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Identification of a N-related shallow acceptor and electron paramagnetic resonance center in ZnO: N_2^+ on the Zn site

Walter R. L. Lambrecht[1,2,*] and Adisak Boonchun[3,4,†]
[1]*Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079, USA*
[2]*Peter Grünberg Institute, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[3]*National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba-city Ibaraki, 305-0044, Japan*
[4]*Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand*
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First-principles calculations of N_2 in ZnO located on the Zn site show that this defect is a shallow double acceptor and can be identified with a N-related shallow level observed experimentally by donor-acceptor-pair recombination. When the shallow acceptor level is occupied with a single electron, it can also explain a N_2-related electron paramagnetic resonance signal observed in ZnO. We show that the g factor and hyperfine structure observed for this center are closer to those of a $N_2{}^+$ radical than to a N_2^- radical as previously proposed in literature and hence consistent with the Zn location.

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I. INTRODUCTION

The wide band gap (3.44 eV at room temperature) and large exciton binding energy (60 meV) make ZnO attractive as optoelectronic material. Unfortunately, the bottleneck for these applications remains the lack of reliable p-type doping. The natural choice of N on the O site leads to a very deep level. While earlier calculations in the local density approximation already gave a somewhat deep level at about 0.4 eV above the valence band maximum[1], more recent calculations with orbital dependent functionals showed the level to become considerably deeper due to orbital polarization, between 1.3[2] and 1.6 eV.[3] A level at 1.3 eV has also been confirmed by recent experiments.[4,5]

Many other candidate acceptors have been studied[6] and found unsuitable because they either form deep levels (Cu_{Zn}[7]) or have compensating donor interstitial sites (Li, Na)[1] or form compensating deep AX centers (P, As, Sb).[1] Another proposal[8] for a shallow acceptor that P, As, Sb would prefer the Zn site but form a complex with two V_{Zn} is unfavorable for entropic reasons.

Nonetheless, a shallow level related to N has been found in ZnO by Zeuner *et al.*[9] While it did not lead to p-type doping by its low concentration and compensation by shallow donors, the related donor-acceptor pair (DAP) recombination at 3.235 eV was used to determine a binding energy of only 165 ± 40 meV. Unfortunately, it has until now remained unclear what is the nature of this N-related level. Recently, Lautenschlaeger *et al.*[6] proposed that N_O pairs combined with H could possibly explain this shallow level. In subsequent computational work,[10] we showed that this is not the case because H would bind strongly to one of the N and thereby remove the level completely from the gap, while the other N remains in a deep level just as for the single N_O case. Another defect complex, N_O-V_{Zn} was recently proposed to have a shallow level by Liu *et al.*[11] These authors proposed that this defect could evolve from N_{Zn}-V_O, which was shown to be preferentially incorporated during growth on the Zn-polar surface but this complex transformation requires a 1.1 eV barrier to be overcome.

On the other hand, N_2 molecular centers are well known in oxides and alkali halides and an electron paramagnetic center corresponding to N_2 was clearly identified in ZnO by its hyperfine interaction with two equivalent ^{14}N, $I = 1$ nuclei by Garces *et al.*[12] These authors identified this center with a N_2^- radical sitting on the O site although no convincing arguments were given for this site or charge state.

Here, we reinvestigate the possibility of a N_2 molecule in ZnO to be related to either of these two experimental findings by means of first-principles calculations. Previous work has already studied N_2 in ZnO in interstitial sites[13] and on the O site.[14]

II. COMPUTATIONAL METHODS

We used both projector augmented wave (PAW)[15] calculations using the Vienna *ab initio* simulations package (VASP)[16] in the generalized gradient Perdew-Burke-Ernzerhof (GGA-PBE)[17] and Heyd-Scuseria-Ernzerhof (HSE) (with standard Hartree Fock mixing $\alpha = 0.25$ and screening) hybrid functional[18,19] approximations and full-potential linearized muffin-tin orbital (FP-LMTO) calculations in the local density approximation (LDA).[20] Supercells of 96 and 128 atoms were used, respectively. Forces were converged to 0.02 eV/Å. A plane wave cutoff of 400 eV was used in the PAW calculations, and shown to be adequate by comparison with the results for 300 eV. Single k-point (Γ-point) sampling was found adequate for converging the calculations in these cells but subsequent partial density of states (PDOS) analysis used a larger $2 \times 2 \times 2$ k-point mesh.

III. RESULTS

A. Qualitative analysis

We start from an analysis of the well-known N_2 molecule electronic states. The highest occupied molecular orbital (HOMO) is the σ_g^+ level. It is a σ-bond between p_z orbitals along the axis of the molecule which is antibonding to the lower lying s-bonding state (σ_g^-) and as a result lies above the π_u bonding state between the p orbitals perpendicular to the molecular axis. The other occupied state is the σ_u^- antibonding s-like state, which further interacts with the p-antibonding state. The three σ-levels each with two electrons and the π_u state with four electrons account for the ten valence electrons in the molecule. The extremely strong bond in N_2 arises from the fact that all bonding states are occupied and all antibonding states are empty.

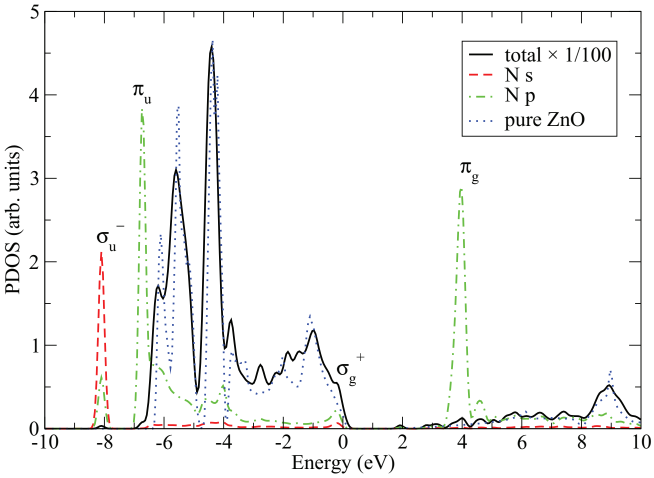
Now we consider what happens if we put this molecule on an O or Zn site in ZnO. On an O site, the molecule, like the O ion, must accept two electrons from Zn, to keep the defect in the neutral state. These would occupy the antibonding π_g state and lead to a $S = 1$ state according to Hund's rules, which, however, has not been observed. On the other hand, on the Zn-site the molecule must give up two of its electrons from the σ_g^+ level. It is already clear that the latter has a better chance to lead to an acceptor level whereas the O site is likely to lead to a donor level. This will become clear once we examine the relative position of the molecular levels to the bands of ZnO. The singly occupied acceptor level for the Zn site corresponds to a $N_2{}^+$ radical, whereas the removing one electron from the donor level for the O site results in a N_2^- radical. Below, we will show that the former is in much better agreement with the observed EPR center for N_2 in ZnO by Garces *et al.*[12]

Now, we discuss the results of the first-principles calculations. First, the structures were relaxed with FP-LMTO in LDA, and with VASP in both PBE and HSE and show consistent results. The N_2 molecule in both Zn and O sites slightly tilts from the vertical axis. The structure for the O site is similar to that reported by Lee *et al.*[14] and shows a clear bonding of the N_2 to the surrounding nearest neighbor Zn. In the case of N_2 on the Zn site, the N-O bond distances (of order 2.5 Å) are significantly longer than a typical N-O bond length of about 1.4 Å. The nearest-neighbor O atoms move somewhat outward from the molecule.

The PDOS calculated for N_2 on the Zn site, shown in Fig. 1(a), allow us to clearly identify the molecular σ_u^- and π_u, π_g levels because they lie in a region of low DOS of the host. The splitting of the $\pi_g - \pi_u$ states is similar to that in the free molecule. We can identify π levels from the fact that their peaks show a pure p-like PDOS, whereas the σ states show both N-s and N-p PDOS character. The σ_g^+ state of the molecule must clearly lie within the valence band because it shows only a weak resonance just below the VBM. A plot of the charge density contribution, not shown here, integrated over the energy range of the σ_g^+ resonance shows a very delocalized bandlike state with a slight O-2p dangling bond character and only a small fraction of the charge located on the N_2 molecule. Nonetheless, the valence band must lack two electrons, so a shallow empty state may be split off from the VBM but is not visible in this PDOS figure. Conceptually, the N_2 molecule with ten valence electrons is a double acceptor when replacing a Zn with 12 valence electrons. The deep σ_g^-, σ_u^-, and π_u states of the N_2 can be viewed as replacing the Zn-3d electrons. The effective mass theory for such an acceptor[21] would give $(2m^*m_ee^4)/(2\varepsilon^2\hbar^2) \approx 0.3$ eV with $m^* \approx 0.7$ and $\varepsilon \approx 8$.

In contrast, in Fig. 1(b) for N_2 on the O site, the highest occupied level is found just below the large peak associated with the π_g molecular level. This split-off state occurs because of the bonding with the surrounding Zn atoms. No significant spin polarization was obtained in this state. As mentioned earlier, it is consistent with a donorlike state, as also mentioned by Lee *et al.*,[14] although because the LDA (and GGA) band gap for ZnO is too small, this state overlaps with the conduction band of ZnO.

(a) N_2 on Zn-site in ZnO



(b) N_2 on O-site in ZnO

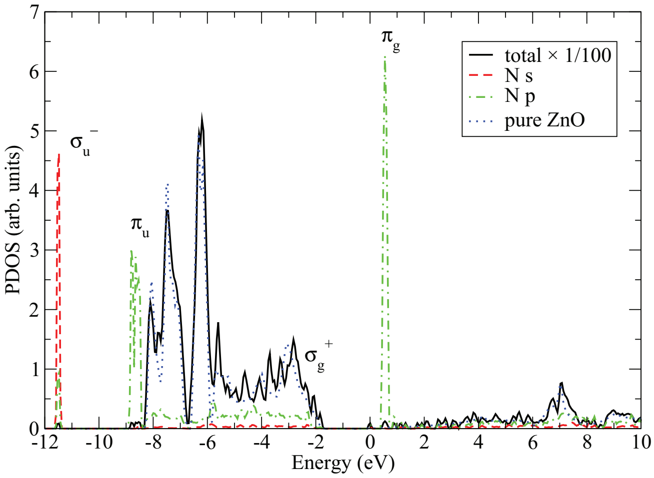


FIG. 1. (Color online) Total and partial densities of states of N_2 on Zn (a) and on O (b) sites obtained in the FP-LMTO calculation.

B. Defect energy levels

We next determine the defect level more precisely. We locate the position of the host VBM in the supercell by aligning a core level between the defect supercell and a primitive cell host calculation and determine the Kohn-Sham energy levels at Γ relative to this VBM. We do this for each charge state. Separately, we also determine the transition levels $\epsilon(q/q') = [E_f(q) - E_f(q')]/(q - q')$ from the energies of formation. Because it is not clear *a priori* whether HSE or PBE is more accurate here, we give results for both methods. The results are summarized in Table I.

While the transition level $(0/-)$ is slightly deeper in HSE, it does not reflect a qualitative change in the nature of the state as occurs for example for the N_O case. This can be seen by comparing the spin densities in the $q = -1$ state in PBE and HSE in Fig. 2. While the apparent mirror symmetry about a plane passing through the molecular axis in PBE is slightly broken in HSE and the spin density is somewhat

TABLE I. Kohn-Sham energy levels $\epsilon(q)$ and transition levels $\epsilon(q/q')$ for N_2 on Zn site in ZnO with both PBE[17] and HSE[19] density functionals and 400 eV cutoff.

method	$\epsilon(0)$	$\epsilon_{\uparrow}(-1)$	$\epsilon_{\downarrow}(-1)$	$\epsilon(-2)$	$\epsilon(0/-)$	$\epsilon(-/2-)$
PBE	0.12	0.21	0.24	0.51	0.25	0.36
HSE	1.53	0.17	1.81	0.28	0.46	0.91

less delocalized, they both show a fairly delocalized state, spread beyond the N and its nearest neighbors O. Because the defect states are delocalized in space in both PBE and HSE, we do not include image charge corrections here in the calculation of the transition levels.[22,23] We note that while the filled Kohn-Sham levels of the defect remain shallow, the empty states in HSE move up significantly relative to the VBM as is typical of HSE. In fact, this is mostly due to the VBM shifting down when going from PBE to HSE. While HSE is preferable over PBE for strongly localized defects, which suffer from the self-interaction error in LDA or GGA, and thus can prevent a symmetry breaking localization of the defect wave function, this is not expected to play a role for a shallow delocalized defect state as encountered here. To examine whether HSE or PBE is preferable here, we consider the fulfillment of the generalized Koopmans theorem (GKT). According to the latter, the vertical transition energy $\epsilon^{v}(0/-)$, i.e., the transition energy from $q = 0$ to -1 calculated at the frozen geometry of the neutral charge state, should equal the one-electron level at the $q = 0$ state. The deviation from GKT, $\Delta^{nK} = \epsilon^{v}(0/-) - \epsilon(0)$ amounts to 0.01 eV for the GGA and -0.10 eV for the HSE. This is in contrast to the N_O case, where the HSE with $\alpha = 0.25$ improves the Δ^{nK}.[3] This results from the much stronger localization of the defect wave function for the N_O case, which leads to a sizable self-interaction and also requires to include image charge corrections in that case. Hence we conclude that PBE is preferable here and $E_A \approx 0.12$ eV. This is consistent with the experimentally observed level of 165 ± 40 meV by Zeuner *et al.*[9] to within the precision of the calculations, which we estimate to be of order 0.05 eV, mainly due to uncertainties in the alignment procedure of the VBM of the supercell and the unperturbed host. We use the one-electron energy or vertical transition energy rather than the relaxed transition level as a measure for the acceptor binding energy because the experimental value is deduced from the optical transition between a shallow donor and this acceptor level.

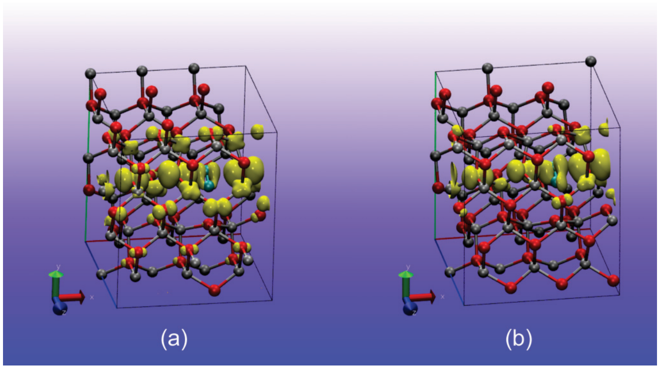


FIG. 2. (Color online) Spin density of the singly occupied acceptor level $q = -1$ in PBE (a) and HSE (b). Grey spheres: Zn, red spheres: O, cyan spheres: N, yellow isosurface set at 0.005 $e/\text{Å}^3$.

C. Site preference

The site preference energy, ΔG_{sp}, or difference in formation energies for N_2 on the Zn and O sites is given by

$$\Delta G_{\text{sp}} = E_{\text{tot}}(N_2/\text{Zn}) - E_{\text{tot}}(N_2/\text{O}) + \mu^0_{\text{Zn}} - \mu^0_{\text{O}} \pm \Delta H_f(\text{ZnO}), \tag{1}$$

where μ^0_{Zn}, μ^0_{O} are the reference chemical potentials of Zn (in bulk Zn) and O (in the O_2 molecule), respectively, and $\Delta H_f(\text{ZnO})$ is the energy of formation of ZnO. The $+$ and $-$ sign apply to O-rich and Zn-rich conditions, respectively. Hence the site preference energy in the two chemical potential conditions differ by $\Delta G_{\text{sp}}(\text{Zn-rich}) - \Delta G_{\text{sp}}(\text{O-rich}) = 2\Delta H_f(\text{ZnO})$. The experimental value of $\Delta H_f(\text{ZnO})$ is -3.61 eV. Thus the Zn site is strongly preferred over the O site in O-rich, Zn-poor conditions.

D. Analysis of EPR spectra

Now, we turn to the interpretation of the EPR center obtained by Garces *et al.*[12] Although a full calculation of the g tensor for the delocalized defect state is challenging, some insights can be obtained already by carrying out a calculation for the simple $N_2{}^+$ radical. A similar treatment of the N_2^- for an anion location can be found in Ref. 24. Within a simple tight-binding model of the N_2 molecule, the states can be obtained completely analytically with parameters determined by the identification of the levels with those calculated in LDA. Within this model, and using the usual second-order perturbation theory,

$$\Delta g_{ij} = -4\lambda \sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n - E_0}, \tag{2}$$

we find that the only contribution to Δg comes from the π_g excited state. One obtains $\Delta g_{\parallel} = 0$ and $\Delta g_{\perp} = -4(\sin^2\alpha)\lambda/(E_{\pi_g} - E_{\sigma_g^+})$. The reason why $\Delta g_{\parallel}$ is zero is that in the σ_g^+ state, the orbital quantum number of the p state is $m = 0$, while in the π_g state it is $m = \pm 1$. Thus the L_z operator with z along the molecular axis will give zero matrix elements. Here, $\lambda \approx 6$ meV is the atomic spin-orbit parameter, which we extract from a calculation of the molecule with spin-orbit coupling and which splits the π levels by 2λ. The factor $\sin^2\alpha$ gives the contribution of the p orbitals in the σ_g^+ state. The resulting $\Delta g_{\perp} = -2564$ ppm is in good agreement with a much more elaborate calculation by Bruna and Greiner[25] giving $\Delta g_{\perp} = -2734$ ppm, $\Delta g_{\parallel} = -249$ ppm. It is important to realize here that if the wave function is spread out beyond the molecule, the matrix elements in Eq. (2) are still expected to be of order 1 but the order of magnitude of the g shift is set by the ratio of the spin-orbit coupling to the $E_{\pi_g} - E_{\sigma_g^+}$ splitting. Thus the order of magnitude of the different Δg-tensor components should stay valid even when the N_2 molecule is incorporated in ZnO and has a more spread-out wave function.

In Table II, we compare our calculated g-factors with those of Bruna and Greiner[25] and with those of Garces *et al.*[12] for the observed EPR center. We also compare them with the g factors

TABLE II. Calculated g-tensor components in $N_2{}^+$, compared to measured ones for the EPR center observed by Garces *et al.*[12]. Also shown are the measured g tensor for N_2^- in MgO and KCl (see Ref. [26]).

	Present	Bruna	Garces	MgO	KCl	
$g_\parallel$	2.0023	2.0021	2.0036	1.9833	1.9065	g_{zz}
$g_\perp$	1.9997	1.9996	1.9935	2.0043	1.9971	g_{xx}
				2.0021	2.000	g_{yy}

TABLE III. Hyperfine parameter comparison.

	Garces	$N_2{}^+$ (Bruna)	N_2^- in MgO	
$A_{\rm iso}$ (MHz)	16.7	88	4.5	$A_{\rm iso}$
$A_{\rm dip}$ (MHz)	−3.4	28	−7.8	T_{xx}
			17.7	T_{yy}
			−9.9	T_{zz}

for N_2^- centers in MgO and KCl.[26] These correspond to N_2 on anion site and aligned in the [110] direction and show an orthorhombic g tensor with opposite changes in g factor from the free electron g_e from that observed by Garces *et al.*[12] We caution that we do not claim a quantitative agreement with the isolated $N_2{}^+$ molecular radical, the $\Delta g_\perp$ in the experiment is in fact larger, −8800 ppm. However, there is a clear qualitative distinction between the $N_2{}^+$ and N_2^- type g tensor, which results from the different underlying quantum state of the singly occupied molecular orbital (SOMO), which is a σ state in our case and a crystal field split π state in the other case.

From the angular dependence of the spectrum, Garces *et al.*[12] concluded that the center is aligned with the c axis of the crystal. In our calculations, we find the N_2 molecule to be tilted from the c axis. However, because of the relatively weak bonding of the N_2 in the crystal, one may expect the molecule to be rotating about the c axis among several minimum energy locations. Since this rotational time scale (of order terahertz) is much faster than the time scale of the EPR experiment (gigahertz), the EPR measurement can be viewed as averaging over the azimuthal angle.

The hyperfine structure is discussed next. Table III compares the hyperfine parameters determined by Garces *et al.*[12] with those calculated for the $N_2{}^+$ by Bruna and Grein[25] and with those for N_2^- in MgO given by Napoli *et al.*[26] The isotropic $A_{\rm iso} = (A_\parallel + 2A_\perp)/3$ and dipolar $A_{\rm dip} = (A_\parallel - A_\perp)/3$ hypefine terms are due to the Fermi contact term related to the s-like spin density at the nucleus and the nuclear dipole interaction respectively. The hyperfine tensor for N_2^- in MgO is orthorhombic $\mathbf{A} = A_{\rm iso}\mathbf{1} + \mathbf{T}$ with $\mathbf{1}$ the unit matrix and $\mathbf{T}$ a traceless diagonal matrix.

We can see that the isotropic hyperfine term of the Garces *et al.*[12] center is smaller than that for the $N_2{}^+$ radical but larger than that for the N_2^- in MgO. The small value for the latter is due to the π_g character of the wave function. For an isolated N_2^- radical, this would be zero since a π orbital has no s-type orbital contribution and hence zero value at the site of the nuclei. The small value for N_2^- in MgO must arise from some admixture of the π_g state with the surrounding lattice. On the other hand, the smaller values than in the free molecule are compatible with the shallow nature of the $N_2{}^+$ on the Zn site. It would indicate that the wave function is about $16.7/88 \approx 20\%$ localized on the N-s compared to the free molecule. This is consistent with the shallow picture of the wave function emerging from our first-principles calculation. Note that the delocalization of the wave function affects the hyperfine tensor much more directly than it does for the g factor because we are directly looking at the contribution right at the nuclear sites of the N atoms.

E. Conclusions and outlook

In summary, we have shown that N_2 on the Zn site has the characteristics of a shallow double acceptor and is thus a good candidate to explain the observed N-related shallow acceptor state by Zeuner *et al.*. At the same time, when this shallow acceptor level catches one electron, it can account for the EPR center observed by Garces *et al.*,[12] which is thereby identified as a $N_2{}^+$ radical, rather than a N_2^- one. We emphasize that the DAP transition at 3.235 eV measured by Zeuner *et al.*[9] is also observed in the samples of Garces *et al.*,[12] thus providing additional evidence that both may be related to the same center.

The major consequence of the present finding is that it points toward a new route for achieving p-type doping in ZnO with nitrogen. First, one should grow ZnO in O-rich and Zn-poor conditions and secondly, one should try to dope with N_2 rather than with activated atomic N species. We have here identified the nature of the N-related defect that can cause a shallow level and hence could be a source of p-type doping. However, we cannot exclude that N_2 could migrate to other sites, such as interstitial sites and this may be the reason why p-type doping in ZnO has remained so elusive. How to stabilize the N_2 molecule on the Zn site and avoid compensating defects remains a challenge to be overcome.

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[*] Permanent address: Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079, USA; walter.lambrecht@case.edu

[†] Permanent address: Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand.

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