortion (Fig. 3) is found in the lowering symmetry of GaN (the symmetry lower from C_{3v} to C_s). As the result, the E level splits into A'(ψ_1) and A"(ψ_2) as in the case of ZnO and A_1 level become A' (ψ_3), as Fig. 4 shows. By analyzing of four-anion dangling model, we find that on the A_1 level the wavefunction is expressed as $\psi_3 = \frac{1}{\sqrt{3+\epsilon^2}}(\varphi_1 + \varphi_2 + \varphi_3 - \epsilon\varphi_4)$, where ϵ is a constant. As in the case of ZnO, the E level splits into A'(ψ_1) and A"(ψ_2) and A_1 (ψ_3) becomes A' due to symmetry lowering from C_{3v} to C_s. We restrict within the spin doublet (S=1/2), two electrons occupy the A' level and A" level is occupied by a single electron. We find that in the both case of ZnO and GaN, the energy of symmetry lowering is small and thus the spin-polarized state is the most stable structures.

We have studied the symmetry lowering effect in cation vacancies of II-VI and III-V semiconductors and found that the symmetry lowering effect is very small. The metastable or unstable states are found in the spin singlet (doublet) C_s geometries and thus the most stable structures in the case II-VI (III-V) semiconductors are triplet (quartet) C_{3v} symmetries. Our results are in sharp contrast with the case of of silicon neutral monovacancy [37-39]. In the Silicon monovacancy, the inward ralaxation occurs at the four nearest Si atoms and the interactions between Si atoms become large. As a result, the spin singlet state becomes the most stable state because the JT distortion inducing the bonding of the dangling bonds

4. Conclusions

We have carried out spin-polarized DFT calculations of cation vacancies in wide-gap semiconductors, i.e, III-V (nitrides and phosphides) and II-VI (oxides and sulfides), wurtzite

structure. We find that the most stable structures are spin-polarized C_{3v} symmetries. The defect E level is occupied (unoccupied) by two majority (minority) spin electrons lead the magnetic moment is 2 μB in the case of II-VI semiconductors. The magnetic moment is found to be 3 μB in the case of III-V semiconductors due to three majority (minority) spin electrons occupy in the defect E and A_1 levels. We find that the spin polarize energies are large in the semiconductors consisting of first-row anions, i.e. oxides and nitrides. This is due to the atomic radii of the oxygen and nitrogen are small. The symmetry lowering effect induces the pairing or depairing types of cation vacancies. We find that the energies of symmetry lowering is smaller than spin-polarized C_{3v} symmetry and thus the spin-polarized C_{3v} symmetry is the most stable structure. This abstract partly follow an article-based style in which it includes complete manuscripts which have been published by the author [41].

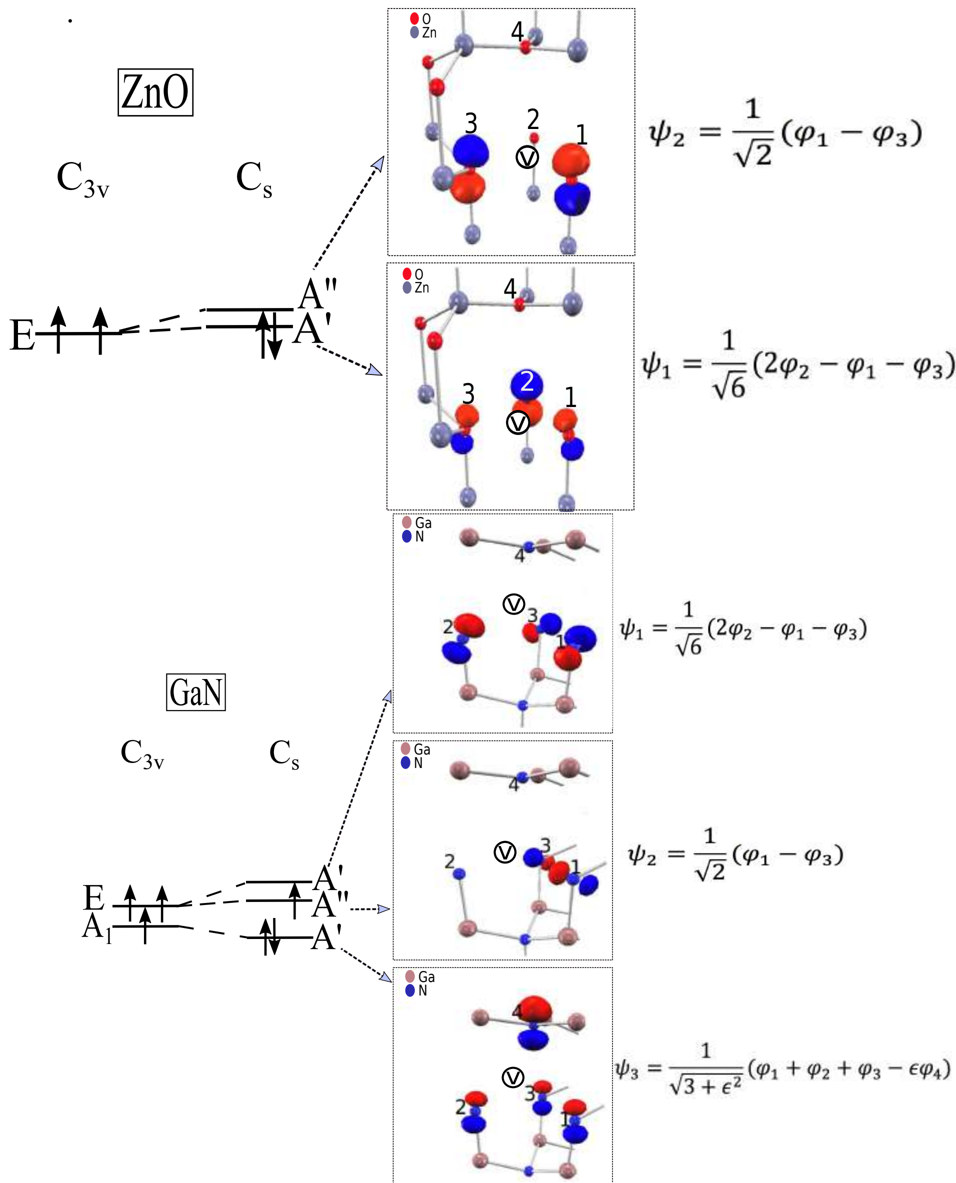

Figure 4. Energy diagram of the C_{3v} and C_s in the case of ZnO and GaN. The wavefunctions is represented as red (blue) colors indicate positive (negative) amplitudes.

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令和　3年　2月　3　日

学位論文審査報告書（甲）

1．学位論文題目（外国語の場合は和訳を付けること。）

First-principles calculations of spin-polarized cation vacancies in wide-gap semiconductors（ワイドギャップ半導体中のスピン分極陽イオン空孔に関する第一原理計算）

2．論文提出者　(1) 所　　属　数物科学　専攻

(2) 氏　　名（ふりがな：むはまど ゆすふ はきむ ういでぃあんと）　MUHAMMAD YUSUF HAKIM WIDIANTO

3．審査結果の要旨（600～650字）

MUHAMMAND YUSUF HAKIM WIDIANTO 氏の学位論文について、審査委員で提出された論文および口頭発表につき詳細な検討を行った後、2月3日に学位論文公聴会を実施した。公聴会の後、審査委員で審議を行った。最近になり、III-V および II-VI ワイドギャップ化合物半導体において、陽イオン空孔がスピン分極することが分かってきた。スピン分極した空孔は強磁性の性質を示す希薄磁性半導体の原因となることから、スピントロニクス応用の観点から注目されている。本研究では、III-V および II-VI 化合物半導体中の陽イオン空孔に対し、密度汎関数法に基づく計算を行い、スピン分極の機構について調べた。陽イオン空孔は C_{3v}の対称性を保ちスピン分極することが明らかになった。スピン密度は近接の4個の陰イオン原子に局在し、酸化物および窒化物において空孔は大きなスピン分極を持つ事が分かった。このことは、これらの半導体でキュリー温度が高い実験事実と矛盾しない。また、対称性の低下により、磁気モーメントが減少した構造は C_{3v}の対称性を持つ構造よりもエネルギーが高くなることを明らかにし、スピン分極した C_{3v}の構造がエネルギー的に最安定であることを明らかにした。対称性の低下した構造が最安定にならないのは、近接の4個の陰イオン原子が互いに遠ざかるように格子緩和し、陰イオン原子の軌道の重なりが極めて小さいことによる事が分かった。本研究は、III-V および II-VI 化合物半導体における陽イオン空孔のスピン分極に対し、有用な知見を与えるものであり、合格と判断した。

4．審査結果　(1) 判　　定（いずれかに○印）　（合　格）・　不合格

(2) 授与学位　博　士（理学）