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Effects of the Geometries of Boron-Rich Crystals on the Lattice Dynamics

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The effects of the geometries of boron-rich solids on dynamical properties are discussed. Traditionally, it has been thought that the intericosahedral bond is stronger than the intraicosahedral bond. In the past, questions concerning this understanding have arisen, based on experimental results. Some of the apparent contradictions can be solved by considering the special geometries of the icosahedron-based structure. The geometrical concept is examined for elastic responses, librational modes, and anharmonic phenomena. An attempt has also been made to address the problem of the strength of the chain bond in boron carbides by *ab initio* calculations. Based on the present results, a model has been proposed to solve contradictions among experimental results. © 2000 Academic Press

I. INTRODUCTION

Since Longuest-Higgins disclosed the nature of the icosahedral bonding of boron molecules (1), it has been generally accepted that the intericosahedral bonding is charaterized as the covalent bond and is stronger than the intraicosahedral bonding. Published results of model calculations have so far strongly supported this concept (2). A recent *ab initio* calculation demonstrated that some modification is needed to incorporate the angle forces (3) (this concern is discussed later). This new discovery, however, only confirms the traditional interpretation as described above. Despite this fact, suspicions of the correctness of this concept sometimes arose in the results of new experimental data. Questions were also found in a number of calculations.

To clarify this confusion, when comparing the strength of different bonds, it should be noted the circumstance in which the comparison is made. In this respect, consideration of geometrical effects of bonding is important (4). Since this point of view is often overlooked, it is worthwhile to discuss various phenomena from this point of view.

To put the problem more concretely, first, numerical values of basic quantities associated with lattice dynamics are presented. In Table 1, the force constants (harmonic term f and cubic anharmonic term g) of α-boron are compared with those of silicon. The force constants compared are those of the strongest covalent bonds. For boron, this is the intericosahedral bond, formed along the edges of the rhombohedral cell, and is termed the rhombohedral bond. By expressing the bonding character in this form, nothing special can be found concerning the covalent bond of boron. The ratio f_a/f_r and g have similar values for two crystals. Many peculiarities arise from the special geometries of the icosahedron-based structure.

An example of this can be seen in the relationship between force constants of the inter- and intraicosahedral bonds of α-boron. Calculations show that the force constant for the former is about three times stronger than that of the latter (2). Force constants represent the strength of bonds. The strength of a bond can be roughly estimated by the magnitude of charge density of the bond. From X-ray structural studies (7), it has been demonstrated that the maxima in charge density were almost the same for inter- and intraicosahedral bonds. The force constants, however, were very different. The reason for this is that for the intericosahedral bond, the bond charge is shared only by its own bond, while that for the intraicosahedral bond is shared by many other bonds, and even by angles (8).

This is an example of what is referred to presently as the geometrical effects, which are further elaborated in the following. In the last part of this paper, an attempt is made to solve the currently difficult problem of boron carbides, along this line of thought.

II. ELASTIC RESPONSES

The first example is that of the elastic properties of boron-rich crystals (9). The Bravais lattice of α-boron modifications is rhombohedral. The angle θ_0 between one of the primitive translational vectors and the c axis has been determined to be 34°. From this, it is easily concluded that the crystal will be stiff along this axis. In terms of the elastic constants c_{ij}, $c_{33} > c_{11}$ is expected. For α-boron crystals, this is the case. A strange matter about boron carbides is that, even though the strongest chain bond is inserted

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TABLE 1
Comparison of the Force Constants of α-Boron and Si[a]

	α-B[b]	Si[c]
f_r	3.4	1.47
f_a	0.066	0.03
f_a/f_r	1.9	2.0
g_r	− 9.8	− 5.1
γ_r	− 4.9	− 8.0
g_a	0.56	0.11
γ_a	14.7	8.4

[a] The strongest bond and angle are taken as representatives of the interactions, i.e., the rhombohedral bond for boron. Harmonic force constants *f* are given in mdyn/Å, while cubic anharmonic force constants *g* are in mdyn/Å^2. The subscript *r* refers to the bond stretching, and *a* to the angle bending. Grüneisen constants γ are also listed.

[b] Reference (5).

[c] Reference (6).

along the *c* axis, the opposite result is predicted, that is, $c_{33} < c_{11}$.

The origin of this unexpected result is due to the subtle difference in structure between these two crystals. In α-boron modifications, the orientation of the rhombohedral bond deviates slightly from that of the primitive translational vectors; i.e., the angle θ' formed between the rhombohedral bond and the *c* axis differs from θ_0. In α-boron, $\theta' < \theta_0$. When applying compression along the *c* axis, θ' is further reduced, owing to deformable icosahedra. This displacement results in a strong resistance to the applied compression, which leads to a large c_{33}. In boron carbides, since $\theta' > \theta_0$, the opposite response takes place. That is, the angle θ' is increased. This manner of displacement is one in which the resistance to the compression is reduced. This leads to small c_{33}. This example demonstrates that even a slight difference in geometry could yield quite different overall effects.

Another example is the elastic response to hydrostatic pressure. For boron carbides, it has been experimentally demonstrated that the icosahedral unit is more reduced under high pressures than is the unit cell (10). This observation seems reasonable from the traditional concept of relative strength between inter- and intraicosahedral bonding. In contrast, for α-boron, calculations reveal the opposite result, as listed in Table 2 (11).

The result for α-boron does not mean that the above-mentioned traditional concept is wrong. Although the individual force of the intericosahedral bond is stronger than that of the intraicosahedral bond, i.e., $f_r^{\mathrm{rh}} \approx 3f_r^{\mathrm{in}}$, the number of intraicosahedral bonds N^{in} is much greater than that of rhombohedral bonds N^{rh}. That is, $N^{\mathrm{in}}{:}N^{\mathrm{rh}} = 30{:}3$. For hydrostatic pressure, all bonds are uniformly deformed; hence the resistance to the pressure is three times stronger in the icosahedral unit than in the lattice frame. For boron carbides, the addition of the chain bond is the reason for the relative stiffness between the icosahedral unit and the lattice frame to appear reversed.

TABLE 2
Comparison of the Compressibility of α-Boron and Boron Carbides in Units of 10^{-3} GPa^{-1}[a]

	α-B[b] $\partial \ln r/\partial p$	B_4C[c] $\partial \ln V/\partial p$
Inter	− 2.1	− 4.9
Intra	− 1.8	− 6.1

[a] It should be noted that the definition of compressiblitty differs, owing to limited data. As indicated in the second column, compressiblity is evaluated by the change in the bond length *r* of α-boron, and in the third column as the change in the volume *V* for the boron carbide.

[b] Calculation: Ref. (5).

[c] Experiment: Ref. (10).

III. LIBRATIONAL MODE

There had been a longstanding problem in the lattice dynamics of α-boron, the nature of the 520-cm^{-1} band in the Raman spectrum (12). The linewidth of this band is exceptionally narrow. This fact, together with others, led researchers to think that this band was not due to the usual phonon scattering. By a cooperative study of *ab initio* calculations and high-pressure experiments, it is now indisputably concluded that this band is no more than phonon scattering of the first order (3). The related phonon is a librational mode. At first, this new finding appeared surprising. The recorded frequency was probably the highest among the librational modes of various crystals (13). The frequency of the librational mode ω_l is usually less than about 100 cm^{-1}. ω_l is dominated by angle forces f_a. Angle forces are usually small, that is, less than 10% of the bond stretching forces f_r. Accordingly, such a high frequency for ω_l implies exceptionally large angle forces. By carefully analyzing the results in terms of a force-constant model, however, nothing special was found concerning the angle forces (5). The magnitude of an individual angle force still falls in a reasonable range (see Table 1). On the other hand, the number of angles involved in the librational mode is indeed large. Special attention should be given to the multiplication factor N_a in the formulas $\omega_l^2 \sim N_a f_a$, as noted in the previous section. Even though individual angle forces are small, the overall effect can be large.

The most interesting question concerning this mode is why the linewidth is so narrow. Compared with other materials, the linewidth $\Delta\omega/\omega_0$ of α-boron is the smallest, < 0.002, at room temperature, as far as the authors could determine from the literature. The linewidth has been studied in terms of phonon–phonon interactions (5). Actually, many factors contribute to this narrow linewidth feature.

It is true that anharmonic coupling constants are small only for this mode, as is discussed in the next section. The most important factor, however, is the thermal effect or, more precisely, the combined effect of the thermal factor and two-phonon DOS. Among the zone-center optic modes of α-boron, the librational mode is the only mode for which the phonon-decay processes are dominated by up-conversion, i.e., $\omega_l + \omega_1 \rightarrow \omega_2$. This type of process vanishes at very low temperature. This fact itself is common in other materials that possess librational modes. The special characteristic of boron is that ω_l is exceptionally high, so that even at room temperature the phonon-decay process of up-conversion type quenches.

IV. ANHARMONICITIES

In a qualitative discussion, anharmonicity can be regarded as indicating the softness of crystals. On the other hand, a quantitative description is complicated, because there are a number of parameters, even at the lowest order. Usually, only and averaging parameter, the Grüneisen parameter γ, can be obtained from thermal data. The anharmonicities of boron crystals obtained in this manner (most data are for β-boron) are quite normal, on the order of unity: 0.63 for thermal expansion (14); 0.76 for specific heat data (14); 1.85 for temperature dependence of the phonon frequency (15). A recent high-pressure experiment provided more detailed information concerning anharmonicites (3). From these data, estimates of many cubic anharmonic force constants could be determined. The values so obtained are not special when compared with those of other crystals, as seen in Table 1. This is consistent with thermal data. The effects of these anharmonic force constants, however, are different depending on observations. There have been cases in which anharmonicities were almost eliminated and cases in which anharmonicities were cooperatively enhanced. Again, the special geometries of boron-rich crystals play important roles in the anharmonic effects. In the following, these examples are examined.

Pressure Dependence

An extreme example in which anharmonicities are totally eliminated is the pressure dependence of phonon frequencies. The pressure dependence of phonon frequencies usually provides a rough estimation of the magnitude of anharmonicity. As shown in Ref. (3), most of the Raman modes have similar pressure dependence on frequency, from which $\gamma = \partial \ln \omega / \partial V = 0.9$ has been deduced. The exception again is the librational mode. The frequency of the librational mode is almost independent of pressure. This should not be interpreted as indicating a weakness in the anharmonicities of angles (see Table 1). The reason for this is simple. The angles involved in the librational mode hardly change under hydrostatic pressures, due to homogeneous deformation.

Cancellation Mechanism

The reason why the librational mode has a very narrow linewidth differs from the above mechanism for the weak pressure dependence. The most important factor is the thermal effect, as stated above. However, it is to some extent true to state that weakness of the anharmonicities still contributes to this narrow feature (5). As shown in Table 1, cubic anharmonic force constants of angles are not small. In special situations, however, these parameters cancel each other, and the overall effects may be greatly reduced. This occurs in the librational mode of α-boron. Figure 1 schematically illustrates how the mechanism works. For the librational mode, the icosahedral units rotate rigidly, and only those angles formed between the rhombohedral bond and the icosahedron vary. The deviations of the angles $\Delta\theta_i$ are almost equally distributed, both positively and negatively, around the rhombohedral bond. By summing up all the contributions, it can be seen that the cubic anharmonic terms, i.e., the mode Grüneisen constant $\Phi^{(3)}(q_1, q_2, q_3) \sim \gamma_i(\Delta\theta_i)^3$, are almost eliminated.

Selection rules determining which combinations of normal modes (q_1, q_2, q_3) are inhibited can be, in principle, predicted by the group-theoretical method, although this is laborious for higher-order phenomena. It should be noted that the range over which the present cancellation mechanism occurs is more than that predicted by the formal selection rules. It is found that many cubic terms associated with this narrow band are not inhibited by the selection rules.

For macroscopic phenomena, such as thermal expansion, the cancellation mechanism does not occur, because the signs of the changes in the bond lengths and angles are all

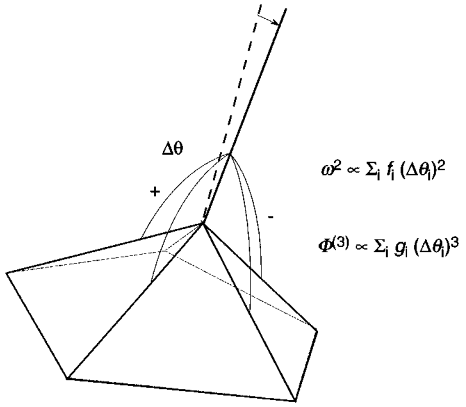

FIG. 1. Schematic illustration of the angles around a rhombohedral bond for the librational mode. The icosahedral unit is shown by the upper pentagonal pyramid only.

the same. Accordingly, it is reasonable that anharmonicities appearing in thermal data look very normal.

Optical Anharmonicities

In crude models of IR and Raman spectra, it is sometimes stated that second-order spectra reflect the DOS of phonons, by assuming weak dependence of the matrix elements on frequency. Actually, this is not the case for boron. As shown in Fig. 2, the higher-order spectrum is very different from the calculated two-phonon DOS. This means that the ω dependence of matrix elements is by no means weak. The matrix elements of higher-order optical spectra are composed of several types of anharmonicities, which sometime work cooperatively.

The prominent IR band appearing at 1100 cm^{-1} has been studied (17). The band is now ascribed to the second-order phonon absorption, but surprisingly the intensity is as large as that of the first order. According to the standard theory of anharmonicities (18), the second-order dielectric susceptibility $\chi^{(2)}(\omega)$ is composed of (a) one-phonon absorption including the effect of the self-energy, (b) two-phonon absorption, and (c) the interaction between the one- and two-phonon processes. Presently, it is found that process (b) is the dominant mechanism for the 1100-cm^{-1} band. In process (b), the matrix element is given by the dipole moment of the second order in atomic displacements, $M^{(2)}(q_1, q_2)$. $M^{(2)}(q_1, q_2)$ is given by the cross term between the effective charge of the first-order $Z^{(1)}$ and the displacement δR. The bond charge model (19) was used; two types of charges, $Z_{\parallel}$ and $Z_{\perp}$, are attached at the center of a rhombohedral bond.

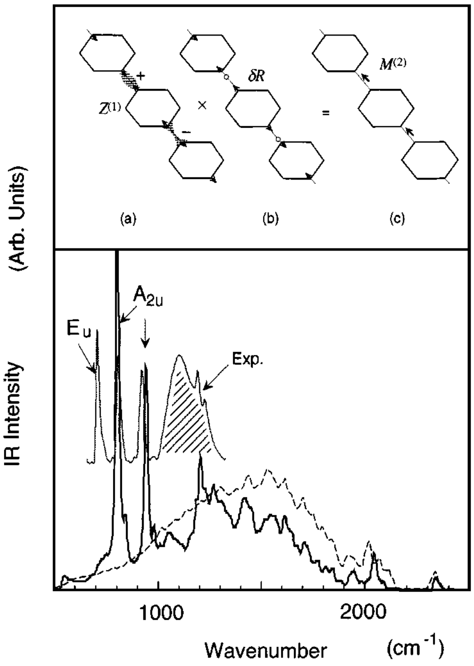

FIG. 2. IR spectrum of α-boron. The gray line indicates experimental results (16). Note that only a portion of the experiment is shown. The three sharp bands are of the first order (the symmetry is indicated). The dashed band indicates a higher-order absorption. The calculation for $\chi^{(2)}_{zz}(\omega)$ is represented by the solid line, and the two-phonon DOS $\rho_2(\omega)$ by the dashed line. The upper figure illustrates the origin of the strong intensity of the 1100-cm^{-1} band for (a) a symmetric mode at the zone boundary carrying the first-order effective charge $Z^{(1)}$, and (b) an antisymmetric mode at the zone boundary. The product of these two modes yields the second order of moment $M^{(2)}$ as shown in (c).

The present calculation reveals that the 1100-cm^{-1} band is due to the combination of symmetric and antisymmetric modes near the zone boundary (see the upper portion of Fig. 2). The symmetric mode carries a large effective charge $Z^{(1)}$, while the antisymmetric mode carries the alternative displacements δR_b among adjacent cells. The coupling of these two modes produces the same dipole moment over all cells. Hence, it is no wonder that this coupling yields an intensity as large as that of the first order.

V. BORON CARBIDES

The most difficult problems in boron-rich solids are concerns of boron carbides, $B_{1-x}C_x$. No simple model succeeds in explaining the variations in their properties over the C concentration $0.13 < x < 0.2$ (20–22). Even for a fundamental property, it is still in dispute as to whether the chain bond is stiff or soft. From the traditional understanding, the chain bond must be the strongest among various bonds in this compound. On the contrary, several experimental results contrary to this concept have been demonstrated, such as the thermal factors in structural data (20–22). A study was conducted on the electronic structure of boron carbides by the *ab initio* pseudopotential method to solve this problem. The potentials were from Troullier and Martins (23). The cutoff energy of the plane waves was about 44 Ry.

First, the various structures of boron carbides were studied. The results were basically the same as those of the study of Bylander and Kleinman (BK), who extensively studied this family of boron carbides (24). The BK results can be summarized as follows:

i. Among various modifications of this family, $B_{12}C_3$ is the most stable.

ii. For the composition of $B_{13}C_2$, the most stable structure is B_{12}(CBC).

iii. The chain bond is strongest among the various bonds of this compound.

Point (ii) disagrees with experimental results (20). It should be noted that conclusion (ii) is derived with rather restricted conditions. First, only disorders resulting from atom interchange were considered. Other types of disorder, such as the experimentally observed insertion of the B_4 unit (25), are not taken into account. A recent refinement of crystal structure reveals that a point defect is found at the center of the chain

(22). Second, a type of atom interchange in a cell is assumed to occur exactly in the same manner over the crystal, owing to the obvious restriction of treating the primitive cell. The present calculation is also subjected to the same restrictions.

Table 3 compares lattice parameters obtained experimentally and by calculation. There is good agreement between the experimental results and calculations for lattice parameters a_0 and α_{rh}. Cell size decreases with increasing C concentration x; the decrease in a_0 from $B_{13}C_2$ to $B_{12}C_3$ is 1.1% in the calculation and 0.7% in the experiment.

The present results, however, demonstrate an important difference from both experiment and BK calculation. This is the variation of bond length of the CBC chain. The present calculation finds that the bond length decreases by 3% as x increases from 0.13 to 0.2. From $B_{13}C_2$ to $B_{12}C_3$, a compositional change occurs only in the icosahedral units. Surprisingly, the largest change occurred for the bond length of the CBC chain. The association of $B_{11}C$ with the CBC chain is so strong, insertion of C into the icosahedral unit could probably affect the other part of the crystal. This contrasts with the experimental results, where the variation is only 0.5%. This discrepancy indicates that, in transformation from $B_{13}C_2$ to $B_{12}C_3$, the method of insertion of extra C atom is not as simple as successive replacement of a B site in the icosahedral unit with a C atom.

A fact supporting the traditional concept of a stiff chain is existence of the topmost band (at 1560 cm^{-1}) in the IR spectrum of boron carbides. Model calculations have attributed this band to an antisymmetric stretching vibration of the chain (2*d*). A weak chain bond could not yield such a high frequency. Presently, the vibrational spectra have been examined by use of the above *ab initio* calculations. The IR-active modes are compared with experimental results (28) in Fig. 3. The present vibration calculations only confirm the traditional interpretation that the chain bond is the strongest. Although the frequency of the topmost mode varies according to the C concentration, which reflects the large variation in the bond length of the chain, the attribution to an antisymmetric mode does not change. Accordingly, a serious gap between theory and experiment still remains as an unsolved problem.

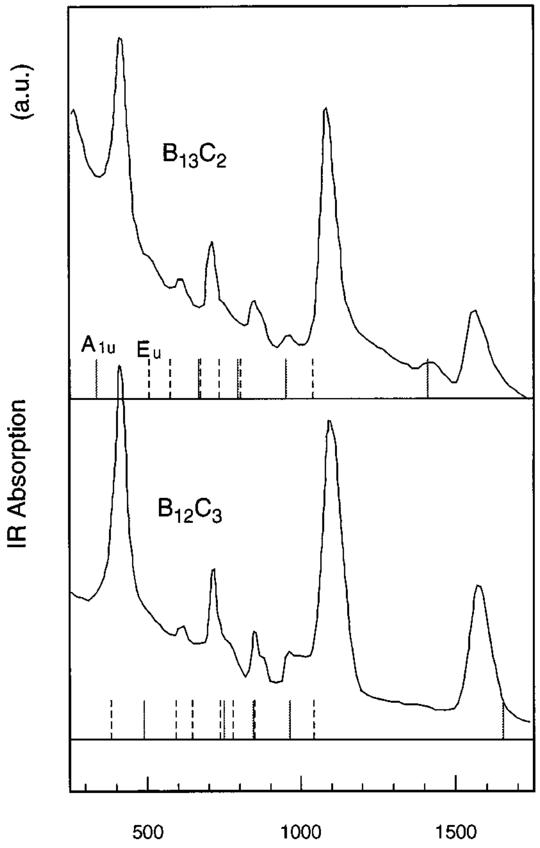

FIG. 3. IR spectra of boron carbides taken from experimental results (27). Calculated spectra are shown by the line spectra: A_{2u} (solid), E_u (dashed).

TABLE 3
Lattice Parameters (in the Rhombohedral System) of Boron Carbides[a]

		B_{12}(CBC)	B_{11}C(CBC)	Change (%)
a_0	Exp I	5.198	5.165	− 0.6
	Exp II	5.191	5.155	− 0.7
	BK	5.198	5.141	− 1.1
	Present	5.147	5.086	− 1.2
α_{rh}	Exp I	65.62	65.71	0.1
	Exp II	65.63	65.67	0.0
	BK	65.54	65.76	0.3
	Present	65.65	65.90	0.4
d_{ch}	Exp I	1.431	1.433	0.1
	Exp II	1.429	1.463	2.4
	BK	1.442	1.441	− 0.07
	Present	1.460	1.420	− 2.7

[a] Length is in units of Å, and the angle is degrees. The bond length of the chain d_{ch} is also listed. Experimental data I are taken from Larson (26) for $B_{12}C_3$, and Kirfel *et al.* (27) for $B_{13}C_2$. Experimental data II are taken from Kwei and Morosin (22). A large discrepancy in d_{ch} between two experimental results is due to the difference in the assumed models in the data analysis. Calculations are compared between the present results and Bylander and Kleinman (BK) (24).

By considering substantial complexities in the structures, one way to resolve this discrepancy might be further seeking different assignment by taking other crystal models into account. The authors, however, believe that the chain bond is originally stiff. Different aspects of the chain bond may then be observed depending on the experiment. To obtain a concrete mechanism, the following remarks related to the special geometry might be useful. First, even though the chain bond is strongest along the chain axis, this is not so for the perpendicular direction. The restoring force in this direction could be weaker than any of the other intraicosahedral bonds, due to the relatively small number of associated angles. Second, once the central boron atom in the chain is removed for some reason (e.g., by thermal agitation or electron excitation), the chain bond is no longer stiff. A recent structural refinement (22) discussed the evidence that some of the central boron atoms were displaced in a direction perpendicular to the axis. Unusual thermal factors in the structural analyses might allow for observation of the atoms after this displacement, while the topmost IR band indicates only one strong component in the restoring force of the original bond.

VI. SUMMARY

It has been demonstrated that geometrical effects play important roles in the properties of boron-rich solids and at some times resolve apparent contradictions between the basic concept of bonding and experimental results. For boron carbides, the problems are much more complicated. Although geometrical considerations are also useful for this compound, it might be worth leaning on the results of a recent study on the defects in semiconductors; strong covalent bonds are not always strong. A strong bonding state could be converted to a strong antibonding state if electrons are doped (29). Further study on this problem is in progress.

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