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Central and Noncentral Forces on the Lattice Dynamics of Boron-Rich Solids

The Bonding Nature of Icosahedral Boron Solids

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The distinct feature of the chemical bonding of boron solids is three-center or icosahedral bonding. The consequences of this peculiar bonding on the lattice dynamics are discussed in terms of the central and noncentral forces, while the recent development in this field is reviewed. The character of noncentral force is very small for the intraicosahedral bonding. Many features of the optical spectra of α-boron can be understood without the help of large noncentral forces of the intraicosahedral bond. The intericosahedral bonding is basically a covalent bond, but is less stable than the usual covalent bond based on the sp^3 hybridization. The balance between these forces has a significant role on the determination of the crystal structure of boron carbide. The icosahedral character further decreases in boron carbide. Roles of the noncentral forces become important for this crystal. A discussion of the mechanical stability provides a reasonable account for the following features of the α-boron modifications: the resistance for shear strains, the deviation of the rhombohedral site from the ideal lattice position, and the relaxation for a strain along the *c*-axis. A variety of boron modifications exhibit various types of distortions of icosahedra. Such distortions are not the cause of the different crystal modifications, but are the consequence of the external influences. © 1997 Academic Press

I. HISTORICAL VIEW OF CHEMICAL BONDING

From the chemical standpoint, the family of boranes is understood as an electron-deficient system (1). The bonding nature has been characterized by the so-called three-center bonding or multi-center bonding, an idea introduced by Longuet-Higgins in the 1940s. This idea has been extensively developed by Lipscomb for higher boranes. In the crystal case, the idea of three-center bonding was extended to icosahedral bonding, which was established again by Longuet-Higgins (2). In this paper, I review the development in the dynamical properties of boron-rich solids and show the consequences of this peculiar bonding on the lattice dynamics. The basic idea underlying the present argument is to interpret the strength and the orientational property of the chemical bonds in classical terms, namely *forces*.

After the fundamental study of Longuet-Higgins, further calculations on the electronic structures of solid boron had been performed only gradually (3, 4). In the past decade, many authors have joined this field, partly because of novel materials based on the icosahedron (5). A series of papers by Kleinman's group gives the most systematic and reliable band structures (6). Regarding chemical bonds, however, in my personal view, the qualitative understanding is basically the same as the original one by Longuet-Higgins, although a detailed description of the charge distribution given by Kleinman's group made some modifications to that. Longuet-Higgins showed that an icosahedral boron molecule is composed of 13 intraicosahedral bonding orbitals, 23 intraicosahedral antibonding orbitals, and 12 outward nonbonding orbitals. At the same time, he showed that an isolated icosahedral molecule is still unstable.

In the case of α-boron, the optimal bonding requirements are almost fulfilled, with a deficiency of only two electrons. This causes the formation of three-center bonds in the equatorial sites. The incorporation of carbon in boron carbide was understood to supply the extra two electrons to the crystal of α-boron, replacing the weak three-center bond with strong covalent bonds. In this case, the role of carbon incorporation is simply regarded as doping. My recent study on the vibrations of boron carbide, however, shows that this role of doping should not be taken too literally. This issue will be discussed later.

The outward orbitals, which are a_g, t_{1u}, t_{2u}, and v_g, in ascending order in energy, form covalent intericosahedral bonding, when two outward orbitals meet each other. Recently, an interesting interpretation has been found on intericosahedral bonding, in connection with aluminum-based quasicrystals (7). Since little is known about this work, it may be worth saying a few words about it. The lowest outward orbital a_g is based on a *sp* hybrid, the bonding of which is strongly oriented. Hence, this orbital

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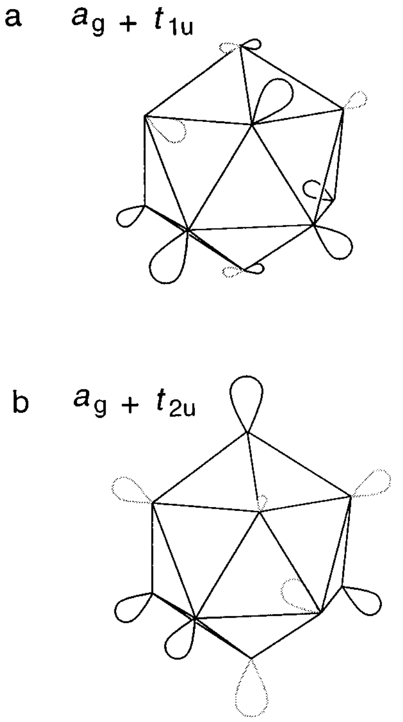

FIG. 1. The outward nonbonding orbitals for two different electronic configurations: (a) $a_g + t_{1u}$, and (b) $a_g + t_{2u}$. The z-axis is taken to be perpendicular to the plane of the figure. The three strong outward bonds in (a) form covalent bonds, which turn to the lattice frame of the rhombohedral crystal in α-boron. The configuration in (b) is favorable for forming metallic quasicrystals, which are characterized by rather isotropic bonding.

basically determines the covalent character of the intericosahedral bonding. The next lowest orbitals t_{1u} (sp^2 hybrid), which are partly occupied, modify the covalent character. As shown in Fig. 1a, the t_{1u} orbitals reinforce 6 of the 12 outward orbitals in the directions of the rhombohedral-lattice frame, while eliminating the others; the covalency is increased. The relatively small coordination number ensures the covalent character of the rhombohedral bonding.

In the case of aluminum-based icosahedra, the order in t_{1u} and t_{2u} is reversed. Modification by t_{2u} (sp hybrid) results in a different character of intericosahedral bonding (Fig. 1b). Each of the 12 outward orbitals survives with different orientations, and the bonding becomes isotropic as a whole. In this case, the highly oriented covalent character is lost, and the metallic bonding is formed instead. This gives a qualitative account for why two different icosahedra produce different classes of solids; the one turns to a semiconductor and the other to a metal. However, later, we will see that the rhombohedral bonding in boron crystals is weaker than the usual covalent bonding based on the sp^3 hybridization and tetrahedral coordination.

Dynamical properties of crystals cast further insight into chemical bonding, in terms of interatomic forces. In the following, I try to discuss versatile properties of the bonding of boron crystals which appear in a variety of aspects of lattice dynamics. For the usual covalent bond, a relatively strong noncentral force is expected, while the ionic bond in alkali halides has a character of almost central force (8). What we can expect for three-center or icosahedral bonding might be a strong angular dependence, and thereby a noncentral character as a large part of the bond. So far, no serious investigation has been made of icosahedral bonding along this line of thought. For this purpose, I use, throughout this paper, the valence force model (VFM) rather than the Keating model, because of its clear physical meaning. For the experimental aspect of boron-rich solids, the reader should consult review papers (9).

II. LATTICE VIBRATIONS OF α-BORON

a. Vibration Frequencies

First of all, let us look at the molecular vibrations of the icosahedral molecule B_{12}. The eight eigenfrequencies are expressed by central and noncentral forces, as listed in Table 1. Here, the terminologies of central and noncentral forces are used, which correspond in the molecular vibrations to the bond-stretching force f_r and the angle-bending force f_a, respectively. Usually, the noncentral force is used in a wider meaning. In the question to which extent the central and noncentral forces contribute to an eigenfrequency, we should distinguish the following two factors: how strong is the individual force, and how many of such bonds participate in the eigenfrequency. The latter aspect corresponds to a geometrical factor, which can be estimated by the quantity listed in the last column of Table 1. We can see that the contribution of the noncentral force f_a to the eigenfrequency is quite large with respect to the geometrical factor, except for A_g. If f_a is ignored, the uniformly breathing mode A_g is almost the highest mode; only one of V_g modes is slightly higher than A_g. When f_a is introduced, several modes become higher than the A_g mode.

The belief in large noncentral forces seemed to be supported by a calculation of lattice vibrations in the 1970s (10). In the vibration spectra of α-boron, broad but apparent IR bands were observed at the higher frequency region ($> 1000\ \mathrm{cm}^{-1}$), beside relatively sharp Raman bands. At that time, symmetry species of the Raman bands had not been known. Weber and Thorpe calculated the vibrations and got good agreement with the experiments, provided that the high-frequency IR bands were of the first order (10). One of their valuable contributions was to show that the intericosahedral bond is (more than twice) stronger than the intraicosahedral bond. This is consistent with the fact that the intericosahedral bonds, which here are called the rhombohedral bonds, have strong covalent character and that boron crystals are not molecular crystals.

TABLE 1
The Nonzero Eigenvalues of the Icosahedral B_{12} Molecule Using Valence Forces f_r and f_a, Where d Is the Bond Length of the Icosahedron

Γ	$M\omega^2$	Ratio	Γ	$M\omega^2$	Ratio
A_g	$(5-\sqrt{5})f_r$	0	U_u	$\frac{7+3\sqrt{5}}{4}\left\{f_r+3\frac{f_a}{d^2}\right\}$	3
T_{1u}	$3\left\{f_r+(3-\sqrt{5})\frac{f_a}{d^2}\right\}$	0.76	V_g	$2f_r+\frac{13-\sqrt{5}}{2}\frac{f_a}{d^2}\pm\left[2f_r^2+2(5-\sqrt{5})f_r\frac{f_a}{d^2}+\frac{39-13\sqrt{5}}{2}\frac{f_a^2}{d^4}\right]^{1/2}$	2.15
T_{2u}	$(3-\sqrt{5})f_r+4\frac{f_a}{d^2}$	5.24			5.85
U_g	$\frac{5+\sqrt{5}}{4}\left\{f_r+5\frac{f_a}{d^2}\right\}$	5	V_u	$f_r+6\frac{f_a}{d^2}$	6

Note. The last column shows the ratio of the contributions of the noncentral force to ω^2 to that of the central force, *i.e.*, the ratio of the coefficient of f_a/d^2 to that of f_r. For V_g, the ratio is given by approximating the exact eigenfrequencies to $(2\pm\sqrt{2})f_r+\{(13-\sqrt{5})/2\pm(5-\sqrt{5})/\sqrt{2}\}(f_a/d^2)$, by assuming $(f_a/d^2)/f_r \ll 1$.

When the rhombohedral force f_r^{rh} is the strongest force, the higher Raman-active modes are much higher than the highest IR mode. The frequency of the highest IR-active mode is almost independent of f_r^{rh}. To obtain an IR band near the highest Raman band, a large noncentral force f_a^{in} for the intraicosahedral bonds is required, and Weber and Thorpe's calculation assumed this.

In the late 1980s, the polarization characteristics of Raman spectra were carried out. Tallant *et al.* showed that the highest Raman band has A_{1g}, while the next highest has E_g symmetry (11). The order in the frequency was opposite to the prediction by Weber and Thorpe. On the basis of this new data, Beckel *et al.* reexamined the calculation of vibrations and found that the contribution of noncentral forces was small (12). The highest A_{1g} mode has its predominant origin in the uniform breathing mode A_g of an icosahedral molecule, and thereby the frequency is independent of f_a^{in}. The E_g mode, on the other hand, has its predominant origin in a V_g mode of the icosahedral molecule, which significantly depends on f_a^{in} as shown in Table 1. The assumption that f_a^{in} is very small is, therefore, an inevitable requirement for agreement with the Raman experiment. An immediate consequence of this finding is that no IR band can have a frequency as high as the highest Raman bands. Consequently, the IR bands observed at $> 1000\ \text{cm}^{-1}$ must be ascribed to a higher order absorption. I also reached this conclusion from my shell model (SM) calculation (13). As far as the zone-center frequencies are concerned, both models, the SM and VFM, give basically the same answer.

b. IR Absorption Intensity

My original intention of using the SM was to demonstrate the IR activity for α-boron, for which there was relatively poor agreement between the calculation and experiment (13). Another interest in studying the IR activity lies in the question why and how the crystal exhibits a nonvanishing dipole moment, although the unit cell is composed of only one type of atom. Regarding the latter concern, the use of the SM was successful. The SM, however, did not agree well with experiment in the intensity of IR absorption. Experimentally, from IR spectra, relatively large effective charges (comparable to those of polar semiconductors) were estimated (14), which must cause discernible separation of TO and LO modes. The SM cannot produce these large effective charges, unless unreasonable large noncentral forces are allowed. Introducing large noncentral forces is impermissible, as described in the preceding session. The difficulty has been solved by using the adiabatic bond-charge model (BCM) (15).

In the language of the SM, a rigid translational motion of shells s_1 carries a nonvanishing dipole moment, and to which extent the core motion of a finite-frequency vibration c_2 couples to the s_1 determines the effective charges. The coupling coefficient a_{12} is determined in a way that the shell motions eliminate the increase in the potential caused by the core motions as largely as possible, in the sprit of the adiabatic approximation. In the SM, the induced shell motion is usually almost the same type of motion as the core motion. This is because the shell and the core are located at the same position in the equilibrium state, and thereby, a coupling between different types of motion is not energetically favorable.

The polar mode T_{1u} of an icosahedral molecule is shown in Fig. 2a. In the BCM, the finite-frequency mode of the bond charges s_2 (Fig. 2b) is quite different from the core motion c_2. In the BCM, coupling to s_1 becomes much easier. A surprising matter is that if only nearest neighbor central

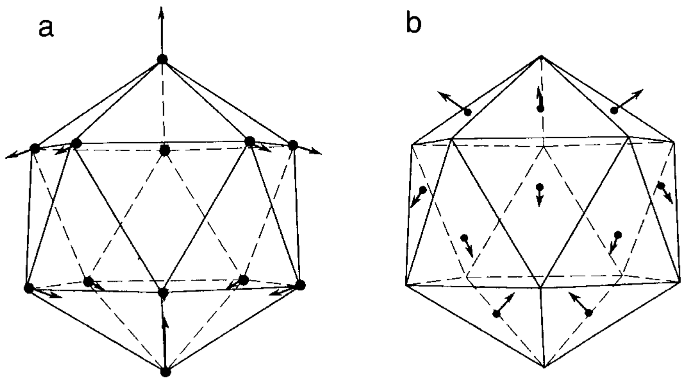

FIG. 2. (a) IR-active core motion c_2 of the icosahedral molecule, and (b) the bond-charge motion s_2 with the same symmetry in the BCM.

forces are assumed, the s_2 is not merely weakly coupled to c_2, but is completely decoupled. Figure 3 shows why the c_2 motion is easily coupled to the different type of the bond charges s_1, even though noncentral forces are very small.

This special situation, however, raises a subtle problem on the validity of the adiabatic approximation. Easiness of coupling to zero-frequency motion implies very weak restoring force for the bond charges. Even though the mass of an electron is so small, the electrons would not follow immediately the core motions, if the restoring force is too small. This breaks the adiabatic approximation. Thus, a caution is needed for using force constants beyond the valid range (15).

The present argument is restricted to the intraicosahedral bonding. In real crystals, the bond charge in the rhombohedral bond may be more important. It has been widely accepted that the BCM is a more realistic model for usual covalent crystals (16). In either case, we can ascribe the large effective charges of boron crystals to the presence of the bond charges. There is no need to introduce large noncentral forces.

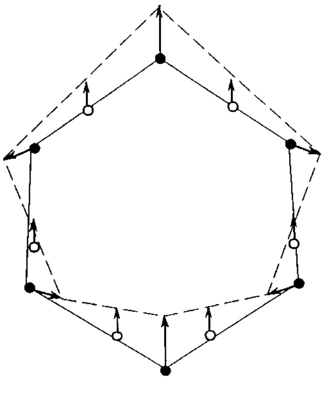

FIG. 3. The core motion c_2 induces the bond-charge motion of type s_1, without much increase in energy.

c. *Vibrations of Amorphous Boron*

Although the structure of amorphous boron has not yet been well known, there is evidence that it contains icosahedral units with short-range order. The vibration spectra of amorphous boron may have some clues to the interpretation of the interatomic forces of boron solids. The spectra of amorphous boron are very broad, as usual for amorphous materials, and seem featureless (17, 18). However, we can identify a secondary band at $> 1000\,\mathrm{cm}^{-1}$, beside the broad primary band from 400 to $1000\,\mathrm{cm}^{-1}$. Judging from the vibrations of the crystal, this secondary band can easily be interpreted to originate from the vibrations of the intericosahedral bonds. The secondary band in amorphous boron is both Raman and IR active. If we regard the spectrum of amorphous boron as a broadened version of the spectrum from the crystal, this fact is interesting, because we have already identified the IR bands at $> 1000\,\mathrm{cm}^{-1}$ in the crystal to a higher-order absorption. Previously, I thought that this fact provided evidence for large noncentral forces, on the basis of the SM.

To study the vibrations of amorphous boron, the Bethe lattice model was used (19), since the short-range order of the structure is preserved in amorphous solids (20). By using this model, it has been shown that the secondary band is activated both in the Raman and IR spectra, even if only central forces are taken into account. Figure 4 illustrates how the secondary peak exhibits both Raman and IR activities. In the crystal case, only zone-center modes can be observed in optical spectra. The highest Raman band ($> 1000\,\mathrm{cm}^{-1}$) is much higher than the highest IR-active band ($\sim 800\,\mathrm{cm}^{-1}$), provided $f_r^{\mathrm{in}} < f_r^{\mathrm{rh}}$. This is because the strain energy due to f_r^{rh} has the maximum value for the zone-center Raman-active mode, owing to its symmetric motion. As going to the zone boundary, the frequency of the Raman band is decreased, because deviation in the phase becomes large from that of the symmetric motion. Conversely, the frequency of the IR band is increased, because deviation in the phase becomes small. If we take this dispersion into account, we can see that the frequency averaged over the entire zone is almost the same for both IR and Raman bands. We can regard that the spectra of amorphous boron reflect this. There is again no need to introduce large noncentral forces.

III. VIBRATIONS OF BORON CARBIDE

So far, we have seen that the noncentral character of the intraicosahedral bond is very small. But, this by no means denies the importance of noncentral forces in the lattice dynamics of boron crystals. Rather, some of the noncentral forces play important roles in the lattice dynamics of boron carbide, in particular in the mechanical stability of the crystal, to which we proceed with our argument.

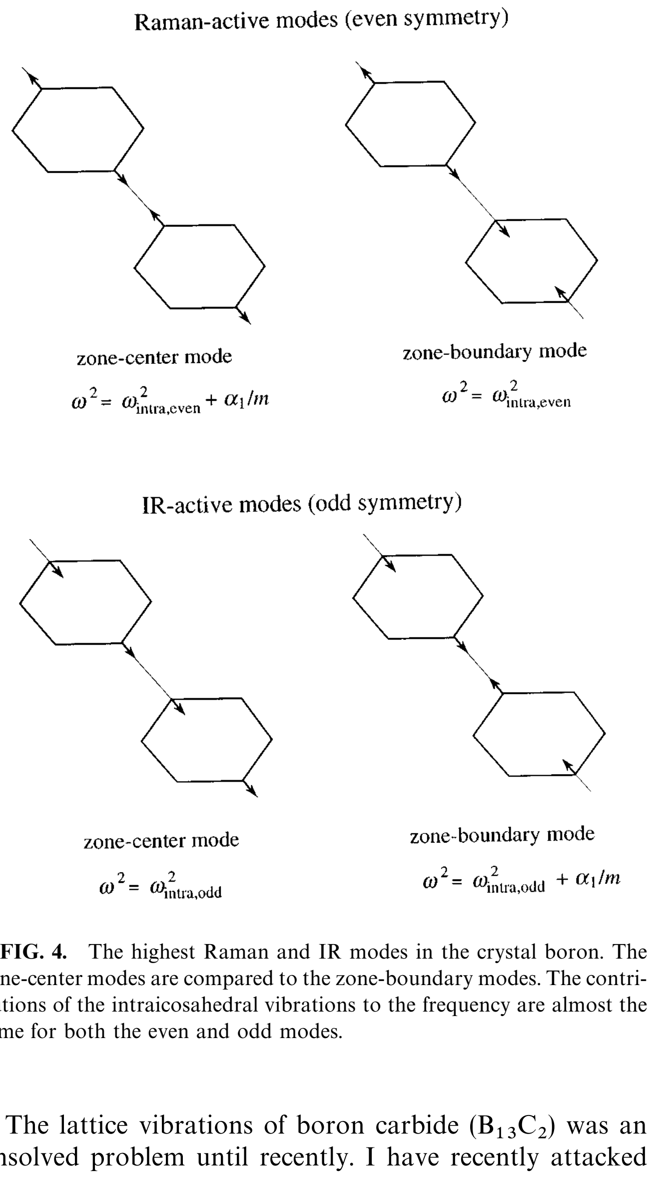

FIG. 4. The highest Raman and IR modes in the crystal boron. The zone-center modes are compared to the zone-boundary modes. The contributions of the intraicosahedral vibrations to the frequency are almost the same for both the even and odd modes.

The lattice vibrations of boron carbide ($B_{13}C_2$) was an unsolved problem until recently. I have recently attacked this issue and obtained good agreement with experiment (21). Here, I pick up the essential results, which are interesting from the viewpoint of chemical bonding.

It is found that the C–B bond in the linear chain C–B–C is by far the strongest bond in the $B_{13}C_2$ crystal, and the stretching motion of this bond gives rise to the highest IR-active mode at 1560 cm^{-1}. Figure 5 shows the balance of various forces in boron carbide, compared to α-boron. We can see that not only the intraicosahedral force f_r^{in} but also the intericosahedral force f_r^{rh} are weakened by insertion of the linear chain. In fact, the icosahedral unit is further deformed in boron carbide compared to α-boron (22). The C–B bond in the chain is, on the other hand, contracted, the bond length being shorter than any single bond of known organic compounds. This balance between forces are consistent with the Raman spectra of α-boron modifications; the frequencies of Raman bands are lowered as the crystal becomes stiff. Lowering of the Raman frequency does not mean softening of the crystal at all, but is a sign that the crystal loses more icosahedral bonding.

This finding is very important in view of what happens when both relatively weak icosahedral bonds and strong covalent bonds occur. If we follow the Longuet-Higgins theory, it would be concluded that the icosahedral bonding is further reinforced, due to doping. Kirfel *et al.* examined in boron carbide the charge transfer from the linear chain to the icosahedral unit from this point of view, but with no success (23). Now, it is clear that what happens is opposite to this prediction. An electronic-structure calculation by Kleinman's group (6) demonstrates that valence electrons are more concentrated around C atoms than as expected by their valences.

In this connection, it may be worthwhile to make a comment on the effects of doping in boron crystals. The potential to exhibit superconductivity by doping is discussed for boron crystals, in analogy to fullerenes (24). For usual semiconductors, doping means supplying free carriers without altering the host material. For boron crystals, however, incorporation of impurity atoms modifies the bonding nature of the host crystals, since even the intericosahedral bonds are not very stable compared to the usual covalent bonds.

Another interesting finding in the vibrations of $B_{13}C_2$ is the contribution of the noncentral forces. Over all, good agreement with the experiment is obtained when a very small (or even negative) f_a^{in} is assumed for the intraicosahedral angles and when a relatively large f_a^{c} is assumed for the chain angles. Since the chain forms tetrahedrally coordinated covalent bonds, large noncentral forces are reasonable for the chain angles. This large noncentral force f_a^{c} of the linear chain is very important for the mechanical stability of the crystal $B_{13}C_2$, which will be discussed in the next section.

The range of intraicosahedral vibrations is wider than a prediction based on a simple model of central forces only, which suggests a negative value of the noncentral force f_a^{in} for the intraicosahedral angles. This is plausible in view of the electronic instability of polyhedral molecules. This subject will be discussed again later.

IV. ELASTIC PROPERTIES

The elastic property is related to the mechanical stability of the crystal structure, for which noncentral forces play an important role and thus shall be discussed here (25).

The mathematical statement of the mechanical stability of crystal structures is that the matrix of the elastic constants is positive definite (26). There are basically two categories for stabilizing crystal structures. One is that only central forces to the nearest neighbors are enough for the stability condition to hold (category I). The stability of the fcc (and

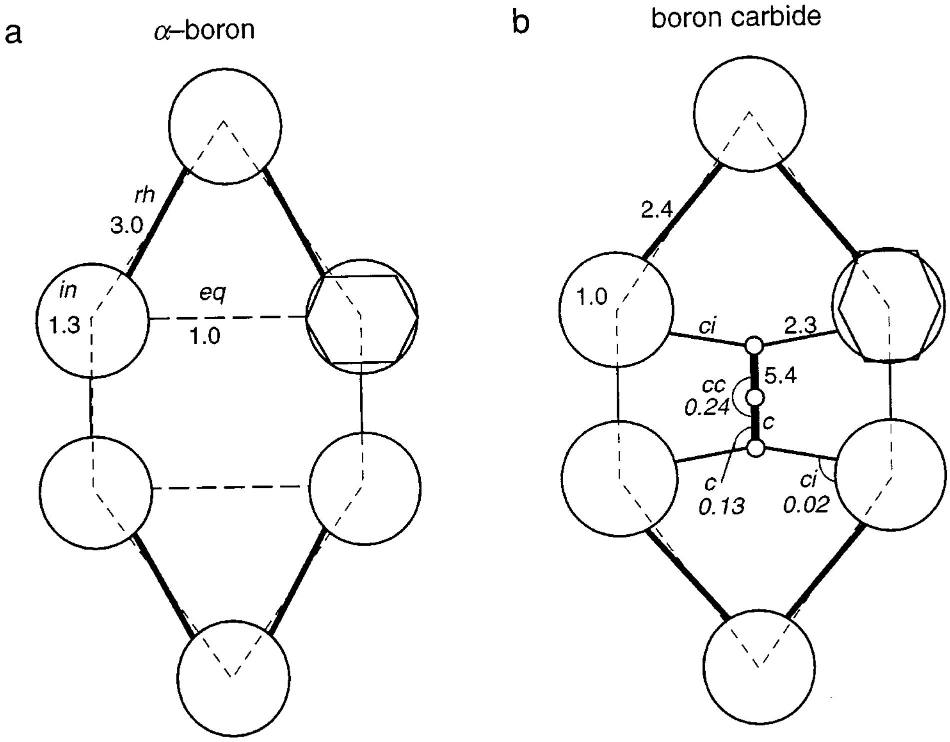

FIG. 5. The force constants of (a) α-boron and (b) boron carbide. Italic numbers indicate the angle-bending forces; the others indicate the central forces, along with the notations indicating the type of bond. The force constants are expressed in units of mdyn/Å. For angle-bending forces, the values are indicated by $f_a/(d_1 d_2)$, where d_i's are the lengths of bonds. The icosahedra are represented by spheres. The figure also qualitatively shows the deformation of icosahedra.

presumably bcc) structure falls in this category. The other is that the stability condition is met assuming noncentral forces (category II). The stability of the diamond crystals falls in the latter type.

For α-boron, it is found that the c_{44} component completely vanishes, if only central forces are assumed. The reason for this unexpected result is that a shear strain ε_4 induces rotations of icosahedra, which completely cancel the shear strain. There is no symmetry reason for this and thus this cancellation must be accidental. In fact, this cancellation would not be complete if noncentral forces are introduced. However, for α-boron, it has been seen that noncentral forces are very small. On the basis of the criterion (I), we can understand that the crystal structure of α-boron is unstable.

Induction of rotations of the icosahedra is a very important mechanism to relax external strains. This rotation-induced relaxation mechanism is not special for boron crystals, but is proven to be a quite ubiquitous feature for molecular crystals, such as fullerenes. The rotation-induced relaxation holds on subtle balance of forces. A slight change in external forces or a slight change in the crystal structure would cause a drastic change in the rotations (27). In this respect, the fact that the rhombohedral site slightly deviates from the ideal lattice vectors (off-line site) has a significant meaning. If the rhombohedral site were located just on this ideal lattice vector, no relaxation mechanism would occur. This situation looks like a magic hand which is fully stretched. Suppose that an external force is applied to it along the arm. There is no way to relax the external force. This situation is unstable for any perturbation which is applied in the perpendicular direction (Fig. 6a). Slight bending of the arm is favorable to the mechanical stability.

The chance that the accidental cancellation takes place will be reduced when the crystal structure has additional elements in the primitive unit cell. In the $B_{13}C_2$ case, insertion of the linear chain, however, does not eliminate the accidental cancellation. Adding atoms at high-symmetry positions, sometimes, does not help the situation either. Instead, it is found that highly oriented covalent bonds formed around the carbon atoms provide strong angle-bending forces, and that these forces make the crystal stable in a way similar to diamond crystals. Therefore, the stability of boron carbide falls into category (II). 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. This prevents the accidental cancellation even if only central forces are used. Hence, we can say that β-boron is quite stable, and that the stability belongs to category (I).

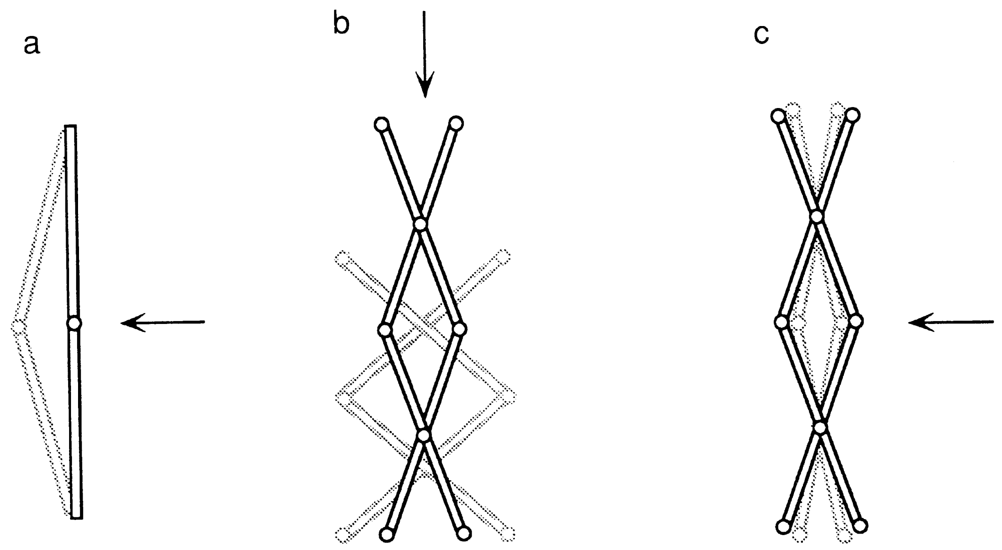

FIG. 6. An analogy of the relaxation by a magic hand. The fully stretched state is unstable (a). The magic hand is significantly deformed, when compressed in the direction of the arm (b). The deformation is not significant, when a force is applied perpendicular to the arm (c).

In the family of boron crystals, only for the strain in the z direction, rotational motion is not induced. The deformity of the icosahedron, instead, leads to an unexpected effect on the elasticity of boron carbide. *Deformity* of the icosahedron here meant that the intraicosahedral force is the weakest among central forces. As shown schematically in Fig. 5, most of the strong forces in $B_{13}C_2$ act along the z-axis. From this, we can expect a rigidity in this direction. However, there is a flaw in this rigidity. The icosahedra are so flexible that they absorb most of the strain energy in this direction. It is amazing to find that a compression in the z direction causes an elongating of the icosahedra in this direction (negative Poisson's ratio!). Again, the off-line rhombohedral site is quite favorable for this distortion. It is interesting to point out that both the crystal structures of α-boron and boron carbide reflect this elastic response: the rhombohedral frame of α-boron is elongated in the z-axis, while the icosahedra is slightly compressed in this direction; in boron carbide the situation is opposite.

The reason boron carbide is soft in the z-axis despite strong bonds in this direction is given in Ref. (25). An analogy to the magic hand may again be helpful. In Fig. 6, the strong intericosahedral bonds (or the chain bonds) are looked on as the stiff bars, whereas the soft icosahedra are looked on as flexible pivots. Despite stiff bars, the magic hand can be greatly deformed in the direction of the axis of the arm (the z-axis). But, in the direction perpendicular to the arm, the deformation cannot be significant, because it is almost fully stretched from the beginning. A large relaxation in this direction itself was predicted by a calculation of the electronic structure (28), but the physical mechanism was understood only after the classical dynamics of the lattice was studied.

Unfortunately, there is as yet no full experiment on the elastic constants of boron carbides. However, the deformity of the icosahedron in the above sense has, recently, been partly resolved experimentally (29).

V. FIRST-PRINCIPLES CALCULATIONS

Our survey for evaluating the force constants must eventually be justified by a more fundamental viewpoint, the electronic structure. The force constants can, in principle, be obtained by first-principles calculations. In fact, for the strongest bond-stretching forces, it is almost always possible to calculate them by using a breathing type deformation. Beckel's group carried out such a calculation for the α-boron modifications (30) and obtained values in good agreement with those obtained by fitting to the experiment.

For noncentral forces in crystals or large molecules, however, there is a practical difficulty in estimating them by first-principles calculations. In the expansion of the adiabatic potential obtained by first-principles calculations, there are so many force constants other than the stretching and bond-angle forces, that the angle-bending forces so obtained usually are inaccurate. This issue is discussed elsewhere (31).

For small molecules, evaluating the noncentral forces is feasible. Working on simple examples, such as a triangular molecule, the following properties are derived. Tetrahedrally coordinate covalent bonds have almost always strong angle-bending forces. Highly oriented bonding is formed in the direction connecting two atoms. Any angle deviation from this orientation would cause a large increase in energy, so that a strong angle-restoring force is expected.

On the other hand, for a square molecule or a triangular molecule, those degenerate orbitals in the ground state which contribute to the bonding, e.g., the e states, behave differently. These states stretch their orbitals in a different way from the direction connecting the two atoms. In other words, these have to some extent nonbonding character. In this case, an angle deviation can sometimes even cause the energy to decrease. This causes the noncentral force to become small or even negative. The icosahedral molecule belongs to this case.

This mechanism is to some extent related to the Jahn–Teller effect. In fact, for the simplest examples of a square and a triangular molecule, either of the degenerate states gains energy by deforming the molecule, i.e., the Jahn–Teller effect takes place. This is the predominant mechanism of the energy gain for these molecules. It should also be noted, however, that not only degenerate states but also other states are able to couple with each other and to decrease energy through deformations. As the structure of a molecule becomes more complex, the pure effect of the Jahn–Teller type will be buried by other effects of coupling between different states. Actually, it was shown that the deformations that do not cause a Jahn–Teller effect, such as U_u, can decrease the energy as much as those deformations that cause a Jahn–Teller effect (31). At any rate, no matter whether a pure Jahn–Teller effect causes negative values of noncentral forces, it is almost certain that an intrinsic instability of polyhedral molecules is a cause of negative values. It is also worth noting that distortions of icosahedra are observed in various boron crystal modifications. However, the distortions in boron crystals are not the cause of the various crystal modifications, but are consequences of the crystal structures. The icosahedron is so flexible that it is able to accommodate itself to a wide range of deformations, as shown in the previous section. What determines the final form of deformation is the external influences, such as the lattice frame and external strains.

VI. SUMMARY

Intraicosahedral bonding is best characterized by a central force. The role of the noncentral force f_a^{in} is very small for this bond. Many properties of the vibrations of boron solids can be described without invoking f_a^{in}. Intrinsic instability of the icosahedron leads to weak and even negative f_a^{in}, which results in the deformity of the icosahedron of boron crystals. It is, however, not appropriate to ascribe this instability only to the Jahn–Teller effect.

Regarding the intericosahedral bonds, the rhombohedral bond basically has the character of covalent bonding, but is weaker than usual tetrahedrally coordinated covalent bonds. From this, it can often happen that the latter is more stabilized at the cost of weakening the former, if both occur. This trend is consistent with the Raman spectra of α-boron modifications.

The linear chain of the boron carbide crystal has tetrahedrally coordinated bonds, which are characterized as strong covalent bonds with corresponding strong noncentral forces. This covalent character of the bonds is indispensable for the mechanical stability of the crystal structure of boron carbide.

When an isolated icosahedral boron molecule is transferred to crystalline boron, the icosahedron is deformed in accordance to the rhombohedral frame. This type of deformation is primarily caused by the requirement of chemical bonding of the outward orbitals. The icosahedral units in the crystal are further deformed, namely the off-line rhombohedral sites. This type of deformation is looked upon as a consequence of the mechanical stability. For boron crystals, it is important to recognize that what actually determines the final form of the distortion is not the intrinsic instability of the icosahedron, but is the external influences, such as the intericosahedral bond, the chain bond, and applied strains.

Note added in proof. After completing this manuscript, another study on the vibrations of α-boron by Vast *et al.* appeared (32). By using *ab initio* calculations and experiments, they showed that the librational mode has a much higher-frequency than as believed before. Since a high-frequency librational mode implies large noncentral forces, this new result might seem to contradict the present conclusion. By analyzing their result in terms of the valence-force model, we are convinced that the present qualitative description about the noncentral forces is still valid. A key thing to resolve this apparent contradiction is that there are indeed a large number of noncentral forces, as noted at the beginning of Section IIa. If we count properly all the noncentral forces on the same order of approximation, we could obtain a relatively high frequency for the librational mode. A more detailed description will be given in a comment paper.

REFERENCES

1. N. N. Greenwood, *in* "Comprehensive Inorganic Chemistry" (J. C. Bailar, H. J. Emeléus, Sir R. Nyholm, and A. F. Trotman-Dickenson, Eds.), Chap. 11. Pergamon, Oxford, 1973.
2. H. C. Longuet-Higgins and M. de V. Roberts, *Proc. R. Soc. A* **230,** 110 (1955).
3. F. Perrot, *Phys. Rev. B* **23,** 2004 (1981).
4. D. W. Bullett, *J. Phys. C* **15,** 415 (1982).
5. S. L. Lee, D. M. Bylander, and L. Kleinman, *Phys. Rev. B* **42,** 1316 (1990); A. C. Switendick, *in* "Physics and Chemistry of Finite Systems: From Clusters to Crystals," Vol. I, pp. 683–690. Netherlands, Kluwer, 1992. [It is to be expected that there are many papers from a similar motivation from all over the world]
6. D. M. Bylander, L. Kleinman, and S. Lee, *Phys. Rev. B* **42,** 1394 (1990); D. M. Bylander and L. Kleinman, *Phys. Rev. B* **43,** 1487 (1991); I. Morrison, D. M. Bylander, and L. Kleinman, *Phys. Rev. B* **45,** 1533 (1992).
7. T. Hatakeyama, *Dr. thesis*, Univ. of Tokyo, 1989; *in* "New Horizons in Low-Dimensional Electron Systems" (H. Aoki, Ed.), pp. 433–444. Netherlands, Kluwer, 1992.

8. J. C. Phillips, “Bonds and Bands in Semiconductors,” Chap. 3. Academic, New York, 1973; R. M. Martin, *Phys. Rev. B* **1,** 4005 (1970).
9. H. Werheit, *in* “Proc. 9th Int. Symp. on Boron, Borides and related Compounds,” pp. 142–153. Universität Duisburg, 1987, *in* “Boron-Rich Solids,” AIP Conf. Proc. 140, pp. 325–339. Am. Inst. Phys., New York, 1986.
10. W. Weber and M. F. Thorpe, *J. Phys. Chem. Solids* **36,** 967 (1975).
11. D. R. Tallant, T. L. Aselage, A. N. Campbell, and D. Emin, *Phys. Rev. B* **40,** 5649 (1989).
12. C. L. Beckel, M. Yousaf, M. Z. Fuka, S. Y. Raja, and N. Lu, *Phys. Rev. B* **44,** 2535 (1991).
13. K. Shirai and S. Gonda, *J. Phys. Chem. Solids* **57,** 109 (1996).
14. K. Shirai, S. Gonda, and Y. Kumashiro, *in* “Proc. 11th Int. Symp. Boron, Borides, and Related Compounds, 1993,” JJAP Series **10**, pp. 102–105, 1994.
15. K. Shirai and S. Gonda, *Physica B* **219/220,** 336 (1996).
16. G. Lucovsky and C. K. Wong, *Philos. Mag. B* **52,** 331 (1985); G. Lucovsky, R. M. Martin, and E. Burstein, *Phys. Rev. B* **4,** 1367 (1971).
17. U. Kuhlmann, H. Werheit, T. Ludström, and W. Robers, *J. Phys. Chem. Solids* **55,** 579 (1994).
18. K. Shirai, S. Emura, S. Gonda, and Y. Kumashiro, *J. Appl. Phys.* **78,** 3392 (1995).
19. K. Shirai, M. F. Thorpe, and S. Gonda, *J. Non-cryst. Solids* **198/200,** 36 (1996); K. Shirai and M. F. Thorpe, *Phys. Rev. B* **55,** 12244 (1997).
20. G. Lucovsky and W. B. Pollard, *in* “The Physics of Hydrogenated Amorphous Silicon II” (J. D. Joannopoulos and G. Lucovsky, Eds.), Chap. 7. Springer-Verlag, Berlin, 1984.
21. K. Shirai and S. Emura, *J. Phys.: Condens. Matter* **50,** 10919 (1996).
22. B. Morosin, A. W. Mullendore, D. Emin, G. A. Slack, and C. Wood, *in* “Boron-Rich Solids” AIP Conf. Proc. 140, (D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, Eds.), pp. 70–86. Am. Inst. Phys., New York, 1986.
23. A. Kirfel, A. Gupta, and G. Will, *Acta. Crystallogr. B* **35,** 1052 (1979).
24. S. Gunji, H. Kaminura, and T. Nakayama, *J. Phys. Soc. Jpn.* **62,** 2408 (1993); “Proc. 11th Int. Symp. Boron, Borides, and Related Compounds, 1993,” JJAP Series **10**, pp. 35–38, 1994.
25. K. Shirai, *Phys. Rev. B* **55,** 12235 (1997).
26. M. Born and K. Huang, “Dynamical Theory of Crystal Lattices,” Oxford Univ. Press, Oxford, 1954.
27. K. Shirai, *J. Solid State Chem.* **133,** (1997).
28. S. Lee, D. M. Bylander, and L. Kleinman, *Phys. Rev. B* **45,** 3245 (1992).
29. R. J. Nelmes, J. S. Loveday, R. M. Wilson, W. G. Marshall, J. M. Besson, S. Klotz, G. Hamel, T. L. Aselage, and S. Hull, *Phys. Rev. Lett.* **74,** 2268 (1995).
30. M. M. Florence and C. L. Beckel, *in* “Boron-Rich Solids” (D. Emin, T. Aselage, C. L. Beckel, A. C. Switendick, and B. Morosin, Eds.), AIP Conf. Proc. No. 231, pp. 37–41. Am. Inst. Phys., New York, 1991; B. S. Abbott and C. L. Beckel, *in* “Boron-Rich Solids” (D. Emin, T. Aselage, C. L. Beckel, A. C. Switendick, and B. Morosin, Eds.), AIP Conf. Proc. No. 231, pp. 344–346. Am. Inst. Phys., New York, 1991.
31. K. Shirai, *J. Solid State Chem.* **133,** (1997).
32. V. Vast, S. Baroni, G. Zerah, J. M. Besson, A. Polian, M. Grimsditch and J. C. Chevin, *Phys. Rev. Lett.* **78,** 693 (1997).