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Anomalous band-gap behavior and phase stability of *c*-BN–diamond alloys

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Electronic-structure calculations allow us to predict that hypothetical ordered mixed crystals of *c*-BN and diamond representative of the expected short-range order in the alloys show a very pronounced band-gap bowing. This anomalous behavior is believed to be related to the staggered band lineup at the corresponding heterojunction. The miscibility phase diagram of this system is estimated using a simple pseudobinary "regular-solution" model for the short-range order and energies of formation of the representative ordered compounds calculated from first principles. It indicates that there is only very limited mutual solubility in the solid state. The band gaps and energies of formation of the disordered ternary alloys are estimated by means of cluster expansions.

I. INTRODUCTION

Diamond and cubic boron nitride (*c*-BN) have recently received considerable attention because of their promising materials properties for abrasives, heatsinks, protective coatings, and even for wide-band-gap semiconductor applications. This interest stems from the extreme values of these two materials' properties such as hardness, thermal conductivity, elastic constants, and band gaps.[1] The recent interest arose as a result of the increased availability of these difficult-to-obtain materials. This in turn resulted from the development of a number of growth techniques among which are energetically enhanced (plasma, hot filament, microwave) chemical vapor deposition (CVD),[2] laser ablation,[3] and ion-beam techniques.[4] A basic difficulty common to both materials is that they are thermodynamically stable only at high pressures; the low-pressure ground states are the layered hexagonal phases, namely, graphite and *h*-BN.

Mixed C-BN layered hexagonal phases have been synthesized by a number of groups[5–7] and studied theoretically by Liu, Wentzcovitch, and Cohen.[8] Badzian[5] has synthesized mixed crystals of diamond and *c*-BN by a high-pressure high-temperature phase-transformation technique starting from the layered hexagonal mixed crystals. Attempts to grow cubic mixed phases by CVD have so far failed.

In this paper the results of electronic-structure calculations of the cubic $(\mathrm{BN})_x\mathrm{C}_{2(1-x)}$ system are presented. This study complements a previous study of the diamond/*c*-BN heterojunction.[9] Our calculations address the question of the band-gap behavior, the energy of formation, and the phase stability. Rather restrictive but plausible assumptions are made about the short-range order in this alloy system.

The paper is organized as follows. Section II describes the computational approach. A discussion of the the assumptions about the short-range order appears in Sec. III. In Sec. IV we first present our results for the band gaps of the ordered compounds, then the phase diagram of the alloys, and finally, the properties of the disordered alloys. Section V is devoted to a discussion of the phase diagram in relation to the experimental data and the theoretical results of other heterovalent alloy systems. The conclusions of this work are summarized in Sec.VI.

II. COMPUTATIONAL METHOD

The results presented here were obtained using Andersen's linear muffin-tin-orbital method (LMTO) in the atomic-sphere approximation (ASA), including the so-called combined correction.[10] The Kohn-Sham local-density-functional theory[11] is used with the exchange-correlation parametrization of Hedin and Lundqvist.[12]

The local-density approximation (LDA) is well known to underestimate the band gaps because the Kohn-Sham eigenvalues are not, strictly speaking, quasiparticle excitation energies. In this work we estimate the quasiparticle self-energy correction using an expression derived by Bechstedt and Del Sole.[13] The latter is based on an approximate treatment of Hedin's *GW* approximation.[14] In Bechstedt and Del Sole's treatment,[13] local-field effects are neglected and matrix elements are calculated with a simple tight-binding approximation to the LDA wave functions. In the final closed expression of the correction,

$$\Delta = \frac{q_{\mathrm{TF}}/\epsilon_\infty}{1 + 7.62 q_{\mathrm{TF}} r_{\mathrm{eff}}}, \tag{1}$$

only well-known quantities appear such as the dielectric constant ϵ_∞, the Thomas-Fermi screening wave vector q_{TF}, and $r_{\mathrm{eff}} = [(1-\alpha_P)r_A/2 + (1+\alpha_P)r_B/2]$ with r_A and r_B effective radii of cation and anion Slater orbitals given by $r_{A/B} = a/4\pi(1.7 \mp 0.05|Z_A - Z_B|)$, with a the cubic lattice constant and the bond polarizabilities α_P based on Harrison's universal tight-binding theory.[15]

Our approach to studying the disordered alloys involves two parts. The first is the calculation of properties of ordered compounds representative of the assumed short-range order. In the second part, the statistically averaged properties of the disordered alloys are determined by a cluster expansion whose coefficients are derived by a mapping of the cluster expansion to the ordered crystal results. This is a generalization of the Connolly-Williams approach.[16] In the following section, we discuss our assumptions about the short-range order and the choice of ordered structures.

III. MODEL OF SHORT-RANGE ORDER

The short-range order in teterahedrally bonded heterovalent ternary alloys, of which the presently studied C-BN system is a particular case, has been discussed vigorously in a set of papers which appeared mainly in the middle 1980s. Extensive experimental and theoretical studies were devoted to $(\mathrm{GaAs})_x\mathrm{Ge}_{2(1-x)}$, $(\mathrm{GaSb})_x\mathrm{Ge}_{2(1-x)}$.[17–26] A recent overview of the field can be found in Ref. 26.

In the dilute limit of the III-V component in the alloy, one may expect isolated group-III and group-V impurities in a diamond lattice. That is, one can expect group-III and group-V elements to occur on either of the two fcc sublattices of the diamond lattice with equal probability. At a higher concentration of the III-V component, one may expect a transition to a nominally zinc-blende lattice in which the group-III element has a statistical preference for one of the sublattices and the group-V element for the other. The simplest way to view this transition is as a percolation problem.[18] More sophisticated treatments will include energetic and/or surface growth considerations.

From an energetic point of view, one may expect that the group-III and group-V elements would tend to be nearest neighbors. This is because the III-IV and IV-V ($\Delta Z = \pm 1$) bonds are undersaturated and oversaturated, respectively, by 1/4 electron/bond. One thus can gain up to $\sim$1/4 of the band gap E_G by charge transfer from one to the other. This compensation leads to charged *donor* and *acceptor* bonds which costs electrostatic energy. As a result, the compensation is most effective for nearest-neighbor III-IV and IV-V bonds in which case the electrostatic energy cost is minimized. These compensation effects between oversaturated and undersaturated bonds have been discussed by Dandrea, Froyen, and Zunger[27] and Lambrecht, Amador, and Segall.[28]

For similar reasons, $\Delta Z = \pm 2$ bonds (V-V and III-III) are unlikely to occur. These basically correspond to antisite defects, which have a large energy of formation.[29] The same conclusion is reached from a study of inversion domain boundaries in GaAs.[28] In the case of the Ge-based alloys, there has been a controversy over the presence or absence of the $\Delta Z = \pm 2$ so-called "wrong" bonds.[20,22] It was shown by Holloway and Davis[22] that their presence in any significant amount would lead to a closure of the gap because of the associated deep levels. This would be in disagreement with the experimental data on the band-gap behavior in these alloys and this was used as an argument for their absence.

Osório, Froyen, and Zunger[26] included the above-mentioned electrostatic effects explicitly in a statistical thermodynamics treatment of these alloys. They con-

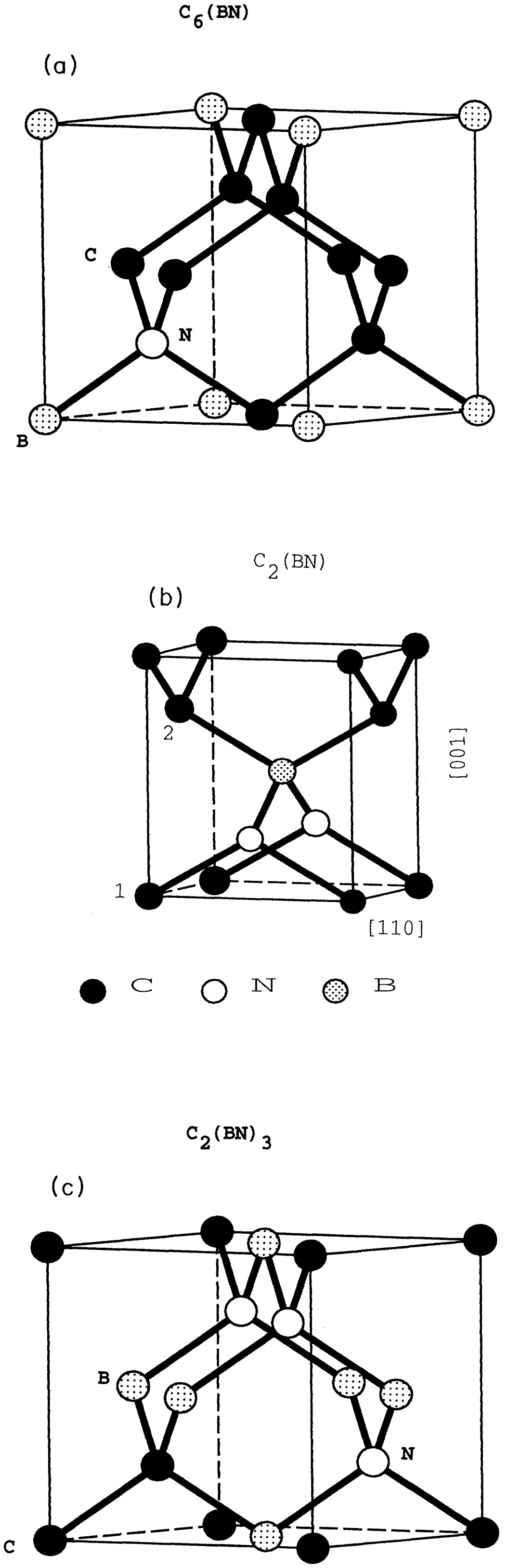

FIG. 1. Ordered crystal structures: (a) 25% BN $L1_2$, (b) 50% BN $L1_0$, and (c) 75% BN $L1_2$.

cluded that the electrostatic effects tend to stabilize the zinc-blende ordering over the diamond structure. Below the melting temperature T_m, however, both phases were found to be unstable towards phase separation over most of the composition range. The energetic arguments against the $\Delta Z = \pm 2$ bonds and for the "clustering" of $\Delta Z = \pm 1$ bonds are even stronger for compounds with larger ionicity and thus are more compelling for *c*-BN than for the GaAs and GaSb cases studied earlier.

From Badzian's x-ray diffraction studies,[5] it appears that at least partial zinc-blende ordering can be assumed for the solid solutions of cubic *c*-BN prepared by him. That is, the B and N ions maintain a preferential occupation on separate fcc sublattices of which a certain percentage are replaced by carbon atoms in the mixed crystal.

In view of the above, we assume that the short-range ordering is characterized by (1) absence of B–B and N–N bonds, and (2) nearest-neighbor positioning of B and N leading to local compensation of B–C and N–C bonds. These plausible assumptions correspond basically to assuming an almost perfect local *charge neutrality* and local *stoichiometry.* Obviously, this cannot be strictly applicable in the dilute limit of small x in $(\mathrm{BN})_x\mathrm{C}_{2(1-x)}$. We choose here not to treat the controversial subject of the zinc-blende-to-diamond transition. Rather, we focus on the coarser problem of the miscibility and the properties of the most plausible short-range-order structure over most of the composition range (excluding $x \ll 1$), which, as argued above, has the zinc-blende structure.

As a starting point, we study hypothetical ordered structures based on the zinc-blende structure. The models we investigated correspond for $x = 0.5$ to the $L1_0$ and for $x = 0.25$ and $x = 0.75$ to the $L1_2$ fcc superlattices of BN and C_2 "molecules" oriented along the $\langle 111 \rangle$ direction. Of course, this does not imply that we atttach a meaning to these molecules as independent or weakly interacting entities. The system obviously is not a molecular crystal. These structures are shown in Fig. 1. This choice corresponds to the Connolly-Williams[16] (CW) $\mathrm{B}_n\mathrm{C}_{4-n}$ structures with $n \in \{0,1,2,3,4\}$ on one of the fcc sublattices. In each of these, there occurs exactly one type of the $\mathrm{B}_n\mathrm{C}_{4-n}$ fcc nearest-neighbor tetrahedra. These tetrahedra form the basis of the cluster expansions used for the statistical treatment of the disordered alloys. For the purpose of statistically averaging the properties of the alloys, there is a one-to-one correspondence between the five basic tetrahedra and the five CW structures.

IV. RESULTS

A. Band gaps of ordered compounds

We start with a discussion of the band gaps of the pure materials. The band gap of *c*-BN has been somewhat controversial in the past because of the difficulty of obtaining single crystals of adequate size. A value of 6.4 eV was obtained by absorption measurements by Chrenko[30] on high-pressure synthesized crystals.[31] Recently, Mishima[32] measured the optical-absorption edge and found it to be 6.1 ±0.2 eV. Our previous calculations yielded a band gap of 4.46 eV within LDA and 6.4 eV including the Bechstedt–Del Sole correction. The band gap of diamond obtained by the same computational approach was 5.6 eV (4.1 eV in LDA) in fair agreement with the experimental value of 5.5 eV. From our and their experience, the Bechstedt–Del Sole approach is usually found to give a slight overestimate with errors of the order of a few 0.1 eV at most.

Based on the fact that the band gap of *c*-BN is larger than that of diamond, one might expect that mixed diamond–*c*-BN crystals would have band gaps larger than that of diamond. The calculated band gaps of ordered compounds are shown in Fig. 2. The LDA values are indicated by squares, the corrected values[33] by diamonds. Contrary to simple expectations, one sees that the gap initially shows a dramatic decrease upon alloying *c*-BN into diamond. Even for the 75% *c*-BN compound, the gap is smaller than that of diamond.

The reason for this anomalously strong bowing of the band gap can be understood in terms of the alignment of the energy bands in *c*-BN and diamond. As was shown in our earlier work on the heterojunctions between these two solids, the band offset is of the so-called type-II, (i.e., staggered type), as shown in Fig. 3. This means that the valence-band maximum of the composed system (mixed crystal or heterojunction) is mainly C-like while the conduction-band minimum is mainly BN-like with, in fact, a significant B component because of the cation nature of the latter. This implies that the effective band gap of the system is lower than that of either of the two pure materials. The effect, in fact, is slightly more pronounced in the $L1_0$ structure studied here, which is a $1+1$ $\langle 001 \rangle$ (and simultaneously a $\langle 110 \rangle$) superlattice, than it is in larger period superlattices approaching the semi-infinite heterojunction.[9] One might expect that smaller size superlattices would tend to have wider gaps because of size quantization. However, the band lineup (and thus the

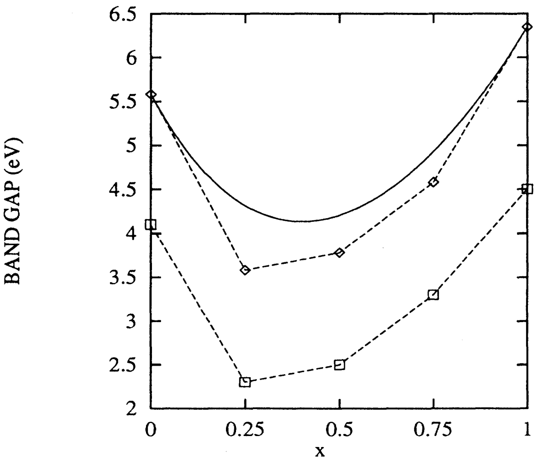

FIG. 2. Band gap as a function of composition for zinc-blende-derived $(\mathrm{BN})_x\mathrm{C}_{2(1-x)}$ ordered crystals: LDA (squares), self-energy corrected (Ref. 33) (diamonds), and random alloys (smooth full line).

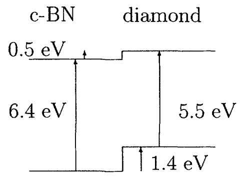

FIG. 3. Band offset at diamond/*c*-BN heterojunction.

effective gap) depends on the lineup of the electrostatic potentials which in turn depends on the nearest-neighbor environment of the atoms at the interface. The latter is different for an atom at the interface between two semi-infinite solids than for an atom in the $1+1$ superlattice. For example, in the $1+1$ cell an N atom has two B atoms and two C atoms whereas at the $\{110\}$ interface it has three B atoms and one C atom as nearest neighbors. There is a more effective intermixing of the states leading eventually to the smaller gap. This large bowing effect clearly may be expected to occur in other alloy systems in which the heterojunctions between the two constituent semiconductors is of type II, e.g., SiC/BP.[34]

B. Phase stability

As already mentioned, it is not clear that this system is a true solid solution in the thermodynamic sense. First of all, this appears not to be the case for the other heterovalent ternary alloy systems, and secondly one may expect phase separation on the basis of the high interface energy of formation that we previously calculated for the heterojunction.[9] We discuss the miscibility phase diagram here within a very simple approximation.

First, in accordance with the assumptions about short-range order discussed in Sec. III, we treat the alloy problem as a pseudobinary system of BN and C_2 "molecules." Second, the total energy of the solid solution is expanded in a cluster expansion using the above described fcc-tetrahedron approximation. The cluster energies are identified with the energies of formation of the corresponding CW structures as explained in Sec. III.

For simplicity, we ignore the small lattice mismatch ($\sim 1\%$) between diamond and *c*-BN. Thus we only need the energy of formation at their equilibrium volume. The results of our first-principles total-energy calculations are shown in Fig. 4. They are found to be well described by a parabola, that is

$$\Delta H_o(x) = 4\Delta H_2 x(1-x) \tag{2}$$

with ΔH_2 the energy of the $L1_0$ compound equal to 0.45 eV/atom. The subscript "*o*" stands for "ordered" compound as opposed to the disordered alloys. While in general the CW-cluster expansion is equivalent to a *generalized* Ising spin model including triplet and tetrahedron interactions, the special case of a parabolic dependence on x is well known to correspond to the Ising model with only nearest-neighbor pair interactions,

$$\hat{H} = -\sum_{\langle ij\rangle} J_2 \hat{S}_i \hat{S}_j . \tag{3}$$

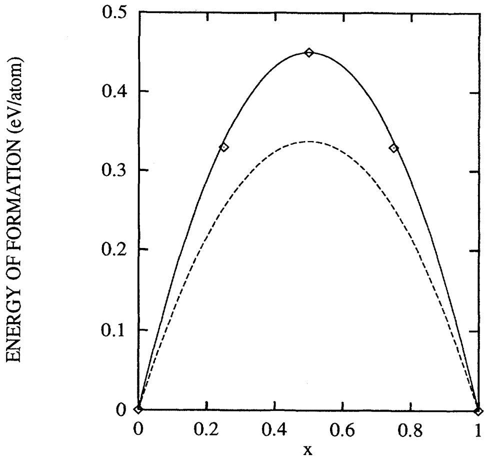

FIG. 4. Energies of formation in eV/atom: calculated ordered structures (diamonds), parabolic interpolation Eq. (2) (solid line), and randomly disordered solid solutions Eq. (7) (dashed line).

In the present case, $J_2 > 0$ since like "molecules" prefer each other over unlike ones as nearest neighbors. This is indicated by the positive energy of formation of the compounds. This means that the alloy statistics in this approximation is mapped on that of the well-known ferromagnetic Ising model.

We briefly recall the "regular solution" or mean-field treatment of this problem. In this model the entropy of mixing is approximated by the point approximation in which $S = -k[x\ln x + (1-x)\ln(1-x)]$ with k the Boltzman constant. The free energy becomes $F(x,T) = \Delta H_o(x) - TS(x)$. At low temperature, this function shows a maximum at $x = 0.5$ and two minima symmetrically located on either side as shown in Fig. 5. With increasing temperature, the two minima converge towards

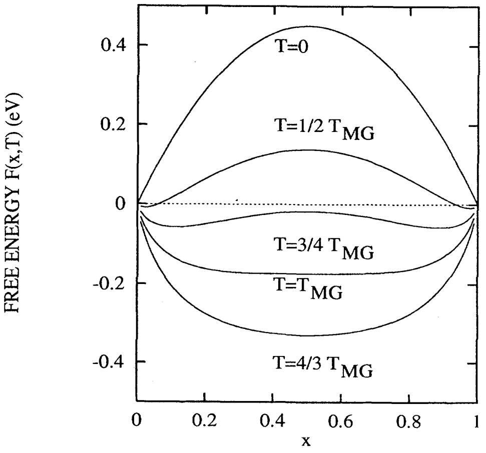

FIG. 5. Free energy of $(BN)_xC_{2(1-x)}$ alloys within the regular-solution model.

the maximum until above a certain critical temperature, $T_{\rm MG}$, they merge together in a single minimum at 50%. The locus of these minima in the x-T plane describes the miscibility gap (MG) (binodal line) and is given by

$$kT/\Delta H_2 = (8x-4)/[\ln x - \ln(1-x)]. \qquad (4)$$

The region where $d^2F/dx^2 < 0$ is unstable and is bounded by the spinodal line

$$kT/\Delta H_2 = 8x(1-x). \qquad (5)$$

The critical temperature $T_{\rm MG} = 2\Delta H_2/k \approx 10\,400$ K.

The ferromagnetic Ising model has been treated by means of more sophisticated statistical methods, such as Kikuchi's cluster variation method (CVM).[35,36] With increasing size of the clusters taken into account in the entropy expression, one obtains a decreasing correction factor of 0.835–0.830 for $T_{\rm MG}$ relative to that for the regular solution approximation. The most accurate value known for the critical temperature was obtained by a high-temperature expansion[37] which gives the critical temperature as 0.816 27 times the critical temperature of the regular solution model. Even with this correction factor, $T_{\rm MG} \approx 8500$ K.

This is much higher than the melting temperature, which was estimated to be ~3500 K for *c*-BN and ~4000 K for diamond at ~10 GPa.[1] A tentative phase diagram including the renormalization of the critical temperature and the position of the liquidus line is shown in Fig. 6(a). As can be seen, our model predicts very limited mutual solubility of *c*-BN and diamond in the solid state, in apparent conflict with Badzian's claim of having synthesized solid solutions of compositions $0.15 < x_{\rm BN} < 0.6$. As will be discussed below, this suggests that the mixing in the experiments took place in the liquid state and that the solid solutions are metastable systems.

C. Properties of disordered alloys

The properties of the disordered alloys such as the energy of formation and the band gap can be expanded in a cluster expansion. We note that within the CVM one might calculate the probability distribution of the tetrahedral clusters from the energy minimization of the free energy. These may deviate from the random (binomial) distribution.

However, since the miscibility gap critical temperature was found to be significantly above the melting temperature, and the mixed compounds are, in fact, likely to have been formed in the liquid state, the use of a random distribution for statistical averaging seems appropriate here.

For the energy of formation, this averaging leads to

$$\Delta H_d(x) = \sum_{n=0}^{4} \binom{4}{n} x^n (1-x)^{4-n} \Delta H_o\left(\frac{n}{4}\right) \qquad (6)$$

$$= 3\Delta H_2 x(1-x), \qquad (7)$$

where the energy of formation of the ordered compounds $\Delta H_o(\frac{n}{4})$ is given by Eq. (2). This statistical averaging is seen to lead simply to a renormalization by a factor of 3/4. The resulting random solid-solution energies of formation are shown in Fig. 4 by the dashed curve.

For the band gaps of the disordered alloys, we obtain in a similar fashion

$$E_G(x) = \sum_{n=0}^{4} \binom{4}{n} x^n (1-x)^{4-n} E_G^{(n)}, \qquad (8)$$

where $E_G^{(n)}$ is the band gap of the nth CW structure associated with the coresponding tetrahedral cluster. As expected, the resulting band-gap bowing, shown in Fig. 2 by the full continuous line, while still very strong, is somewhat less pronounced than that of the ordered compounds. We note that the tetrahedron approximation used for our cluster expansion is probably less well converged for the band gaps than for the total energies.

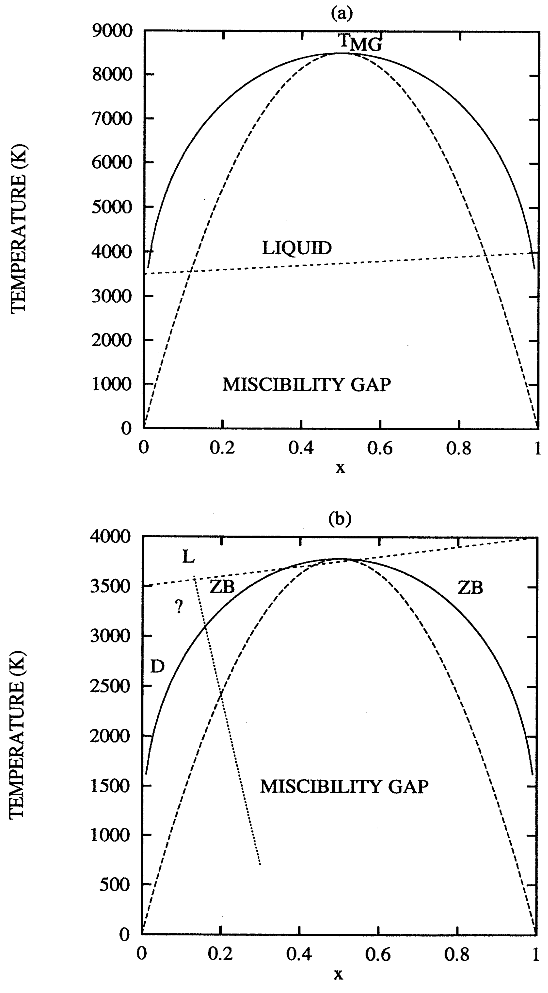

FIG. 6. Tentative phase diagrams of $(\mathrm{BN})_x\mathrm{C}_{2(1-x)}$. (a) "Ferromagnetic Ising" model treated within the regular solution approximation renormalized by ~82%. (b) Same as (a) but including a hypothetical lowering of the miscibility gap down to the melting point by long-range correlations. A hypothetical diamond (D) to zinc-blende (ZB) order-disorder transition is tentatively indicated with ? and a dotted line. The liquidus line separating the liquid (L) from the solid portion of the phase diagram is indicated in both.

V. DISCUSSION

In Sec. IV B we found the miscibility critical temperature to be well above the melting temperature. Here, we consider possible improvements to the simplified treatment given above.

Including the lattice mismatch of about 1% requires expanding diamond and compressing *c*-BN to the common lattice constant of the mixed crystal which will cost an additional energy ΔE_v. This should be followed by a relaxation of the bond lengths in the alloy, releasing an energy ΔE_r. These two effects partially cancel each other. We estimate that this may change the energies of formation and thus the temperature scale by at most a few percent. This would thus not alter our conclusion that the miscibility critical temperature lies well above the melting temperature.

A more important consideration might be the inclusion of long-range correlations. In some common-anion pseudobinary systems, this has been shown to lead to a miscibility critical temperature which is only 60% of its uncorrected value.[38] In particular, the fourth-nearest-neighbor pair interaction, which is between cations linked along the bond chains in the $\langle 110\rangle$ direction, was found to be quite important in the work of Ferreira, Wei, and Zunger.[38] Since this has been found to be a rather general feature,[38,39] a similar effect may well occur in the present system. At present, it is difficult to predict how much this effect might lower the critical temperature because there are significant differences between the common anion and the heterovalent alloy systems.

A complete treatment of long-range effects is beyond the scope of the present paper. Such a treatment should probably be based on extensions of the Blume-Emery-Griffiths $S = 1$ spin Hamiltonian[40] which was first applied to the problem of heterovalent ternary (III-V)-IV alloys by Newman *et al.*[20] The generic phase diagram of this model Hamiltonian is characterized by the presence of a miscibility gap and an order-disorder transition between the zinc-blende and diamond phases in the solid-solution region above the miscibility gap which ends at the binodal line in a tricritical point. Although our results suggest that it is very unlikely that T_{MG} would be lowered below the melting temperature T_m, we consider in Fig. 6(b) an alternative tentative phase diagram with $T_{\mathrm{MG}} \approx T_m$. In this figure we have also tentatively indicated a zinc-blende-to-diamond transition with the understanding that the position of the transition is, of course, not known at this point, as is indicated by the question mark. We tentatively placed the line close to the diamond limit because Badzian's[5] results indicate that at least partial zinc-blende ordering was present in his samples down to $x = 0.15$. We emphasize that the form of the phase diagram shown here is very schematic. See for, e.g., the papers of Newman *et al.*[20] and Osório, Froyen, and Zunger[26] for realistic phase diagrams of the $S = 1$ Hamiltonian for various values of the relevant parameters.

In the situation depicted by Fig. 6(b), one may imagine quenching the system from above the miscibility gap to lower temperatures. Above the miscibility gap, but below the melting line, the system would either have the diamond or zinc-blende—depending on which side we are of the order-disorder transition line—solid-solution phase as thermodynamic equilibrium state. The corresponding phase would thus be frozen in at low temperature. The argument behind this is that at temperatures low with respect to the melting-point phase separation would be hindered by kinetic barriers which we will see are large. In a slight variation of this picture, one imagines the order-disorder transition line continued inside the miscibility gap as a metastable transition. In that case, if we are at a point vertically below a thermodynamic equilibrium zinc-blende phase, but on the left of the metastable transition line, the diamond phase would have a lower free energy than the zinc-blende phase, even though both have higher free energies than the phase-separated state. The argument that such a transition could occur is that the change from zinc-blende to diamond ordering requires only local rearrangement of the atoms. This is less hindered by kinetic barriers than is phase separation. Of course, the speed at which the temperature of the system is lowered could determine which of the the two outcomes prevails.

We note that there has been significant controversy regarding this picture in either of its two variants. A proposed alternative theory is that the order-disorder transition between the diamond and zinc-blende phases, found experimentally for the Ge-based alloys, is purely of surface-growth kinetic origin.[21,22] Still another possibility suggested by Osório, Froyen, and Zunger[26] but remaining to be explored is that a surface thermodynamic equilibrium phase gets frozen in because of the absence of full bulk thermodynamic equilibration.

One way to test the validity of the "bulk thermodynamic" approach to this problem is to calculate the relevant interaction parameters from first principles. There have only been limited attempts to calculate the interaction parameters of the $S = 1$ Hamiltonian from electronic-structure calculations. The existing calculations[24–26] lead to parameters which would give a very high miscibility temperature (significantly higher than the liquidus line). Those results are similar to our present findings for the *c*-BN system. Osório, Froyen, and Zunger[26] found this to be true even when $\Delta Z = \pm 2$ bonds were excluded and the electrostatic and $\Delta Z = \pm 1$ compensation effects were taken into account as, in effect, has been done in the present work by our assumptions about short-range order. Now, a miscibility gap temperature above the melting point, as we obtained in our calculations and as depicted in Fig. 6(a), makes the scenario of quenching in the zinc-blende form from a high-temperature solid solution impossible. This fact lends indirect support to the idea that surface (kinetic or pseudoequilibrium thermodynamic) effects need to be invoked to explain the zinc-blende ordering. Indeed, a miscibility gap temperature above the melting temperature would indicate that the mixed crystals or alloys can only be formed by condensation or solidification of a mixed gas or liquid phase in which, of course, a zinc-blende ordering does not make sense.

The "solid solutions" of *c*-BN–diamond obtained in

Badzian's work[5] were obtained by direct (i.e., noncatalytic) solid-state transformation of hexagonal c-BN crystals (obtained by CVD) at high temperature > 3300 K and pressures of ~ 14 GPa. As stated in the paper, temperatures above the melting temperature may have occured in the center of the sample. Thus, the synthesis of mixed crystals does not contradict our prediction of the miscibility gap temperature being above the melting point.

In summary, by analogy to the more extensively studied Ge-based ternaries, the phase diagram of Fig. 6(a) following directly from our calculations, appears more likely than that of Fig. 6(b). Nevertheless, we note that none of the calculations of heterovalent ternaries so far have included the type of long-range effects which were found to be important for common-anion pseudobinaries. We can thus not completely exclude the situation indicated in Fig. 6(b). The experimental evidence is at present insufficient to distinguish between the two pictures.

Relaxing some of the assumptions about short-range order in our treatment (e.g., the requirement that B and N always occur as nearest neighbors) would introduce configurations of higher energy and thus presumably *increase* $T_{\rm MG}$. As mentioned earlier, only the existence of special long-range order would seem to allow for an appreciable lowering of $T_{\rm MG}$. We note that a reduction by more than a factor of 2 is required to get $T_{\rm MG}$ below the melting temperature. Even then, it seems very unlikely that $T_{\rm MG}$ could be lowered appreciably below the melting point. The conclusion of limited miscibility at reasonably low temperatures would thus remain valid even in this case.

Although the diamond-c-BN alloys are thus "in principle" unstable towards phase separation at room temperature, it can easily be seen that alloys are hindered from phase separating by large kinetic barriers. Indeed, we note that phase separation would require bond breaking and substantial diffusion. Since the bond strengths are of the order of 4 eV, kinetic barriers will be huge compared to the "driving force" towards phase separation. The latter can be identified with the energy of formation which is an order of magnitude smaller as mentioned above.

For all practical purposes, these mixed crystals thus appear like true solid solutions even though they are in principle metastable. As is well known, this system is in addition metastable towards the hexagonal-layered phases at ambient pressure.

VI. CONCLUSION

The main finding of this work is that c-BN–diamond mixed crystals and alloys exhibit an anomalously large band-gap bowing, which we propose to be related to the staggered band offsets at the corresponding heterojunction.

We also discussed the phase stability within the tetrahedron approximation of a cluster expansion. Our model of the alloys is based on the absence of B–B and N–N bonds (because of their expected high energy) and nearest-neighbor clustering of B–C and C–N bonds to ensure local charge neutrality. Within this restrictive model for the short-range order, the problem can be treated as a pseudobinary alloy problem. The energies of formation within this model were found to map onto the ferromagnetic Ising model. Their values lead to the prediction that the miscibility gap temperature would be well above the liquidus line. Although this conclusion is in agreement with more complete treatments of other heterovalent ternary semiconductor alloy systems, some uncertainty remains with regards to this conclusion. Indeed, long-range correlations have not been taken into account in any of these treatments. These correlations have been found to lower the miscibility gap temperature significantly in some common-anion semiconductor alloy systems. The experimental situation was discussed in terms of our calculated phase diagram and a hypothetical alternative phase diagram with a miscibility temperature close to the melting temperature. The experimental conditions in which the mixed crystals were synthesized could be consistent with either of the tentative phase diagrams of Fig. 6 although our analysis seems to favor Fig. 6(a). Further work will be required to sort out which of these two alternatives applies.

The "in principle" metastability of the system should, however, not be a practical impediment to their use and further study since kinetic barriers towards phase separation are expected to be huge, even at fairly elevated temperatures. We hope this study will lead to further experimental work on this system which could verify our predictions about the band gaps.

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[33] For systems of about constant density, the self-energy correction Δ is approximately inversely proportional to the dielectric constant (in this case, $\Delta \approx 8.3/\epsilon_\infty$ eV). We used 5.6, 4.5, and 6.5 as values of ϵ_∞ for diamond, *c*-BN, and the three ordered alloys, respectively. Further refinement to the individual alloys would lead to changes in E_G smaller than other uncertainties in that quantity. The value used for the alloys is a rough estimate based on their smaller LDA band gap. This leads to values of Δ of 1.5, 1.9, 1.3, respectively.

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