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Theoretical study of boron nitride modifications at hydrostatic pressures

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This paper presents a detailed study of boron nitride modifications at hydrostatic pressures. Cohesive properties of zinc blende (c-BN), wurtzite (w-BN), hexagonal (h-BN), rhombohedral (r-BN), and rocksalt structure are calculated by systematic optimization of unit cell parameters and atomic positions using total-energy density-functional methods. With focus on the very rarely discussed layered modifications the p-V equations of states are derived. It is confirmed that the isothermal bulk modulus of the sp^2-bonded phases is more than 10 times smaller in comparison to the dense phases. Additionally, the equilibrium line of c-BN and h-BN in phase p-T diagram is calculated. According to recent experimental reports c-BN is predicted as a stable modification at standard conditions. [S0163-1829(97)06409-6]

I. INTRODUCTION

In recent years there have been a lot of experimental and theoretical activities in studying the physical and chemical properties of boron nitride in detail. The extraordinary properties of the zinc blende modification (c-BN), such as extreme hardness, chemical inertness, high melting temperature, wide band gap, and low dielectric constant, which are important for many commercial applications in modern microelectronic devices and protective coating materials, are the reason for that considerable interest. Starting with the work of Kleinmann and Phillips[1] a lot of theoretical studies of boron nitride have been presented in the last decades. Using different, more or less accurate, first principles methods these works are focused predominantly on the electronic properties of the different modifications (see Refs. 2–20 and references therein). But only a few authors have paid attention to detailed investigations of structural ground state properties. Wentzcovitch *et al.*[8] discussed the transition path from rhombohedral to zinc blende structure and investigated dense phases[6] at high pressures. Knittle *et al.*[9] derived the equation of state for c-BN in experiment and theory with high reliability. Finally, one of the most comprehensive works was given by Furthmüller *et al.*[13]

Regarding all these studies two things are remarkable. First, the bulk modulus, which is of considerable importance in understanding the relationship between a crystal's structure, hardness, and stability, has been calculated for the cubic phase with high consistency by all authors, but for the sp^2-bonded phases with surprisingly deviating values from 77 GPa to 335 GPa.[16,13,11] Second, it is a present dispute which of all observable phases has the lowest total energy.

These differences are evident and prevent a reliable estimation of the equilibrium phase p-T diagram, which is of considerable interest in understanding, e.g., the growth mechanism of boron nitride.

This paper presents a detailed study of several solid modifications of boron nitride using well-established pseudopotential density-functional (DF) methods within the local density approximation. All atomic positions and cell parameters are optimized independently using the Broyden-Fletcher algorithm and a twofold Birch-Murnaghan fitting procedure, respectively, which is described in Sec. III B. The equations of states are deviated and in the case of the sp^2-bonded phases the calculations are compared with the recently available experimental data of Solozhenko *et al.*[21,22]

Finally, the Gibbs free energy of c-BN and h-BN is calculated using the Debye-Grüneisen approximation[25] and the equilibrium line in the phase p-T diagram is predicted. According to Solozhenko[23,24] it is found that c-BN is the thermodynamically stable modification at standard conditions (Sec. III C).

II. METHOD OF CALCULATION

The calculations are based on density functional theory within the local density approximation (LDA) using a plane-wave expansion for the pseudopotentials and wave functions[26,27] as well as the Ceperley-Alder exchange-correlation functional.[28] Boron and nitrogen norm-conserving pseudopotentials were generated following the Troullier-Martins pseudopotential generation scheme.[29]

The energy cutoff for the electronic wave functions has been systematically optimized to reach full convergence and has been set at $E_{\mathrm{cut}}=1630$ eV. A uniform mesh of k points was generated by the method of Monkhorst and Pack.[30] For the zinc blende and rocksalt structure ten special k points have been used. For the hexagonal, rhombohedral, and wurtzite structure six k points were sufficient to achieve convergence better than 0.001 eV/f.u. The atom positions have been relaxed inside the cell volume using the Broyden-Fletcher algorithm.[31] Additionally, nonlocal corrections to exchange and correlation functionals as given by Becke[32] were calculated as final non-self-consistent correction.

III. RESULTS

A. Structures

This paper deals with the structures which are experimentally observed: The hexagonal structure (space group D_{6h}^4) is the common form (h-BN),[33] which has an $AaAa\ldots$ stacking sequence and is slightly different to hexagonal graphite ($ABAB\ldots$ stacking). The rhombohedral modification (r-BN) with $ABCABC\ldots$ stacking sequence is the other lay-

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ered structure[34] (space group C_{3v}). Analogs to cubic and hexagonal diamond are the dense modifications of boron nitride: the cubic phase (c-BN) with zinc blende structure (space group T_d^2), which can be synthesized in the laboratory under pressure,[34,35] and the wurtzite structure (w-BN) (space group C_{6v}^4), which is the analog to stable AlN. Additionally, BN has been calculated in the rocksalt structure.

B. Cohesive properties

The equilibrium properties of a crystal can be derived from thermodynamic potentials, e.g., the Helmholtz free energy $F(T,V)=F_0(V)+F_{\mathrm{vib}}(T,V)$, where F_0 is the static lattice energy without vibrational contributions, F_{vib}. The equation of state determining the pressure is

$$p=-\left(\frac{\partial F}{\partial V}\right)_T, \tag{1}$$

and the isothermal bulk modulus of hydrostatic compression is given by

$$B=-V\left(\frac{\partial p}{\partial V}\right)_T. \tag{2}$$

There are several approximative theories[25,36] describing the isothermal p-V relation (1), but the most common and simple form has been proposed by Murnaghan,[37] who assumed that the isothermal bulk modulus is a linear function of pressure. A slightly better description especially for high pressure delivers the Birch equation,[38] which is an expansion in the strain (f):

$$p=3B_0f(1+2f)^{5/2}\{1+af+bf^2\}, \tag{3}$$

Here f is Eulerian strain parameter $([V/V_0]^{-2/3}-1)/2$, B_0 the isothermal bulk modulus, and a and b constants. The pressure derivative of the bulk modulus B_0' is related to the constant a by $B_0'=2a/3+4$. This equation provides an excellent description of the compression of most solids,[39] while inclusion of the term bf^2 is almost negligible.

Using relations (1) and (3) it is possible to derive the bulk modulus, its pressure derivative, and the minimum of energy and volume from energy-volume data via

$$F_0(V)=\frac{9}{16}B_0V_0\left(6-B_0'+\left(\frac{V_0}{V}\right)^{2/3}\left[(B_0'-4)\left(\frac{V_0}{V}\right)^{4/3}-(3B_0'-14)\left(\frac{V_0}{V}\right)^{2/3}+3B_0'-16\right]\right)+F_0(V_0). \tag{4}$$

For cubic symmetries the generation of energy-volume data can be easily done by total energy calculations of isotropically compressed or expanded unit cells. In the case of noncubic unit cells this method is not valid and yields misleading results, especially if the structures are strongly anisotropic. So the energy-volume data of isotropic expanded and compressed graphitelike structures (h-BN, r-BN) yield erroneous results for the bulk modulus and its derivative, because the c-axis length, which is determined by weak van der Waals bonding, varies much more under hydrostatic pressure than the a axis length.

Therefore, the minimum energy has to be found for each volume by independent variation of the cell parameters. This is in principle the scanning of the energy of compressive and shear deformations for the minimum at a given volume.

In this study the energy-volume data for h-BN, r-BN, and w-BN are determined with help of a twofold Birch fitting procedure: At first, the total energies are calculated for a grid of a-c cell parameters. These data are projected onto an energy-volume plot. Then the Birch equation is fitted to corresponding values of several cell parameters assuming that the equation of state is valid for this case of anisotropic compression. For discrete volume steps all these Birch equations are evaluated and an additional fit is done to the deviated data, resulting in the ideal a-c combination for a fixed volume. So it is possible to deviate the energy-volume data and relations between volume and axis lengths.

The results are reported in Table I in comparison to other selected works. Figure 1 shows the calculated cohesive energies as a function of volume.

1. Zinc blende

The zinc blende structure has the lowest static lattice energy of all modifications. This result agrees with most calculations reported by others. The calculated bulk modulus is 395 GPa for the static lattice. Respecting vibrational energies by the empirical Debye-Grüneisen theory (as reported in Sec. III C) the LDA result is in very good agreement with experimental data (see Table II). Anharmonic effects raise the cell length and lower the bulk modulus with increasing temperature as plotted in Figs. 2 and 3, respectively. The vibrational correction increases by compression, so that the equilibrium volume at 0 K is higher and the bulk modulus is smaller than for the static lattice.

Furthermore, calculations were done using Beckes[32] nonlocal corrections in comparison with the LDA. The results are given in Table II. The nonlocal approximation corrects the LDA overbinding and delivers, as expected, a higher equilibrium distance, whereas the bulk modulus gets too low. Obviously, the agreement with experiment is not evidently improved by these corrections.

The cohesive energy was determined as 12.94 eV/f.u. without zero point corrections using a linear combination of atomic orbitals (LCAO) method[27] with the local spin density approximation. All plane wave (PW) calculations are related to this result, which is in good agreement with estimations from experimental data.[10]

2. Wurtzite

The lattice energy of the wurtzite structure is slightly higher than for c-BN. This structure is a metastable modification. The optimization of lattice parameters yields that the unit cell axes scale in the same manner with increasing hydrostatic pressure. This is not surprising with respect to the sp^3-bonded structure of this modification. The atomic positions vary slightly from ideal values. Boron positions are $\{\frac{1}{3},\frac{2}{3},\xi\}$, $\{\frac{2}{3},\frac{1}{3},\frac{1}{2}+\xi\}$ and nitrogen positions $\{\frac{1}{3},\frac{2}{3},\frac{3}{8}-\xi\}$, $\{\frac{2}{3},\frac{1}{3},\frac{7}{8}-\xi\}$, with $\xi=0.0005$ at equilibrium volume.

TABLE I. Calculated structural and cohesive properties of BN in various phases compared to other LDA calculations and experiment: Volume per atom V, lattice constant a, cohesive energy E_0, ratio of interlayer distance to lattice constant c/a, energy difference to the cohesive energy of the zinc blende structure ΔE, bulk modulus B, and pressure derivative of the bulk modulus B'.

	Present work	Furthmüller *et al.*[a]	Wentzcovitch and co-workers[b]	Xu and Ching[c]	van Camp and van Doren[d]	Expt.
Zinc blende						
V (Å^3)	5.797	5.718	5.860	5.905	5.954	5.930 [e]
a (Å)	3.593	3.576	3.606	3.615	3.625	3.615[e]
E_0 (eV/atom)	−6.47	−8.152	−7.15	−7.00		−6.6 [f]
B (GPA)	395	397	367	370	392	369–400 [g]
B′	3.65	3.59	3.6	3.8	3.31	4.0[e]
ΔE (eV/atom)	0	0	0	0		0
Wurtzite						
V (Å^3)	5.813	5.731		5.845	6.73	5.966 [h]
a (Å)	2.532	2.521		2.536	2.6883	2.553 [h]
c/a	0.827	0.826		0.828	0.8	0.828 [h]
ΔE (eV/atom)	0.011	0.020	0.027	0.075		
B (GPa)	394	401		390	107	
B'	3.68	3.59		6.3	4.24	
Hexagonal						
V (Å^3)	8.747	8.613		8.970	10.02	9.04 [i]
a (Å)	2.496	2.468		2.494	2.592	2.504 [i]
c/a	1.300	1.295		1.335	1.330	1.330[i]
ΔE (eV/atom)	0.057	0.055	0.06	−0.35		
B (GPa)	30.1	261[j]		335 [j]	77	36.7 [k], 29.9[l]
B'	10.1	3.66		3.76	4.41	5.6[k], 9.3 [l]
Rhombohedral						
V (Å^3)	8.693	8.603				9.04[m]
a (Å)	2.493	2.495				2.504[m]
c/a	1.296	1.294				1.996[m]
ΔE (eV/atom)	0.057	0.052				
B (GPa)	32.3	262 [j]	0.06			33.4 [m], 34.6[n]
B'	10.3	3.87				5.25 [m], 5.23[n]
Rocksalt						
V (Å^3)	5.244	5.168	5.327			
a (Å)	3.474	3.458	3.493			
ΔE (eV/atom)	1.758	1.723	1.70			
B (GPa)	410	416	425			
B'	3.81	4.00				

[a] Reference 13.
[b] References 4, 6, 8, and 10.
[c] Reference 11.
[d] Reference 16.
[e] Reference 9 and 49.
[f] Reference 10.
[g] References 45 and 49.
[h] Reference 49.
[i] References 22 and 50.
[j] Calculated by isotropical compression of the unit cell.
[k] Reference 22.
[l] Fit with Birch equation to values given by Solozhenko (Ref. 22).
[m] Reference 21.
[n] Fit with Birch equation to values given by Solozhenko (Ref. 21).

3. Hexagonal

The theoretical static lattice energies and bulk moduli of h-BN given in the literature disagree evidently. A few authors[11,19] report that h-BN has the lowest static lattice energy, whereas most favor the dense phase. It is obvious that the reason for this is the uncertainties of some methods. In this study the energy minimum for h-BN is determined 0.1 eV/f.u. above the minimum of c-BN. Exactly the same result has been reported by Furthmüller *et al.*[13] and Wentzcovitch and co-workers.[4,10,6,8]

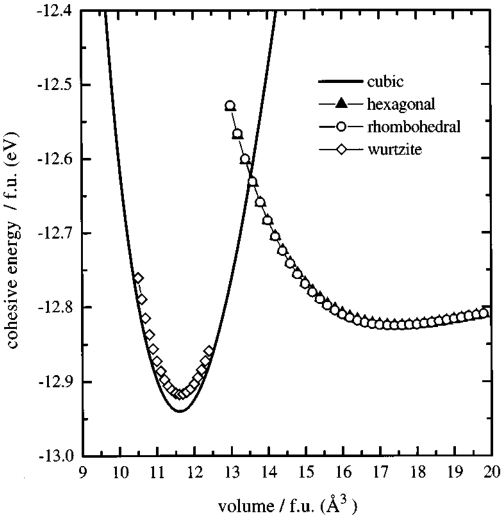

FIG. 1. Calculated cohesive energies of BN as a function of cell volume in the zinc blende, wurtzite, hexagonal, and rhombohedral structure.

Theoretical values for the bulk modulus range from 77 to 335 GPa. These remarkable deviations were the impulse for a systematical recalculation of the layered structures. Using the twofold fitting procedure described above total energies of h-BN have been calculated for optimized unit cells and compared to experimental data, which are recently available.[22] The c axis length which is determined by a weak van der Waals interaction varies much more under hydrostatic pressure than the a axis length, which is given by the extremely short and strong ionic-covalent sp^2 bondings. This is found both experimentally and theoretically as shown in Fig. 4. Up to 12 GPa the relative compression of the a axis is insignificant, while the c axis is compressed to about 85%. Indeed, the theoretical result is surprisingly good, taking into account that a very low interplanar electron density generally represents a problem for the LDA.

The theoretical bulk modulus is 30.1 GPa in comparison to the experimental value of 29.9 GPa, which was obtained by fitting the data of Solozhenko *et al.*[22] to the Birch equation again. This is more than 10 times smaller than the value for c-BN. The pressure derivative is determined theoretically and experimentally as 10.1 and 9.3, respectively. Figure 5 shows the good agreement of experiment and calculation.

4. Rhombohedral

The calculated energies for h-BN and r-BN are nearly the same as shown in Fig. 1. This is due to the fact that the LDA is inadequate to distinguish between different stackings of sp^2-bonded planes. The small difference in curvature between both planar structures is revealed in a slightly higher minimum energy and a higher bulk modulus for r-BN in comparison to h-BN. Although Solozhenko *et al.*[22,21] reported a higher bulk modulus for h-BN, a fit of their data to

TABLE II. Cohesive properties of cubic BN calculated with local and nonlocal density approximation for a static lattice, at $T=0$ K and $T=300$ K, in comparison to experiment.

		B (GPa)	B'	V_0/atom (Å^3)
LDA	static	395	3.65	5.797
	$T=0$ K	387		5.884
	$T=300$ K	385	3.66	5.888
GGA	static	344	3.69	6.120
Expt.[a]	$T=300$ K	369–400	4.0	5.905

[a] References 9 and 45.

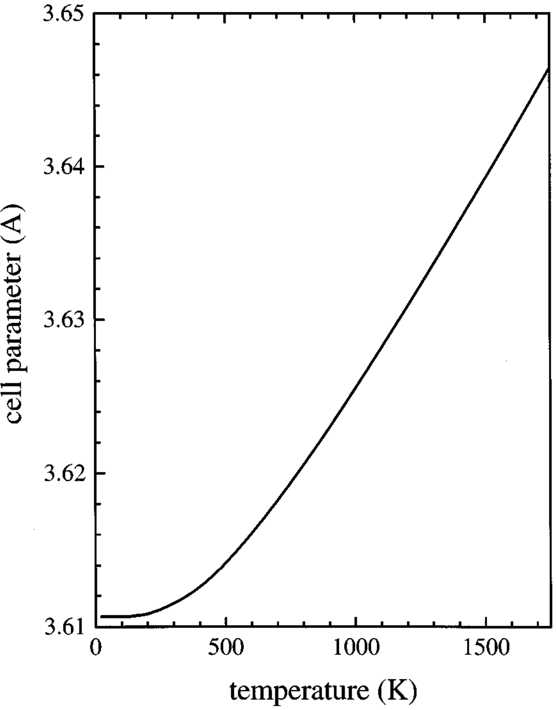

FIG. 2. Lattice constant of c-BN as a function of temperature calculated by Debye-Grüneisen theory.

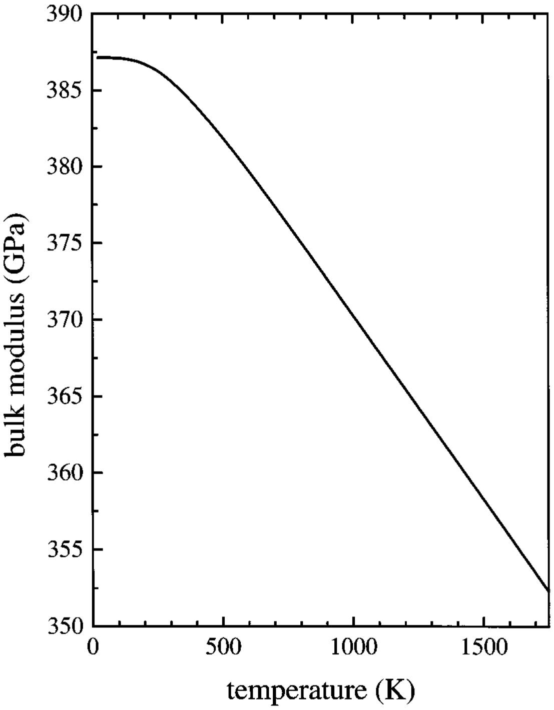

FIG. 3. Bulk modulus of c-BN as a function of temperature calculated by Debye-Grüneisen theory.

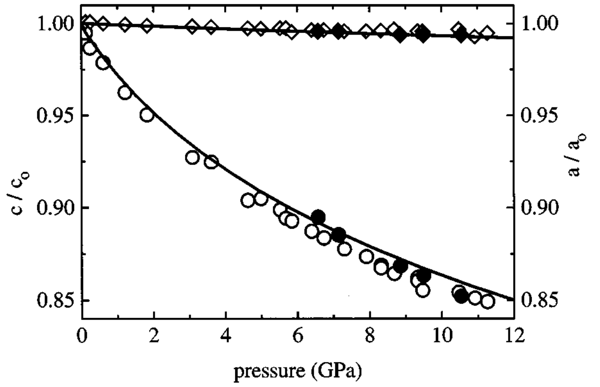

FIG. 4. Relative length of *a* and *c* axes of hexagonal BN vs pressure as given by Solozhenko (Ref. 22). The solid line is the theoretical result.

the Birch equation yields the opposite. The theoretical result is shown in comparison to the experiment in Fig. 6.

C. Phase diagram

The p-T phase diagram of boron nitride is controversially discussed in the literature. There are two proposals which differ fundamentally. The generally accepted one was given two decades ago by Corrigan and Bundy,[43] which predicts h-BN as a thermodynamically stable modification at standard conditions in analogy with the carbon phase diagram. By way of contrast Solozhenko[23,24] presented a phase diagram where c-BN is thermodynamically stable at standard conditions, while the equilibrium line intersects the temperature axis at 1600 K.

Regarding these differences, it seems likely to draw some conclusions from total-energy calculations, particularly since knowledge of the phase diagram is of fundamental interest.

The phase transition between the cubic and hexagonal polymorphs of boron nitride is a reconstruction phase transition, which is always a phase transition of the first order.[40] Therefore, the transition line in the p-T phase diagram can be derived from the thermodynamic potentials of the coexisting phases. The static part of the Helmholtz free energy $F_0(V)$ is given by the *ab initio* calculations shown before (Fig. 1), which predict that c-BN is energetically favored in comparison to h-BN by about 0.114 eV/f.u. This is sufficiently more than the accuracy of the calculations ($\Delta E = 0.001$ eV/f.u.). Furthermore, vibrational contributions must be discussed.

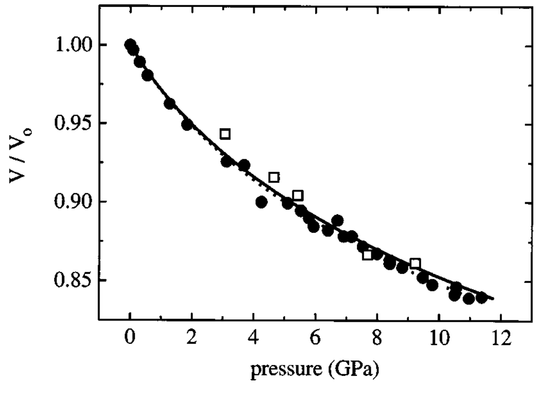

FIG. 5. V/V_0 vs pressure for h-BN. Solid circles (●) represent data of Solozhenko (Ref. 22) while the dotted line is the fit to the Birch equation. Open squares (□) are measured by Coleburn and Forbes (Ref. 48). The solid line is the theoretical result.

There are no experimental phonon spectra for the dense phases as well for the graphitelike modifications available, but recently several theoretical phonon spectra have been published by Karch *et al.*[41] and Nozaki and Itoh,[42] as well as Widany *et al.*[19] (Fig. 7). These data were used in order to derive the zero point energies, which are half of the first moments of the normalized densities. The evaluation of the data of Karch *et al.*[41] yields 0.32 eV/f.u. for the zero point vibrational energy of c-BN. For h-BN an energy of 0.35 eV/f.u. can be derived using the data of Nozaki and Itoh.[42] The data of Widany *et al.*[19] are quite different but yield similar zero point vibrational energies, which are 0.27 eV/f.u. for c-BN and 0.32 eV/f.u. for h-BN. The energy differences at zero temperature are $\Delta F_{\mathrm{vib}} = F_{\mathrm{vib}}(\text{hexagonal}) - F_{\mathrm{vib}}(\text{cubic}) = 0.05$ eV/f.u. using the data of Widany *et al.* or $\Delta F_{\mathrm{vib}} = 0.03$ eV/f.u. using the other results. This confirms the assumption of Lam *et al.*,[10] who have discussed this question in detail and concluded that the zero point vibrational energy of c-BN and h-BN should not differ more than a few hundredths of eV.

Since the difference of the static lattice energies ($\Delta F_{\mathrm{stat}} = 0.114$ eV/f.u.) is significantly larger, it can be definitely concluded that the c-BN ↔ h-BN equilibrium line in the p-T phase diagram does not intersect the pressure axis at zero temperature as proposed by Corrigan and Bundy,[43] because a Gibbs construction on the energy-volume data is impossible, even if zero point contributions are regarded.

These purely qualitative predications make a more detailed calculation highly desirable. Thermodynamic potentials can be calculated by molecular dynamics or Monte Carlo (MC) methods. But these are costly, because the phase space must be sampled calculating the potential energy several times, which is hardly possible by full self-consistent-field DF calculations.

Therefore the empirical Debye-Grüneisen approximation was used in order to calculate the Helmholtz free energies of h-BN and c-BN in a sufficiently accurate but more simple way.

The vibrational contribution to the Helmholtz free energy is given in harmonic approximation by[25]

$$F_{\mathrm{vib}} = 2 \times 3 N k_B T \int 2 \sinh\left(\frac{\hbar \omega}{2 k_B T} \right) g(\omega) d\omega. \tag{5}$$

The phonon density of states $g(\omega)$ can be approximated for cubic systems using the three-dimensional (3D) Debye model:

$$g_D^{(3\mathrm{D})}(\omega) = \begin{cases} 3\dfrac{\omega^2}{\omega_D^3}, & \omega \leq \omega_D , \\ 0, & \omega > \omega_D , \end{cases} \tag{6}$$

where the cutoff frequency ω_D is related with the Debye temperature by $k_B \theta_D = \hbar \omega_D$.

Gielisse *et al.*[44] proposed a Debye temperature of 1700 K for c-BN. This yields a zero point vibrational energy of

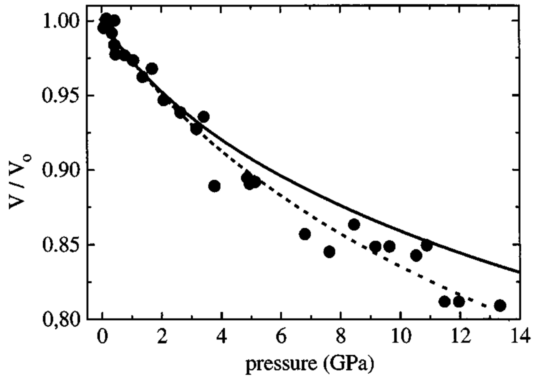

FIG. 6. V/V_0 vs pressure for *r*-BN. Solid circles (●) represent data of Solozhenko (Ref. 21). The dotted line is the fit to the Birch equation. The solid line is the theoretical results.

$\frac{9}{4}k_B\Theta_D=0.33$ eV/f.u. and a temperature dependence, which agrees very well with the result calculated by the theoretical spectra of Karch *et al.*[41] (Fig. 8). For graphitelike phases a two-dimensional Debye approximation is more suitable due to the weak interplanar binding. The phonon density of states is then

$$g_D^{(2D)}(\omega)=\begin{cases} 2\dfrac{\omega}{\omega_D^2}, & \omega\leqslant\omega_D, \\ 0, & \omega>\omega_D. \end{cases} \tag{7}$$

For low temperatures a Debye temperature of 598 K fits the specific heat quite well.[46,47] For higher temperatures this fit is unadaptable and the zero point energy is much too low (0.10 eV/f.u.). Therefore 1900 K was chosen as the Debye temperature for *h*-BN. This yields a vibrational free energy that corresponds nearly ideal to the result received by the

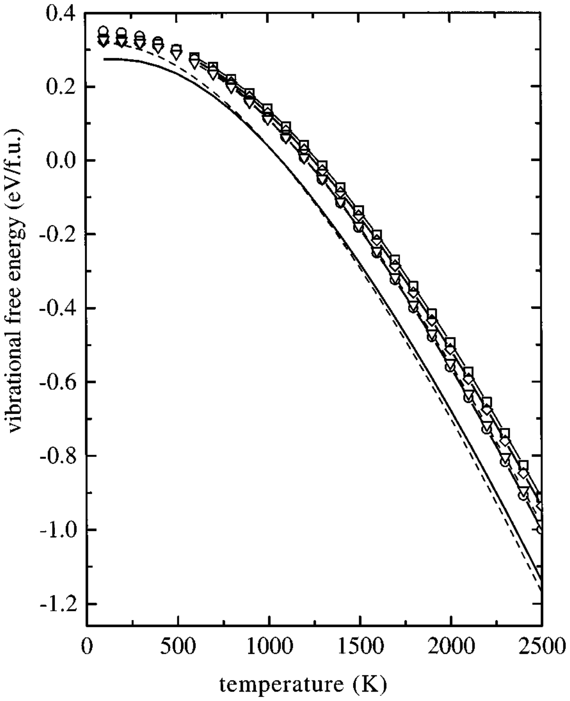

FIG. 8. Vibrational free energy of BN calculated with different phonon densities of states. *h*-BN: dashed line calculated using data of Widany *et al.* (Ref. 19), circles (○) calculated using data of Nozaki *et al.* (Ref. 42), triangles (▽) represent the result in two-dimensional Debye approximation ($\theta_D=1900$ K). *c*-BN: solid line calculated using data of Widany *et al.* (Ref. 19), diamonds (◇) calculated using data of Karch *et al.* (Ref. 41), squares (□) represent the result in three-dimensional Debye approximation ($\theta_D=1700$ K).

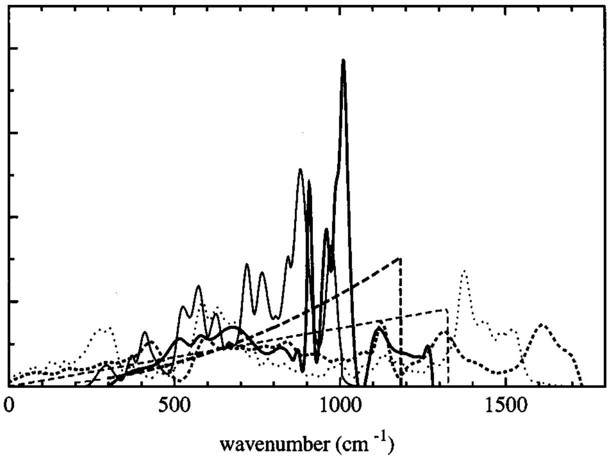

FIG. 7. Phonon density of states for *c*-BN: The thick solid line represents the data of Karch (Ref. 41), the thin solid line the data of Widany *et al.* (Ref. 19). Phonon density of states for *h*-BN: the thick dots represent the data of Nozaki *et al.* (Ref. 42), the thin dots the data of Widany *et al.* (Ref. 19). Phonon density of states in Debye's approximation: The thick dashed line corresponds to the three-dimensional model; the thin dashed line corresponds to the two-dimensional model.

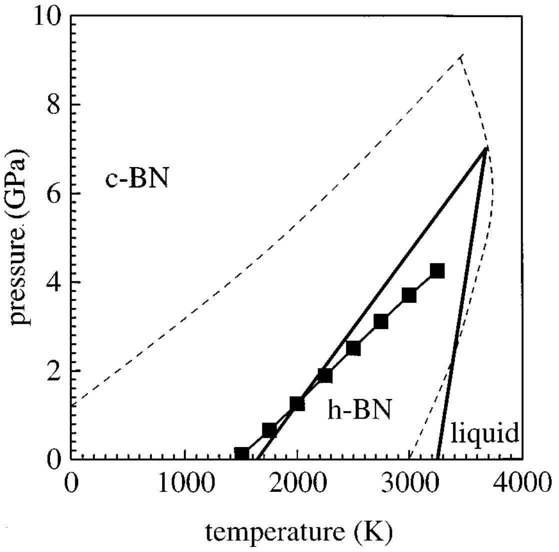

FIG. 9. *p-T* phase diagram of boron nitride. The dashed line is Corrigan and Bundy's diagram (Ref. 43), the thick solid line Solozhenko's proposal (Ref. 23). The line with solid squares represents the equilibrium line calculated in the present work.

data of Nozaki and Itoh[42] (see Fig. 8) with a small mismatch at low temperatures ($<$ 600 K).

Anharmonic effects are respected in the Debye-Grüneisen theory by a volume-dependent Debye temperature, which is determined by the global Grüneisen parameter[25] $\gamma=-(d\ln\theta_D/d\ln V)$. The integration yields $(\theta_D/\theta_D^0)=(V/V^0)^{-\gamma}$ for constant γ.

The Grüneisen parameter can be derived for cubic systems from the bulk modulus' pressure derivative by $2\gamma\approx B'-1$. So $\gamma=1.3$ was chosen for c-BN. This agrees well with results referred by Kim *et al.*,[20] where γ is 1.2–1.5. The Grüneisen parameter for h-BN was set quite arbitrarily to $\gamma=1$. But it should be stated that this choice does not affect the achieved result in principle.

Finally, the free enthalpy $G(T,P)=F_0+F_{\mathrm{vib}}+PV$ can be derived by Legendre transformation from the Helmholtz free energy and the c-BN ↔ h-BN transition line is determined by the equilibrium condition $G_{\mathrm{cubic}}(T,P)=G_{\mathrm{hexagonal}}(T,P)$.

The result is shown in Fig. 9. The equilibrium line corresponds strongly to Solozhenko's proposal and has quite the same shape. The intersection point with the temperature axis is somewhat lower at 1400–1500 K, which depends on the choice of γ for h-BN. Therefore, the thermodynamically stable phase at standard conditions is c-BN. This is consistent with general chemical trends. If a material is able to form strong covalent bonds, a low coordination is favored due to the Pauli exclusion and electrostatic repulsion between bond charges. So carbon is stable in layered structures while silicon is not. Boron nitride has an ionic-covalent bonding with a higher ionicity in h-BN. Therefore, it is conceivable that the zinc blende structure is favored.

IV. SUMMARY

This paper presents *ab initio* calculations of all known structures of boron nitride. In contrast to other studies it is focused exclusively on the pressure dependence of structural properties. The results for the tetragonal coordinated structures achieve full agreement with the most accurate calculations published so far, which are based on different computational techniques. In the case of layered structures an extended fitting procedure is introduced, which determines the dependence of volume and axis lengths on pressure in excellent agreement with experimental measurements. The achieved energy-volume data allow a reliable estimation of the phase diagram features. This prediction is suitable to settle an existing dispute on the shape of this diagram.

ACKNOWLEDGMENT

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[1] L. Kleinmann and J. C. Phillips, Phys. Rev. **117**, 460 (1960).

[2] A. Zunger, A. Katzir, and A. Halperin, Phys. Rev. B **13**, 5560 (1976).

[3] A. Zunger and A. J. Freeman, Phys. Rev. B **17**, 2030 (1978).

[4] R. Wentzcovitch, K. J. Chang, and M. L. Cohen, Phys. Rev. B **34**, 1071 (1986).

[5] K. T. Park, K. Terakura, and N. Hamada, J. Phys. C **20**, 1241 (1987).

[6] R. M. Wentzcovitch, M. L. Cohen, and P. K. Lam, Phys. Rev. B **36**, 6058 (1987).

[7] A. Catellani, M. Posternak, A. Baldereschi, and A. J. Freeman Phys. Rev. B **36**, 6105 (1987).

[8] R. M. Wentzcovitch, S. Fahy, M. L. Cohen, and S. G. Louie, Phys. Rev. B **38**, 6191 (1988).

[9] E. Knittle, R. M. Wentzcovitch, R. Jeanloz, and M. L. Cohen, Nature **337**, 349 (1989).

[10] P. K. Lam, R. M. Wentzcovitch, and M. L. Cohen, in *Synthesis and Properties of Boron Nitride*, Materials Science Forum Vols. 54 and 55, edited by J. J. Pouch and S. A. Alterovitz (Trans Tech Publications, Zürich, Switzerland, 1990), pp. 165–192.

[11] Y.-N. Xu and W. Y. Ching, Phys. Rev. B **44**, 7787 (1991).

[12] N. E. Christensen and I. Gorczyca, Phys. Rev. B **50**, 4397 (1994).

[13] J. Furthmüller, J. Hafner, and G. Kresse, Phys. Rev. B **50**, 15 606 (1994).

[14] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Phys. Rev. B **51**, 6868 (1995).

[15] H. Bross and R. Bader, Phys. Status Solidi B **191**, 369 (1995).

[16] P. E. van Camp and V. E. van Doren, Int. J. Quantum Chem. **55**, 339 (1995).

[17] R. Rodriguez-Hernández, M. González-Diaz, and A. Muñoz, Phys. Rev. B **51**, 14 705 (1995).

[18] Y. Miyamoto, M. L. Cohen, and S. G. Louie, Phys. Rev. B **52**, 14 971 (1995).

[19] J. Widany, Th. Frauenheim, Th. Köhler, M. Sternberg, D. Porezag, G. Jungnickel, and G. Seifert, Phys. Rev. B **53**, 4443 (1996).

[20] K. Kim, W.R.L. Lambrecht, and B. Segall, Phys. Rev. B **53**, 16 310 (1996).

[21] V. L. Solozhenko, G. Will, and F. Elf, Solid State Commun. **90**, 65 (1994).

[22] V. L. Solozhenko, G. Will, and F. Elf, Solid State Commun. **96**, 1 (1995).

[23] V. L. Solozhenko, Thermochim. Acta **218**, 221 (1993).

[24] V. L. Solozhenko, Diamond Relat. Mater. **4**, 1 (1994).

[25] D. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).

[26] M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

[27] Computational results were obtained using a version of the software programs PLANE-WAVE and DSOLID of Molecular Simulations of San Diego.

[28] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[29] N. Troullier and J. L. Martins, Solid State Commun. **74**, 613 (1990).

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

[31] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerial Recipes in Fortran* (Cambridge University Press, Cambridge, England, 1992).

[32] A. D. Becke, J. Chem. Phys. **96**, 2115 (1992).

[33] R. Pease, Acta Crystallogr. **5**, 536 (1952).

[34] F. P. Bundy and R. H. Wentorf, J. Chem. Phys. **38**, 1144 (1963).

[35] R. H. Wentorf, J. Chem. Phys. **26**, 956 (1957).

[36] P. Vinet, J. Ferrante, J. Smith, and J. Rose, J. Phys. C **19**, L467 (1986).

[37] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30**, 244 (1944).

[38] F. Birch, J. Geophys. Res. **57**, 227 (1952).

[39] F. Birch, J. Geophys. Res. **83**, 1257 (1978).

[40] B. K. Vainshtein, V. M. Fridkin, and V. L. Indenbom, *Structure of Crystals*, *Modern Crystallography*, 2nd ed. (Springer-Verlag, Berlin, 1982), Vol. 2.

[41] K. Karch, F. Bechstedt, P. Pavone, and D. Strauch, Physica B **219 & 220**, 445 (1996).

[42] H. Nozaki and S. Itoh, Phys. Rev. B **53**, 14 161 (1996).

[43] F. R. Corrigan and F. P. Bundy, J. Chem. Phys. **63**, 3812 (1975).

[44] P. Gielisse *et al.*, Phys. Rev. **155**, 1039 (1967).

[45] M. Grimsditch, E. S. Zouboulis, and A. Pollan, J. Appl. Phys. **76**, 832 (1994).

[46] A. S. Dworkin, D. J. Sasmor, and E. R. van Artsdelen, J. Chem. Phys. **22**, 837 (1954).

[47] J. Krumhansl and H. Brooks, J. Chem. Phys. **21**, 1663 (1953).

[48] N. L. Coleburn and Y. W. Forbes, J. Chem. Phys. **48**, 555 (1968).

[49] T. Soma, S. Sawaoka, and S. Saito, Mater. Res. Bull. **9**, 755 (1974).

[50] R. W. Lynch and H. G. Drickamer, J. Chem. Phys. **44**, 181 (1966).