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Lattice vibrations and the bonding nature of boron carbide

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Abstract. The vibrations of boron carbide $B_{13}C_2$ have been studied by the valence force model. There have been so far several ambiguities in the interpretation of experimental spectra, which made theoretical study difficult. This paper solves the main difficulties, that is, characterization of the highest 1560 cm^{-1} band and most of the Raman bands, providing reasonable interpretations for low-frequency modes. The 1560 cm^{-1} band is ascribed to the anti-symmetric stretching of the linear chain. The necessity of large angle-bending forces of carbon atom arose for better fitting, which fact can be regarded as evidence for formation of strong covalent bonds around this atom. The present analysis also throws a new light on the Longuet-Higgins interpretation of the role of carbon incorporation. The coexistence of the strong covalent bonds of carbon atoms and the relatively weak icosahedral bonds results in such a balance of bonding that the intra-icosahedral and rhombohedral bonds are further weakened, and the covalent bonds of the carbon chain are instead reinforced.

1. Introduction

Boron crystals have several polymorphic modifications having the icosahedral unit in their crystal structures. Boron carbide ($B_{12}C_3$ or $B_{13}C_2$) is the most stable one in this family, and has interesting properties [1]. The crystal structure of the stoichiometric $B_{13}C_2$ is depicted in figure 1. The proceedings of recent conferences on boron-rich solids are abundant sources for the study of this material [2–5]. In the case of other boron modifications of α-rhombohedral type, although these are less stable, the vibration spectra have been well analysed both experimentally and theoretically. For boron carbide, there are difficulties in the interpretation of experimental data. The following issues are the chief ambiguities in the experimental data which make things more complicated.

(i) The crystal structure is not so simple as predicted before. Recent structural study shows that the main diagonal chain is composed of C–B–C, and an extra carbon atom may substitute a boron atom in the B_{12} unit [6–9]. This leads to symmetry breaking and renders the selection rule useless.

(ii) The highest band at 1560 cm^{-1}, which appears both in IR and Raman spectra, has been a controversial issue for a long time, as to whether it is a true phonon band of the crystal [10–17]. It was reported that the band disappeared from the Raman spectra when good-quality specimens were used [15]. From this observation, this band was believed to be due to C inclusion. In IR spectra, in contrast, it seems indisputable that it is a true crystal mode. The polarization characteristics [11] and the isotope effect [14] are definite evidence.

(iii) Raman spectra of boron carbides have recently been subject to re-investigation by Werheit's group [18, 19]. They showed Raman spectra very different from those obtained by traditional methods. They insist that the traditional methods disturb the electronic states considerably, and accordingly the spectra so obtained do not reflect the true phonon bands.

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In addition to these ambiguities, there is a fundamental question.

(iv) Among α-type boron modifications, boron carbide is the most stable and hardest one, while pure α-boron is the most unstable one. Qualitatively, we can easily expect that the phonon frequency increases as the material becomes harder unless other conditions change significantly. Experimental Raman spectra of boron-rich crystals contradict this simple prediction [16]. The crystal of α-boron has the highest-frequency Raman band. What causes this situation?

For these reasons, study of the vibrations of boron carbide is a challenging subject.

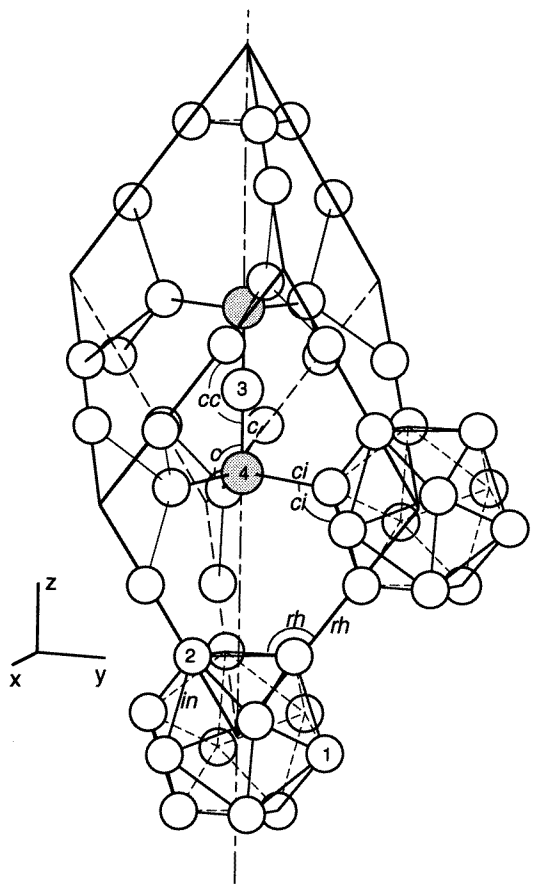

Figure 1. The crystal structure of the stoichiometric compound $B_{13}C_2$. Grey spheres represent carbon atoms. The boron site 1 is customarily called the equatorial site, whereas site 2 is called the rhombohedral site. Also are shown the names of bonding types.

Fortunately, the problem (i) seems not to be important in the present study. We will discuss only the stoichiometric compound $B_{13}C_2$. Even for the stoichiometric compound, there is a complexity in that alternation in the chain structure may occur [20]. Detailed experiments show, however, that the variation of the C fraction does not influence the frequency significantly [12, 14]. We can thus treat as a representative the vibrations of the stoichiometric compound $B_{13}C_2$ having complete D_{3d} symmetry without causing much

error. On this assumption, the usual group-theoretic analysis becomes effective, giving the following decomposition:

$$5A_{1g} + 2A_{1u} + 2A_{2g} + 6A_{2u} + 7E_g + 8E_u. \quad (1)$$

There are 12 distinct modes for Raman and 12 distinct modes for IR spectra. The chief aims of this paper are to dispel the ambiguities (ii) and (iv), and hopefully to give useful insight into the problem (iii). Frequently use is made of the calculations on α-boron [21–23], and a preliminary calculation of boron carbides by Beckel's group [24]. [24] is particularly important, although only a short note.

2. Estimation of the force constants

Experimental data for IR and Raman spectra are listed in table 1, along with the symmetry type if available. The numeric values are the ones which the present authors read off from the original figures cited there. As to Raman data, a serious problem is involved, as mentioned in (iii). In the present paper, we note this, but we do not discuss this problem at the present level of study. Here, we refer to the Raman data obtained by a traditional method [16]. One of the present authors (SE) also obtained a spectrum basically the same as those of traditional methods. As mentioned before, optical spectra do not vary significantly with the C fraction from $B_{13}C_2$ to $B_{12}C_3$. An exception occurs for the low-frequency part of the Raman spectra [16]. The intensity of sharp bands at 485 and 527 cm^{-1} increases significantly with increasing C fraction. In addition, the frequencies of the librational modes are decreased, and a new feature appears at 270 cm^{-1}. The data listed in table 1 are the spectrum of the compound $B_{13}C_2$.

The valence force model is used in this study. The bond-stretching forces are denoted by f_r, while the angle-bending forces are denoted by f_a, with the appropriate superscripts referring to the type of bond or angle. In figure 1 are shown the locations of various types of bond and angle.

We did not attempt an exhaustive survey for the best fitting. Rather, we scanned a realistic range of the parameters on physical grounds. The force constants can be calculated from the more fundamental viewpoint, the electronic structure. The first-principles calculation is usually carried out in a rather limited situation, such as a small cluster, and, of further importance, it depends critically on the electronic configuration of the ground state. There is thus no *a priori* reason why the first-principles calculation is more reliable than the parameter fitting. The first-principles calculation has in any case a great value, if available. Beckel's group carried this out for boron carbides [24, 25]; this is a useful source for reference.

A simple rule for the force constant of the bond stretching is that it decreases as the bond length is increased. In table 2, we list the inter-atomic distances for boron carbides, compared with α-boron [8, 26]. The force constants for α-boron obtained by Beckel's group are also listed [21]. By referring these data, we will discuss the force constants of boron carbides.

2.1. Linear chain modes

First of all, we notice that the bond length of the chain is the shortest one, so a large bond stretching force can be expected. As an extreme, we can regard the chain as a linear XY_2 molecule which is isolated from its surroundings. This molecule has the highest odd mode (IR active) with frequency ω_{odd} and an even mode (Raman-active) with frequency ω_{even}.

Table 1. A comparison of calculated frequencies to experimental data of boron carbide, $B_{13}C_2$. The frequencies are given in cm^{-1}. The experimental intensity is evaluated qualitatively by the following notations: ss, sharp and strong; sw, sharp but weak; m, middle; w, weak; b, broad. In the calculation, Raman-active modes of A_{1g} and E_g are listed in the same column, but the former type is denoted by (z). The predominant motions are also described, if possible. The last row lists the parameters used. The abbreviations are used as follows: sy, symmetric; a, anti-symmetric; st, stretching; be, bending; rot, rotation; tr, translation; ico, icosahedron; ch, chain.

Experiment					Calculation						
Raman [16]		IR[a]			Raman			A_{2u}		E_u	
1060	ss	1560	A_{2u}	s	(z)	1078	breathing	1575	a-st-ch		
1039	w	1418		b		1016	rot-ch+st-ico				
998	m	1076	E_u	s		1004				1041	a-st-ico+be-ch
938	w	1004		w	(z)	964	sy-st-ch				
845		951		s	(z)	828					
813	b	875		w		692					
780		846	A_{2u}	s		655		772		748	
721	s	744		w	(z)	589		738			
527	sw	697		s		551	no ch				
485	sw	608	E_u		(z)	546	no ch	673		690	
374	m	506		w		335	rot-ch+wag-ico			487	be-ch
330	w	407	E_u	s						434	
168	b					172	rot-ico			393	no ch
								268	tr-ch	314	a-ico+tr-ch
					Optically inactive			A_{1u}		A_{2g}	
								740		529	
								380	twist-ico	166	rot-ico
					force constants: f_r (mdyn Å^{-1}), f_a (mdyn Å)						
					$f_r^{in} = 1.1$			$f_a^{in} = -0.1$		$f_a^{cc} = 0.5$	
					$f_r^{rh} = 2.4$			$f_a^{rh} = 0.02$			
					$f_r^{c} = 5.4$			$f_a^{c} = 0.3$			
					$f_r^{ci} = 2.3$			$f_a^{ci} = 0.05$			

[a] The frequencies are read off from [12]. The assignment of symmetry follows [11].

The ratio of $\omega_{odd}/\omega_{even} = [1 + 2(M_Y/M_X)]^{1/2} = 1.79$ is close to the ratio of the highest IR mode to the highest Raman mode, if we disregard the possibility that the Raman band at 1560 cm^{-1} is a true crystal mode. Werheit pointed out that the IR band exhibits the polarization characteristic that the electric field is parallel to the crystal c-axis [27]. From these facts, it is reasonable to ascribe the 1560 cm^{-1} band to a true lattice mode with IR activity only, whose symmetry belongs to A_{2u}.

If we seek the origin of the 1560 cm^{-1} band in another part, such as the chain–icosahedron bond, higher Raman bands would be associated with the highest IR band. The strong chain bond is able to exclusively bring about such a situation that only the 1560 cm^{-1} band is singled out from the others. The entity of the 1560 cm^{-1} is thus definitely the anti-symmetric stretching of the linear chain. The stretching force f_r^c is determined to be 5.4 mdyn Å^{-1}, in order to fit the frequency.

Table 2. The bond lengths of boron carbide and α-rhombohedral boron in ångströms. For α-boron, the appropriate values of the central forces f_r are quoted in millidynes per ångström.

Type of bond		$B_{13}C_2$	α-boron	
				f_r
Intra-icosa.	B(1)–B(1)	1.773	1.78	
	B(2)–B(2)	1.821	1.73	1.3
	B(1)–B(2)	1.796	1.79	
		1.807	1.79	
Inter-icosa.	B(2)–B(2)′	1.732	1.71	3.0
Three-centre	B(1)–B(1)′	2.756	2.03	1.0
Chain	C(4)–B(3)	1.429		
Chain–icosa.	B(1)–C(4)	1.617		
Refs		[8]	[26]	[21]

2.2. Intra-icosahedral modes

In the α-boron case, vibrations from 500 to 1000 cm^{-1} are ascribed to the intra-icosahedral vibrations [21, 23]. The highest vibrations near 1100 cm^{-1} are ascribed to inter-icosahedral vibrations. The fact that the inter-icosahedral vibration is higher than any intra-icosahedral vibration is evidence that this crystal is not a molecular crystal, which is well known in the physics of boron solids.

We can easily expect similar situation for other boron modifications. The inter-icosahedral vibrations appear around 1000 cm^{-1}, and below this band the intra-icosahedral vibrations appear. In the series of modifications, α-boron, $B_{12}As_2$ (or $A_{12}P_2$), and boron carbide (in this order the crystal becomes harder), this crude classification is valid. However, the frequencies of most of the Raman bands are decreased as the crystal becomes harder [15, 16]. This indicates that the intra- and inter-icosahedral bondings become weaker as the crystal becomes harder. Actually, the lengths of the intra- and inter-icosahedral bonds increase in this order in the crystals [9]. Accordingly, it is reasonable to assume small force constants f_r^{in} and f_r^{rh} for boron carbides, compared with those of α-boron. Beckel's prediction clearly shows this trend [24].

For a numerical estimation, the highest A_{1g} mode is used to determine the two forces f_r^{in} and f_r^{rh}, because this mode is the uniform breathing mode and the frequency is dominated by these two forces. Experimentally, there is no explicit record to show the symmetry of the highest Raman band at 1060 cm^{-1}. However, it is almost certain from a study of other boron modifications that the A_{1g} mode is the highest Raman mode. The force constants are then determined as $f_r^{in} = 1.0$ and $f_r^{rh} = 2.2$ mdyn Å^{-1}.

It is interesting to see the effect of the angle-bending forces on the intra-icosahedral vibrations. If only the stretching forces f_r^{in} and f_r^{rh} are used, the frequencies of the intra-icosahedral vibrations which are Raman active fall into a range from 570 to 1060 cm^{-1}. The effect of introducing the angle-bending force f_a^{in} is a change in frequency more appreciable for low-frequency modes than for high-frequency modes. Introducing any positive f_a^{in} would, therefore, cause the range of the intra-icosahedral vibrations to be narrowed. The experimental range is rather wider; the lower bound is around 500 cm^{-1}. A negative f_a^{in} is suggested. Negative force constants are not abnormal in crystals. It is permissible as long as the dynamic matrix is positive definite. Born and Huang show a form of potential which gives a negative value even for the central force constant [28]. A negative value is

particularly expected for non-central forces of polyhedral molecules, for the same reason as the Jahn–Teller effect is expected for those molecules. The Jahn–Teller type distortion contributes a negative adiabatic potential near the equilibrium position, and the potential easily exhibits a negative curvature. A simple calculation gives a negative value for the angle-bending force for an icosahedral molecule [29].

Another way to obtain a wide range of intra-icosahedral vibrations is to reduce f_r^{in}, while retaining the highest Raman band at 1060 cm^{-1}. In this case, the spectrum of the intra-icosahedral vibrations clearly becomes split: the one group lies from 900 to 1000 cm^{-1} and the other group from 450 to 580 cm^{-1}. Experimentally observed Raman bands are distributed rather uniformly over the above range. This way is thus not appropriate. Accordingly, introducing a negative f_a^{in} is preferred. A negative value -0.1 mdyn Å is temporary deduced for f_a^{in}. Before, this non-central force was estimated to be very large [30], because the three-centre bond was expected to have some angle-dependent character. Beckel's group found this force to be small on the basis of the Raman data [21]. Now, we find that even a negative value is plausible.

2.3. Librational modes

The lowest frequency modes are the libration modes, which originate from free rotations of molecular units. Angle-bending forces dominate the frequency.

In the present problem, there are two types of rotation, and correspondingly two libration modes are expected. One is a rotation of the icosahedron, and the other is of the linear chain. Both rotations about the x- and y-axes exhibit Raman activity. There are three Raman bands observed at low frequencies (see table 1). The 330 cm^{-1} band is very weak for $B_{13}C_2$ and the frequency is appreciably decreased to 270 cm^{-1} as the C fraction increases until the composition $B_{12}C_3$ [16]. This band may be the same type of mode as the 374 cm^{-1} mode, but be modified by a structural disorder introduced by extra carbon atoms.

The lowest one, which is experimentally observed at 168 cm^{-1}, corresponds to a rotation of the icosahedron, analogous to the other α-type modifications. The frequency is dominated by f_a^{rh}. From the experimental data, we obtain $f_a^{rh} = 0.02$ mdyn Å. The other, at 330 cm^{-1}, corresponds to a rotation of the chain, and the frequency is greatly influenced by both f_a^c and f_a^{ci}. Of these two, f_a^{ci} has great influence on both rotations of the icosahedron and of the chain. If f_a^{ci} is increased, the two bands approach each other. Good separation of the two libration modes (168 and 330 cm^{-1}) suggests that f_a^c is the dominant mechanism for the 330 cm^{-1} band. In order to fit with experiment, $f_a^c = 0.3$ and $f_a^{ci} = 0.05$ mdyn Å are deduced. This relatively large value for f_a^c is not surprising. The bonding of the central linear C–B–C chain is characterized by a strong covalent bonding. Covalent bonds have highly oriented bonding, and have a large resistance against the derivation in the orientation of bonds. Actually, semiconductors have relatively large non-central forces.

A relationship, $f_a^{rh} < f_a^{ci} < f_a^c$, is also reasonable, in the regard that the covalency of the bonds is increased in this order. The presence of f_a^c is of particular importance for the elasticity of the boron carbide crystal. In the absence of this force, the crystal would be unstable for shear strain. We will discuss this issue in a forthcoming paper [31].

By using the force constants discussed so far all together, with a slight adjustment, we obtain a frequency spectrum of zone-centre modes of $B_{13}C_2$. The result is shown in table 1. A short description of vibrational characteristics is noted for some modes. Concrete pictures for important modes are displayed in a companion paper [32]. Comparison to the experiments is also made in figure 2, with the actual spectra duplicated from the original papers.

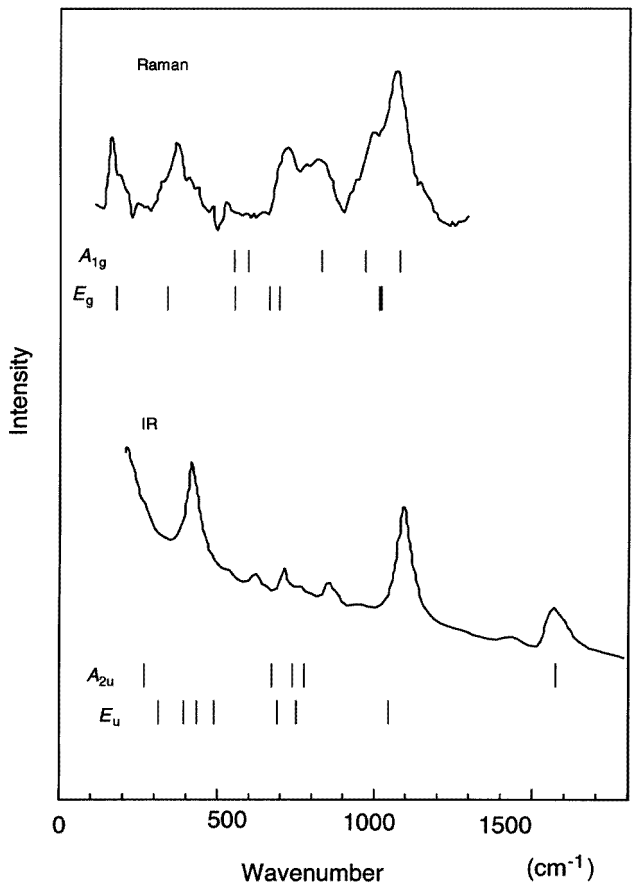

Figure 2. A comparison of the calculated line spectrum to Raman and IR spectra. The experimental data are duplicated from [16] (Raman) and [12] (IR).

3. Discussion

Let us check the calculation with the Raman data. The main features of the Raman bands are well reproduced in the calculation. For the lowest intra-icosahedral vibrations, the frequency is computed to be 546 cm^{-1}, which is much higher than the lower bound, 485 cm^{-1}, in the experiment. The experimental 527 and 485 cm^{-1} bands are very similar in the fact that the band widths are exceptionally narrow compared with other bands [16]. The intensity of the 527 cm^{-1} band is relatively decreased as the C fraction increases, and, conversely, the 485 cm^{-1} band is increased. From this observation, it seems that both bands have the same origin and only the 527 cm^{-1} band survives in the perfect stoichiometric limit $B_{13}C_2$. If this is the case, the lower bound of the intra-icosahedral vibrations must be 527 cm^{-1}, which is close to the calculation. The 527 cm^{-1} mode has almost no contribution from the linear chain. Accordingly, the change in the frequency with increasing C content may be caused by the substitution of a boron at the rhombohedral site with a carbon.

The same situation seems to occur for the experimental 330 and 374 cm^{-1} bands, as discussed in the preceding section. The 330 cm^{-1} band may be a version of the 374 cm^{-1} band modified by a structural disorder. The calculated 325 cm^{-1} band is characterized by

a rotation of the chain associated with a wagging icosahedron. The frequency must be sensitive to the structural disorder at the end site of the chain but not at the centre site, because of the symmetric motion. When phosphorus is doped into the boron carbide, it is observed that the broad Raman bands around 300 cm^{-1} are greatly influenced [33]. This fact is reasonable, provided a phosphorus atom is placed at the end site of the chain. The remaining part of the rotation of the chain appears at a higher mode at 1007 cm^{-1}.

Next, let look at the IR bands. In the final calculation, we further added the angle-bending force of the linear chain f_a^{cc}, which is expected to be large because of the strong covalent character of this bond. Profound effects of this force appear exclusively for E_u modes, in particular for the lowest mode.

Since, as can be seen, most of the calculated E_u modes at low frequencies are lower than experiment, introducing f_a^{cc} is favourable. The lowest E_u mode is mainly due to the bending motion of the linear chain, when f_a^{cc} is very small. In the case of a linear chain molecule XY_2, the bending motion could have a high frequency above 400 cm^{-1}, as pointed out by Werheit *et al* [13]. This would be correct only if the chain were isolated from the surroundings. What happens in the crystal is different in the fact that the stiff chain is connected to rather soft icosahedral units, so that the bending motion is relaxed more or less by the deformation of icosahedra. In this case, several lowest modes are mixed, and the f_a^{cc} alone does not help to raise the low-frequency IR modes. In this way, three IR-active modes are predicted to reside below 400 cm^{-1}, where no IR band is discernible in the experiment.

At this stage, it is important to notice that, although the rotations and bending motions of the chain alone have low-frequency character, these chain motions are actually mixed with icosahedral motions, and their influence appears even in the high-frequency region around 1000 cm^{-1}.

Experimentally, two or more IR bands are identified in a range from 800 to 1000 cm^{-1}. In particular, the 846 cm^{-1} band is clear. There is, however, no prediction of the calculation in this range. Instead, in the calculation, there are many E_u modes around 750 cm^{-1}. If we want to raise the relatively low-frequency E_u modes, there are two possibilities within our present treatment. The one is to raise f_r^{in}. In this case, while the E_u modes are raised, the other undesirable effect of this manipulation is to raise the highest inter-icosahedral vibrations of both Raman and IR bands considerably, which spoils the agreement with the experiment. The other way is use of a positive f_a^{in}. Here is a disadvantage of use of a negative f_a^{in}, say, the decrease in the frequencies of the IR bands in the intermediate-frequency range. However, even if we use a positive value, say $f_a^{in} = +0.1$ mdyn Å, the increase of the frequencies is at most 40 cm^{-1} for the bands concerned, and hence the difficulty cannot be removed. Hence, there seems to be no way to solve the discrepancy in the intermediate-frequency IR bands within the present treatment.

In this respect, it might be nothing but fortuitous that the number of IR-active modes in the present reading is coincident with the group-theoretical prediction, that is, 12 in all. This coincidence does not guarantee at all that all the frequencies read off are correct, nor that these are first-order absorptions. In the α-boron case, broad but intense IR bands above 1000 cm^{-1} are now understood as due to higher-order absorption [21, 23]. Furthermore, even in the well studied α-boron case, agreement between the calculation and experiment is poor for the IR-active modes. The primary difficulty may lie in the effect of the Coulomb interaction on the IR-active modes. In the presence of the Coulomb interaction, the number of polar vibrations does not agree with the group-theoretical prediction [34]. The Coulomb interaction lifts degenerate polar vibrations, and modifies the frequency. This effect of the Coulomb interaction for α-boron was studied by the shell model [23]. The prediction

by the shell model is quantitatively too small to account for the experimental intensity of absorption, assuming the non-central forces to be small. It has recently been demonstrated that this large discrepancy is greatly improved by the adiabatic bond-charge model [35]. This was shown for an isolated icosahedron only, but the effect is reasonably expected for the crystal. It is plausible that the effect is larger in boron carbides than in α-boron because different types of atoms are involved.

Lastly, it is worth mentioning the general trend found in the vibrations among α-type modifications. Since Longuet-Higgins successfully explained the bonding nature of the icosahedral boron solids [36], it has been believed that the chief role of the carbon incorporation in boron crystal is simply doping; a free B_{12} unit is deficient in electrons to form the covalent bond, which urges it to form the three-centre bonds instead. The carbon incorporation supplies an electron for each three-centre bond and replaces it with covalent chain–icosahedron bonds. From this, it is easily expected that the carbon incorporation stabilizes the icosahedral bonding, but the present study shows that this role of the carbon atom is subtle. Rather, incorporation of the carbon atom seems to reinforce the covalent bonds in the linear chain itself at a cost of weakened icosahedral bonding. In fact, the icosahedra are further deformed when α-boron is transferred to $B_{13}C_2$, as shown in table 2. In contrast, the bond length of the chain is shorter than the average C–B bond length (1.56 Å) found in organic compounds, but is close to the double bond [8].

It is interesting that the insertion of the covalent bond in this way weakens not only the weak intra-icosahedral bonds but also the relatively strong rhombohedral bonds. The rhombohedral bond, which is basically characterized as a covalent bond, originates from the a_g (sp hybrid) orbital of the regular icosahedral molecule, with a slight modification by the t_{1u} (sp^2 hybrid) orbital [29, 36]. It is thus plausible that this bond is weaker than the covalent bond of carbon atom, which is based on sp^3 hybridization. In the case where the two types of covalent bond happen to meet each other, it is reasonable that the electron distribution is so re-arranged that the stronger one overcomes the other.

4. Conclusions

The vibrations of the stoichiometric compound $B_{13}C_2$ have been studied by means of the valence force model. Regarding the stretching forces, the prediction of Beckel's group by the first-principles calculation is correct overall.

As to problem (ii), a conclusion is drawn that the 1560 cm^{-1} band is a true crystal mode, which is IR active but not Raman active. This mode is ascribed to the anti-symmetric stretching of the linear chain.

As to problem (iv), the trend is found in this family of crystals that lowering of the highest Raman frequency does not imply softening of the crystal at all, but is rather a sign that the crystal loses the character of icosahedral bonding.

The effects of non-central forces have been revealed. From the range of the intra-icosahedral vibrations, a negative value is suggested for the intra-icosahedral angle-bending force f_a^{in}, which implies an electronic instability of the icosahedral structure. The angle-bending forces of the linear chain f_a^c and f_a^{ci} are found to be relatively large. This is reasonable in the regard that the covalent bond has a large angle-bending force. It will be seen that the fact is essential for the elastic stability of the crystal.

For the IR bands, beside the highest band, it seems that the calculated bands are lower than the experimental bands as a whole. Within the present model of the valence force, it is difficult to solve this discrepancy. Taking the Coulomb effect into account may solve this difficulty, and a study along this line is hoped for.

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