

Comment on “*Ab Initio* Electronic and Optical Properties of the $N - V^-$ Center in Diamond”

In a recent Letter [1], Hossain *et al.* claimed that a generalized gradient correction type functional within the density functional theory (PBE-DFT) [2] reproduces accurately the energy of the measured zero-phonon line (ZPL) excitation of the $N - V^-$ center in diamond. In this Comment we show the following: (i) The excitation energies obtained with the PBE functional do *not* agree with experiment: PBE results underestimate the fundamental band gap of diamond by 24% (1.32 eV), and the ZPL energy of the $N - V^-$ center by 12% (0.24 eV). (ii) The calculated PBE vertical absorption energy found by Hossain *et al.* is erroneously assigned to the ZPL and is fortuitously very close to the experimentally measured ZPL energy. The erroneous assignment is due to the neglect of phonon modes and of the defect relaxation upon excitation; the latter produces a shift in the absorption energy (Stokes shift). The fortuitous agreement with experiment is due to the fact that the measured Stokes shift (0.235 eV) happens to be very close to the value by which the PBE calculation underestimates the measured ZPL value.

The experimental ZPL of the $N - V^-$ center is 1.945 eV both in absorption and emission [3]. For $T > 77$ K, a broad phonon side band was detected in absorption with maximum intensity at 2.180 eV. This is attributed to the vertical (no relaxation) $A \rightarrow B$ transition in Fig. 1, the energy difference with the ZPL, 0.235 eV, being the Stokes shift. The ZPL transition involves change in *both* the electronic

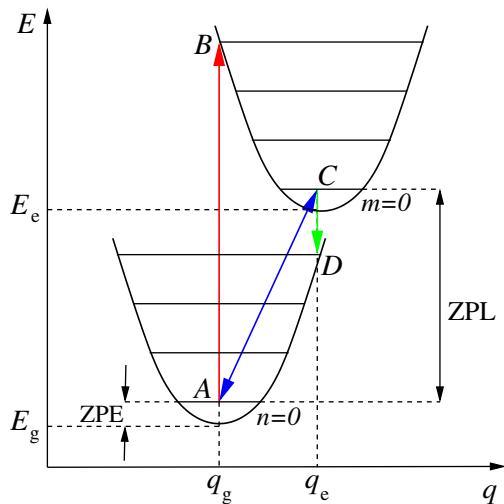


FIG. 1 (color online). Energy (E) vs configuration coordinate (q) of defect excitation in the Franck-Condon approximation. E_g , q_g , and E_e , q_e correspond to the lowest-energy structure for the ground and excited states, respectively. Zero-point energy (ZPE) of the ground state, and $n = 0$, $m = 0$ are the lowest phonon levels in each case. $A \rightarrow B$ and $C \rightarrow D$ are the vertical absorption and emission and $A \rightarrow C$ is the zero-phonon line.

TABLE I. The calculated vertical absorption ($A \rightarrow B$), the zero-phonon line (ZPL) and Stokes shift (S) using PBE-DFT, compared to experiment. The value calculated in Ref. [1] and erroneously assigned to the ZPL, is here compared to the $A \rightarrow B$ transition.

	ZPL (eV)	$A \rightarrow B$ (eV)	S (eV)
PBE	1.706	1.910	0.204
Exp. [3]	1.945	2.180	0.235
PBE [1]		1.912	

and the ionic configurations. The zero-point energy in the ground state and excited configurations is ~ 10 meV and can be ignored [3]. We calculated the excitation energies corresponding to the $A \rightarrow B$ and the ZPL transitions, using the PBE functional, in a supercell of 512 C atoms, with the VASP code [4], which gives well converged properties for this system [5].

The PBE results (Table I) underestimate both the ZPL and the ($A \rightarrow B$) transition, by 0.239 and 0.270 eV, respectively. The calculated Stokes shift, 0.204 eV, is close to the experimental value. Since Hossein *et al.* [1] neglected defect relaxation upon excitation, their excitation energy (1.912 eV) must be assigned to the vertical excitation rather than the ZPL, and is in excellent agreement with our result for the same transition (1.910 eV). The error between theory and experiment for the ZPL happens to be very close to the experimentally measured Stokes shift. This conclusion is not affected by the direction of the applied electromagnetic field, which affects only the absorption strength but not the position of the peak.

A. G. is supported by the Hungarian OTKA No. K-67886.

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Received 29 January 2009; published 10 April 2009

DOI: 10.1103/PhysRevLett.102.149703

PACS numbers: 71.15.Mb, 31.15.ae, 31.15.ag, 71.55.-i

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