

Elastic properties and the mechanical stability of icosahedral boron crystals

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The elastic constants of the icosahedral boron crystals have been studied by the formulation of Born and Huang. First of all, a technique of symmetry decomposition has been developed for general crystals possessing molecular units in order to see the relaxation mechanism by the internal shift. It is proven that if a librational mode is Raman active, which is often the case, the mode is able to relax the external strain considerably. For α boron, when only central forces are assumed, the c_{44} component completely vanishes. A shear strain ε_4 induces rotations of icosahedra, which cancel the shear strain completely. This gives a qualitative account for why this crystal is metastable. The rotations of icosahedra frequently happen in order to relax other types of strain too. This rotation-induced relaxation mechanism is looked upon as a special example of the above general property. The cancellation for ε_4 would remain in boron carbide, if only central forces are assumed, even though additional elements are introduced in the unit cell. In this case, the stability of the crystal has been ascribed to large noncentral forces, which emerge from the covalent bonds of the linear chain in the unit cell. Another way of stabilizing the crystal structure of α boron is suggested: the surface contact of icosahedra, which is realized in the crystal of β boron. In this family of crystals, the only direction in which a rotational motion is not induced is the z direction. The deformity of the icosahedron, instead, leads to an unexpected effect on the elasticity of boron carbide. The crystal is shown to be less stiff in the c axis than in the ab plane, despite the strongest interatomic forces being oriented parallel to the c axis. The rhombohedral site slightly deviates from the lattice vector, and this geometry gives rise to a great relaxation in the compression along the c axis. [S0163-1829(97)04518-9]

I. INTRODUCTION

The crystal structures of boron crystals have icosahedra B_{12} as the common building block, and have several polymorphic modifications. Among them, α -rhombohedral boron is the simplest one, while metastable. This crystal structure can be stabilized by introducing impurity atoms, the way of which is embodied in the crystals of boron carbides ($B_{13}C_2$). Another way of stabilization is to form a larger icosahedral unit (a B_{12} unit enclosed with a large B_{60} shell), which is embodied in the crystal of a β -rhombohedral boron.¹ These have the rhombohedral Bravais lattices with the same space group D_{3d}^5 symmetry. Some crystal structures of this family are depicted in Fig. 1,^{2,3} along with the names of the bonds. Note that the atom site 1, which is called the rhombohedral site, slightly deviates from the lattice vector [Fig. 1(c)]. This deviation is, while slight, an inevitable requirement for the mechanical stability of this family, which will be seen later.

The stability of boron modifications has been understood in terms of the chemical bonding requirement.^{1,4,5} The property of being electron deficient is the chief motivation by which boron crystals find their way to stabilize the structures. So far, this viewpoint has been so accepted that the other viewpoints might be overlooked. The mechanical stability provides a useful insight into the stability of crystals, and thus is also important. In this paper, the elastic constants of α -boron modifications have been calculated, and the stability of the crystal structures is discussed on this basis. We will see that rotational motions of icosahedra relax external strains a great deal. Considering the importance of this mechanism of rotation-induced relaxation, we will begin our

discussion with a general formalism of the internal relaxation for an external strain for those crystals which possess molecular units in the crystal structure. Fullerenes are promising crystals for the application of this theory.

The mechanical stability of crystal structures has been thoroughly studied by Born and Huang.⁶ The following is a brief summary of the important results of their study. The elastic constants $c_{\rho\sigma}$ are customarily represented in a matrix form of 6×6 dimensions. The mechanical stability of a crystal is expressed in the most general form: *theorem 1 (stability condition)*: the matrix $[c_{\rho\sigma}]$ is positive definite.

We should note that negative values are not prohibited for $c_{\rho\sigma}$. For cubic crystals, the stability condition has particularly simple forms,⁷

$$c_{44} > 0, \quad c_{11} > c_{12}, \quad \text{and} \quad c_{11} + 2c_{12} > 0. \quad (1)$$

If we take only nearest-neighbor forces into account and if these forces are central forces, the conclusion is then drawn that the simple-cubic (sc) structure is unstable. This is because c_{12} depends only on the next-nearest-neighbor or further-distant forces, so that it would vanish if only nearest-neighbor central forces are assumed. In reality, there are many forces beyond the nearest-neighbor distance. However, the nearest-neighbor forces are by far stronger than any other, so that the above simple conclusion is qualitatively valid.

A way to avoid this instability is to form the fcc structure, where all the conditions (1) are met by assuming only central forces of the nearest neighbors. This example indicates the first category for crystals to stabilize their structures: (*category 1*) the stability condition is satisfied even when only

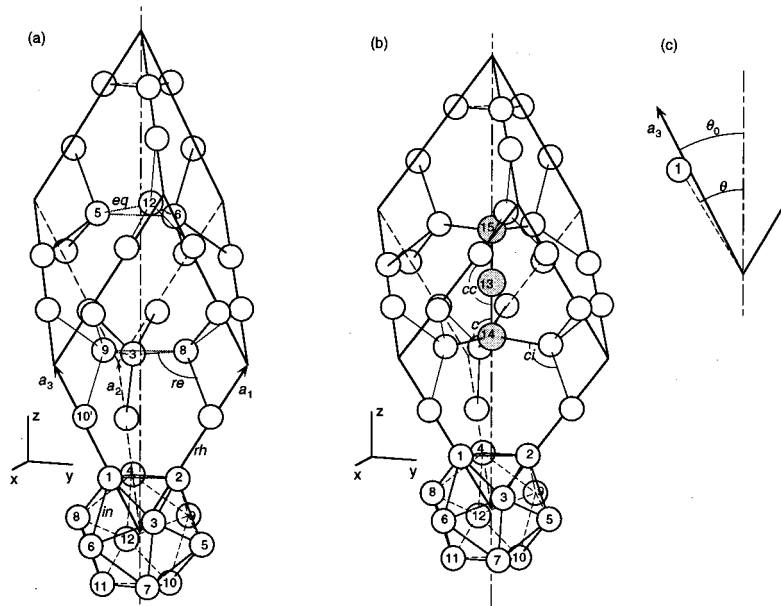


FIG. 1. The crystal structures of (a) α -rhombohedral boron, and (b) boron carbide ($B_{13}C_2$). The site which is symmetry equivalent to atom 1 is customarily called the rhombohedral site, and the site symmetry equivalent to atom 3 is called the equatorial site. The abbreviations of the types of bond are indicated. The equatorial bonds in α boron are replaced with the covalent bonds of the linear chain C-B-C in boron carbide. The rhombohedral site is slightly deviated from the lattice vector (c). The polar angles θ and θ_0 are defined about the center of an icosahedron (inversion center). For α boron $\theta > \theta_0$, but reversed in boron carbide.

central forces of the nearest neighbors are assumed. In the bcc structure, the second condition of Eq. (1) does not hold. However, the distance of the next-nearest neighbors is close to that of the nearest neighbors, so that this crystal structure is more stable than sc.

For the diamond crystals, the crystal structure would be unstable in view of the criterion (I). The c_{44} component becomes zero when only the nearest-neighbor central forces are used, because the c_{44} is given by

$$c_{44} = \text{const } f_r f_a / (f_r + f_a), \quad (2)$$

where f_r and f_a are the bond-stretching and the angle-bending forces, respectively.⁸ Of course, the diamond structure is stable. In this case, we should not ignore the contribution of the noncentral force f_a . By the nature of the covalent bond, the noncentral force is relatively large in diamond crystals, in contrast with ionic crystals.⁹ This example gives the second category for crystals to stabilize their structures: (*category II*) noncentral forces are strong enough for the stability condition to hold. These criteria are simple, but are applicable for a surprisingly wide range of crystals. In the following, we will see that these criteria are useful also for boron crystals.

A closely related criterion is given by the constraint theory.¹⁰ The zero-frequency vibrations other than rigid translational and rotational motions are called *floppy modes*. They have a special consequence for the elastic properties.

Theorem II: The existence of floppy modes implies no restoring force for a deformation in some direction, so that the component of the elastic constant in that direction vanishes.

A good example is provided by a two-dimensional square lattice. The converse is not necessarily correct; that is, even

when a crystal does not have any floppy mode, we cannot exclude the possibility that no restoring force is exerted in a particular direction of strain.

Bearing these theorems in mind, we proceed to a discussion on a special property of rotational motions which plays in the elasticity. Interesting properties of rotational motions in elastic continua used to be discussed in connection with the strain gradient theories.¹¹ Unfortunately, these effects are only microscopic or second-order effects, so that experimental observation is difficult. In contrast, the present effect is macroscopic, and is easily observed.

II. THEORY OF THE INTERNAL RELAXATION FOR AN EXTERNAL STRAIN

The elastic constants can be calculated by the force constants in problems of lattice vibrations. A general formulation has been established by Born and Huang.⁶ Here, we follow them, but use a slightly different version of the theory as given by Lax,^{12,13} because it has a convenient form for discussing the symmetry properties. The effect of the long-range Coulomb force is disregarded from the present argument.

The elastic constants $c_{\mu\alpha, \nu\beta}$ are given by

$$c_{\mu\alpha, \nu\beta} = [\mu\nu, \alpha\beta] + [\alpha\nu, \mu\beta] - [\alpha\mu, \nu\beta] + (\mu\alpha, \nu\beta) \quad (3)$$

according to the notations of Born and Huang. The first three terms on the right-hand side represent the contribution of the homogeneous external deformation. The last term represents the contribution of the internal shift, that is, relative displacements of the atoms in the primitive unit cell (optic modes). Throughout this paper, $\alpha, \beta, \mu,$ and ν refer to the Cartesian coordinates, while ρ and σ are used for the Voigt notation,

which runs from 1 to 6. The indices l and κ refer to the lattice site and the atom site in the unit cell ($\kappa=1,\dots,s$), respectively. The calculation of the external part is rather straightforward:

$$[\mu\nu, \alpha\beta] = -\frac{1}{2} \frac{1}{\Omega_0} \sum_{\kappa\kappa'l'} K_{\mu\nu}^{l\kappa l'\kappa'} (X^{l\kappa} - X^{l'\kappa'})_{\alpha} \times (X^{l\kappa} - X^{l'\kappa'})_{\beta}, \quad (4)$$

where Ω_0 is the volume of the primitive unit cell, and $K_{\mu\nu}^{l\kappa l'\kappa'}$ are the force constants between atoms $l\kappa$ and $l'\kappa'$, whose equilibrium positions are expressed by X . The internal shift is induced in order to relax the external deformation, and hence the contribution to the elastic energy must be negative. For special classes of crystals, however, the internal shift does not occur. A general criterion as to whether the internal shift is induced or not, and if induced, which type of optic mode is induced, is determined by a selection rule, to which we proceed with our argument.

The internal shift u_{μ}^{κ} induced by an external strain $u_{\mu\alpha}$ is given by

$$u_{\mu}^{\kappa} = - \begin{bmatrix} \kappa & \kappa' \\ \mu & \nu' \end{bmatrix}^{-1} \begin{bmatrix} \kappa' \\ \nu' & \nu & \beta \end{bmatrix} u_{\nu\beta}, \quad (5)$$

and, correspondingly, the part of the internal shift in $c_{\mu\alpha, \nu\beta}$ is given by

$$(\mu\alpha, \nu\beta) = - \begin{bmatrix} \kappa & \mu & \alpha \\ \mu' & \mu & \alpha \end{bmatrix} \begin{bmatrix} \kappa & \kappa' \\ \mu' & \nu' \end{bmatrix}^{-1} \begin{bmatrix} \kappa' \\ \nu' & \nu & \beta \end{bmatrix}. \quad (6)$$

The minus sign indicates a negative contribution. The matrices in these equations are defined by

$$\begin{bmatrix} \kappa & \kappa' \\ \mu & \nu' \end{bmatrix} = \frac{1}{\Omega_0} \sum_{l'} K_{\mu\nu}^{l\kappa l'\kappa'}, \quad (7)$$

$$\begin{bmatrix} \kappa & \mu & \alpha \\ \mu & \nu & \beta \end{bmatrix} = \frac{1}{\Omega_0} \sum_{l'\kappa'} K_{\mu\nu}^{l\kappa l'\kappa'} X_{\beta}^{l'\kappa'}.$$

By transforming the displacement vectors u_{μ}^{κ} to the symmetry vectors u_a^r , we have alternative expressions for Eqs. (5) and (6),

$$u_a^r = - \begin{bmatrix} r & r \\ a & a' \end{bmatrix}^{-1} \begin{bmatrix} r \\ a' & \nu & \beta \end{bmatrix} u_{\nu\beta} \quad (8)$$

and

$$(\mu\alpha, \nu\beta) = - \begin{bmatrix} r & \mu & \alpha \\ a & \mu & \alpha \end{bmatrix} \begin{bmatrix} r & r \\ a & a' \end{bmatrix}^{-1} \begin{bmatrix} r \\ a' & \nu & \beta \end{bmatrix}. \quad (9)$$

Here, r denotes the label of the irreducible representation, and a denotes the index of a different set belonging to the same irreducible representation.

The coefficients $[{}^r_a \mu \alpha]$ tell us the selection rule for which type ra of the optic mode couples to an external deformation $u_{\mu\alpha}$. The pair of indices $\mu\alpha$ is transformed as is the symmetrized product of the Cartesian coordinates, $(\Gamma_p \times \Gamma_p)_s$. Hence, only those symmetry vectors which are transformed as $(\Gamma_p \times \Gamma_p)_s$ can be coupled to the external strain. In other

words, *theorem III*: only symmetric Raman-active modes can be induced as the internal shift by external strains.

As an example, NaCl-type crystals have no Raman-active mode, so that no internal shift is induced. This fact is known as the statement that there is no contribution by the internal shift to the elastic constants, if the crystal has an inversion center and if every atom is located in the center.¹⁴ Furthermore, by investigating the decomposition of the individual product $\mu\alpha$ to the irreducible representations, we can easily find selection rules for which type of Raman mode ra can be coupled to the particular $u_{\mu\alpha}$.

In view of Eq. (8), first a specific type of optic mode ra is discriminated by $[{}^r_a \mu \alpha]$ for a given deformation $u_{\mu\alpha}$. The magnitude of the contribution is then determined by the inverse of $[{}^r_a \nu \beta]$. The matrix $[{}^r_a \nu \beta]$ gives the dynamic matrix for the zone-center modes, on weighting with masses. Roughly speaking, the ra component of this inverse matrix is given by the inverse of the square of eigenfrequency of that mode. Therefore, the lowest-frequency mode dominates the magnitude of the relaxation. From this follows the general property that *corollary I*: Raman-active librational modes, if they exist, are able to greatly reduce the strain energy. Librational modes are based on rotations of molecular units. The symmetry of rotation is represented by the antisymmetrized product of the Cartesian coordinates, $(\Gamma_p \times \Gamma_p)_a$, which are frequently consonant with the symmetry of Raman activity, $(\Gamma_p \times \Gamma_p)_s$. The contribution of the librational mode with the frequency ω_l depends on inversely ω_l^2 . Since the frequency of the librational mode is dominated by noncentral forces, the effect of corollary I drastically appears as the noncentral forces are decreased. In the same line of proof, we can reach theorem II, which states the relaxation mechanism in terms of floppy modes.

Besides the selection rule, another advantage of the symmetry decomposition is nonsingularity of the dynamic matrix in the form $[{}^r_a \nu \beta]$. A rather annoying problem when evaluating Eq. (6) is that the original matrix $[{}^{\kappa}_{\mu} \nu']$ is singular, owing to the acoustic modes, and hence the inverse does not exist. Because only the symmetry blocks possessing Raman activity is involved in Eq. (9), the selected blocks have already been nonsingular.

III. CALCULATIONS OF α -BORON MODIFICATIONS

Rhombohedral crystals of the α -boron modifications have the point symmetry D_{3d} . There are six independent components of the elastic constants, say, c_{11} , c_{33} , c_{44} , c_{12} , c_{13} , and c_{14} .¹⁵ According to the stability condition, we can obtain the interrelationships between $c_{\rho\sigma}$. Out of the six relationships, $c_{44} > 0$, $c_{33} > 0$, and $c_{11} > c_{12}$, have simple forms. The remaining relationships have relatively complicated forms. Instead of using these inequalities, it is easier to use an alternative form of the stability condition, in which all the eigenvalues of the matrix $[c_{\rho\sigma}]$ must be positive. This form is used in the following calculations.

In order to discuss the selection rule, we should explicitly give the coordinates of the system and the representations. The crystal axes are taken in such a way that a C_2 axis is

TABLE I. The elastic constants of α -rhombohedral boron in units of GPa. Results of different models are compared; (I) only central forces are used; (II) and (III) noncentral forces are added. These parameters are listed in the last row. In (I), the contribution of the external deformation alone and the result of including the internal shift are separately shown. The c_{44} component is compared with the average of the diagonal components c_d . The frequency of the E_g librational mode ω_l is also tabulated. The stability has been judged by the positive-definite property of the elastic matrix. The experimental data are the elastic constants of β boron, not α boron.

	Calculation			Experiment ^a	
	(I) (ext)	(II) (+int)	(III)		
C_{11}	389.5	302.2	314.5	323.9	467
C_{33}	455.1	309.4	327.4	333.7	473
C_{44}	123.1	0.0	0.0	33.4	198
C_{12}	129.8	137.1	130.1	122.4	241
C_{13}	123.1	166.4	160.8	158.6	?
C_{14}	-9.2	0.0	0.0	-5.8	15.1
C_{44}/C_d (%)		0	0	10	42
ω_l (cm ⁻¹)		28	30	163	
Stability		No	No	○	
Force constants	$f_r^{\text{in}}=1.3$ $f_r^{\text{th}}=3.0$		(I)+ (II)+		
f_r (mdyn/Å)	$f_r^{\text{ca}}=1.0$		$f_a^{\text{in}}=0.15$	$f_a^{\text{re}}=0.04$	
f_a (mdyn Å)					

^aExperiment data: for β -rhombohedral boron, I. M. Silvestrova, L. M. Belayev, Y. V. Pisarevski, and T. Niemyski, Mater. Res. Bull. **9**, 1101 (1974).

parallel to the x axis, and the y axis is in a plane of a mirror. The basis set for E_g is so arranged that the first and second partners are transformed as (xz, yz) .

A. α boron

First, let us examine the preceding theory for the simplest boron modification, α boron. The lattice vibrations of this crystal are well understood by the studies using the valence-force model¹⁶ and the shell model.¹⁷ In the present paper, the valence-force model is used because of its clear physical meaning. Two types of forces, the bond-stretching forces f_r and the angle-bending forces f_a , are assumed, but more general terminologies, the central and noncentral forces, respectively, are sometimes used. The superscripts of the force constants refer to the types of bond or angle (see Fig. 1 for the abbreviations).

The results of the calculation are listed in Table I. When only central forces are used, the results are presented separately in column (I), the case in which only the contribution of the external deformation is considered, and the case in which the contribution of the internal shift is taken into account. Then, noncentral forces are subsequently added in columns (II) and (III). The frequency of the E_g librational mode ω_l is a measure of the contribution of the librational mode to the internal relaxation, and is included with this utility.

A notable result is that some components, say c_{44} , vanish when only central forces are used. The effect of the internal

TABLE II. The selection rules in the matrix $[r_{\nu\beta}]$ for D_{3d} . For E_g , the label of the partner is followed. For the coordinates of the system and the representation, see the text.

$\nu\beta$	Allowed r
1	$A_{1g} + E_g 2$
2	$A_{1g} + E_g 2$
3	A_{1g}
4	$E_g 2$
5	$E_g 1$
6	$E_g 1$

shift completely cancels the contribution of the homogeneous external deformation. This result is an unexpected one from the viewpoint of the constraint theory. In the Appendix, we will show that there is no floppy mode in a network which is topologically equivalent to the crystal structure of α boron. There are so many constraints for the bonding in this crystal structure that it is unlikely that the strain ε_4 ($\equiv u_{23} \equiv \partial u_y / \partial z$) does not change any bond length. The component c_{44} becomes nonzero only after the angle-bending forces between the adjacent icosahedra are included, as shown in column (III) of Table I. The angle-bending force within the icosahedron is not enough. There is no symmetry reason for canceling the external contribution. In this sense, the cancellation is just accidental. For the case in which the Cauchy relations hold, extra symmetry properties appear in the elastic constants.^{6,18} But, this is not the case here.

Let us investigate what happens with a vanishing component, say, c_{44} , when only central forces are used. The c_{44} component is the elastic response for the shear strain ε_4 . The induced optic modes are determined by the selection rule about the coefficient $[r_{a\mu\alpha}]$. The selection rules for D_{3d} symmetry are summarized in Table II. For the strain ε_4 , only $E_g 2$ -type optic modes are excited. In α boron, there are six E_g modes. The induced internal shifts u_μ^K are expressed by a linear combination of these allowed modes.

The induced internal shift by the strain ε_4 is found to be a perfect rotation of an icosahedron. It should be noted that the librational mode is close to a perfect rotation about the x axis, but is slightly different. A linear combination of six E_g modes plus the external deformation completes a perfect rotation of the icosahedron. Obviously, a perfect rotation of an icosahedron causes no strain on intricosahedral bonds. But, it is amazing that it is also true for intericosahedral bonds. A detailed analysis shows that this special situation actually happens. Let us see this situation by taking a rhombohedral bond as an example. The polar angle θ is slightly larger than θ_0 in α boron (Fig. 1), and thereby the angle θ' formed by the bond 1-10' and the c axis is smaller than θ_0 (Fig. 2). Free rotations of the two icosahedra induce a change in the length of the bond 1-10', i.e., a slight expansion. However, for the net displacement of atom 10' relative to atom 1, we should add the contribution u_{ext} of the external strain ε_4 . As shown in Fig. 2, the rotation by an angle ω is induced in such a way that a contraction of the bond 1-10' by the shear strain is canceled by an expansion caused by the rotation, from which ω is determined as

$$2\omega \cdot (\mathbf{a}_3 \times \mathbf{X}^1) = u_{yz} a_{3z} (2\mathbf{X}^1 - \mathbf{a}_3)_y. \quad (10)$$

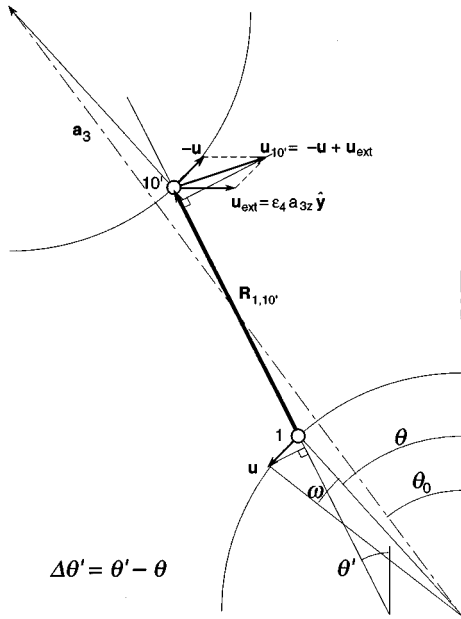


FIG. 2. When a shear strain ϵ_4 is applied, this figure shows how the bond 1-10' is changed. A contraction of the bond due to the external contribution u_{ext} is canceled by an expansion caused by the rotations of two icosahedra.

Note that for the case in which atom 1 is on the lattice vector a_3 , this rotation never occurs, since $\omega=0$ according to Eq. (14). For equatorial bonds, it is easier to show that the bond length is invariant, because there is no external contribution in this direction.

Judging from the category (I), the crystal of α boron must be unstable, which is consistent with experimental fact. The accidental cancellation for c_{44} is removed by introducing angle-bending forces, as shown in (III) in Table I. The parameters used here are basically the same as those given by Beckel *et al.*,¹⁶ except for f_a^{re} . In the present study, for f_a^{re} , five angles are taken into account about an equatorial atom, while the two angles of 143° are taken into account in the Beckel calculation. These values presently have the best agreement with experimental spectra. Even taking angle-bending forces into account, the c_{44} component is still small, namely, 10% of the main diagonal component c_d , which is defined by $(2c_{11} + c_{33})/3$. Therefore, the above conclusion is qualitatively correct.

Unfortunately, there are no experimental data for elastic constants of α boron. Situations are similar for other α modifications. As far as the author is aware, there is only one experimental report on the elastic constant of β boron, although not complete.¹⁹ The data are listed in the last column of Table I. Before obtaining the present result, the author simply predicted that the values were similar between α and β boron, because of similarity in the crystal structures. Thus, the original intention for citing the data of β boron was a better comparison between the calculation and experiment in a poor experimental situation. But, the purpose has now been changed to show the difference between these two crystals. The c_{44} component relative to the main-diagonal components is larger in β boron, namely 40%, than in the calculation of α boron. The largeness of c_{44} seems to contribute to the stability of β boron.

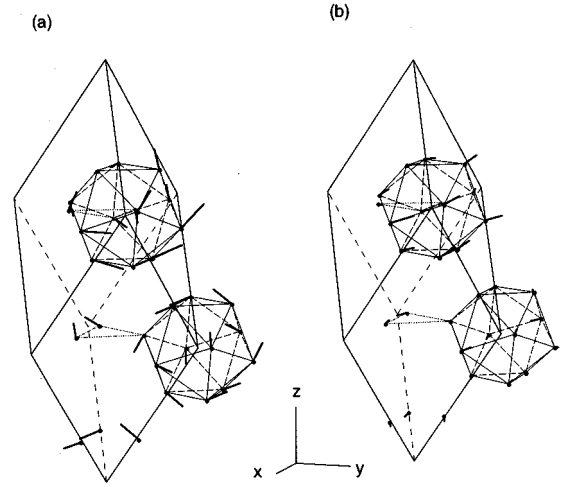


FIG. 3. The relaxation in α boron for the compression in the x direction, ϵ_1 , for the case of central forces only (a), and for the case of angle-bending forces included (b). The used parameters are those of (I) and (III), respectively, in Table I. The external displacements are shown relatively by taking the center of the main diagonal as the origin.

If we regard the icosahedron as a rigid sphere, the crystal of α boron is topologically the same as the sc structure. As mentioned in Introduction, the sc structure is unstable in that no restoring force is exerted for a shear strain, i.e., $c_{44}=0$. Accordingly, the instability of α boron is reasonable. The only unexpected result in α boron is that the strain of any intericosahedral bond is completely relaxed by free rotations of the icosahedra.

As for the other components $c_{\rho\sigma}$, the internal shift also contributes to the relaxation, although not as seriously as for c_{44} , as shown in Table I. For example, the effect of the internal shift on c_{11} is shown in Fig. 3. For the case of central forces only, we can see that nearly perfect rotations of icosahedra occur [Fig. 3(a)]. From the selection rule in Table II, coupling to rotations takes place for all the components except c_{33} . Further examples are given in another publication,²⁰ where one can see that even a small variation in the structure or in forces causes a drastic change of the rotations in both the magnitude and orientation. Indeed, the mechanism of the rotation-induced relaxation would be a ubiquitous response appearing in those crystals which have librational modes, if only central forces are exerted on the atoms. A prominent effect of this rotation-induced relaxation may be free rotations of icosahedra in fullerenes at high temperatures. In this connection, the fact that both high- and low-temperature phases of a crystal C_{60} have a point group T_h is not accidental. In cubic symmetry, only T and T_h are point groups in which rotational motions have Raman activity.

At the same time, in Fig. 3(b), we can see that even small angle-bending forces have the apparent effect of suppressing the rotational motions. Table I shows that as angle-bending forces are added, the frequency of the librational mode is quickly increased. This prevents the librational mode from participating in the relaxation mechanism, as expected in the theory of Sec. II. An important implication to fullerenes lies at this point. It is not very appropriate to say that weakness

of the intermolecular force (van der Waals force) itself is the cause for free rotations of icosahedra. Weakness in the non-central character of the force is responsible for this. Actually, the present case of boron is opposite to the molecular crystals, that is, the intermolecular forces are stronger than the intramolecular forces. In spite of this, we have seen that rotations are easily induced if only central forces are assumed.

In the analogy with the other crystal cases mentioned in the Introduction, the crystal of α boron can be stabilized by introducing further elements in the crystal structure. Boron carbide and β boron are the examples. In the following sections, we will see details as to how the crystal structure is stabilized, through evaluation of the elastic constants.

B. Boron carbide

The vibrations of boron carbide ($B_{13}C_2$) have lately been calculated.²¹ We now know a set of appropriate force constants, and these values are used in this study. For $B_{13}C_2$, some difficulties in the interpretation of experimental data are involved, as described in Ref. 21, so that careful analysis is needed. The reader is referred to Ref. 21 in order to know the meaning of the values of the force constants in this crystal, in particular, the angle-bending forces.

We notice that the linear-chain force f_r^c is much larger than any other forces. The next strongest one is the rhombohedral force f_r^{rh} , while the chain-icosahedral force f_r^{ci} is a little smaller than f_r^{rh} . The intraicosahedral force f_r^{in} is the smallest of the nearest-neighbor central forces. Let us first compute the elastic constants by the central forces only. The balance of forces is schematically shown in Fig. 4, compared with the situation for α boron.

In this figure, we can see that the strongest two types of bonds are along or almost along the crystal c axis, while the other weak bonds are nearly perpendicular to the c axis. From this observation, we could expect that the crystal is more stiff in the z direction than in the x - y plane, that is, $c_{33} > c_{11}$. The calculated result is opposite to this intuition. The result is listed in column (I) in Table III. In the case of the external contribution alone, the inequality $c_{33} > c_{11}$ holds, as expected. Once the contribution of the internal relaxation occurs for c_{33} , resulting in $c_{33} < c_{11}$. Lee *et al.* showed this apparent decrease in c_{33} by the first-principles calculation.²² In α boron, c_{33} is slightly larger than c_{11} , as expected from the balance of forces [Fig. 4(a)]. In order to see what happens with boron carbide, we again check which types of internal shift are induced.

An analysis similar to the α -boron case shows that the deformation of icosahedra greatly reduces the strain energy in the z direction. Let us consider the situation for c_{33} . Suppose the crystal is subject to a compression in the z direction. In the α -boron case, the internal shift is induced in such a way that the icosahedra are compressed in the z direction and are elongated in the x - y plane, as shown in Fig. 4(c). The restoring forces which act on the icosahedron in the x - y plane are weak, because only f_r^{ci} are such forces, and these are much weaker than f_r^{rh} . In the $B_{13}C_2$ case, on the other hand, the situation is different. Since f_r^c is much stronger than any others, a way to keep the bond length of the chain invariant is energetically most favorable.

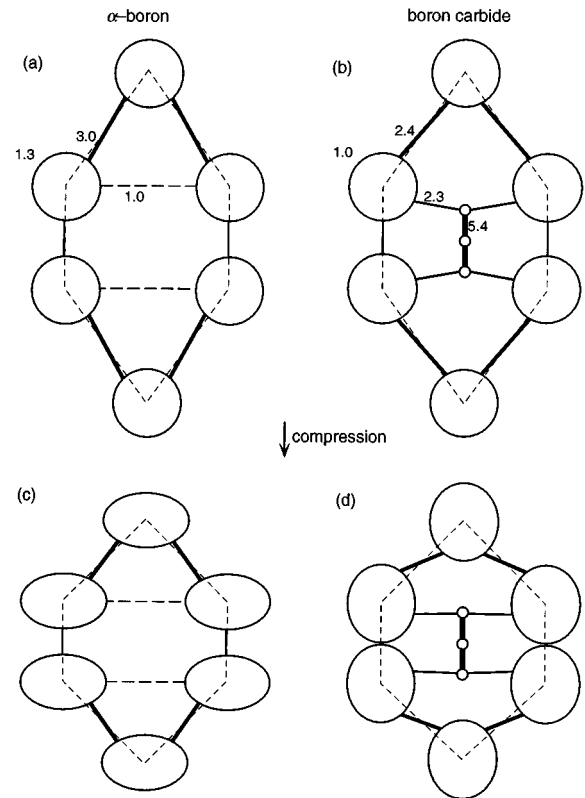


FIG. 4. Schematic comparison of the relaxation for the compression in the z direction, ϵ_3 , between α boron and boron carbide. The icosahedra are represented by the spheres. (a) and (b) show the equilibrium positions, and (c) and (d) show the positions after compression. The force constants for the stretching forces are indicated in (a) and (b). Note that the deformation is exaggerated for illustration.

Then, let us fix the bond lengths in the chain, and consider what are going on with the other bonds. Since f_r^{rh} is the next-strongest force, a way in which the bond lengths of rhombohedral bonds remain unchanged as far as possible is energetically favorable. We should note that, in the equilibrium positions, the relationships between the polar angles θ' and θ_0 are opposite between $B_{13}C_2$ and α boron; $\Delta\theta' \equiv \theta' - \theta_0 > 0$ for $B_{13}C_2$ and $\Delta\theta' < 0$ for α boron. For a compression in the z direction, in the α -boron case, a further negative decrease in $\Delta\theta'$ is desirable for the strain energy in the rhombohedral bond, because much energy loss due to a compression of the rhombohedral bond is saved in this direction. But, the direction of this deformation is opposite to the external compression in the z direction. A relaxation in this way is, therefore, not effective [Fig. 4(c)]. In the $B_{13}C_2$ case, on the other hand, it is easier to increase in $\Delta\theta'$, the compression of the rhombohedral bond is greatly saved, and this deformation is consonant with the external compression in the z direction [Fig. 4(d)]. That is why c_{33} is greatly reduced for $B_{13}C_2$.

It is a surprising matter that the icosahedra are rather elongated in the z direction under the compression of this direction. An essential point is that a deformity of the icosahedra, i.e., weak forces of intraicosahedral bonds, completely spoils stronger forces in the z direction, which would otherwise lead to the stiffness in this direction.

TABLE III. The elastic constants of boron carbide in units of GPa. The arrangement and the notations are the same as in Table I.

	Calculation			
	I (ext)	(+ int)	II	III
C_{11}	300.2	182.0	190.1	235.6
C_{33}	341.8	81.3	87.9	113.7
C_{44}	86.8	0.0	27.2	44.4
C_{12}	100.1	182.0	176.6	132.6
C_{13}	86.8	141.9	138.9	133.6
C_{14}	4.6	0.0	-10.3	-4.7
C_{44}/C_d (%)		0	17	23
ω_l (cm^{-1})		14	120	171
Stability		No	No	○
Force constants	$f_r^{\text{in}}=1.0$ $f_r^{\text{th}}=2.4$		(I)+ $f_a^{\text{th}}=0.02$	(II)+ $f_a^{\text{in}}=-0.1$
f_r (mdyn/Å)	$f_r^c=5.4$			$f_a^c=0.3$
f_a (mdyn Å)	$f_r^{\text{ci}}=2.3$			$f_a^{\text{ci}}=0.05$ $f_a^{\text{cc}}=0.5$

For a compression in the x - y plane, a similar situation must happen, but the situation about the polar angle must be reversed from the case of the compression in the z direction. Hence, the relaxation of α boron for the x direction could be greater than that of B_{13}C_2 , if other conditions are not changed. However, the polar angles are relatively close to $\pi/2$ in this case: in other words, the bond has already been almost fully stretched, so that the effect of the relaxation is not appreciable in both α boron and B_{13}C_2 . In this way, we can see that a slight deviation of the angle θ from θ_0 leads to a great consequence on c_{11} and c_{33} .

Let us check the stability of the crystal. As shown in Table III the c_{44} component is still zero when only central forces are used. In addition to free rotations of icosahedra, a free rotation of the linear chain is induced in order for any chain-related bonds to be left invariant. It would be concluded, on the basis of category (I), that the B_{13}C_2 crystal is unstable. Insertion of a linear chain does not help the mechanical stability, if only central forces are considered.

Next, let us introduce angle-bending forces and check the stability. The results are listed in the remaining columns of Table III. As expected, the stability is recovered by introducing angle-bending forces. However, one thing to note is that only a small value of f_a^{th} is not enough to stabilize the crystal, even though it makes c_{44} nonzero; the elastic matrix $[c_{\rho\sigma}]$ is not yet positive definite. A relatively strong, angle-bending force f_a^c is necessary for stability. The set of parameters in the last column is presently the best fit to the experimental spectra. The force f_a^c is formed in the angles with a carbon atom as the apex atom. The associated bonds are similar to the usual covalent bonding based on the sp^3 bond. Hence, it is reasonable that the f_a^c is large.

The ratio c_{44} to the average diagonal component c_d increases by more than 20%. We can say that the stability of the B_{13}C_2 crystal falls in category (II). The angle-bending forces are the primary cause of the resistance to shear strains. Experimentally, only averaged quantities like Young's

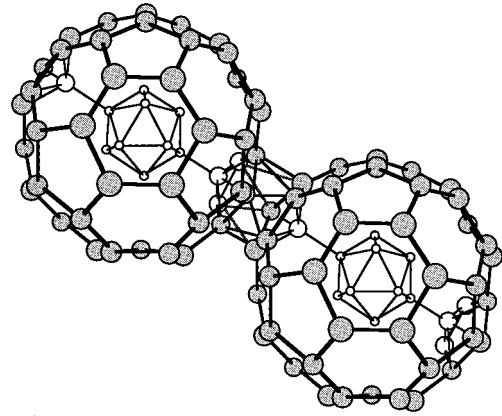


FIG. 5. The type of intericosahedral bonding of β -rhombohedral boron. Two adjacent B_{84} units contact each other by a face, where ten intermolecular bonds are formed. In the B_{84} unit, many internal bonds are omitted to avoid unnecessary complication.

modulus E have been measured for boron carbide.²³ Young's modulus E has dependence on the direction in which the measurement is done. The explicit formula is given in Ref. 7 (p. 145). The measured value in Ref. 23 must be the orientational average of E . But, this way of comparison to experiment is no more than a simple order estimation by $E \approx c_{11}$, by which estimation agreement is obvious at the outset.

C. β boron

Because of the very complicated crystal structure of β boron, e.g., the unit cell contains 105 atoms, no calculation was made for this crystal. Instead, an implication for β boron which can be drawn from the foregoing arguments will be given.

In β boron, the primary building block is a B_{84} unit, which is looked upon as a double-layered icosahedron.^{24,25} This B_{84} unit is located at each vertex of the rhombohedral lattice, instead of the B_{12} unit in α boron. A further structural unit, like a linear chain in B_{13}C_2 , is located in the main diagonal in the primitive unit cell, but we can disregard the effect of this extra unit from the present argument. In α boron, two adjacent icosahedra are connected by only one bond. In this sense, the intericosahedral bonding is a *point contact*. In the point contact case, free rotations of icosahedra induce no restoring force, because the displacements are always perpendicular to the intericosahedral bonds. For β boron, the double-layered icosahedra contact each other by face, namely, *face contact*, as shown in Fig. 5. In this situation, any rotation of the double-layered icosahedra necessarily changes in the lengths of the intericosahedral bonds more or less. Hence, net restoring forces for a shear strain are exerted by the central forces, which are much stronger than any noncentral force. As a consequence, we expect that the c_{44} component does not vanish even when only central forces are used, and that the value is larger than that of B_{13}C_2 . Therefore, the stability of β boron falls in category (I).

IV. CONCLUSIONS

Our argument first shows the selection rule that only Raman-active modes are induced for external strains. Gen-

eral properties of the relaxation mechanism for external strains have then been proven for those crystals which have molecular units in the unit cell. The relaxation is dominated by the lowest-frequency mode. It often happens that the librational mode of such a crystal is Raman active. Then, the relaxation is predominantly caused by that mode. As an immediate consequence, this effect drastically appears, if non-central forces are ignored.

The present study on the elastic properties of the α -boron modifications well illustrates this general theory. As to the specific properties of the α -boron modifications, the following conclusions have been deduced, although no direct comparison between the calculation and experiment is possible at the present time.

In the case in which each icosahedron contacts the adjacent icosahedra by point contacts, free rotations of icosahedra completely relax the shear strain energy accumulated in the intericosahedral bonds; an accidental cancellation between the external strain and the internal shift takes place. This leads to $c_{44}=0$. On the basis of category (I), we can conclude that the crystal structure of α boron is unstable.

The chance that this accidental cancellation takes place will be reduced when the crystal structure has additional elements in the unit cell. In the $B_{13}C_2$ case, insertion of the linear chain, however, does not eliminate the accidental cancellation. Instead, in this case, highly oriented covalent bonds formed around the carbon atoms provide strong angle-bending forces, which make the crystal structure stable in a way similar to diamond crystals. In the case of β boron, the icosahedral unit is quite enlarged, and this enlarged icosahedron is bonded to the adjacent units by face contacts, which prevents the accidental cancellation even when only central forces are used. This leads to the conclusion that β boron is quite stable.

For the above argument, it was a good description to approximate the icosahedral unit by a rigid sphere. For the elastic components which are not coupled to librational modes, the deformity of the icosahedron plays an important role in the internal relaxation. In the $B_{13}C_2$ case, most of the

strong bonds lie in the crystal c axis, which must make c_{33} larger than c_{11} . There is, however, a flaw in the stiffness in the z direction. The icosahedron in boron crystals is rather flexible. This relaxes considerably the strain energy caused by compression in the z direction. A special geometry of the crystal $B_{13}C_2$, i.e., the initial orientation of the rhombohedral bond relative to the lattice vector, is quite favorable for this relaxation. In this respect, a slight deviation of the rhombohedral site from the lattice vector is an inevitable requirement for the mechanical stability of the α -boron modifications.

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APPENDIX

In this Appendix, we will show that the crystal structure of α boron is stable in view of the constraint theory, when central forces f_r^{in} , f_r^{rh} , and f_r^{eq} are considered. For an N -particle system, the number of floppy modes F is given by $F=3N-6-N_c/2$, where N_c is the number of constraints. A positive F means that the system is mechanically unstable.¹⁰ For an isolated icosahedral unit B_{12} , there are 12 atoms and 30 intraicosahedral bonds f_r^{in} , and accordingly the icosahedron is stable. Then, we can regard the icosahedron as a rigid sphere. The crystal structure of α boron is thus topologically regarded as the sc structure. The only difference is that the lattice point is replaced by the rigid rotor, so that the degrees of freedom of the lattice point (sphere) is six. For each icosahedron, there are 6 rhombohedral bonds f_r^{rh} and 12 equatorial bonds f_r^{eq} , resulting in 18 constraints N_c in all. The number of floppy modes $F=6N-N_c/2$ becomes negative, from which the above conclusion follows.

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