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Electronic structure of $BeCN_2$: A proposed nearly direct wide-band-gap semiconductor

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The electronic band structure of a hypothetical compound $BeCN_2$ in the chalcopyrite structure has been calculated using the linear-muffin-tin-orbital method and the local-density approximation (LDA) for exchange and correlation. The calculations predict a lattice constant of 3.67 Å, a bulk modulus of 315 GPa, and a cohesive energy of 6.1 eV/atom. The band gap is found to be nearly direct at the Γ point. The conduction-band minimum, which occurs at $\mathbf{k} = \frac{2\pi}{a}(0.89, 0, 0)$, is only 0.03 eV below the lowest conduction-band state at the Γ point. The minimum band gap is estimated to be 5.7 eV including corrections beyond the LDA. The band-gap hydrostatic deformation potential is calculated to be 0.4 eV.

Recently, there has been a considerable increase in the interest in wide-band-gap semiconductors.[1] These materials offer a wide range of possible electro-optical, high-temperature, and high-speed applications. In addition, they are very hard and have large elastic constants. In connection with the optical properties, not only the magnitude of the gap but whether or not it is direct is very important. Unfortunately, diamond (5.5 eV) and *c*-BN (6.4 eV) have indirect band gaps. The only semiconductor with a direct band gap larger than 5 eV known to date seems to be wurtzite AlN (6.2 eV). A material with a direct band gap well into the UV range would clearly be of great interest.

The tetrahedrally bonded chalcopyrites form an alternative to the traditional group-IV or -III-V semiconductors with the diamond and zinc-blende structures, respectively. In this work, we consider the hypothetical compound $BeCN_2$. It can be thought of as being derived from the III-V compound *c*-BN by the replacement of every other group-III atom (B) by a group-II atom (Be) and the other B by a group-IV atom (C). Clearly, the octet rule of local bonding is on average still statisfied. Several II-IV-V chalcopyrites are known.[2] Among them is $ZnGeP_2$, which was recently grown heteroepitaxially on GaP by Xing *et al.*[3]

Here we use first-principles electronic-structure calculations to predict some of the properties of $BeCN_2$, a crystal, which to our knowledge is yet to be synthesized. We assume the chalcopyrite structure[2] with an ideal c/a ratio and ideal atomic positions of the eight atoms in the unit cell. The calculations were performed using the linear muffin-tin orbital method in the atomic-sphere approximation (ASA) including the so-called combined correction.[4] The density-functional theory[5] was used to obtain total energies. The local-density approximation (LDA) was used for the exchange-correlation energy and potential which were represented by the von Barth–Hedin expression.[6] Empty spheres were introduced in the tetrahedral interstitial sites as is usually done within the ASA for open structures. A set of 11 Monkhorst-Pack[7] special irreducible $\mathbf{k}$ points was used for the reciprocal space sampling. The computational method used here was recently sucessfully used by us in calculations of several other wide-band-gap semiconductors.[8–10]

Table I summarizes the results of our total energy calculations. By comparing the bulk moduli, we find that $BeCN_2$ is a considerably softer material than diamond (480 GPa) or *c*-BN (412 GPa), the hardest known materials. However, it is appreciably stiffer than SiC (233 GPa) or BeO (224 GPa), which are quite hard materials. The above values are theoretical values obtained using the same computational method.[8–10] The latter are typically within 5–20 % of the experimental value. The lattice constant is slightly larger than that of *c*-BN and diamond. Nevertheless, the lattice mismatch to diamond is less than 4%, which opens the possibility of growing this material heteroepitaxially on diamond.

The cohesive energy (i.e., the energy difference between the solid and the free atoms) in Table I includes spin-polarization corrections for the atoms and an estimated zero-point motion correction for the solid. The latter is given by $\frac{9}{8}k\Theta_D$ per atom, where Θ_D is the Debye temperatue and k the Boltzman constant. We estimate Θ_D for $BeCN_2$ to be between 1000 and 1500 K by an interpolation as a function of the bulk modulus using the values of diamond, *c*-BN, BeO, and SiC. This corresponds to a zero-point motion correction of only 0.1 eV. The cohesive energy per atom is seen to be considerably smaller than that of diamond, for which the theoretical value is 8.75 eV/atom.[8] We note that the LDA is known to overestimate cohesive energies typically by 10–20 % (20% for diamond and *c*-BN). In summary, $BeCN_2$ appears to be strongly bonding, but considerably less so than diamond.

Next, we consider the electronic band structure. The energy bands along some lines of the Brillouin zone of the body-centered tetragonal lattice are shown in Fig. 1. Note that the $\mathbf{k}$ points $D = \frac{2\pi}{a}(1, 0, 0)$ and $Z = \frac{\pi}{a}(0, 0, 1)$ are related by a reciprocal lattice vector and thus have

TABLE I. Predicted properties of $BeCN_2$ in the chalcopyrite structure.

Lattice constant a (Å)	3.67
Bulk modulus B (GPa)	315
Pressure derivative of the bulk modulus dB/dp	3.9
Cohesive energy (eV/atom)	6.1
Band-gap (eV) (LDA value in parentheses)	5.7 (4.23)
Band gap hydrostatic deformation potential (eV)	0.4

the same eigenvalues. There are also twofold degeneracies at the Brillouin zone edge [at the $X = \frac{\pi}{a}(1,1,0)$ and Z points], which are a result of the nonsymmorphic nature of the space group, which is $I\bar{4}2d$ or D_{2d}^{12}.

The occupied bands fall into two groups separated by a band gap. From an inspection of the eigenvectors, it is found that the lower four bands are essentially N 2s derived with (bonding) admixture of C 2s and Be 2s at the bottom and C 2p and Be 2p near the top. The next 12 bands have predominantly N 2p character. The lowest state at the Γ point is a bonding combination of N 2p and C 2s with about equal weight of both. The states around −8 eV at the Z point and −6 eV at the Γ point have a significant Be 2s component in addition to the C 2s and N 2p components. The valence-band maximum has predominantly N 2p character with a fairly strong admixture of C 2p and Be 2p as well as d character on those atoms and on the empty spheres. The bottom of the conduction band has considerable weight on the empty sphere orbitals. This, of course, means that its wave function has a large amplitude in the interstitial region. This is similar to the nature of the lowest conduction-band state at the X point in zinc-blende crystals. The zinc-blende X point is folded onto the Γ point here because of the doubling of the unit cell in the c direction. As can be seen in Fig. 2, the valence band has overall considerably more C admixture than Be admixture. This is consistent with the fact that the atomic levels of Be lie relatively higher. The predominance of N character in the valence band indicates that N plays the role of anion in this compound. That, of course, is to be expected from the depth of the atomic N levels.

The most important feature of the band structure is without doubt the band gap. As can be seen in Fig. 1, the valence-band maximum occurs at the Γ point.

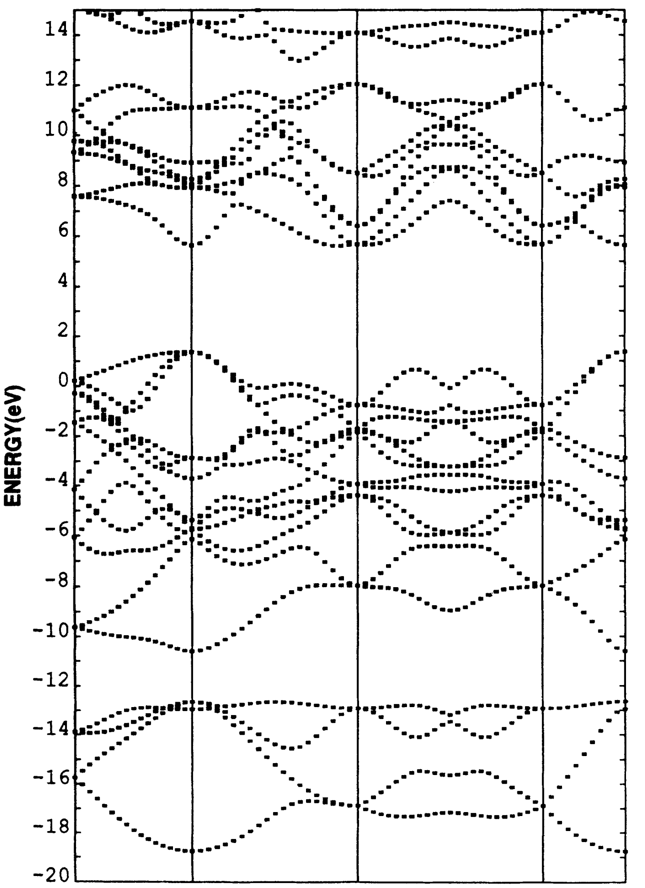

FIG. 1. Electronic band structure of $BeCN_2$ in the chalcopyrite structure. See the text for a description of the displayed lines in reciprocal space. The zero of energy is the ASA reference level (Ref. 12).

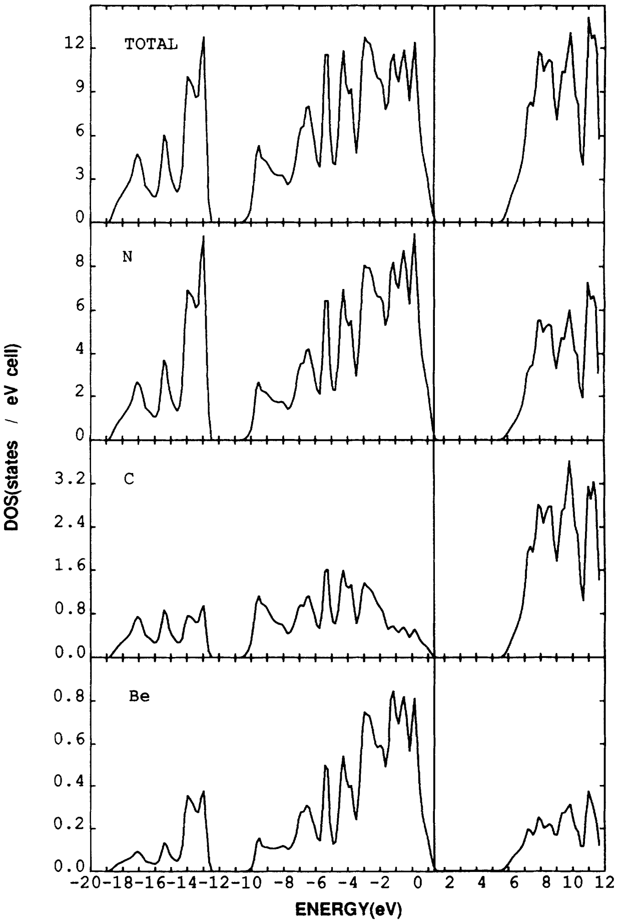

FIG. 2. Total and partial densities of states (DOS) for $BeCN_2$ in the chalcopyrite structure. Note that the unit cell corresponds to two formula units and that the total per type of atom is shown. The tetrahedron method (Ref. 13) was used with 59 irreducible k points for the DOS calculation.

Strictly speaking, the conduction-band minimum occurs at $\frac{2\pi}{a}(0.89,0,0)$. However, the lowest conduction-band state at the Γ point is in fact only 0.03 eV higher in energy. The lowest eigenvalue at the Z or D points also only lies slightly (0.06 eV) above the conduction-band minimum. The band gap is thus very nearly direct. A conduction-band minimum slightly away from the Brillouin-zone edge along the x direction is reminescent of the diamond band structure. The downward slope of the lowest band is a result of the interaction with the other nearby band with which it becomes degenerate at the Brillouin-zone edge, similar to the situation in diamond.

We note that such a very near degeneracy of different **k**-point states with the conduction-band minimum as observed here is rather unusual. It will have significant effects on the optical and transport properties and on the nature of the shallow defect states. Its optical properties would be closer to that of a direct than an indirect semiconductor. Clearly, in absorption, the strong direct absorption edge will dominate the indirect absorption. Of the latter, only a small temperature-dependent tail extending the appropriate one-phonon energy (~0.1 eV) below the indirect transition value would, in principle, be detectable. In emission, the direct transition will become important when kT is of the order of 0.03 eV, which means room temperature. Also, based on effective-mass theory, the "shallow" impurity levels are expected to lie at an energy which is not small compared to the splittings between the various conduction-band minima. The "shallow" states would thus have a significant Γ-point character and thus lead to a fairly strong emission.

The LDA value of the band gap is 4.23 eV. As is well known, the LDA Kohn-Sham eigenvalue band structure does not accurately represent the quasiparticle excitations, and, in particular, underestimates the band gap. Since the LDA band gap lies in between that of diamond (4.13 eV) and that of c-BN (4.46 eV), it is reasonable to interpolate the quasiparticle self-energy correction. From Bechstedt and Del Sole's work,[11] it appears that within a class of compounds of the same row of the Periodic Table, the band-gap correction beyond the LDA is basically inversely proportional to the dielectric constant. That in turn is roughly inversely proportional to the band gaps themselves. The correction should thus be proportional to the LDA gaps. Using the experimental gaps of diamond (5.5 eV) and c-BN (6.4 eV), we thus estimate the band gap of $BeCN_2$ to be 5.7 eV. In view of the uncertainties in the quasiparticle correction (including its **k** dependence) and other details of the structure such as the use of an ideal c/a ratio and ideal atomic positions, it is in fact possible that the conduction-band minimum would actually occur at the Γ point and the material would be strictly direct.

Our calculations show that the "nearly" direct gap situation exists over the entire range of 6% compression and expansion over which we calculated the band structure. The indirect minimum band gap, the band gap at the Z point, and the direct band gap at the Γ point all vary linearly over that range of lattice constants with a hydrostatic deformation potential $a_G = dE_G/d\ln a = 0.4$ eV. The positive value indicates that the band gap *increases* when the lattice constant is increased.

In summary, we have shown that $BeCN_2$ in the plausible chalcopyrite structure would be a strongly bonding material (somewhat softer than diamond but harder than SiC) with a "nearly direct" band gap which is slightly larger than that of diamond, i.e., well within the UV range. The term "nearly direct" means that its properties would be close to that of a direct-band-gap semiconductor. Although we are currently not aware that this material has ever been synthesized, it could conceivably be grown heteroepitaxially on diamond or c-BN because of its reasonably close lattice match (4%) to both.

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[1] See, for example, *Diamond, Silicon Carbide and Related Wide Bandgap Semiconductors*, edited by J. T. Glass, R. Messier, and N. Fujimori, MRS Symposia Proceedings No. 162 (Materials Research Society, Pittsburgh, 1990).

[2] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1964), Vol. 2, p. 336.

[3] G. C. Xing, K. J. Bachmann, J. B. Posthill, and M. L. Timmons, in *Diamond, Silicon Carbide and Related Wide Bandgap Semiconductors* (Ref. 1), p. 615.

[4] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[5] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[6] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[7] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[8] W. R. L. Lambrecht and B. Segall, Phys. Rev. B **40**, 9909 (1989); **41**, 5409 (1990).

[9] W. R. L. Lambrecht and B. Segall, Phys. Rev. B **43**, 7070 (1991).

[10] W. R. L. Lambrecht and B. Segall, J. Mater. Res. (to be published).

[11] F. Bechstedt and R. Del Sole, Phys. Rev. B **38**, 7710 (1988).

[12] W. R. L. Lambrecht, B. Segall, and O. K. Andersen, Phys. Rev. B **41**, 2813 (1990).

[13] O. Jepsen and O. K. Andersen, Solid State Commun. **9**, 1763 (1971).