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Lattice Vibrations of Boron Carbide

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The vibrations of boron carbide $B_{13}C_2$ have been studied by the valence force model. The 1560-cm^{-1} band is ascribed to the antisymetric stretching of the linear chain, and thereby it is IR active only. Large angle-bending forces of the carbon atoms are estimated to agree with the experiment. This conclusion is reasonable, by considering the strong covalent character of the linear chain. At the cost of forming strong covalent bonds in the linear chain, the character of icosahedral bonding is weakened. The decrease in most Raman bands of boron carbides compared with those of α-boron can be understood on this basis. © 1997 **Academic Press**

I. INTRODUCTION

Calculation of the lattice vibrations of boron carbides is a stimulative issue in physics of boron-rich solids. For other boron modifications of α-rhombohedral type, although less stable, the vibration spectra have been well analyzed both experimentally and theoretically. For boron carbide, there are difficulties in the interpretation of experimental data. Recently, we have studied theoretically the spectra of a boron carbide, $B_{13}C_2$, by assuming a strict order C–B–C for the chain and no substitution of the C atom in the icosahedra (1). The qualitative results well describe the experimental spectra. For full explanation, Ref. (1) should be referred to. The purpose of this paper is to give further supplemental information by illustrating the atomic displacements, which will help to interpret the calculation result. There are difficulties in the interpretation of spectra of boron carbide as summarized in Ref. (1). Out of these listed, two are especially worth mentioning again.

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

(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 becomes high as the material goes harder unless other conditions change significantly. Experimental Raman spectra of boron-rich crystals are opposite to this simple prediction. The crystal of α-boron has the highest frequency Raman band. What makes the situation opposite to the simple prediction?

In the following, we assume the stoichiometric compound $B_{13}C_2$ having complete D_{3d} symmetry. Then, the vibrations are classified as $5A_{1g} + 2A_{1u} + 2A_{2g} + 6A_{2u} + 7E_g + 8E_u$. There are 12 distinct modes for Raman and 12 distinct modes for IR spectra.

II. COMPUTATIONAL RESULTS

First, we summarize the main results of Ref. (1). The valence force model is used. The bond-stretching forces are denoted by f_r, while the angle-bending forces are denoted by f_a. For further notations, Ref. (1) should be referred to. The calculated frequencies are listed in Table 1, compared with experimental data of IR and Raman spectra (2, 3).

We should emphasize the significance of these parameters, that these are not merely giving better fitting, but are reasonable on the physical ground. The interpretation given in Ref. (1) is consistent with the result of a first-principle calculation (4, 5).

The strongest force is the bond stretching force of the linear chain f_r^c. The antisymmetric vibration of the linear chain is responsible for the 1560 cm^{-1} band, and thereby it is IR-active only. Accordingly, the observation of a Raman band at this frequency for some specimens must be ascribed due to a disorder: substitution of a carbon in the chain with a boron atom or a domain of carbon inclusion. If we replace the original linear chain C–B–C with a C–B–B chain, and if we assume the force constant unchanged, the frequency is changed from 1563 to 1577 cm^{-1}. The change in the frequency is not significant, but the selection rule for optical activity will be abruptly changed.

The next strongest force is the rhombohedral stretching force f_r^{rh}. Compared to α-boron, we can see that this force is decreased from 3.0 for α-boron to 2.4 (mdyn/Å) for $B_{13}C_2$.

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TABLE 1
Comparison of Calculated Frequencies to Experimental Data of Boron Carbide, $B_{13}C_2$

Experiment					Calculation						
Raman[a]		IR[b]			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 +				
998	m	1076	E_u	s		1004	st-ico			1041	a-st-ico +
938	w	1004		w	(z)	964	sy-st-ch				be-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 +			487	be-ch
330	w	407	E_u	s			wag-ico			434	
168	b					172	rot-ico			393	no ch
								268	tr-ch	314	a-ico +
											tr-ch

optical-inactive	A_{1u}		A_{2g}	
	740		529	
	380	twist-ico	166	rot-ico

Force constants: f_r (mdyn/Å), f_a (mydn Å)

$f_r^{in} = 1.1$ $f_a^{in} = -0.1$ $f_a^{cc} = 0.5$
$f_r^{rh} = 2.4$ $f_a^{rh} = 0.02$
$f_r^{c} = 5.4$ $f_a^{c} = 0.3$
$f_r^{ci} = 2.3$ $f_a^{ci} = 0.05$

Note. The frequencies are given in cm^{-1}. The experimental intensity is evaluated qualitatively by notations (ss) sharp and strong, (sw) sharp but weak, (m) middle, (w) weak, and (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 used parameters. The abbreviations used are as follows: sy (symmetric), a (anti-symmetric), st (stretching), be (bending), rot (rotation), tr (translation) ico (icosahedron), and ch (chain).

[a] D. R. Tallant, T. L. Aselage, A. N. Campbell, and D. Emin, *Phys. Rev. B* **40,** 5649 (1989).

[b] The frequencies are read off from H. Werheit and H. Haupt. *in* "Boron-Rich Solids," AIP Conf. Proc. 231, pp. 355–359. Am. Inst. of Phys., New York, 1991. The assignment of symmetry follows H. Binnenbruck and H. Werheit, *Z. Naturforsch. A* **34,** 787 (1979).

For the intraicosahedral force f_r^{in}, a similar decrease in the force constant is also observed. This decrease is interpreted as the weakening of the icosahedral bonding by changing the crystal structure from α-boron to boron carbide. The decrease in the icosahedral bonding is reasonable, in view of the structural change. The bond lengths in both intra- and intericosahedral bonds are increased in boron carbide, compared to α-boron (see Table II in Ref. 1). A first-principle calculation by Beckel *et al.* also predicts this decrease in the force constants (5). Now, it is clear that the icosahedron is further deformed in boron carbide.

The range of the frequency of the intraicosahedral vibrations reflects the contribution of the angle-bending force of intraicosahedral bonds f_a^{in}. The fact that the experimental range is wider than expected implies a negative f_a^{in}. It is found that the negative force constant is plausible on the ground of the electronic instability of polyhedral molecules (6).

The angle-bending forces of the intraicosahedral bonds have been determined by two librational modes (168 and 330 cm^{-1}). A relationship, $f_a^{rh} < f_a^{ci} < f_a^{c} < f_a^{cc}$, is deduced. This relationship is reasonable, considering 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 (7).

In the remaining part of this paper, we will see the characteristics of individual vibrations. Some of the Raman-active and IR-active vibrations are depicted in Figs. 1 and 2, respectively. These have significant meaning in the procedure of the determination of the force constants and in interpretation of the spectra.

Let us first look at the Raman-active 546-cm^{-1} band (A_{1g}). Around this frequency, two Raman bands are observed experimentally at 527 and 485 cm^{-1}, which have very narrow widths. Such exceptionally narrow bands are

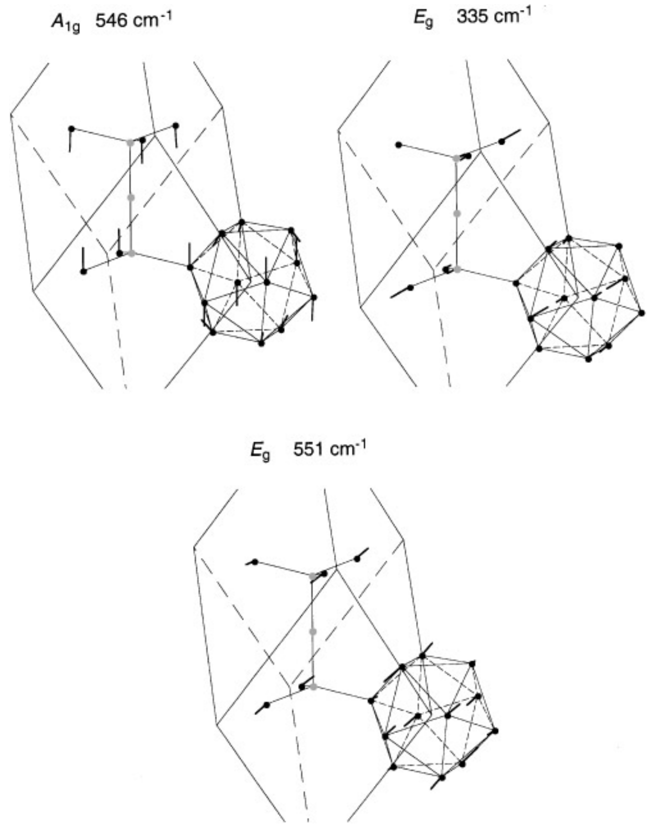

FIG. 1. Raman-active vibrations.

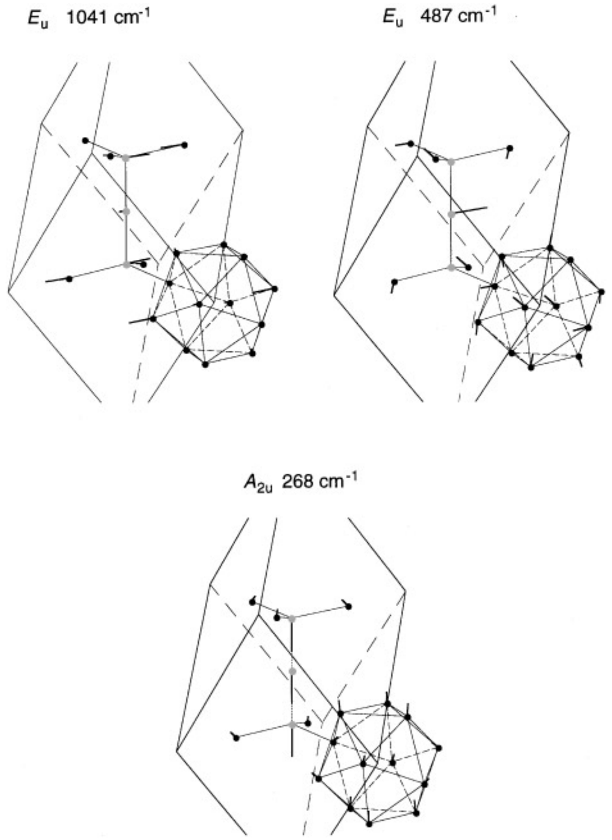

FIG. 2. IR-active vibrations.

observed in common in α-boron modifications, but the origin is open to question. For α-boron, it is doubted that the narrow line observed at 527 cm^{-1} is due to a true phonon excitation, because of unusual polarization characteristics and disagreement with a calculation (2) For $B_{13}C_2$, in contrast, one of the two narrow lines is close to the calculation, and hence we are convinced that the higher one is due to a phonon excitation. The lower one may be the same type of vibration as the higher one but it is modified by introducing disorder.

In considering why this mode has a narrow width, it is useful to see the displacements of individual atoms. As seen in Fig. 1, for the 546-cm^{-1} band, there is no contribution from the linear chain. If we assume that the structural disorder which causes broadening of the Raman bands is that of the linear chain, it would be reasonable that the 546-cm^{-1} band has a narrow width because of its chain-free motion (this interpretation was made in Ref. 2). If this interpretation is true, this mechanism of narrowing could not apply to α-boron. Another calculated mode at 551 cm^{-1} (E_g), which is close to the 546-cm^{-1} mode, has a similar character in that there is no chain motion. From this, one could regard this mode as the other narrow band experimentally observed. But, in this case, the substitution of a boron at the terminal site of the linear chain is able to influence the frequency through a change in f_r^{ci}, because some of the chain–icosahedron bonds are changed in the bond length.

The calculated 335-cm^{-1} band (E_g) is characterized by a rotation of the chain associated with a wagging icosahedron. From this, it may be seen that the frequency must be sensitive to the structural disorder at the end site of the chain but not at the center site, because of the symmetric motion. Experimentally, a change in the frequency of this mode was observed by phosphorus incorporation (8). This change can be understood as substitution at the terminal site of the linear chain.

It is noted that the rotation of the chain appears even for a higher mode at 1007 cm^{-1}, despite that the frequency of rotation itself is low. This is also true for the bending motion of the linear chain, which appears in the IR-active 1041-cm^{-1} mode, as shown in Fig. 2. In this way, the intra-icosahedral vibrations with high frequencies have the component of the chain motions of low frequencies. Hence, it is not surprising that even high-frequency intraicosahedral vibrations show influence of the C motion in the linear chain. The C-isotope effects on these high-frequency modes show this correlation (9, 10).

Next, let us look at the IR bands (Fig. 2). As mentioned before, the bending motion of the linear chain appears at a rather high frequency (1041 cm^{-1}), while the lower E_u 487-cm^{-1} mode has only a little component of this bending motion. This is because the stiff chain is connected to rather soft icosahedral units. A consequence of this is that the bending motion is relaxed by the deformation of icosahedra for the low-frequency mode at 487 cm^{-1}. The lowest A_{2u} mode at 268 cm^{-1} is a combination of nearly rigid translational motions of the chain and the icosahedra with opposite phases. But, no IR band is observed in the experiment.

As for α-boron, agreement with the experimental IR bands is not good for boron carbide. The primary difficulty may lie in the effect of the Coulomb interaction on the IR-active modes (11). Taking the Coulomb effect into account may be necessary.

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