

Interlayer binding of hexagonal boron nitride in the rigid-layer approximation

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(Received 17 December 1984)

A phenomenological model on the basis of the Coulomb and Lennard-Jones potentials is applied to investigate the interlayer binding of layered hexagonal BN. The values of the relevant potential parameters are examined by fitting the lattice sums of the potential derivatives to the values derived from experimental values. It is shown that the model cannot explain the experimental values consistently when the full lattice sum of the repulsive inverse-12th-power interaction is included. However, when the repulsion terms, except those corresponding to the nearest-neighbor B-B, N-N, and B-N atoms, are neglected, the model providing the effective charges as much as $\pm 1.6e$ is compatible with the experimental values. In this case discussions are given on the binding energy, the van der Waals attractive potential constants, the phonon dispersions, and the elastic constants of the crystal.

I. INTRODUCTION

Layered hexagonal boron nitride (hereafter abbreviated as hexagonal BN or simply as BN) consists of layers of hexagonal networks with a monatomic thickness similar to graphite's.¹ Since the primitive unit cell of hexagonal BN contains only four atoms in two adjacent layers, its crystal structure is one of the simplest among crystals with layer structures. The interlayer binding of BN and graphite is known to be very weak. For graphite, a simple Lennard-Jones model has been shown to work well in most cases except those involving *c*-axis shears,²⁻⁸ though a density-functional theory by DiVincenzo, Mele, and Holzwarth⁹ provides a better description of it.

As for hexagonal BN, to the authors' knowledge, its interplanar binding has been studied exclusively on the basis of a phenomenological model with the van der Waals and Coulomb interactions.¹⁰⁻¹² In these previous works the potential constants have been estimated by a nomographic method. There seems, however, ambiguity in the construction of and the linear interpolation from nomograms. In addition, the elastic constant c_{44} in Green's model¹¹ is only a half of the value estimated with the frequency of the zone-center rigid-layer shear mode.¹³⁻¹⁵ It suggests an alternative approach based on relevant experimental results. Similar approaches have successfully been applied to a few layer crystals by Katakahama *et al.*¹⁶ and Mori.¹⁷

The purpose of the present paper is to investigate the interplanar binding of hexagonal BN on the basis of the van der Waals and Coulomb potentials, but without any nomographic method. We make, instead, use of relevant available, though very limited, experimental results, including the frequency of the zone-center rigid-layer shear mode. The potential constants can be obtained by fitting appropriate lattice sums of potential terms and of their derivatives to the relevant experimental values or to the values easily estimated with them. We apply the results

of the calculation to get the dispersion relations of rigid-layer phonons and the two relevant third-order elastic constants, c_{333} and c_{443} .

This paper consists of five sections. Section II will present a calculation of lattice sums. The fitting procedure to obtain the relevant potential parameters will be given in Sec. III. Section IV will contain the results of the calculation and the discussions on them. Section V will deal with conclusions.

II. CALCULATION

In this section, after a brief description of interlayer potential energy, we will examine basic assumptions for its calculation and calculate the lattice sum for each of the relevant potential terms.

The intralayer binding of hexagonal BN shown in Fig. 1(a) is considerably strong compared with its interlayer binding.¹⁵ It allows us to deal separately with the interlayer binding within the total lattice binding. Hereafter, we confine ourselves to the case where each layer itself is rigid and only its relative position may be slightly changed under relevant constraints. The crystal is assumed to be large enough to neglect surface effects.

We further assume that the total potential energy for interlayer binding E_t can be expressed as the sum of the two-center potentials ϕ_{ij} between all pairs of atoms i and j belonging to different layers,

$$E_t = \frac{1}{2} \sum_{i,j} \phi_{ij} . \quad (1)$$

Hereafter, we will refer to an arbitrary pair of a nitrogen atom and an adjacent boron atom in an arbitrary layer which is located far from the surface. We define $\phi_i(\text{N})$ as the potential between the nitrogen atom of the above-mentioned pair and any atom i in a different layer. Similarly, $\phi_i(\text{B})$ is defined for the boron atom. Equation (1) is rewritten as

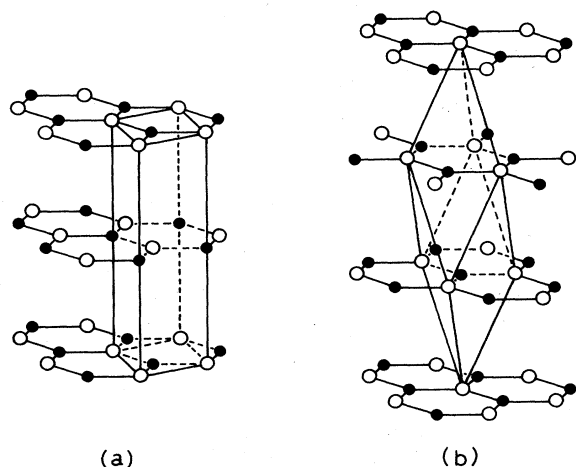


FIG. 1. Crystal structures and unit cells of (a) layered hexagonal and (b) rhombohedral boron nitride. The solid and the open circles denote the boron and the nitrogen atoms, respectively.

$$E_t = \frac{n}{4} \sum_i [\phi_i(\text{N}) + \phi_i(\text{B})], \quad (2)$$

where n is the total number of atoms constituting the crystal. The potential energy per pair of B and N atoms can be expressed as

$$E = \frac{1}{2} \sum_i [\phi_i(\text{N}) + \phi_i(\text{B})]. \quad (3)$$

Thus E is the sum of the potential over a semi-infinite lattice.

We assume that the two-center potential is given by

$$\phi_{ij} = -A_{ij}r_{ij}^{-6} + D_{ij}r_{ij}^{-12} + q_iq_je^2r_{ij}^{-1}, \quad (4)$$

where A_{ij} and D_{ij} are the Lennard-Jones potential constants, e the charge of the electron, q_i and q_j the effective charges of the atom i and j in units of $|e|$, and r_{ij} the distance between the atoms i and j . This form of expression is equivalent to that given by Danilenko *et al.*¹² It is based on the implicit assumption that the charge distributions of the valence electrons of the nitrogen and boron atoms can be approximated to be spherically symmetric. The real distributions, however, should be anisotropic according to the dominant covalent bonding within the layer as is observed in graphite.¹⁸ Consequently, expression (4) can be considered to be the lowest-order approximation, including the anisotropic effect only, via the anisotropic configuration of the lattice.

The difference of the charge distributions from the spherical symmetry can be expressed as the dipole, quadrupole, and higher-order poles around each atom. The dipolar part is zero because of the local symmetry. The quadrupolar distribution is not zero. However, the leading term of their contribution to the interlayer potential, which is the monopole-quadrupole interaction, decays with the inverse fourth-power of distance and the sign of this value is alternating in the lattice sum. Consequently, the contribution of the monopole-quadrupole interaction to the total interlayer binding energy may be small enough to be neglected. The second leading term, which is the quadrupole-quadrupole interaction, can be small but it is not certain that this term is smaller than the first since the sign of the second is not alternating. Fortunately, this quadrupole-quadrupole term depends on the inverse sixth-power of distance similar to the attractive part of the van der Waals potential and can be included to it as an effective van der Waals constant.

Hereafter, we calculate the sum of each term in the potential (4) separately for a few adjacent layers, using the lattice parameters of $a = 2.504$ Å and $c = 6.661$ Å reported by Pease.¹ We denote this energy sum for the n th-nearest layer by $E(n)$. Likewise, E_C denotes the sum of the Coulomb term, the third term on the right-hand side of Eq. (4), between a reference pair of BN atoms and the atoms in a neighboring layer. E_a denotes the sum of the van der Waals attractive term, the first term, between the reference pair and a sublattice in a neighboring layer. E_r refers to the repulsive term.

For the calculation of E_C and its derivatives, we have used a formula by Green *et al.*¹¹ which is based on a modified Ewald method. The absolute value of the effective charge is, only here, assumed to be equal to that of the electron charge. When the u and the w denote, respectively, the in-plane projection (u, v) and the z component of the small relative displacement vector of the relevant layer, the energy is expressed for the hexagonal BN lattice as

$$E_C = (-2\pi e^2/S) \sum_{\mathbf{g}} \{ \cos(\mathbf{g} \cdot \mathbf{u}) - \cos[\mathbf{g} \cdot (\mathbf{r}_0 + \mathbf{u})] \} \times (1/|\mathbf{g}|) \exp[-(z+w)|\mathbf{g}|], \quad (5)$$

where z is the one-dimensional position of the layer at equilibrium, \mathbf{g} a reciprocal-lattice vector, \mathbf{r}_0 the distance vector between the nearest-neighbor B and N atoms, and S the area of the two-dimensional unit cell. Here we note that Eq. (5) reduces to the formula by Green, except the difference of the factor $3/a^2$ is due to the difference of

TABLE I. Coulomb potential E_C and its derivatives between a pair of B and N atoms and neighboring layers at equilibrium. The absolute value of the effective charges is assumed to be equal to that of the electron charge.

Layer	$E_C(n)$	$\frac{\partial E_C(n)}{\partial w}$	$\frac{\partial^2 E_C(n)}{\partial w^2}$	$\frac{\partial^2 E_C(n)}{\partial u^2}$
n	(10^{-14} erg)	(10^{-14} erg Å $^{-1}$)	(10^{-14} erg Å $^{-2}$)	(10^{-14} erg Å $^{-2}$)
1	-1.0686	3.0963	-8.9718	4.4859
2	0.0001	-0.0004	0.0012	-0.0006
3	0.0000	0.0000	0.0000	0.0000

TABLE II. Layer lattice sum of $-r_{ij}^{-6}$, L_a , and its derivatives between a reference atom and a neighboring layer in BN. For each value, the contributions from the two sublattices are shown in different columns. Sublattices 1 and 2 (abbreviated as Subl. 1 and 2) refer, respectively, to those between the unlike species of atoms and those between the same species.

Layer n	$L_a(n)$ (10^{-3} \AA^{-6})		$\frac{\partial L_a(n)}{\partial w}$ (10^{-3} \AA^{-7})		$\frac{\partial^2 L_a(n)}{\partial w^2}$ (10^{-3} \AA^{-8})		$\frac{\partial^2 L_a(n)}{\partial u^2}$ (10^{-4} \AA^{-8})	
	Subl. 1	Subl. 2	Subl. 1	Subl. 2	Subl. 1	Subl. 2	Subl. 1	Subl. 2
1	-2.2018	-2.0771	2.8081	2.6186	-4.4807	-3.9899	1.3242	0.2936
2	-0.1074	-0.1158	0.0345	0.0371	-0.0549	-0.0587	0.0157	0.0149
3	-0.0206	-0.0191	0.0029	0.0027	-0.0046	-0.0043	0.0012	0.0011
4	-0.0057	-0.0061	0.0004	0.0005	-0.0007	-0.0008	0.0002	0.0002
5	-0.0024	-0.0022	0.0001	0.0001	-0.0002	-0.0002	0.0000	0.0000
6	-0.0010	-0.0011	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

the unit of length. The calculation of E_C and their derivatives at equilibrium is briefly described in Appendix A. Table I summarizes its results.

For the calculations of E_a and E_r and their derivatives, we must know the corresponding lattice sums of $-r_{ij}^{-6}$ and r_{ij}^{-12} and their derivatives in hexagonal BN lattice. We have obtained these values by the direct summation supplemented with use of the hexagonal symmetry as described in Appendix B. The results are shown in Tables II and III. Because of the very-short-range nature of the repulsive interaction, we show its sum only for the nearest-neighbor B-B, N-N, and B-N atoms separately in the first row, as well as the usual layer sums in Table III.

III. FITTING PROCEDURE

The lattice sums calculated in the preceding section allow us to link the Lennard-Jones potential parameters to the parameters obtained experimentally. Since there seems no reliable parameter on boron and nitrogen in partially ionic situations, we estimate these values by fitting the first and the second derivatives of the potential function to the values indirectly obtained in experiment.

According to the condition of charge neutrality, the absolute values of the effective charges of the boron and the nitrogen atoms are equal to each other ($=q$) and their signs are opposite. Furthermore, we take notice of the fact that the configuration of the lattice is invariant under the interchange of the boron and the nitrogen sites. Consequently, the lattice sums for like atoms, that is, B-B and N-N, are equal to each other and it is sufficient for us to deal with only the sum of the two potential constants of

like atoms instead of two constants themselves between B and B and between N and N.

Now the number of the independent unknowns are five: the effective charge, the two attractive constants corresponding to the one between B and N and the half of the sum of B-B and N-N, and the two corresponding repulsive constants. The number of the available experimental values are four: the frequency of the zone-center rigid-layer shear mode, the elastic constant c_{33} , and the two interlayer distances at equilibrium of hexagonal BN and rhombohedral BN shown in Fig. 1(b). To decrease the number of the unknowns by one, we assume that the parameter for the attractive interaction between B and N is equal to the half of the sum of the constants between B and B and between N and N. The attractive part of the van der Waals interaction is due to the interaction between fluctuating dipoles, and the polarizability may not be much different for the atoms in the same row of the Periodic Table. While the atom of larger atomic number contains more electrons, the polarizability per electron is smaller. This simple consideration may support the above assumption.

When the relevant summations of the layer sum $E(n)$ are used, we can obtain the following four equations, in each of which the summation extends from $n = 1$ to infinity. Here, A is the attractive parameter, D the repulsive one between B and N, and F the half of the sum of the repulsive ones between B and B and between N and N. The lattice constants of rhombohedral BN are assumed to be equal to the corresponding constants in the hexagonal form since the differences between these seem very small.¹⁹

TABLE III. Lattice sum of r_{ij}^{-12} , L_r , its derivatives, and those obtained by referring to the distance vectors only between an atom in a reference layer and the nearest atoms in one of the nearest layers in BN. The number of the sublattices is defined as in the heading to Table II.

Layer n	$L_r(n)$ ($10^{-7} \text{ \AA}^{-12}$)		$\frac{\partial L_r(n)}{\partial w}$ ($10^{-6} \text{ \AA}^{-13}$)		$\frac{\partial^2 L_r(n)}{\partial w^2}$ ($10^{-6} \text{ \AA}^{-14}$)		$\frac{\partial^2 L_r(n)}{\partial u^2}$ ($10^{-7} \text{ \AA}^{-14}$)	
	Subl. 1	Subl. 2	Subl. 1	Subl. 2	Subl. 1	Subl. 2	Subl. 1	Subl. 2
NN ^a	5.3689	5.7172	-1.9345	-1.7334	7.5508	5.6106	-5.8083	0.5716
1	7.6311	6.3966	-2.4474	-1.8654	8.7635	5.8755	-3.4008	1.4284
2	0.0057	0.0061	-0.0009	-0.0009	0.0060	0.0063	-0.0008	-0.0006
3	0.0001	0.0001	0.0000	0.0000	0.0001	0.0001	0.0000	0.0000

^aNN refers to the sum only for the nearest neighbors.

When the repulsion terms except those for the nearest-neighbor B-B, N-N, and B-N atoms are neglected, the equations are

$$\sum_n \left[\frac{\partial E(n)}{\partial w} \right]_0 = 6d(5.51A - 1.936D - 1.734F + 15.50p) = 0, \quad (6)$$

$$\sum_n \left[\frac{\partial^2 E(2n-1)}{\partial u^2} \right]_0 = 6(0.540A - 1.936D + 0.1906F + 74.8p) = S\rho\omega^2 d/4, \quad (7)$$

$$\sum_n n^2 \left[\frac{\partial^2 E(n)}{\partial w^2} \right]_0 = 6(-30.16A + 25.18D + 18.70F - 149.5p) = Sc_{33}/d, \quad (8)$$

$$\sum_n \left[\frac{\partial E(n)_{\text{rhomb}}}{\partial w} \right]_0 = 6d(5.41A - 0.968D - 1.734F + 7.75p) = 0, \quad (9)$$

where p denotes the square of the effective charge in units of the electron charge, and d is the interlayer spacing in equilibrium and taken to be equal to $c/2$. S denotes the area of the two-dimensional primitive cell and is equal to $(\sqrt{3}/2)a^2$. ρ is the density and ω the angular frequency of the zone-center rigid-layer shear mode. The x and the y axes are taken within a layer and the z axis along the crystalline c axis. The u , v , and w are, respectively, the x , y , and z components of the displacement vector of the rigid layer. The sign of w is taken to be positive for dilatation. The subscript 0 on the left-hand side means the respective derivative at the equilibrium position. The effective charges for the rhombohedral form are assumed to be equal to those for the hexagonal form.

Equations (6) and (9) are the conditions of the equilibrium in the hexagonal and the rhombohedral forms, respectively. The summation on the left-hand side of Eq. (7) means to sum the shear force from each of the odd-number nearest-neighbor layers. The summation sign in Eq. (8) indicates summation of the compressional forces between all layers across a specific layer gap. For simplicity, we have excluded the factors 10^{60} , 10^{105} , and 10^{105} , in the cgs units from the numerical coefficients on A , D , and F in the above four equations, respectively.

We have used the value 3.0×10^{11} dyn cm $^{-2}$ as the elastic constant c_{33} which is derived from the arithmetic mean of the three reported values of compressibility.²⁰⁻²² The ω is taken as 52.5 cm $^{-1}$ according to Ref. 14. The calculation gives 1010 and 4890 ergs cm $^{-2}$ as the values of Eqs. (7) and (8), respectively.

The solution of Eqs. (6)–(8) is as follows:

$$A = (3.65 - 0.541p) \times 10^{-59} \text{ erg cm}^6, \quad (10)$$

$$D = (-5.89 + 3.27p) \times 10^{-104} \text{ erg cm}^{12}, \quad (11)$$

$$F = (18.19 - 4.48p) \times 10^{-104} \text{ erg cm}^{12}. \quad (12)$$

These three parameters must be not negative, and the solution gives an estimate of the range of the absolute value q ($=\sqrt{p}$) of the effective charge in units of the electron charge,

$$1.34 < q < 2.02. \quad (13)$$

The supplementary equation (9) offers an estimated value itself: $q = 1.58$.

Thus $A = 2.31 \times 10^{-59}$ erg cm 6 , $D = 2.2 \times 10^{-104}$ erg cm 12 , and $F = 7.1 \times 10^{-104}$ erg cm 12 . The interlayer interaction energy per pair of BN atoms for hexagonal BN is expressed as

$$E = -(10.7p + 91.2A - 10.74D - 11.44F) \times 10^{-15} \text{ erg} \\ = -(188.0 - 22.5p) \times 10^{-15} \text{ erg}.$$

It is equal to $-(2.71 - 0.32p)$ kcal/mol, which reduces to about -1.92 kcal/mol. Equivalently, the interplanar energy per area is -243 ergs cm $^{-2}$.

So far we have neglected the repulsive terms, except those for the nearest-neighbor B-B, N-N, and B-N atoms. When we include the contributions to the repulsive interaction from all the pairs, it is shown that the present model can provide no consistent set of potential parameters compatible with the available values obtained easily from the relevant experimental results. Thus, hereafter we confine ourselves to the first case, providing the consistency between the model and the experimental results.

IV. RESULTS AND DISCUSSIONS

A. Effective charge

The present calculation has given the effective charges of $\pm 1.6e$. Here, we will briefly examine the meaning of the effective charge in the present model. If the charge distribution around an ion is spherically symmetric, the effective charge has a very simple meaning as far as the electrostatics is concerned. In the present system with considerable anisotropy, however, the effective charge can be defined within the framework of the best one-parameter approximation to the charge distributions around ions constituting the system.

Though we can not specify the sign of the effective charge solely by the present calculation, the nitrogen atom should have excess electrons according to a consideration

of electronegativity and to a band-structure calculation.²³ Thus the dominance of the repulsive interaction between the same kinds of atoms over that between boron and nitrogen as shown in Sec. III may be reduced to the dominance of repulsion between nitrogens. It corresponds to the importance of the nitrogen π -electron distribution near the middle of adjacent layers. The half of the distance between the nearest nitrogen atoms across the layer gap is about 1.82 Å, which is considerably larger than the nearest-neighbor boron-nitrogen distance of 1.45 Å. This suggests that, according to the approximation of the spherical distribution, an appreciable amount of electrons assigned to boron may be included in this approximated spherical distribution of electrons in the nitrogen atom. It may explain the apparent largeness of the relevant effective charge.

Previous calculations^{11,12} have given the value 1.15 for the effective charge q . The value estimated here is much larger than the previous one. The difference stems from the fact that our calculation is based on the fitting of the shear elastic constant c_{44} which is about 2 times larger than in the previous result.

B. Potential parameters and interlayer interaction energy

The calculated mean value A of the van der Waals attractive constant is about 2.3×10^{-59} erg cm⁶, which agrees well with the value 2.14×10^{-59} erg cm⁶ obtained with nomograms by Green *et al.*¹¹ While their procedure with nomograms does not seem to have sufficiently clear physical grounds, the value calculated by us is based only on the experimentally obtained values.

As for the repulsive constants, our calculation gives the value D between B and N and the mean value F of the constants defined between B and B and between N and N. While the D value by us is about two-thirds of the value by Green, the F value by us is about twice as much as Green's. Though D is nearly equal to F in Green's results, our calculation shows that the repulsive interaction constant between the same species of atoms is considerably larger than the constant between the different species. Taking into account the relevant lattice sum, our result indicates that the repulsive interaction itself may be more significant for the first-nearest-neighbor B-B and/or N-N pairs of atoms than for the first-nearest B-N pairs across the nearest layers.

The calculated interlayer interaction energy per area is -243 ergs cm⁻², which agrees well with -244 ergs cm⁻² by Green *et al.*¹¹ The energy per formula unit is -1.92 kcal/mol, which agrees well with -1.908 kcal/mol by Danilenko *et al.*¹²

C. Dispersion relations of rigid-layer phonons

The lattice sums of the second derivatives of the potential terms calculated in Sec. II allow us to estimate the constants of force between layers. We have seen that only the first- and second-nearest-neighbor interactions are important and that the sum of the contributions of the third and further interactions is at most about 2% of the total force.

We deal with the normal modes of vibration in a one-

dimensional periodic array of rigid layers whose masses are assumed to be equal to unity for simplicity. When we use the conventional Born-von Kármán cyclic boundary condition, the equation of motion of the n th layer is

$$\frac{d^2 u_n}{dt^2} = f(u_{n+1} + u_{n-1} - 2u_n) + g(u_{n+2} + u_{n-2} - 2u_n), \quad (14)$$

where u_n is the displacement of the n th layer and f and g are the force constants corresponding to the first- and second-nearest-neighbor interactions.

If we assume that this equation has the solution

$$u_n = U \exp[i(kx_n - \omega t)] + \text{c.c.}, \quad (15)$$

the dispersion relation is

$$\omega^2 = 4f[\sin(kd/2)]^2 [1 + (4g/f)\cos^2(kd/2)], \quad (16)$$

where ω is the frequency, k the wave number, x_n the position of the n th layer, U the amplitude, and d the interlayer separation.

According to the calculation in Secs. II and III, the compressional force constants are

$$f = 5.16 \times 10^3 \text{ ergs cm}^{-2} \text{ and } g = -52 \text{ ergs cm}^{-2}.$$

The shear force constants are

$$f = 1.01 \times 10^3 \text{ ergs cm}^{-2} \text{ and } g = 1.4 \text{ ergs cm}^{-2}.$$

We see that the two dispersion relations are well approximated by sine curves. The shift from the sine curve is at most 2% for the compressional or longitudinal branch and 0.3% for the shear or transverse branch. The directions of change in energy of the two dispersion curves are opposite to each other, which corresponds to the difference of sign in these two constants of the second-neighbor interactions.

The above consideration affords us the correction term for the shear elastic constant c_{44} , which is calculated by the approximated general relation given in Ref. 15. The factor of the first correction term for c_{44} of BN is positive and only about 0.6%.

D. Third-order elastic constants

The above calculations can be extended for two components of third-order elastic constants of hexagonal BN. These are c_{333} and c_{443} obtained by taking the derivatives of c_{33} and c_{44} with respect to the z component of the strain.

According to the relevant calculations on the third-order derivatives of the potential terms, the sums of the contributions of the second and the higher nearest-neighboring layers can be neglected. Thus the third-order constants are expressed as

$$c_{333} = \frac{d^2}{S} \left[\frac{\partial^3 E(1)}{\partial w^3} \right]_0, \quad (17)$$

$$c_{443} = \frac{d^2}{S} \left[\frac{\partial^3 E(1)}{\partial w \partial u^2} \right]_0, \quad (18)$$

where $E(1)$ is the potential energy between a formula unit of BN in a layer and all ions in one of the adjacent layers. The calculation gives $c_{333} = -4.1 \times 10^{12}$ dyn cm $^{-2}$ and $c_{443} = -6.1 \times 10^{11}$ dyn cm $^{-2}$.

We can estimate c_{333} from the pressure dependence of the interlayer separation of BN.^{20,11} The result is $c_{333} = -3.3 \times 10^{12}$ dyn cm $^{-2}$. The absolute of the value calculated by us is larger than the experimental one by about one-fourth. It seems that the degree of the discrepancy is not serious, considering that the present calculation is based on an elementary phenomenological model and that there seem to be variations between the nonlinear parts of the compressibility data on hexagonal BN.

The constant c_{443} can be estimated if we know the pressure and temperature dependence of the angular frequency ω of the zone-center rigid-layer shear mode of BN,

$$c_{443} = d \frac{\partial c_{44}}{\partial p} \frac{\partial p}{\partial \omega} + d \frac{\partial c_{44}}{\partial T} \frac{\partial T}{\partial \omega}, \quad (19)$$

where p is the pressure and T the temperature. We can use the approximated relation between c_{44} and ω given in Ref. 15. The first term on the right-hand side of Eq. (19) is estimated to be -4.7×10^{11} dyn cm $^{-2}$. There seems to be no report on the temperature dependence, but we are dealing with a quasi-isothermal process and can neglect the contribution of the second term. Thus we see that the absolute of the calculated value is, by about 30%, greater than that estimated with experimental values. The model seems not to have such a high accuracy as is provided by a quantitatively correct value related to a higher derivative of interaction energy.

E. Concluding discussion

As described in Sec. III, the inclusion of all the repulsion terms leads to the inconsistency between the model and the set of the relevant experimental results. In this case, if we do not take into account the frequency of the shear phonon, the model provides an effective charge q smaller than about 1.3 and the estimated c_{44} is less than about a half of the value calculated with the shear phonon energy. Green *et al.*¹¹ previously reported that the Lennard-Jones potential seriously underestimates the shear force in graphite. If the similar situation in hexagonal BN stems from more or less common origin, the π electrons related to the remarkably strong anisotropy might be responsible for it. For BN, however, as shown in Sec. III, the truncation of the repulsive interaction saves the simple empirical formula.

V. CONCLUSIONS

We have studied the interlayer binding of layered hexagonal boron nitride with a semiempirical method combining the Lennard-Jones potential and the Coulomb potential due to the partially ionic binding. Without any reference to the potential parameters, we have calculated each of the lattice sums responsible for the total binding energy and their derivatives. It has been found that each sum of the contributions of the second- and higher-

nearest-neighbor layers is less than about 6% of that of the first-nearest layer. It leads to the conclusion that the dispersion relations of rigid-layer phonons are close to sine curves. It is shown that the dominant contribution from the second-neighbor layer stems from the van der Waals attractive potential.

By using the interlayer distances in two crystalline forms, the compressibility and the frequency of the zone-center rigid-layer shear mode, as fitting parameters, we have studied the compatibility of the present model with these values. It is shown that the inclusion of all the repulsion terms leads to the inconsistency between the model and the set of the experimental results. However, when the repulsion terms—except those for the nearest-neighbor B-B, N-N, and B-N atoms—are neglected, the model provides consistent values of the responsible potential parameters.

According to the calculated repulsive constants, it is not the first-nearest B-N but the first-nearest N-N atoms that play the most significant role in the repulsive interaction in layered boron nitride. It may correspond to the importance of N-N repulsion in layer-stacking forms of boron nitride.

Recently, Katahama, Nakashima, Mitsuishi, Ishigame, and Arashi¹⁶ have shown that the energy formula expressed as the sum of an attractive potential in inverse-sixth-power form and a repulsive potential in exponential form successfully describes interlayer bindings of a few kinds of layer crystals on the basis of experimental studies including Raman scattering and x-ray diffraction under high pressures. An extension of the present work along a procedure similar to theirs is in progress.

ACKNOWLEDGMENTS

One of the authors (T.K.) would like to express his gratitude to Dr. Minoru Iwata, the former leader of the sixth research group of the National Institute for Research in Inorganic Materials, for his encouragement and suggestions. He is very grateful to Dr. Koh Era in the Institute for valuable discussions. He is indebted to Professor Shinichi Nakashima, The University of Osaka, for kind suggestions.

APPENDIX A: CALCULATION OF DERIVATIVES OF COULOMB ENERGY

The partial derivative of Eq. (5) with respect to w is obtained simply by adding the factor $|\mathbf{g}|$ in each of the summand once by every order. The derivative by a component of the in-plane coordinates does not depend on the direction because of the hexagonal symmetry. If we pay attention to the factor

$$f = \{\cos(\mathbf{g} \cdot \mathbf{u}) - \cos[\mathbf{g} \cdot (\mathbf{r}_0 + \mathbf{u})]\} \exp(-z |\mathbf{g}|), \quad (A1)$$

f is negligibly small for large $|\mathbf{g}|$. Thus, only the terms with small $|\mathbf{g}|$ contribute to the energy. For small displacement $|\mathbf{u}|$, we have the approximate expression

$$f = \{[1 - \cos(\mathbf{g} \cdot \mathbf{r}_0)][1 - (\mathbf{g} \cdot \mathbf{u})^2/2] + (\mathbf{g} \cdot \mathbf{u}) \sin(\mathbf{g} \cdot \mathbf{r}_0)\} \exp(-z |\mathbf{g}|). \quad (A2)$$

We see that the term linear to $|\mathbf{u}|$ vanishes according to third-order symmetry.

**APPENDIX B: TWO-DIMENSIONAL
SUM OF DERIVATIVES OF POTENTIAL
IN HEXAGONAL LATTICE**

Here, we briefly describe simple expressions for derivatives of a potential between an atom in a layer and all atoms in a neighboring layer under the constraint of small and rigid displacement of the layer. The origin is located at the site of the reference atom. An arbitrary atom i in the l th-nearest-neighbor layer is assumed to have the coordinates (x_i, y_i, ld) at equilibrium, where d is the distance between the nearest layers.

The distance between the reference atom and the atom i is

$$r_i^2 = (x_i + u)^2 + (y_i + v)^2 + (ld + w)^2. \quad (\text{B1})$$

Thus, the following relations hold:

$$\frac{\partial}{\partial u} \frac{1}{r_i^n} = -n \frac{x_i + u}{r_i^{n+2}}, \quad (\text{B2})$$

$$\frac{\partial}{\partial w} \frac{1}{r_i^n} = -n \frac{ld + w}{r_i^{n+2}}, \quad (\text{B3})$$

$$\frac{\partial^2}{\partial u^2} \frac{1}{r_i^n} = n \frac{(n+2)(x_i + u)^2 - r_i^2}{r_i^{n+4}}, \quad (\text{B4})$$

$$\frac{\partial^2}{\partial w^2} \frac{1}{r_i^n} = n \frac{(n+2)(ld + w)^2 - r_i^2}{r_i^{n+4}}. \quad (\text{B5})$$

According to the hexagonal symmetry, the sum of Eq. (B2) vanishes at equilibrium. The sum of the factor x_i^2/r_i^{n+4} can be replaced by that of $\frac{1}{2}(x_i^2 + y_i^2)/r_i^{n+4}$.

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