Theory of Oxygen-Boron Vacancy Defect in Cubic Boron Nitride: A Diamond NV⁻ Isoelectronic Center

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A color center in c-BN which is isoelectronic to diamond NV^- is predicted based on first-principles electronic structure calculations using the Heyd-Scuseria-Ernzerhof hybrid functional. The defect consists of a substitutional oxygen and an adjacent boron vacancy ($\mathrm{O_N} - V_\mathrm{B}$). We find that the $\mathrm{O_N} - V_\mathrm{B}$ center is optically accessible with a zero-phonon line of about 1.6 eV. The $\mathrm{O_N} - V_\mathrm{B}$ center also shares much of the characteristics of the GC-2 center often observed in c-BN. A prominent vibronic coupling peak is predicted to be around 55 meV, which is in excellent agreement with the characteristic phonon frequency (56 meV) observed in the luminescence spectra of the GC-2 center.

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A successful transition from a transistor-based computing paradigm to quantum computing requires identifying systems with desired properties such as having a long quantum coherence time and being scalable. In this regard, the negatively charged nitrogen-vacancy (NV^-) center in diamond, with its unique spin and optical properties, has emerged as a promising solid system for quantum information applications. The promises of the NV^- center have inspired unprecedented research interests in optical manipulations of defect states, and have fostered the search for alternative isoelectronic defect systems [1]. Since cubic boron nitride (c-BN) shares many of the interesting properties with diamond, it is likely the best system to host an NV^--like isoelectronic defect center. In the past, technical difficulties in growing high quality and thick c-BN films had limited its potentials. Recently, however, there are very encouraging developments in the synthesis and annealing techniques [2–8], thereby, prompting renewed interest in this material.

In this Letter, we predict a diamond NV^--like color center in c-BN. This defect center consists of a substitutional oxygen and an adjacent boron vacancy, $\mathrm{O_N} - V_\mathrm{B}$ (shown in Fig. 1), and displays most of the interesting properties found in the NV^- center. We find that the electronic structure of the $\mathrm{O_N} - V_\mathrm{B}$ center resembles that of the NV^- center in diamond, thus, providing a potential alternative to the NV^- center. The $\mathrm{O_N} - V_\mathrm{B}$ center is optically accessible with a zero-phonon line (ZPL) of about 1.6 eV, to be compared with 1.95 eV for the NV^- center. The $\mathrm{O_N} - V_\mathrm{B}$ center also shares much of the characteristics of the GC-2 center often observed in c-BN [9–13].

Experimentally, optical properties of defects in c-BN have been investigated using photoluminescence and cathodoluminescence (CL) techniques [9–15]. Identification of defect center in c-BN using electron spin resonance experiments have also been reported. [16,17] Surprisingly, to the best of our knowledge, there has been no reported work using optically detected magnetic resonance to characterize defect centers in c-BN. From the CL measurements, vibronic spectra of three defect centers, labelled GC-1, GC-2, and GC-3 with ZPL of 1.76 eV, 1.63 eV, and 1.55 eV, respectively, have been identified [9]. It is suggested that GC-1 be vacancy related, while GC-2 be a vacancy complex [9–11]. The precise origins of these centers, however, have not been clearly identified. The measured energy of the ZPL of the GC-2 center agrees

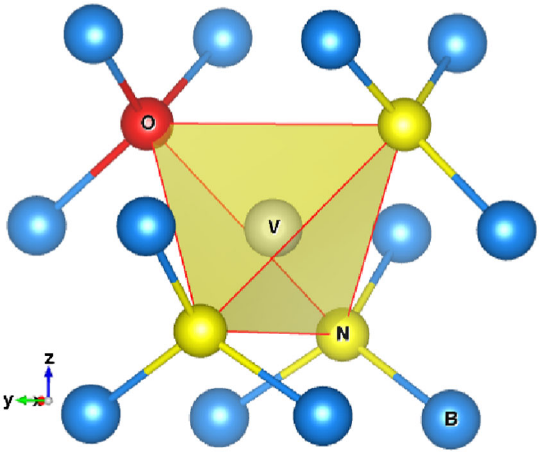

FIG. 1 (color online). Structure of a $\mathrm{O_N} - V_\mathrm{B}$ center in c-BN. Nitrogen atoms are shown in yellow (light color), boron in blue, and oxygen in red (dark). The boron vacancy (V_B) at the center of the tetrahedron is also shown.

well with our theoretical value of 1.60 eV. Our assignment that the $\mathrm{O_N} - V_\mathrm{B}$ be the observed GC-2 center is also consistent with the understanding that the GC-2 is a vacancy complex. In addition, the measured characteristic phonon frequency accompanied by the cathodoluminescence of the GC-2 center is about 56 meV [10,12] which is in excellent agreement with our theoretical estimate of 55 meV.

Our density functional theory (DFT) calculations are carried out using the QUANTUM ESPRESSO package.[18] Optical excitation energies of the $\mathrm{O_N} - V_\mathrm{B}$ center are calculated within the well-established constrained DFT approach using the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [19]. For comparison, we have also used the Perdew-Burke-Ernzerhof (PBE) functional [20] in our calculations. A 50 Ry energy cutoff is used for the plane wave expansion of the wave functions, and 500 Ry is used for the charge density. We use a supercell containing 216 atoms to characterize the electronic and phonon properties of the defect using a Γ-point sampling scheme. We believe that our model is sufficiently large that important features of this defect can be captured. For example, we observe nearly dispersionless in-gap defect states for both diamond $\mathrm{NV^-}$ and the $\mathrm{O_N} - V_\mathrm{B}$ centers, indicating negligible interactions between periodic defect images. The structures are fully relaxed both for the ground state occupation and the constrained excited state occupation.

The $\mathrm{O_N} - V_\mathrm{B}$ defect complex introduces substantial local structural changes: The volume of the tetrahedron formed by the substitutional oxygen atom and the three nitrogen atoms surrounding the vacancy expands by about 27% calculated within the HSE06 functional. The O-B and the N-B bond lengths near the vacancy shorten by about 2% and 3%, respectively, relative to the ideal B-N bond length. This local structural relaxation is very similar to that in the $\mathrm{NV^-}$ center in diamond for which the N-C and the C-C bonds near the vacancy shrink by about 4% and 3% compared to the ideal C-C bond length in diamond. We have also investigated the stability of the neutral $\mathrm{O_N} - V_\mathrm{B}$ defect complex and find that the neutral defect is stable as long as the Fermi level lies within 2 eV (see Supplemental Material [21]) from the valence band maximum. Since c-BN can be both $p-$ and $n-$doped [22], it is possible to tune the Fermi level across the band gap so that the above condition can be achieved.

Figure 2 compares the electronic structures of an $\mathrm{NV^-}$ and an $\mathrm{O_N} - V_\mathrm{B}$ center calculated using the HSE06 functional with a 216-atom supercell. The calculated band gap is about 6.0 eV for c-BN within the HSE06 functional, this compares well with the recently measured value of 6.4 eV [23] for the minimum gap of c-BN. Similar to the $\mathrm{NV^-}$ center in diamond, the $\mathrm{O_N} - V_\mathrm{B}$ center also introduces optically active defect states, i.e., occupied a_1 and unoccupied e minority-spin states (shown in blue in the figure), deep inside the band gap, thereby, enabling optical probe and/or control of the defect states. The ground state of the $\mathrm{O_N} - V_\mathrm{B}$ center is a spin triplet with an electronic configuration $(a_1^2 e^2)[^3A_2]$, which is identical to that of the $\mathrm{NV^-}$ center. The optically inactive majority-spin defect states, however, show significant difference between the two systems: whereas the majority-spin defect states for the $\mathrm{NV^-}$ center are well isolated and located inside the band gap, those for the $\mathrm{O_N} - V_\mathrm{B}$ center seem to be in resonance with bulk valence states. As far as optical probe of defect states is concerned, however, the $\mathrm{O_N} - V_\mathrm{B}$ and $\mathrm{NV^-}$ defect centers should show very similar behavior since only minority-spin states are involved in spin-conserving optical excitations.

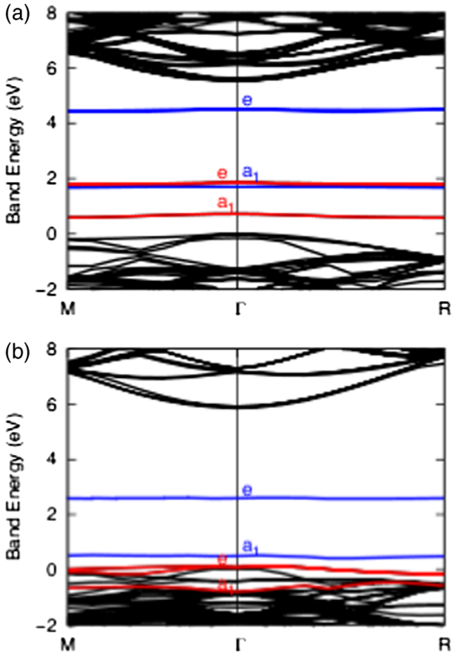

FIG. 2 (color online). Band structures of (a) $\mathrm{NV^-}$ center in diamond, and (b) $\mathrm{O_N} - V_\mathrm{B}$ center in c-BN calculated using a 216-atom supercell and the HSE06 functional. The spin resolved defect states (e and a_1) are shown in red and blue lines for the majority and minority spins, respectively.

The localization of defect states is illustrated in Fig. 3, which compares the minority-spin a_1 and e defect states in the $\mathrm{NV^-}$ and the $\mathrm{O_N} - V_\mathrm{B}$ centers calculated within the HSE06 functional. For the $\mathrm{NV^-}$ center, the a_1 state [Fig. 3(a)] is primarily localized on the substitutional nitrogen and on the three carbon atoms near the vacancy; the e doublet [Fig. 3(b)], on the other hand, is highly localized on the three carbon atoms around the vacancy, and has no contribution from the substitutional nitrogen. The defect states of the $\mathrm{O_N} - V_\mathrm{B}$ center display similar behaviors to those of the $\mathrm{NV^-}$ center: the a_1 state [Fig. 3(c)] is localized on the substitutional oxygen and the three nearby nitrogen atoms, and the e state [Fig. 3(d)] is highly localized only on the three nitrogen atoms near the vacancy.

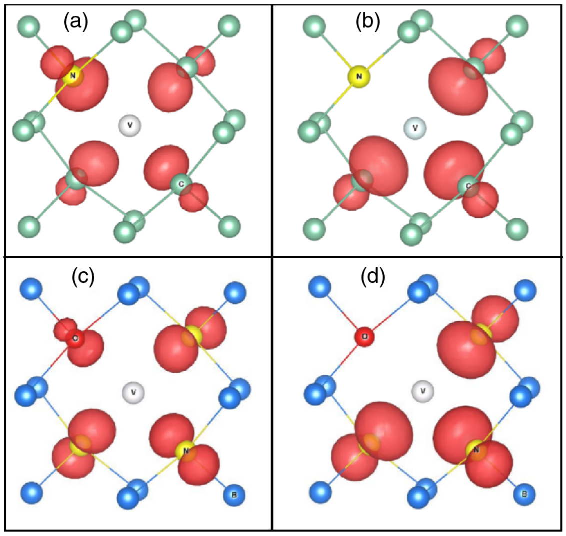

FIG. 3 (color online). Charge density plots for the minority spin a_1 [(a) and (c)] and e [(b) and (d)] defect states for the NV$^-$ center in diamond and the $\mathrm{O_N} - V_\mathrm{B}$ center in c-BN, respectively. Only atoms near the defect center are shown for clarity. The value of the charge density for the isosurface plot is $1.0 \times 10^{-2} e/a_0^3$.

The optical properties of the NV$^-$ center have been investigated in great detail. For example, the ZPL is measured to be 1.945 eV [24], and the Stokes shift (ΔS) and the anti-Stokes shift (ΔAS) are 235 meV and 185 meV, respectively. A schematic illustration of the optical transitions of a defect center is shown in Fig. 4. For the GC-2 center, however, only the ZPL (1.63 eV) and the characteristic phonon frequency (56 meV) have been identified [10,12]. Theoretically, the optical transitions of defect states can be approximated by the total energy difference between the two electronic states involved within the Franck-Condon principle using the constrained DFT approach. For example, the energy of the vertical transition $A \rightarrow B$ (Fig. 4) can be calculated using the total energy of the excited state and that of the ground state within DFT, i.e, $\Delta E(A \rightarrow B) = E_e(Q_g) - E_g(Q_g)$, where the energy of the excited state is calculated using the ground state structural configuration Q_g but with a constrained occupation by promoting one electron from the minority-spin a_1 to the minority-spin e state. Similarly, the energy of the vertical transition $C \rightarrow D$ is calculated using the excited state structural configuration Q_e, i.e., structure relaxed with the excited state occupation. Within this approximation, the transition $A \rightarrow C$ (or $C \rightarrow A$) gives rise to ZPL assuming that the zero-point phonon energies are the same for both the ground state and the excited state. The Stokes shift ΔS and the anti-Stokes shift ΔAS can also be estimated as illustrated in Fig. 4.

Table I compares the optical transitions of the NV$^-$ center in diamond and those of the $\mathrm{O_N} - V_\mathrm{B}$ in c-BN. The accuracy of the HSE06 functional in the prediction of the optical transitions of highly localized defects such as the NV$^-$ center has been previously demonstrated [25], as we have quoted in the table. For example, the calculated energy of the ZPL for the NV$^-$ center is about 1.96 eV, to be compared with the experimental value of 1.95 eV [25]. Our calculated ZPL for $\mathrm{O_N} - V_\mathrm{B}$ is 1.60 eV, which is very close to the measured value (1.63 eV) of the GC-2 center in c-BN. For comparison, we also included results calculated using the PBE functional. As was mentioned earlier, the precise nature of the GC-2 defect center in c-BN is still not well characterized experimentally. To the best of our knowledge, there have been no measurements of the Stokes shift ΔS and the anti-Stokes shift ΔAS for the GC-2 center. Therefore, our results call for future experimental verification.

The assignment of the GC-2 in c-BN center based only on the energy of the ZPL may not be convincing. More evidence comes from the phonon structure. Experimentally, a characteristic phonon energy of about 56 meV is observed in the cathodoluminescence spectra of the GC-2 defect center [10,12]. Therefore, it would be very interesting to investigate the phonon structure of this defect center. Although rigorous quantum mechanical calculations of vibronic transitions of localized defect states is still not feasible today, the Franck-Condon principle provides a convenient theoretical foundation for identifying the local vibration modes (LVMs) involved in electronic transitions. We identify the characteristic phonon energy involved in luminescence experiments in a few steps. First, we calculate the phonon structure of the $\mathrm{O_N} - V_\mathrm{B}$ center in a 216-atom supercell. All phonon modes, i.e., bulk phonons as well as the LVMs, are calculated. Second, we identify the LVM associated with the defects using the localization measure $\xi_\alpha = (\sum_i |\vec{p}_{\alpha i}|^4 / \sum_i |\vec{p}_{\alpha i}|^2)$, where $\vec{p}_{\alpha i}$ is the ith atomic component of the polarization vector of the αth phonon mode. This measure of the localization of phonon modes is similar to the inverse participation ratio for measuring electronic localization [26,27]. A phonon mode

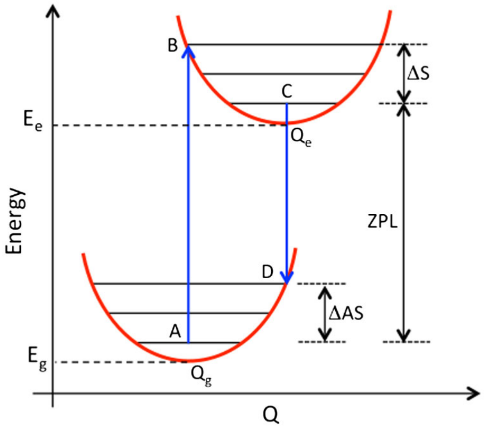

FIG. 4 (color online). Schematic for the energy versus configuration coordinate Q for two electronic states involved in optical transitions within the Franck-Condon principle.

TABLE I. Optical transition energies for the $O_N - V_B$ center in c-BN and the NV^- in diamond calculated using the HSE06 and the PBE functionals. The HSE06 results for the NV^- center is taken from Ref. [25].

System	Method	ZPL (eV)	$A \rightarrow B$ (eV)	$C \rightarrow D$ (eV)	ΔS (meV)	ΔAS (meV)
O_N-V_B	PBE	1.12	1.21	1.04	91	83
	HSE06	1.60	1.75	1.47	150	130
	PBE	1.74	1.93	1.58	189	160
NV^-	HSE06 [25]	1.96	2.21	1.74	258	217
	Expt. [24]	1.95	2.18	1.76	235	185

is identified as a LVM if its ξ_α is significantly greater than the averaged value. The LVMs associated with the $O_N - V_B$ center are listed in Table II. These results may serve as a guide for future experiments aimed at characterizing defects in c-BN.

Next, we define a displacement vector between the structural configuration of the ground state and that of the excited states as

$$\Delta\vec{R}_i = [\vec{R}_i(Q_g) - \vec{R}_i(Q_e)]; i = 1, 2, \ldots, N, \tag{1}$$

where $\vec{R}_i(Q_g)$ and $\vec{R}_i(Q_e)$ are the positions of the ith atom relaxed with the ground state and excited state occupations, respectively, as indicated in Fig. 4, and N is the total number of atoms in the cell. Finally, we calculate the projection of the displacement vector onto the polarization vectors of the identified LVM

$$\eta_\alpha = \sum_i \frac{1}{\sqrt{m_i}} \vec{p}_{\alpha i} \cdot \Delta\vec{R}_i, \tag{2}$$

where m_i is the mass of the ith atom and $\vec{p}_{\alpha i}$ is the ith atomic component of the polarization vector of the αth phonon mode. Symmetry requires that the displacement vector $\{\Delta\vec{R}_i\}$ have the a_1 symmetry. Therefore, only LVMs with the a_1 symmetry will give a nonzero projection. The calculated projections $|\eta_\alpha|^2$ for the LVMs are also listed in Table II. This projection should provide a faithful estimate for the Franck-Condon factor for the LVM involved in luminescence experiments. Figure 5 plots projections $|\eta_\alpha|^2$ versus the energy of the LVM. There should be at least six LVMs involved in the luminescence spectra of the $O_N - V_B$ center. The vibration pattern for a typical a_1 LVM is shown in the inset. To account for various broadening mechanisms, we apply a broadening of 3 meV for each LVM weighted by the projection $|\eta_\alpha|^2$, as shown with the dotted line in Fig. 5. The first three LVMs together give rise to a prominent vibronic coupling peak at about 55 meV. This result compares very well with the experimental result of 56 meV for the GC-2 center [10,12].

We would like to mention that the existence of singlet excited states [28–31] in the NV^- system plays a crucial role in the optical pumping mechanism [32]. Considering their similarities, one would expect that these singlet states also exist in $O_N - V_B$. However, further investigation is needed before we can draw a close comparison between the two color centers. The diamond NV^- also enjoys additional advantages such as the absence of nuclear spins for the ^{12}C isotope.

In conclusion, we have predicted a color center in c-BN which is isoelectronic to the NV^- center in diamond. The defect complex consists of an oxygen substitution and an adjacent boron vacancy ($O_N - V_B$). Similar to the NV^- center, the defect states in the $O_N - V_B$ center are well

TABLE II. Calculated LVM of the $O_N - V_B$ center in c-BN and their Franck-Condon factors estimated by a projection procedure described in the text.

a_1 modes		e modes	
E (meV)	$\lvert\eta\rvert^2 \times 10^4$	E (meV)	$\lvert\eta\rvert^2 \times 10^4$
51.6	1.5	51.5	0.0
53.4	1.0	56.6	0.0
57.2	2.1	64.2	0.0
64.6	0.5	102.1	0.0
67.3	1.0	106.7	0.0
81.7	0.4	108.4	0.0
89.2	0.0	126.3	0.0
a_2 mode		128.2	0.0
132.6	0.0		

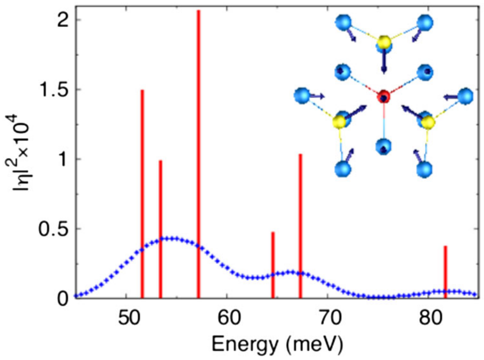

FIG. 5 (color online). Identified LVM phonon modes (vertical bars) and projection $|\eta_\alpha|^2$ weighted broadening (dotted line). These LVMs are predicted to be strongly involved in the luminescence of the $O_N - V_B$ center. The inset shows a vibration pattern for a typical a_1 LVM.

localized and are optically accessible with a ZPL of about 1.6 eV. In addition, we find that this defect complex shares many of the characteristics of the often observed GC-2 center in *c*-BN. Vibronic coupling associated with the luminescence process of $\mathrm{O_N} - V_\mathrm{B}$ is analyzed using a projection scheme within the Franck-Condon principle. The estimated vibronic coupling peaks at about 55 meV, which agrees well with the observed characteristic phonon frequency (56 meV) of the GC-2 center in *c*-BN.

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