Comment on "Huge Excitonic Effects in Layered Hexagonal Boron Nitride"

Recently, the high luminescence yield in hexagonal boron nitride (*h*-BN) has raised the interest in BN compounds as potential candidates for UV light-emitting materials. Arnaud *et al.* [1] have provided an explanation of the measured optical absorption spectrum of *h*-BN [2] in terms of four close-lying Frenkel-like excitons. We agree with the global shape of the spectrum and that the nature of the main absorption peak is a strongly bound π-π^* exciton (see Fig. 1). However, our first principles calculations [3] put in evidence two problems in the analysis of Arnaud *et al.*: (i) The low-lying excitonic structure consists of a bright doubly degenerate exciton that takes most of the oscillator strength of the spectrum as shown in Fig. 1. About 90 meV below the bright exciton, we find a dark doubly degenerate exciton. In contrast, Arnaud *et al.* observe a splitting of the dominant absorption peak into 4 subpeaks between 5.7 and 5.9 eV which they presumed to explain the detailed fine-structure in the measured absorption spectra of Watanabe *et al.* [2]. (ii) The excitonic wave function in Fig. 3 of Arnaud *et al.* violates the symmetry of *h*-BN: since the hole is located on top of a nitrogen atom, the electron probability density should obey the threefold rotation symmetry of *h*-BN, unless the exciton is degenerate.

In order to understand the degeneracy of the main excitonic peak at 5.7 eV, we show in the inset of Fig. 1 the excitonic wave function, considering that the hole is located close to the top of the N atom: The electron probability densities of the two states are not rotationally symmetric, but adding the densities of the two states, we recover the expected threefold rotation symmetry. If we break the symmetry of the crystal, e.g., by slightly displacing one of the atoms, we observe a splitting of the two lowest degenerate excitons. Furthermore, the lowest-lying exciton, which is dark for the perfect crystal, acquires some oscillator strength. Therefore, we conclude that the experimental fine structure of Watanabe *et al.* is not an intrinsic property of the perfect *h*-BN lattice. It can only be understood if symmetry-breaking effects such as dislocations or defects are taken into account.

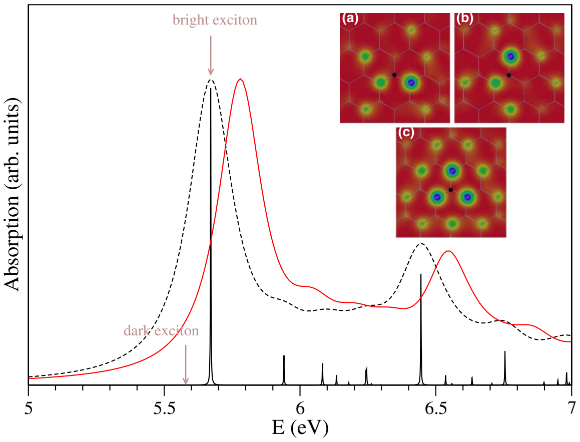

FIG. 1 (color online). Optical absorption spectrum of *h*-BN with a broadening of 0.001 eV (black solid line) and with an estimated experimental broadening of 0.1 eV calculated with YAMBO (black dashed line) and with VASP (red solid line). Inset: Two-dimensional projections of the probability density $|\Psi^\lambda(r_h, r_e)|^2$ of the degenerate exciton states with (a) $\lambda = 3$ and (b) $\lambda = 4$. The hole is located 0.4 a.u. above the nitrogen atom in the center (black circle). Summing the two densities (panel c) restores the threefold rotation symmetry.

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[3] In order to avoid implementation uncertainties we have performed calculations using both pseudopotentials [4] and PAW [5]. The two calculations agree among each other and with previous experimental data obtained from optical absorption and electron-energy loss spectroscopy [6] (see the broader spectrum in Fig. 1). The main experimental absorption peak lies between 6 and 6.1 eV, at about 5.8 eV in the calculation of Arnaud *et al.* and at 5.7 eV in our calculation with SELF and 5.8 in our calculation with VASP. Small differences (of 0.1 eV) in the absolute position of the peak stem from differences in the (pseudo-)potentials.

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