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# Optical properties of $\beta$-$C_3N_4$ and its pressure dependence

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The electronic and the optical properties of $\beta$-$C_3N_4$ are studied by means of first-principles local-density calculations. The structural properties obtained via total-energy calculations are in good agreement with the results of Liu and Cohen [Phys. Rev. B **41**, 10 727 (1990)]. The frequency-dependent optical properties are calculated after an approximate self-energy correction scheme is applied to the energy spectrum. It is found that the band gap in $\beta$-$C_3N_4$ increases linearly with pressure. The absorption spectrum shows two major peaks at 7.9 and 13.9 eV with a static dielectric constant of 3.2 predicted.

Recently, there has been a great interest in searching for and synthesizing the low-compressibility covalently bonded $\beta$-$C_3N_4$. This crystal was theoretically predicted to have a bulk modulus close to, or even greater than that of diamond, based on a simple semiempirical rule of Cohen.[1] Subsequent first-principles pseudopotential local-orbital calculations agreed with this prediction.[2,3] More recently, experimental evidence has been obtained that such a material does exist with a crystal structure close to that predicted by theory.[4,5] Because of the difficulty in obtaining large grain samples for this crystal, many important experiments on its physical properties remain to be done. Carbon nitride may also exist in amorphous form.[6,7]

In this paper, we present the results of theoretical calculations on the optical properties of $\beta$-$C_3N_4$ and its pressure dependence. We start with the calculation of the electronic and structural properties within the framework of the local-density approximation of the density-functional theory. Based on the electronic-structure results and the theoretically determined crystal structure, we evaluate the optical-absorption spectrum in the form of real and imaginary parts of the complex dielectric function. We further study the pressure dependence of the band gap and the optical properties. We use the first-principles all-electron orthogonalized linear combinations of atomic orbitals (OLCAO's) method[8] for the electronic-structure and total-energy calculations. This method is noted for its efficiency for systems with complex structures. As a matter of fact, the first realistic band structures of $\beta$-$Si_3N_4$ and $\alpha$-$Si_3N_4$ were calculated using this method,[9] albeit non-self-consistently. Self-consistent band structure and total-energy calculations for $\beta$-$Si_3N_4$ were carried out a few years later.[10,11] In that calculation, the crystal structure of $\beta$-$Si_3N_4$ as reported by Wild, Grieveson, and Jack was used,[12] which has internal parameters slightly different from the later work of Borgen and Seip.[13]

In the present calculation for $\beta$-$C_3N_4$, the basis function of C and N consists of $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, $3s$, $3p_x$, $3p_y$, and $3p_z$ orbitals of C and N, which are in the form of linear combinations of Gaussian-type orbitals (GTO's). The crystal potential and charge density are cast as sums of atom-centered functions, which are also expressed as GTO's. To increase accuracy, we treat the two crystallography inequivalent N atoms with independent potential functions. Self-consistency iterations in potential were carried out using 16 special **k** points in the irreducible wedge of the Brillouin zone (BZ). The final calculation for the optical properties was carried out using 216 regularly spaced **k** points in the same zone and the analytic linear-tetrahedron method. Because of the well-known problem of gap underestimation for insulators associated with the local-density approximation (LDA) theory, we have also applied a recently developed approximate self-energy correction scheme[14] to improve the gap value. This simple scheme is based on a two-band model of Sterne and Inkson,[15] and is not as rigorous as the first-principles *GW* method[16,17] using the plane-wave pseudopotentials scheme. However, this simple scheme does not involve any arbitrary parameters and thus retains the first-principles nature of the calculation. Test calculations on a number of semiconductors[14] and on $LiNbO_3$ show very satisfactory results.[18]

Our total-energy calculation for $\beta$-$C_3N_4$ is based on the crystal structure suggested by Lui and Cohen (LC), which is the same as for $\beta$-$Si_3N_4$ (space group $P63/m$).[13] We did not search for the optimal internal parameters of the structure, but we did explore the variation of the $c/a$ ratio. Figure 1 shows the calculated total energy as a function of unit-cell volume. Also shown are the total-energy contours with the variations in both the lattice constant $a$ and $c/a$ ratio. As can be seen, our calculation gives an equilibrium structure very close to that predicted by LC. The lattice constants $a$ and $c$ are within 0.5% of the LC result. Recent experimental data[5] give lattice constants a few percent smaller than predicted by the calculations. By fitting the calculated $E$ vs $V$ curve to Murnaghan's equations of state,[19] we obtained a bulk modulus of 4.21 MBar and a pressure coefficient of 5.12 for $\beta$-$C_3N_4$. This value of bulk modulus is very close to the value of 4.27 Mbar obtained by LC. Both values are close to, but smaller than, the value of 4.43 Mbar for diamond.

Figure 2 shows the calculated band structure and density of states (DOS) for $\beta$-$C_3N_4$ at the equilibrium structure. Again, our band structure is almost identical with that of LC. We obtained a direct LDA gap of 3.56 eV at $\Gamma$. The indirect gap is 3.43 eV with the top of the valence band (VB) being at a point along $\Gamma A$ and the bottom of the conduction band (CB) at $\Gamma$. The VB DOS can be viewed as composed of three regions $A$, $B$, and $C$, separated by indirect gaps. The upper region $A$ is from 0 to $-0.53$ eV. The middle one, $B$, is from

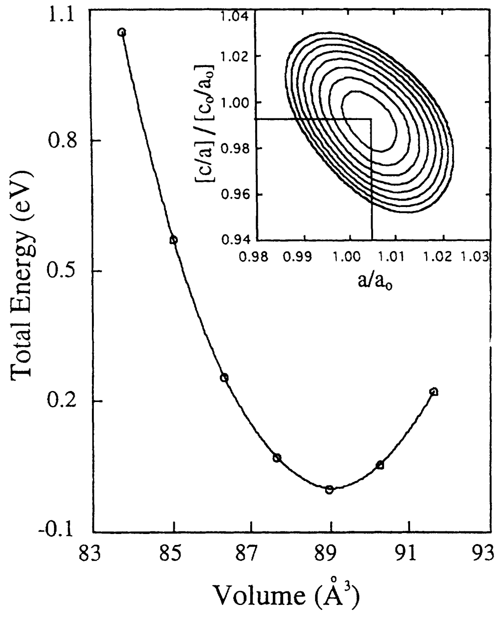

FIG. 1. Calculated total energy of $\beta$-$C_3N_4$ as a function of volume. Inset: total-energy contours as a function of ratios of $a$ and $c/a$ to $a_0$ and $c_0/a_0$, where $a_0$,$c_0$ are the equilibrium lattice constants obtained by LC (Ref. 3). The energy contours are separated in units of 0.03 eV.

TABLE I. Calculated electronic and structural properties of $\beta$-$C_3N_4$.

| | Present calculation | LC (Ref. 3) | Experiment (Ref. 5) |
|---|---|---|---|
| LDA gap (Γ) (eV) | 3.56 | 3.60 | |
| VB width (eV) | 24.9 | 24.8 | |
| $B$ (Mbar) | 4.21 | 4.27 | |
| $B'$ | 5.12 | | |
| $a$ (Å) | 6.47 | 6.44 | 6.3 |
| $c$ (Å) | 2.45 | 2.46 | 2.38 |
| $c/a$ | 0.379 | 0.383 | 0.375 |

$-5.3$ to $-16.6$ eV, and the lower one, $C$, is from $-16.6$ to $-25.0$ eV. In the case of $\beta$-$Si_3N_4$,[3,10] the portions $A$ and $B$ fuse together, leaving a gap of about 4 eV with the lower region $C$. From the partial components of the DOS (not shown), it is found that $A$ is mainly derived from the $2p$ orbitals of N, with no participation from the C states. The middle portion $B$ consists of a mixture of C $2p$ and N $2p$ orbitals. The lower portion $C$ is mainly from the $2s$ orbitals of both N and C with some admixture from the C $2p$ orbitals as well. The CB edge is dominated by the states with C $2p$ character. Both the CB and the VB edges are very sharp, indicative of very large electron and hole effective masses in $\beta$-$C_3N_4$. The main results on the electronic-structure and total-energy calculations are summarized in Table I. Some preliminary experimental data on the structure and those calculated by LC are also listed for comparison.

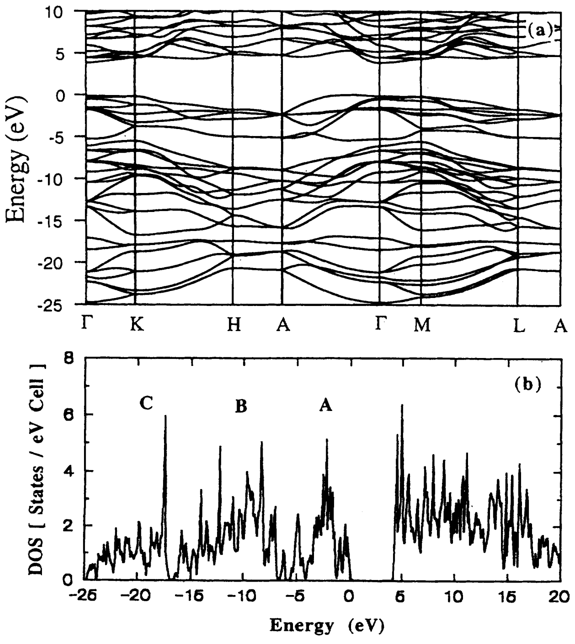

FIG. 2. Calculated (a) band structure; (b) DOS of $\beta$-$C_3N_4$.

Our main focus of this paper is on the optical properties of $\beta$-$C_3N_4$. Understanding the optical properties can lead to a deeper insight on the electronic structure. Although no measurement of optical properties has been reported, mainly because of the lack of a single crystal of sufficient size for this material, we believe it is only a matter of time before large-size samples will become available and optical measurements will be carried out. We thus consider our work to be a theoretical prediction of the optical-absorption profile of this superhard material. Since the gap size is an important issue in the discussion of optical properties, and since it is well known that the LDA theory generally underestimates the experimental gap by as much as 50% we used an approximate self-energy correction scheme within the OLCAO method to address this problem.[14] Our self-energy-corrected direct gap at Γ is 4.58 eV, which is almost 30% larger than the LDA gap. Corkill and Cohen (CC) have recently carried out a quasiparticle band calculation for $\beta$-$C_3N_4$ using the *GW* approximation with the plane-wave pseudopotential band structure.[20] They found the direct band gap at Γ to be increased from 3.6 to 6.75 eV, almost double the LDA gap. Although the *GW* approximation used by CC is considered to be more rigorous, and hence should give a more reliable quasiparticle band gap, it is still surprising to see such a large correction for $\beta$-$C_3N_4$. One possible reason is that the static dielectric constant used by CC is an estimated one. As we shall see below, our calculated value from the LDA result for $\varepsilon_0$ is 3.8, much smaller than the value of 5.25 used by CC. Another possible reason is that the method we employed is based on a simple two-band model, and therefore may not be accurate enough for the $\beta$-$C_3N_4$ crystal. However, the same scheme applied to $LiNbO_3$, which also has a very localized CB and VB near the gap, produced results in excellent agreement with experiment.[18] It is obvious that the actual size of the band gap in $\beta$-$C_3N_4$ cannot be established before experimental data become available. We may mention in passing

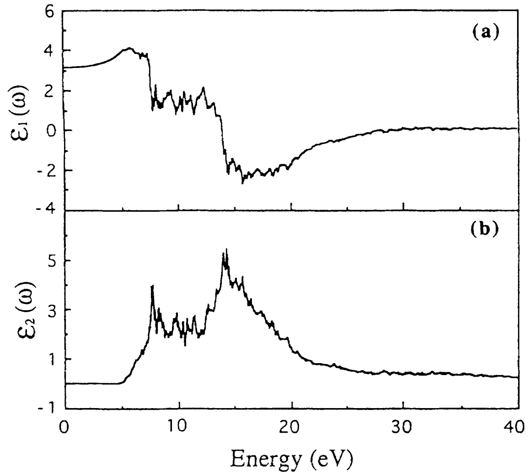

FIG. 3. Calculated (a) real and (b) imaginary parts of the dielectric function for $\beta$-$C_3N_4$.

that a similar type of optical-absorption calculation[23] for $\beta$-$Si_3N_4$ shows good agreement with the measured data on amorphous $Si_3N_4$ in both the peak position and amplitude. The LDA gap is almost the same as the experimental optical gap. We are not aware of any optical measurements on single-crystal $\beta$-$Si_3N_4$.

Figure 3 shows our calculated real and imaginary parts of the dielectric function for $\beta$-$C_3N_4$, using the self-energy-corrected band structure. The optical calculation takes into account the actual transition-matrix elements at each of the 216 **k** points in the irreducible portion of the BZ. The $\varepsilon_2(\omega)$ spectrum is calculated first for photon energies up to 50 eV, and the $\varepsilon_1(\omega)$ curve is then obtained by Kramers-Kronig conversion. The $\varepsilon_2(\omega)$ curve shows two major absorption peaks, one at 7.9 eV and the other at 13.9 eV, with some additional structures between the two peaks. The absorption increases vary rapidly above the threshold as would be expected, because both the CB and VB have very sharp edges. The $\varepsilon_2(\omega)$ curve decreases rapidly above 19 eV. The zero-frequency value of $\varepsilon_1(0)$ gives us an estimated dielectric constant of 3.2. If we use the uncorrected LDA band for the optical calculation, a similar absorption spectrum is obtained. The two major peaks are shifted down to 6.9 and 13.5 eV with a slight increase in amplitudes, and the static dielectric-constant value is increased to 3.8. We have also found that there is negligible optical anisotropy for light polarizations parallel and perpendicular to the $c$ axis.

It is instructive to compare the optical spectrum for $\beta$-$C_3N_4$ with that of other covalent crystals such as diamond,[21] BN,[22] and $\beta$-$Si_3N_4$,[23] calculated using the same OLCAO method. For diamond, the absorption spectrum consists of a single major peak at 12 eV with a LDA gap of 5.7 eV and a static dielectric constant of 4.3. In the case of BN, there are three phases, a graphiticlike hexagonal phase, and cubic and wurtzite phases ($w$-BN). The optical properties of all three phases of BN have been calculated.[22] The hexagonal phase shows a large anisotropy between the in-plane and the perpendicular directions, which is related to its layered structure. The cubic phase has a major peak at 12.5 eV. For the wurtzite structure, the absorption curve has a two-peak structure similar to $\beta$-$C_3N_4$ with a small degree of anisotropy. The peak positions are at 11 and 14 eV, respectively, and the calculated static dielectric constant is about 4.1.[22] Thus, from the viewpoint of optical properties, $\beta$-$C_3N_4$ resembles more $w$-BN than diamond. We also find that the optical spectrum of $\beta$-$C_3N_4$ is very different from that of $\beta$-$Si_3N_4$.[23] The latter shows a major peak at 9.5 eV, a weak peak at 11 eV, and a shoulderlike structure at 7.5 eV.

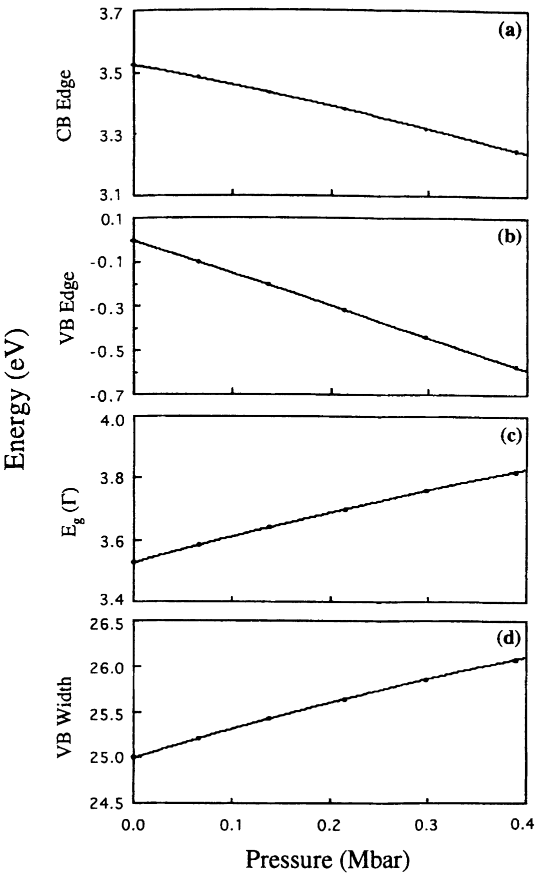

FIG. 4. Pressure dependence of (a) CB edge; (b) VB edge; (c) direct gap at Γ; and (d) VB width for $\beta$-$C_3N_4$.

The pressure dependence of the properties of $\beta$-$C_3N_4$ is also studied using the LDA result without the self-energy correction. Figure 4 shows the pressure dependence of the direct gap at Γ, the shifts in CB and VB edges, and the VB width as a function of pressure $P$. Pressures at compressed volumes are calculated as the tangents of the $E$ vs $V$ curve shown in Fig. 1. The gap increases as $P$ increases in $\beta$-$C_3N_4$, at least initially, at a rather slow rate of 0.82 eV/Mbar. This increase in the gap under pressure is due to the fact that the VB edge decreases faster than the CB edge. The total width of the VB also increases as $P$ increases. This behavior is similar to diamond, in which the band gap increases as $P$ increases at a slow rate of 0.6 eV/Mbar.[24] The first-principles calculation gives a pressure coefficient of diamond in the range of 0.53–0.66 eV/Mbar.[25] A larger pressure coefficient for $\beta$-$C_3N_4$ is consistent with the calculated bulk modulus being slightly smaller than that of diamond. We have also recalculated the optical spectrum of $\beta$-$C_3N_4$ at a pressure of 0.21 Mbar. We find the spectrum to be essentially similar to that of Fig. 3 at zero pressure, the main difference being a slight shift of the order of 0.2 eV in the peak positions to higher frequency, and a slight reduction in the peak heights.

In conclusion, we have calculated the optical properties of the material $\beta$-$C_3N_4$ and studied its pressure dependence. Our calculation is based on the first-principles LDA theory with the implementation of an approximate self-energy correction procedure. Our calculated ground-state structural properties are in good agreement with the earlier work using the first-principles pseudopotential theory. We also predict a positive pressure coefficient of the band gap slightly larger than that of diamond. Our study indicates that $\beta$-$C_3N_4$ is a very hard optical material, but it is unlikely that its bulk modulus will exceed that of diamond.

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