Comment on "Quantum Confinement Effect in Diamond Nanocrystals Studied by X-Ray-Absorption Spectroscopy"

In a recent Letter [1], Chang *et al.* report on an increase in the binding energy of the C1s core exciton in diamond nanopowders which is ascribed to quantum confinement. The core exciton shows up as a peak at the threshold of the C1s → conduction band transitions. The binding energy of the core exciton, ΔE_{ex}, is defined as the photon energy difference between the absorption peak energy E_x of the exciton and the threshold E_{CB} that marks the onset of a continuum of transitions from the C1s core level to the unoccupied states. Chang *et al.* derive values for ΔE_x that increase from 0.19 eV for particles with an average size of 5 μm to 1.0 eV for particles with diameters of 3.6 nm. Experimentally, the change in ΔE_x has two contributions. The energy of the exciton peak E_x increases by 0.4 eV between 5 μm and 3.6 nm grain size while the conduction band threshold E_{CB} increases by 1.20 eV over the same range. The increase in ΔE_x rests crucially on the proper determination of E_{CB}. The authors of Ref. [1] use the superposition of "Lorentzian and arctangent functions to describe the exciton state and the conduction band edge." E_{CB} is identified with the inflection point of the arctangent function which is adjusted to the pre-edge part of the spectrum. However, there is no resemblance of the arctangent function which is essentially a broadened step function with the absorption spectrum in the range of C1s-to-conduction band transitions. The authors do not explain what criteria they used to choose the width of the arctangent function nor, more importantly, its position relative to the absorption spectra. Consequently, there appears to be no foundation for the 1.20 eV increase in E_{CB} in going from 5 μm to 3.5 nm grains and thus no experimental basis from which effects of quantum confinement on the exciton energy or the conduction band edge can be inferred.

Chang *et al.* remark that their exciton binding energy of 0.19 eV for the 5 μm grains agrees with the binding energy reported by Morar *et al.* for single crystal diamond [2]. Morar *et al.* derived the binding energy from a fit of their data with the theory of Elliot [3] which treats the core exciton as a Wannier exciton. The excellent fit achieved with this theory using reasonable values for the parameters entering the description of the exciton and the conduction band edge gives their exciton binding energy a certain degree of credibility. One thus questions why Chang *et al.* did not use Elliot's theory. The answer is given in Fig. 1 where we show C1s absorption data obtained form a clean and (2×1) reconstructed single crystal diamond (111) surface [4]. Also shown are three fits using Elliot's theory and the parameter of Morar *et al.* (solid and dashed lines) with a Gaussian broadening of $w_g = 0.2$ eV and $w_g = 0.1$ eV, respectively. For the short dashed line the exciton binding energy was increased to 0.3 eV. Evidently, all three curves do not fit the data above the exciton peak because of the pronounced minimum ~1.5 eV above E_x which was missing in the data of Morar *et al.* The spectrum of Fig. 1 is virtually identical with all spectra of Chang *et al.* and it appears that the description of the core absorption in terms of a Wannier exciton preceding the conduction band is not appropriate. Shirley [5] has recently calculated the C1s absorption spectrum in diamond including electron-hole interaction. The result does indeed yield the experimentally observed threshold singularity. The spectral shape beyond the threshold singularity is changed so drastically compared to the density of conduction states, however, that any interpretation of the core absorption spectrum in terms of a single particle excitation augmented by a bound core exciton with a definite binding energy appears to be questionable.

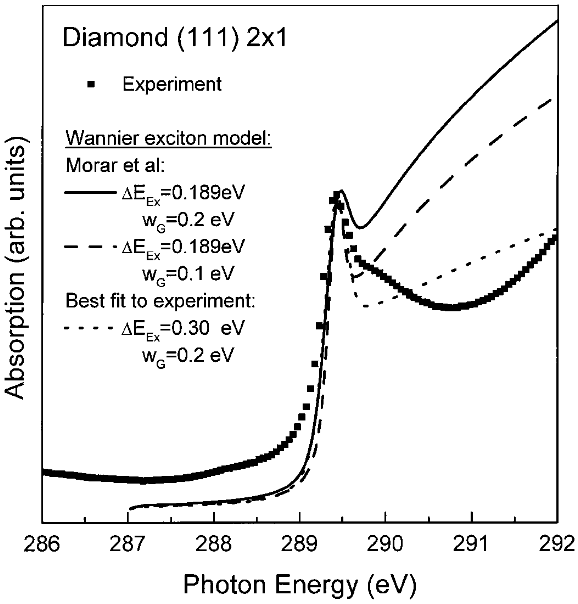

FIG. 1. C1s absorption spectrum of diamond (111) measured in the total electron yield mode (data points). The meaning of the different lines is given in the text.

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