Triple group-V donors in ZnO ^{EP}

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Manu Hegde ^{id}, F. Mohammadbeigi, T. Kure ^{id}, E. Senthil Kumar ^{id}, M. R. Wagner ^{id}, A. Hoffmann, and S. P. Watkins ^{id}

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Manu Hegde,¹ F. Mohammadbeigi,^{1,a)} T. Kure,² E. Senthil Kumar,^{1,b)} M. R. Wagner,² A. Hoffmann,²
and S. P. Watkins^{1,c)}

AFFILIATIONS

¹Physics Department, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada

²Institut für Festkörperphysik, Technische Universität, Hardenbergstrasse 36, D-10623 Berlin, Germany

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a) Present address: Department of Physics, Astronomy and Engineering, Kwantlen Polytechnic University, Surrey, BC, V3W 2M8, Canada.

b) Present address: 2D Materials Laboratory (2DML), Department of Physics and Nanotechnology, Nanotechnology Research Center, SRM Institute of Science and Technology (SRMIST), Kattankulathur 603203, Chennai, India.

c) Author to whom correspondence should be addressed: simonw@sfu.ca

ABSTRACT

Triple donors have been explored in a few semiconductor materials; however, the conventional effective mass theory treatment fails at short length scales due to the high degree of localization implied by a 3+ nuclear charge. Using density functional theory, we consider the various charge states of group-V elements substituting for the Zn sublattice in ZnO under oxygen-rich conditions. For the case of Sb and Bi substitutional impurities, the (1+/0) charge state transition is shallow and has strong similarities to a (1+/0) charge transition of the more common shallow group III donors such as Ga and Al. We compare these calculations with extensive photoluminescence (PL) measurements that now exist for the Sb-related donor bound exciton in ZnO, which is known to contain substitutional Sb on Zn sites. We present new experimental data on the magneto-PL properties of the Sb-related donor bound exciton. These data confirm the strong similarity of the (+1/0) charge state transition of this center to the common group III shallow donors in ZnO. We propose that the very low binding energy (40.2 meV) of the neutral Sb donor is due to a combination of increased screening due to the two inner donor electrons, as well as the exclusion principle, resulting in a repulsive central cell potential close to the defect core.

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I. INTRODUCTION

Much effort has been expended on the study of group-V elements like N, P, As, and Sb in ZnO due to the so-far elusive search for robust p-type dopants. The substitution of group-V elements on the oxygen sublattice was initially assumed to provide a path to p-doping but was later shown to be unlikely due to high formation energies¹ and large acceptor ionization energies.² In fact, density functional theory (DFT) calculations uniformly predict that group-V elements have much lower formation energies on the zinc sublattice, making them potential triple donors.^{1,3} Clear experimental confirmation of the preferred Zn site configuration for As and Sb impurities has been obtained by ion channeling⁴ and radioisotope implantation studies.⁵ Surprisingly, triple donors have been scarcely investigated in the past several decades of research into semiconductor defects. Effective mass theory (EMT), often successful for single donors, must break down for the inner electrons of a

triple donor due to the strong localization of the high core charge, particularly when the effective mass is large.

Firm evidence for shallow donor behavior in group-V dopants in ZnO has been increasingly reported on the basis of electrical^{6,7} and optical measurements.^{8–10} In particular, the optical studies show a donor bound exciton (D^0X) associated with substitutional Sb impurities on the Zn lattice having an emission energy of 3364.3 meV and a very shallow donor binding energy of 42.2 meV.

In this work, we present DFT calculations performed under conditions relevant to typical oxygen-rich growth conditions, which show that the larger group-V elements Sb and Bi should exhibit shallow donor behavior. In particular, the calculations indicate that the first ionization energy of the triple donor should be shallow for Sb and Bi, while the inner two donor electrons are much more localized around the Sb-impurity in nonbonding orbitals. Thus, the behavior of the neutral state of the Sb triple donor is

very similar to that of the single group III donors such as Ga, Al, and In but with a reduced binding energy compared with other shallow donors, indicating increased screening due to first two donor electrons, as well as an effective repulsion due to the exclusion principle. We present high resolution photoluminescence (PL) measurements under a magnetic field which clearly show the shallow donor origin of the low temperature luminescence peak, at 3364.3 meV, which we attribute to the triple Sb donor predicted by DFT.

II. METHODS

Sb-doped ZnO nanowires were grown on c-sapphire substrates by catalyst-free metalorganic chemical vapor deposition (MOCVD) using dimethylzinc and nitrous oxide as the group II and VI precursors, respectively, and nitrogen as the carrier gas.⁸ Trimethylantimony was used as the dopant at very low group-V/group II ratios of $\sim 10^{-4}$. The growth temperature was nominally 605 °C. Magneto-PL measurements were obtained at 2 K using a split-pair solenoid allowing optical access both parallel and perpendicular to the B field. The sample holder was rotatable, allowing angle-resolved measurements by changing the sample c axis with respect to the orientation of the magnetic field. A HeCd laser with a 5 mW power was used to excite the sample. Measurements were done in the backscattering geometry. A double grating spectrometer with a Hamamatsu H10721-210 Mini-PMT was used to collect the PL.

All the calculations were performed using plane-wave pseudopotential DFT as implemented in the *QUANTUM ESPRESSO* package.¹¹ Norm-conserving pseudopotentials with the Perdew, Burke, and Ernzerhof (PBE) gradient corrected exchange-correlation functional (PBE-GGA) were used for all atoms. The 3d electrons of Zn were included in the valence configuration of the pseudopotential. The wavefunctions were expanded in plane waves with an energy cutoff of 80 Ry. The ZnO unit cell in a hexagonal symmetry was fully relaxed using an $8 \times 8 \times 8$ Monkhorst-Pack *k*-point mesh. We found a bandgap of ~ 0.9 eV within the PBE-GGA approximation. In order to overcome the severe bandgap underestimation within the PBE-GGA formalism, the GGA + U level theory was used. The Hubbard U correction of 7 eV for Zn 3d electrons and 5.9 eV for O 2p electrons was used, respectively.¹² A bandgap of ~ 2.9 eV was obtained using the GGA + U approximation. Fully optimized lattice parameters and atomic coordinates from the ZnO unit cell were used to build a 96-atom supercell in a orthorhombic symmetry.¹³ All the atoms in the ZnO supercell were fully relaxed using a $2 \times 2 \times 2$ Monkhorst-Pack *k*-point mesh. The Sb defect was introduced in the ZnO matrix by substituting on one of the Zn sites. This gives us a doping concentration of $\sim 2\%$. The total energy obtained from the geometrically optimized supercell was used for formation energy calculations. For the density of state calculations, a 72 atom ZnO supercell was used.

The formation energy of a defect in a charge state *q* can be calculated using the expression

$$E^f[D^q] = E_{\text{tot}}[D^q] - E_{\text{tot}}[\text{ZnO}] - \sum_{\text{X}} n_{\text{X}} \mu_{\text{X}} + q[E_F + E_v + \Delta E_{\text{corr}}^q], \quad (1)$$

where $E^f[D^q]$ is the total energy of the supercell with a defect, $E_{\text{tot}}[\text{ZnO}]$ is the total energy of a perfect supercell without a defect.

n_{X} and μ_{X} are the number and the chemical potential of atoms added (n_{X} is positive) to, or removed (n_{X} is negative) from, the supercell, respectively. E_F and E_v are the Fermi energy and energy of the VBM, respectively. ΔE_{corr}^q is the potential alignment term due to the presence of the charged defect. The chemical potential μ_{X} depends on the ZnO growth conditions. We only consider O-rich conditions as our samples were grown by MOCVD under O overpressure. In this case, $\mu_{\text{Zn}} = \mu_{\text{Zn}}(\text{bulk}) + \Delta H_f$ and $\mu_{\text{O}} = 0$. We obtained the enthalpy of formation $\Delta H_f = -2.99$ eV for ZnO. In this work, we consider X_2O_3 ($\text{X} = \text{As}, \text{Sb}, \text{Bi}$) as possible sources of dopants; hence, we have to consider their chemical potential too. For X ($\text{X} = \text{As}, \text{Sb}, \text{Bi}$) under O-rich conditions, the chemical potential will be $\mu_{\text{X}} = \mu_{\text{X}}(\text{bulk}) + 1/2\Delta(H_f)_{\text{X}_2\text{O}_3}$. The charge correction term was calculated using the *sxdefectalign* program proposed by Freysoldt *et al.*¹⁴ The charge transition levels $\epsilon(q/q')$ introduced by defects can be estimated from the formation energy calculations. They are defined as the Fermi-level position at which the formation energies of two charge states *q* and *q'* are equal. They can be calculated from

$$\epsilon(q/q') = \frac{E^f(D^q; E_F = 0) - E^f(D^{q'}; E_F = 0)}{q'}, \quad (2)$$

where $E^f(D^q; E_F = 0)$ is the formation of the defect *D* in charge state *q* when the Fermi level is at the VBM ($E_F = 0$). The physical meaning of the transition level is that charge state *q* is stable for the Fermi-level positions below $\epsilon(q/q')$, while the charge state *q'* is stable for Fermi-level positions above $\epsilon(q/q')$. The formation energies corresponding to the experimental bandgap were obtained using the extrapolation method of Janotti and Van de Walle¹⁵ within both the GGA and GGA + U approximations.

III. RESULTS

A. Formation energies

There are a couple of previous reports of calculations of formation energies of group-V donors in ZnO.^{1,3} Limpijumrong *et al.* calculated the formation energies of As and Sb donors within the local density approximation (LDA), with severe underestimation of the bandgap.¹ Petretto and Bruneval did a more detailed calculation of the formation energies of P, As, and Sb substitutional donors using hybrid functionals, resulting in a more accurate bandgap; however, their calculations were only performed for Zn-rich conditions.³

Figures 1(a)–1(c) show our DFT calculations of the formation energies of simple substitutional dopants As_{Zn} , Sb_{Zn} , and Bi_{Zn} with different charge states as a function of Fermi energy under O-rich conditions. The slopes of these lines are determined by the charge state *q* and the kinks represent transition energies. Our results are qualitatively similar to previous predictions for As and Sb triple donors of Petretto *et al.*,³ however, our overall formation energies are higher due to the assumption of O-rich conditions relevant to the MOCVD growth method. For the simple substitutional donors Sb_{Zn} and Bi_{Zn} , we find that there are no neutral states inside the bandgap, which is consistent with the shallow Sb substitutional donor observed in PL.^{9,10} For both cases, the most stable charge state under n-type conditions (E_F near the conduction band) is the $q = +1$ state. The charge transition energies were calculated with

FIG. 1. Formation energy calculations E_f for substitutional defects X ($X = \text{As}, \text{Sb}, \text{Bi}$) as a function of Fermi energy. All calculations were performed under O-rich conditions. The top panels [(a)–(c)] correspond to substitutional dopants on a Zn site with X being in different charge states. The bottom panels [(d)–(f)] show substitutional X_{Zn} paired with a nearest neighbor Zn vacancy.

respect to the VBM maximum using Eq. (1). The $\epsilon(+/0)$ transition energy was found to be 3.56 eV and 3.41 eV for Sb- and Bi-doped ZnO, respectively. In a situation like this where the neutral state is predicted to be above the conduction band, the Coulombic potential of the $q = +1$ state can still bind an electron in a loose hydrogenic bound state at low temperatures, although the binding energy cannot be predicted by DFT methods.¹⁵

The formation energies obtained for all three group-V impurities show very small formation energies, when E_F is close to the VBM maximum. Sb and Bi show positive values of the formation energy for E_F close to the CBM, making them shallow donors. In contrast, As shows deep behavior with a transition energy $\epsilon(3+/0)$ located 0.7 eV below the CBM. These results are consistent with Petretto and Bruneval, who obtained $\epsilon(3+/0)$ at 0.73 eV below the conduction band using Heyd-Scuseria-Ernzerhof (HSE) based DFT calculations.³

We also considered the formation energies of As, Sb, and Bi on Zn sites paired with nearest neighbor Zn vacancies in Figs. 1(d)–1(f). A group-V element on a zinc site is expected to be a triple donor, whereas a zinc vacancy can act as a double acceptor, therefore it seems reasonable to consider the pair as a single donor. The formation energy data in Figs. 1(d)–1(f) argue against this model since they indicate amphoteric behavior. The charge transition energy $\epsilon(+/0) = 1.61$ eV with respect to the VBM indicates that it is a deep donor. The transition energy for $\epsilon(-/0)$ is 2.39 eV. For the case of $\text{Sb}_{\text{Zn}} + \text{V}_{\text{Zn}}$, a neutral state is found well inside the gap,

making it a deep donor/acceptor. Thus, $\text{Sb}_{\text{Zn}} + \text{V}_{\text{Zn}}$ is unlikely to be the explanation for the observed Sb-related donor. A similar trend was observed in the case of the $\text{Bi}_{\text{Zn}} + \text{V}_{\text{Zn}}$ vacancy complex, where charge transition energies of 0.55 eV and 0.99 eV were obtained for the $\epsilon(+/0)$ and $\epsilon(-/0)$ transition states, respectively.

B. Electronic structure of Ga- and Sb-doped ZnO

Contributions from different orbitals (orbital angular momentum projected density of states) to the total density of states (TDOS) for bulk ZnO, Ga- and Sb-doped ZnO are shown in Fig. 2. Figure 2(a) shows the density of states plots for pure ZnO. The top of the valence band is predominantly made up of O 2p orbitals, while Zn 4s orbitals primarily contribute to the conduction band states. The TDOS of Ga-doped ZnO looks similar to that of undoped ZnO Fig. 2(b). This is expected as the valence orbitals of Ga are made up of 4s and 4p orbitals similar to those of the Zn orbitals, with which they undergo strong hybridization. The extra electron due to Ga is fully transferred to the CBM. The situation is different when doping with group-V elements, Sb and Bi, as shown in Figs. 2(c) and 2(d), respectively. These dopants induce narrowband intermediate states above the VBM, made up of hybridized O 2p and dopant s orbitals. The localized midgap states indicated in Fig. 2 are consistent with the deep transition levels observed in Figs. 1(a) and 1(b) for the simple Sb_{Zn} and Bi_{Zn}

FIG. 2. (a) The contribution of Zn 4s and O 2p resolved orbitals to the total density of states (TDOS) in bulk ZnO. (b)–(d) density of state plots for Ga-, Sb-, and Bi-doped ZnO. The top panel is the comparison of the TDOS of doped ZnO with corresponding orbital angular momentum resolved valence orbitals. A 72 atom supercell was used for the DOS calculations.

defects. We attribute these states to the localized nonbonding electrons of the triple donor. Sb and Bi also contribute additional states to the CBM composed of Zn 4s and dopant *p* states. These states, which we attribute to the third electron of the triple donor should be dispersed in the conduction band, similar to the situation for Ga-doped ZnO.

C. Experimental evidence for group-V donors

Conclusive evidence for a shallow Sb donor in ZnO comes from radioisotope implantation experiments.⁹ Radioactive ¹¹⁷Ag was implanted into ZnO bulk crystals and Sb was generated by transmutation along the decay chain ¹¹⁷Ag → ¹¹⁷Cd → ¹¹⁷In → ¹¹⁷Sn → ¹¹⁷Sb.⁹ This resulted in the appearance of a shallow D⁰X transition at 3364.3 meV, which grew with the rate expected from the radioisotope decay kinetics. This unambiguously confirmed (1) that Sb was involved in the donor center and (2) that it is localized on a Zn lattice site. MOCVD was found to be a useful method for intentionally introducing the Sb-related emission using trimethylantimony.⁸ Samples were grown in which the Sb-related emission was the dominant shallow exciton emission peak.¹⁰ Resonant optical excitation was used to confirm that the transition was due to a donor bound exciton based on the observation of the 2s/2p “two electron transition” which constrained the donor binding energy to 42.2 ± 0.5 meV, making it shallower than any previous donor in ZnO, and shallower than the effective mass donor binding energy of 50.2 meV. PL excitation spectroscopy confirmed the strong similarity of the D⁰X excited states to those of the shallow group III donors Ga and In.¹⁰ The Sb-related donor was found to satisfy the same linear relationship (“Haynes’ rule”) between the D⁰X binding energy and the donor binding energy as the other common shallow donors (Al, Ga, In, and H).¹⁰

In addition to conclusive donor behavior of Sb, there have been reports of n-type electrical properties arising as a result of P- and Bi doping.^{7,16}

1. Zeeman spectroscopy measurements

PL measurements of D⁰X emission lines under a magnetic field have been performed for several shallow donors in ZnO and have been used to verify the charge state of the exciton, as well as the ordering of the valence bands.¹⁷ It is, therefore, of value in confirming the shallow donor nature of the Sb PL emission. Under a magnetic field, both the D⁰X initial state and the D⁰ final state split due to residual spin degeneracy as indicated in Fig. 3.

In a D⁰X ground state transition, the magnitude of the splitting under an applied magnetic field is determined by the *g*-factor of the electron in the final (donor) state and the hole in the initial (exciton) state. In wurtzite ZnO, free electrons occupy an s-like conduction band and have an almost isotropic *g* value of 1.96.¹⁸ Holes are derived from electron states with p-like properties, and the hole *g*-factor is anisotropic and given by

$$g_h = \sqrt{|g_h^{\parallel}|^2 \cos^2 \theta + |g_h^{\perp}|^2 \sin^2 \theta}, \quad (3)$$

FIG. 3. Energy level diagram for D⁰X in (a) the Voigt configuration, (b) the Faraday configuration.

TABLE I. Electron and hole g-factors of bound exciton complexes in this work and other references.

D^0X	g_e	$g_h^{\parallel}$	$g_h^{\perp}$	Reference
I_8 (Ga)	1.96	-1.28	0.18	This work
I_8 (Ga)	1.92	-1.24	0.08	20
I_{Sb}	1.97	-1.29	0.21	This work
I_9 (In)	1.98	-1.36	0.1	21

where θ is the angle between the magnetic field B and the c axis. Typical values of g_h extracted from analysis of group III D^0X transitions are given in Table I. The splitting of the D^0X transitions is then given by

$$\Delta E = \frac{1}{2} |g_e \mp g_h| \mu_B B. \quad (4)$$

The magneto-PL spectra of the Sb-doped ZnO sample are shown in Fig. 4. The PL spectra were recorded at $T = 2$ K in the Faraday ($B \parallel C$) configuration, with $E \parallel c$ [Fig. 4(a)], as well as the Voigt ($B \perp C$) configuration, with $E \perp c$ [Fig. 4(c)], and at different angles between B and the c axis of the sample [Fig. 4(b)]. A maximum magnetic field B of 5 T was used. All the spectra are shifted vertically for clarity and are taken in the same spectral range. The angle dependent measurements started at $B \parallel C$ and ended at 75° with a fixed magnetic field of 5 T. In this section, we only focus on excitons bound to Ga and Sb donors. The Zeeman splittings of I_8 and I_{Sb} in the Faraday configuration are shown in Fig. 4(a). The splitting is small because the g-values of the initial and final states are comparable for this case. Two more split peaks outside of the split peaks at $B \parallel C$ appear when θ is nonzero. Figure 4(c) shows a clear

linear splitting of the I_8 and I_{Sb} lines into two distinct components under magnetic field application in the Voigt configuration. In this case, the g-factor of the initial state (D^0X) is ~ 0 , so the splitting is primarily due to the electron final state, resulting in a larger overall splitting. Both split components showed equal intensity at 2 K, which indicates no thermalization behavior between them.

2. Analysis of the Zeeman data

The peak positions of the Zeeman split lines were obtained from Lorentzian line shape fits to the data in Fig. 4. The peak positions are plotted in Fig. 5 as a function of magnetic field in different configurations. Figure 5 shows that the I_{Sb} transition follows the same behavior of the Ga I_8 line under an external magnetic field and undergoes a linear splitting which confirms the neutral donor charge state for this transition.¹⁹ A D^+X transition can be ruled out since it would exhibit strong nonlinear dependence on the B field.¹⁹ In addition, this would be inconsistent with the observation of a two electron transition.¹⁰ When the angle θ between the applied magnetic field and the crystal c axis changes, additional Zeeman components which were forbidden at $\theta = 0$ appear. The four observed Zeeman line energy positions can be fitted to the following equations:

$$E^\pm = E_0 \pm \frac{1}{2}(g_e + g_h)\mu_B B \quad (\text{outer Zeeman pair}), \quad (5)$$

$$E^\pm = E_0 \pm \frac{1}{2}(g_e - g_h)\mu_B B \quad (\text{inner Zeeman pair}). \quad (6)$$

From Fig. 5(b), it can be seen that as the angle θ changes from 90° to 0° , the splitting of the inner transitions decreases and the splitting of the outer transitions increases. This behavior can be explained by the anisotropy of the hole g-factor in Eq. (3). The experimental data

FIG. 4. Zeeman splitting of neutral bound excitons I_8 and I_{Sb} in (a) Faraday ($B \parallel C$) configuration, (b) varying angles θ between B and c axis at $B = 5$ T and (c) Voigt ($B \perp C$) configuration. Vertical lines show the position of transitions at zero-field.

FIG. 5. Zeeman splitting of neutral bound excitons I_8 and I_{Sb} in (a) Faraday configuration, (b) arbitrary angles between the magnetic field B and the c axis and (c) Voigt configuration. The solid lines are the fits to the data.

have been fitted by Eqs. (5) and (6) for the different angles between the magnetic field and c axis and shown by the solid lines. The best fit parameters for the electron and hole g -factors in different transitions are listed in Table I. There is good agreement between our results and previously reported g -factors for I_8 .^{17,20,21} Comparing the Zeeman splitting in the Faraday and Voigt configurations, it can be seen that the size of the splitting is smaller in the Faraday configuration. This is due to the negative hole g -factor ($|g_h^{\parallel}| < g_e$).²⁰ This confirms that the holes involved in the excitons bound to Ga and Sb donors originate from the A-valence band (Γ_7) and not the B-valence band (Γ_9).²¹ The fact that very similar hole g -factors are observed for the Sb donor and the other group III donors argue for a simple tetrahedral symmetry of the defect.

While it is now clear that the I_{Sb} transition is due to a shallow D^0X , it is also possible to further rule out an acceptor bound exciton (A^0X) origin by looking at the thermalization behavior of the Zeeman split lines.²² If the center is a D^0X , the splitting in the Voigt geometry is primarily determined by the electron final state splitting and there is no thermalization of the split components. In contrast for A^0X in the Voigt geometry, the splitting occurs in the initial state (two paired holes and one unpaired electron) and the split lines are expected to thermalize²² according to

$$\frac{I_{upper}}{I_{lower}} = \exp\left(-\frac{\Delta E}{k_B T}\right), \quad (7)$$

where ΔE is the energy splitting of the two components. At the maximum magnetic field, $\Delta E = 0.6$ meV and the intensity ratio at $T = 2$ K according to Eq. (7) will be 0.03. As can be seen in Fig. 6(a), the intensities of the split components are almost equal at 2 K. Fits to the integrated intensity were made to the split line components over a range of temperatures for both I_8 and I_{Sb} [Fig. 6(c)], confirming the lack of thermalization, which confirms that both transitions are due to a D^0X rather than A^0X transition.

Furthermore, I_8 and I_{Sb} have very similar temperature dependence of the peak exciton energies [Fig. 6(b)].

IV. DISCUSSION

The Sb donor identified in this work is very shallow with a binding energy (42.2 meV), 8.0 meV less than the effective mass theory (EMT) value (50.2 meV). Magneto-PL spectroscopy of the Sb- D^0X transition shows strong similarities with the other shallow group III donors substituting for Zn sites. There are very few experimental reports of triple donors in the extensive literature on shallow defects over the past 60 years. EMT calculations have been made for double and triple donors.^{23,24} An ionization energy of $2.5Ry^*$ (Ry^* is the single donor effective mass binding energy), was predicted for the first ionization energy of an effective mass triple donor,²⁴ which would give a value of ~ 125 meV for ZnO based on an effective mass binding energy of 50.2 meV. This is in strong disagreement with our very low observed value of 42.2 ± 0.5 meV for I_{Sb} , which amounts to $0.84 Ry^*$. However, the use of effective mass theory to attempt to describe a triple donor is highly problematic since the predicted localization of the inner two donor electrons is comparable to the atomic valence orbital dimensions. The shallow binding energy of the Sb donor provides support for our model of a simple substitutional defect. As a general rule, the binding energy of effective mass single donors in semiconductors is observed to increase as one moves down the periodic table as indicated for the group III donors in Table II. Phillips pointed out that the magnitude of the central cell correction (chemical shift) usually scales with the difference in electronegativity between the host atom and the dopant, at least when comparing donors from the same column of the periodic table.²⁵ More generally, increased binding energy relative to the EMT value is attributed to the reduction of screening of the valence electrons at short distances for atoms with a larger atomic core radius relative to the host atom (in this case Zn).^{26,27}

FIG. 6. (a) 5 T spectra showing the lack of thermalization of the Zeeman split transitions I_8 and I_{Sb} in Faraday ($B \parallel c$) and Voigt ($B \perp c$) configurations. (b) Temperature dependence of the peak energies (c) temperature dependence of the peak amplitudes at 5.0 T as a function of temperature showing the lack of thermalization.

Sb $3+$ and In $1+$ have the same inner electron core structure. Inspection of Table II shows that In has an increased binding energy of 12.2 meV relative to the effective mass theory (EMT) estimate, whereas Sb has a reduction of binding energy of -8.0 meV. The formation of the Sb $1+$ charge state requires the addition of

TABLE II. Binding energies of the effective mass theory (EMT) donor, group III donors, and the Sb donor, showing the trend in the central cell shift relative to the EMT value, ΔE .

Donor	Binding energy (meV)	ΔE (meV)
EMT	50.2	0
Al	51.55	+1.4
Ga	54.6	+3.4
In	62.4	+12.2
Sb	42.2	-8.0

two additional valence electrons compared with In $1+$. These electrons are added to a nonbonding localized orbital resulting in a more extended charge distribution. The effect of this on the central cell potential seen by a third donor electron is hard to calculate quantitatively but we can argue qualitatively using simple physics arguments. For the $1+$ charge state of Sb to bind a third electron and form the neutral state, the extra electron would have to occupy a different nonbonding orbital due to the exclusion principle. In addition, the more extended charge density of the outer two electrons should result in an increase in screening, which also leads in the direction of reducing the binding energy. Detailed calculation is beyond the scope of this paper, but the work of Binggeli and Baldereschi²⁶ suggests a possible quantitative treatment combining *ab initio* calculations for the first two electrons with effective mass theory for the third electron, by a suitable choice of short range impurity potential.

While Sb has clearly been shown to reside on the Zn site,⁹ we cannot rule out the possibility that the defect involves an additional constituent, such as a double acceptor. Clearly, if the triple donor model is correct, it should be possible, in principle, to observe the other charge states, such as $2+$ and $3+$. However, given the low density of the Sb centers (based on the narrow linewidths of the D^0X emission), it is not likely that these will be observed under the typical n-type conditions prevailing in ZnO grown by MOCVD and other techniques.

$\text{Sb}_{\text{Zn}}-\text{V}_{\text{Zn}}$ complexes have also been proposed as a possible candidate for the donor behavior observed in Sb-doped ZnO.⁸ Compensation of group III donors by Zn vacancies has been previously reported based on electron paramagnetic resonance measurements.²⁸ Sb is a triple donor and V_{Zn} is a double acceptor, which might indicate single donor behavior, however our DFT calculations [Figs. 1(d)–1(f)] and those of others^{1,3} indicate that $\text{Sb}_{\text{Zn}}-\text{V}_{\text{Zn}}$ should be an amphoteric defect with a neutral state well inside the energy gap. It is therefore unlikely to be responsible for the observed I_{Sb} transition. It is possible that it is responsible for quenching the Sb triple donor under conditions favorable for Zn vacancy formation.

Regarding other group-V donors, DFT calculations indicated that N_{Zn} and As_{Zn} should be deep donors under Zn-rich conditions, whereas P_{Zn} should result in a shallow donor.³ Bound exciton emission in P-doped ZnO was observed, consistent with a donor binding energy of 37.5 meV and attributed to P donors.¹⁶ In the case of As, radioisotope studies confirmed that implanted As resides on a Zn site, yet shows no shallow donor bound exciton emission,²⁹ in agreement with the predictions of DFT calculations that it should act as a deep donor.³ Preliminary reports of Bi doping indicated the presence of n-type conductivity;⁷ however, the quality of the samples published so far has not been high enough to detect high resolution shallow donor PL. So far, Sb_{Zn} remains the most likely candidate for a well characterized substitutional group-V donor in ZnO.

V. CONCLUSIONS

Based on DFT investigations, we conclude that group-V donors Sb and Bi should result in triple donors which should behave in a very similar fashion to ordinary group III single donors, in terms of

the electronic states of the most easily ionized donor electron. We conclude that the observed shallow donor related to substitutional Sb is consistent with a $(1+/0)$ transition level due to substitutional Sb on a Zn site. Magneto-PL measurements of the Sb-related D^0X center are consistent with the behavior of other shallow group III donors in ZnO, and thermalization measurements rule out an A^0X origin. The shallow nature of the Sb donor binding energy (40.2 meV) is likely due to screening by the inner two donor electrons, coupled with effective repulsion due to the exclusion principle, which should provide a negative central cell potential.

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