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Ab initio optical properties of BN in the cubic and in the layered hexagonal phase

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Abstract

We present our ab initio calculation of linear optical properties in cubic (c-BN) and layered hexagonal BN (h-BN). Our results show a reasonable agreement with existent theoretical results and with measured data for the imaginary part of the dielectric function in the case of h-BN, while for c-BN discrepancies arise between theory and experiment. We discuss the possible reasons of this mismatch. © 2001 Elsevier Science B.V. All rights reserved.

In recent years the properties of Boron Nitride (BN) have been studied in great detail, both theoretically and experimentally. This is mainly due to some attracting properties of BN, such as its extreme hardness, high melting point, low dielectric constant, and large band gap which make this material interesting for applications in modern microelectronic devices and as a protective coating material [1].

Linear optical functions of cubic (c-BN) and hexagonal BN (h-BN) have been studied within DFT-LDA theory [2]. The electron wave-functions have been expanded in plane waves and the electron–ion interaction is treated by non-local norm-conserving ab initio pseudopotentials [3].

The cutoff energy needed to obtain convergence of both the total energy and Kohn–Sham eigenvalues is found to be equal to 55 Rydberg for c-BN and h-BN. The use of 10 Chadi and Cohen special

k points [4] for charge integration in the irreducible Brillouin Zone (IBZ) is found to be sufficient to achieve a good accuracy for the computed total energy and eigenvalues of the cubic phase. For h-BN the use of 12 special k points turns out to be enough [5].

We determine the optical properties of h-BN and c-BN by evaluating the momentum matrix elements associated to the dipole transitions at a large number of k points within the IBZ. According to the scheme described in [6] we compute the frequency-dependent imaginary part of the dielectric function as

$$\epsilon_2(\omega) = \frac{(8\pi)^2 e^2}{\omega^2 m^2 V} \sum_{v,c} \sum_{\vec{k}} |\langle v, \vec{k} | \vec{p} | c, \vec{k} \rangle|^2 \times \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega), \quad (1)$$

where v and c label the valence and conduction states associated with the energies $E_v(\vec{k})$ and $E_c(\vec{k})$, V is the crystal volume and $\langle \rangle$ is the matrix element of the momentum operator. In our case

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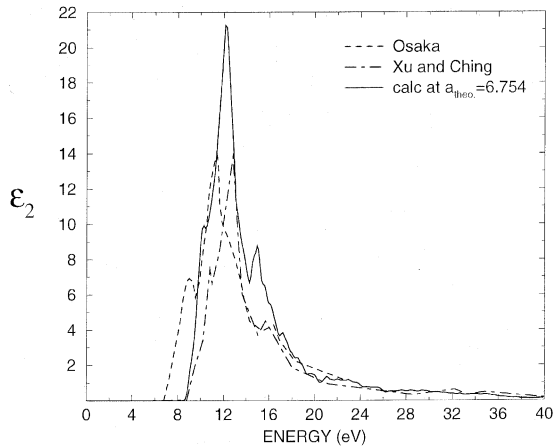


Fig. 1. Imaginary part of dielectric function of c-BN vs. the experimental data from [7] and previous LCAO theoretical result from [8].

eigenvalues and eigenfunctions used in Eq. (1) are the DFT-LDA ones.

In Fig. 1 we report the imaginary part of dielectric function in comparison with the experimental data obtained for a crystalline sample by Osaka et al. [7] by reflectance measurements. We also reported the LCAO theoretical results by Xu and Ching [8] for comparison. The experimental data show major structures at 9.05 and 11.7 eV and shoulders at 13.2 and 16.7 eV. For the onset a value of 6.8 eV can be estimated. The calculated curve by Xu and Ching shows a rigid shift to higher energies with respect to the experimental one by about 1.7 eV. Our results, which agree reasonably well with the LCAO ones, show also a blue shift with respect to the measurements, by about 2 eV at the onset.

For h-BN our results (see Fig. 2) for the dielectric function are also in good agreement with the LCAO one. Lower intensities are reported relatively to this phase, with respect to larger oscillator strengths found for c-BN.

A possible explanation of the mismatch between theory and experiment for the spectrum of c-BN is the presence of defects or surface disturbances within the sample, which may have caused a lowering of the onset energy. Moreover, one could suppose the coexistence of cubic and hexagonal phase domains within the same sample

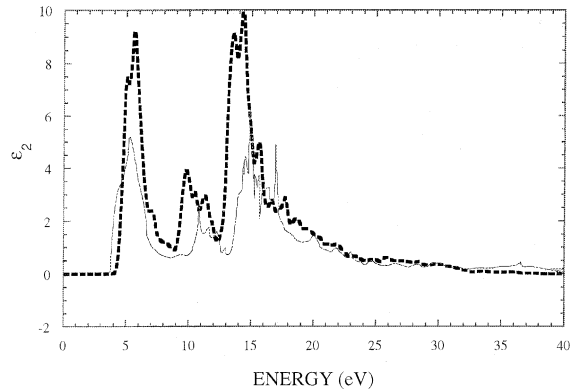


Fig. 2. Imaginary part of dielectric function averaged over the three crystallographic directions of h-BN (dashed line) vs. LCAO theoretical result of [8] (continuous curve).

[9]. In fact, merging hexagonal and cubic contributions to the dielectric functions determines a shift of $\epsilon_2(\omega)$ towards lower energies, but also causes a mismatch with the experimental curve at higher energies. Another matter of discussion is the strong dependence of ϵ_2 on the lattice parameter values. This issue can be crucial in case of a strong mismatch between substrate and grown samples [7,10]. Moreover, our calculation does not take into account self-energy corrections and excitonic effects (neither these effects have been considered up to now in the calculations of optical properties of BN). However, self-energy corrections tend to shift the spectrum toward higher energies, enhancing the discrepancies with the experiments, while excitonic effects tend to modify the shape of the ϵ_2 curve in the right direction. We are convinced then that both more refined experimental measurements and theoretical calculations on this interesting material are now timely.

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