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Calculated quasiparticle band gap of β-C_3N_4

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The quasiparticle electronic band structure of C_3N_4 carbon nitride in the β-Si_3N_4 structure is calculated using the *GW* approximation. The indirect band gap is predicted to be 6.4±0.5 eV and the minimum direct gap is found to be at Γ with a value of 6.75 eV. A plane-wave local-density-approximation band structure is also presented.

Solids made of first-row elements are of particular importance because these materials often have high bulk moduli, high thermal conductivity, low density, and large band gaps. Applications range from use in materials processing to heat-dissipative substrates for devices to use in short-wavelength photodiodes. While prediction of useful metastable materials using first-principles theory has been a purely academic pursuit in the last few decades, recent advances in materials research has made production of these compounds a reality.[1]

In predicting materials with high bulk moduli, covalent solids with small lattice constants are targeted. This is based on the predictive power of a semiempirical model[2,3] which relates the bulk modulus B_0 of a solid to the ionicity λ and bond length d by

$$B_0(\text{GPa}) = \frac{\langle N_c \rangle}{4} \frac{(1971 - 220\lambda)}{d^{3.5}} . \tag{1}$$

Here, λ is an empirical ionicity parameter which is 0, 1, and 2 for group IV, III-V, and II-IV semiconductors, respectively, and $\langle N_c \rangle$ is the coordination number of the compound. A covalent solid made of C and N was predicted by this model to have a bulk modulus comparable to diamond[4] and first-principles calculations of the structural properties gave a bulk modulus of 427 GPa, confirming the model's prediction. Calculations of the electronic properties[5] predicted an insulating material. The band structure and hence the band gap was calculated within the local-density approximation (LDA) which is known to underestimate band gaps.[6] The LDA calculated gap was found to be 3.2 eV and it was expected that the experimental value could be larger by several eV.

The structure investigated, β-C_3N_4, is related to the β-Si_3N_4 structure.[7,8] In this material, CN_4 tetrahedra are linked by the threefold coordinated N atoms. A model of the β-C_3N_4 structure is shown in Fig. 1. Nitrogen atoms are shown as the larger spheres. Each C atom has four nearest-neighbor N atoms forming an almost regular[9] tetrahedron while each N has three nearest-neighbor C atoms forming 120° bond angles. This arrangement satisfies the octet rule, indicating that the charge distribution would be primarily in the bonding regions stabilizing the compound. In contrast, zinc-blende CN is not a good candidate for a stable C-N solid since the first antibonding band would be occupied.

Recent experiments[10–12] have produced a covalently bonded C-N solid thought[13] to be β-C_3N_4 using various techniques. Although characterization of the compositional, structural, and electronic properties of the samples are consistent with the predicted compound β-C_3N_4, at present an adequate sample to perform optical measurements has not been produced. Hence the fundamental and higher energy band gaps have not been measured.

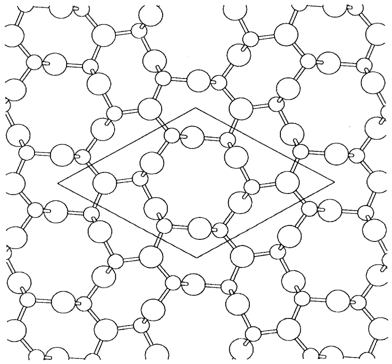

FIG. 1. Structure of β-C_3N_4 in the *a-b* plane. Half of the atoms shown lie in the $z = c/4$ plane, while the other half lie in the $z = -c/4$ plane. The solid consists of these buckled planes stacked directly on top of each other. Nitrogen atoms are represented by the larger spheres.

Here we present calculations of the fundamental (indirect) gap and the slightly larger direct gap using accurate methods for describing the quasiparticle properties, and present a plane-wave LDA band structure over a wide energy range.

As a first step the standard *ab initio* pseudopotential method[14–16] within the LDA (Ref. 17) is used to describe the ground state. The exchange and correlation potential derived[18] from the Monte Carlo calculations of Ceperley and Alder[19] is used. Troullier-Martins[20] soft pseudopotentials are used for the strong C and N cores to achieve good convergence for the energy eigenvalues with a moderate size basis set. The self-consistent calculation uses a plane-wave basis set with a cutoff energy of 45 Ry. Because of the large unit cell which contains two formula units (14 atoms), increases in the cutoff energy for the plane wave calculation are costly with present techniques.

The *GW* method[21,22] is used to calculate the self-energy correction to the LDA energies at Γ, *M*, *L*, and *A* in the hexagonal Brillouin zone. We use the wave functions obtained from the LDA calculation as input to the quasiparticle calculation and extrapolate the *GW* energy levels to determine the band gaps. This approach results in 0.1 eV (Ref. 21) accuracy for band gaps calculated using a random-phase approximation (RPA) dielectric matrix or 0.1–0.3 eV accuracy when an appropriate model dielectric matrix is used.[21,23]

In this work, the Hybertsen-Louie[21] scheme is used to calculate the electron self-energy. Typically the static dielectric response matrix is obtained by either a model or a linear-response perturbation calculation in the RPA.[21] Here we use a generalized form of the static Levine-Louie model dielectric function.[23,24] This model incorporates the correct limiting cases of the long-range ($\mathbf{q} \to 0$) and short-range ($\mathbf{q}$ is approximately the inverse lattice constant) behavior of the response function. The static dielectric matrix is extended to finite frequencies ω by a generalized plasmon-pole model[21] using exact sum rules to fix the frequencies and strengths of the poles in the inverse dynamical dielectric matrix elements $\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\omega)$ (Ref. 23) (where $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors).

The Levine-Louie model requires only the dielectric constant ε_∞ of the material as input. In principle this can be evaluated from *ab initio* calculations, but in the present case the computational requirements to do so are prohibitively large. We estimate the dielectric constant as a weighted average of ε_∞ of sp^3-bonded C (5.5) and sp^2-bonded BN (4.10–4.95).[25] Since the C-N bond in β-C_3N_4 is more similar[4] to the C-C bond than to the B-N bond we weigh the ε_∞ of diamond more heavily than that of hexagonal BN and obtain a rough estimate of 5.25. The error this estimate introduces has been estimated by repeating the present calculations for a dielectric constant of 5.15.

In the calculation of the many-body contribution to the self-energy Σ, several numerical cutoffs are involved. The dielectric matrix is truncated at $|\mathbf{q}+\mathbf{G}| = 3.1$ a.u. We have included eight $\mathbf{k}$ points in the irreducible wedge of the Brillouin zone and 400 bands in the calculation of the matrix elements of Σ in summing over the intermediate scattering states. The magnitudes of the variations due to each of the cutoffs are determined to estimate errors. The largest error arises from the cutoff in energy for the initial LDA plane-wave calculation. This accounts for 0.3–0.4 eV of the total error. Variation due to the choice of ε_∞, the truncation of the dielectric matrix and the number of bands used is less than 0.1 eV total.

As in Ref. 5, we did not relax the structural parameters of this structure. The structure belongs to space group $P6_3/m$ with $c/a = 0.3827$ which is the same value as Si_3N_4 and a calculated[4] lattice constant of 6.44 Å. Atomic coordinates are those of β-Si_3N_4 from Ref. 8.[26]

The LDA band structure is shown in Fig. 2. The agreement between this calculation using a plane-wave basis set and a previous LDA calculation[5] which used Gaussian orbitals is very good. We calculate a band gap of 3.11 eV compared to 3.2 eV from Ref. 5. The LDA valence bandwidth calculated here is 24.5 eV compared to 24.8 eV of Ref. 5. In addition, we note that the direct gap lies 0.5 eV above the lowest indirect transition. For both studies, however, the calculated gap is expected to be smaller than the true gap because the LDA does not accurately model excited state properties and has been shown to systematically underestimate band gaps.

From the *GW* correction, the lowest indirect gap is predicted to be 6.4 eV while the direct gap at Γ is 6.75 eV. Since these gaps lie almost an eV above that of diamond, this material may find many uses as a hard transparent solid. As in GaP where the indirect and direct gaps are close in energy, it may be possible to dope β-C_3N_4 to alter the indirect gap and make direct transitions favorable. In GaP, the difference between the indirect and direct gaps[25] is about 0.5 eV (the gaps are 2.272 and 2.780 eV at 300 K, respectively). While doping to produce a direct gap would lower the transition energy, the large initial gap of β-C_3N_4 may allow flexibility to engineer a useful material in the ultraviolet or visible blue region. The flat bands imply that the carrier mobility would probably be

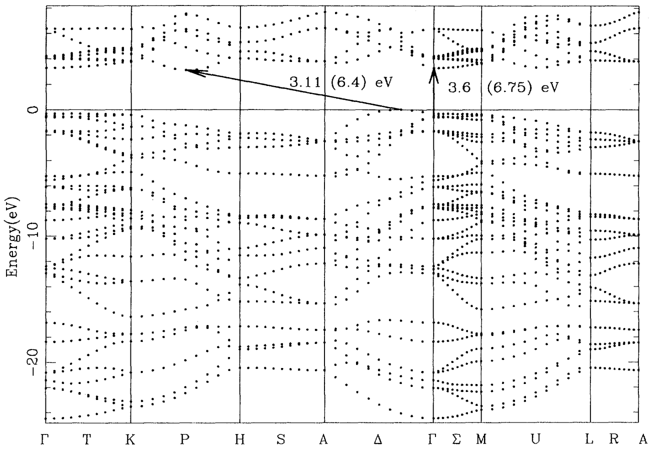

FIG. 2. The calculated LDA band structure for C_3N_4 is shown along with values of the quasiparticle band gaps in parentheses. Energies are measured relative to the top of the valence band. The lowest indirect and direct transitions are indicated by arrows with values labeled for the LDA (*GW*) calculation in eV.

low as is the case for most large gap semiconductors. In addition, we note that the low dispersion at Γ may be an asset since it produces a large joint density of states at the direct gap energy.

Using quasiparticle calculations we predict a large indirect gap of 6.4 eV and slightly larger direct gap of 6.75 eV for β-C_3N_4. The error in these calculated values is ±0.5 eV. While doping to produce an efficient direct gap material would reduce the gap, the initially large value indicates that use of this material for large-gap devices may be possible.

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