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# On surface Raman scattering and luminescence radiation in boron carbide

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## Abstract

The discrepancy between Raman spectra of boron carbide obtained by Fourier transform Raman and conventional Raman spectrometry is systematically investigated. While at photon energies below the exciton energy (1.560 eV), Raman scattering of bulk phonons of boron carbide occurs, photon energies exceeding the fundamental absorption edge (2.09 eV) evoke additional patterns, which may essentially be attributed to luminescence or to the excitation of Raman-active processes in the surface region. The reason for this is the very high fundamental absorption in boron carbide inducing a very small penetration depth of the exciting laser radiation. Raman excitations essentially restricted to the boron carbide surface region yield spectra which considerably differ from bulk phonon ones, thus indicating structural modifications.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Raman spectroscopy is a sensitive tool for investigating phonon spectra of crystalline solids and their variation caused by structural imperfection. However, misinterpretation of the spectra can occur when other optical emissions like luminescence or electronic resonance effects occur in the same energy region. Usually such emissions can be excluded by selecting lasers with suitable excitation energies. As the laser beam necessarily penetrates the sample surface and the adjacent region, related excitations like surface phonons cannot be avoided. A great penetration depth of the exciting laser light makes the contribution of such effects sufficiently weak or even negligible compared with volume effects. Unfortunately, this does not hold for conventional Raman spectroscopy for boron carbide, since there is experimental evidence that these prerequisites are not fulfilled.

In consequence, Raman spectra of boron carbide obtained with conventional spectrometers [1–13] using for example Ar

lasers for excitations at 488.0 nm (2.546 eV) and 514.5 nm (2.415 eV) or even 325 nm (3.815 eV) [20] are qualitatively different from those measured with FT (Fourier transform) Raman spectrometers using Nd:YAG lasers at 1064 nm (1.165 eV) [14–16]. Applying both techniques to exactly the same boron carbide sample, Werheit *et al* [17] provided evidence that the conventionally measured Raman spectra of boron carbide are essentially not determined by bulk phonons. The dependence of Raman spectra on the energy of the exciting laser was afterward reported by Domnich *et al* [18], Dandekar *et al* [19], and Ghosh *et al* [20] as well, but not interpreted.

The main reason for this problem may be the very high absorption coefficient of boron carbide in the range of fundamental absorption above the absorption edge at 2.09 eV or even above the exciton absorption at 1.560 eV. On the basis of the absorption coefficients  $\alpha > 2000 \text{ cm}^{-1}$  in polycrystalline and  $\alpha > 6000 \text{ cm}^{-1}$  in single-crystalline boron carbide [21], the corresponding penetration depths are  $< 5$  and  $< 1.7 \mu\text{m}$  respectively. Accordingly, in commonly used

mechanically polished boron carbide samples the exciting laser light is essentially absorbed within the Beilby layers at the surface, even if layers of adsorbed foreign atoms or molecules can be excluded. Therefore, as discussed in [17], in the range of the fundamental absorption of boron carbide, the small penetration depth of the exciting laser and surface effects must not be disregarded.

In this context it has to be considered that already the ideal surface of a crystal causes a substantial change of the volume properties. The periodicity of the crystal lattice and spatial symmetry of bonding forces are abruptly terminated, and surface atoms and subjacent layers are rearranged; this is accompanied by a modification of properties.

Physical properties related to the surface region, surface phonons included, are usually related to layers whose thickness does not exceed a few unit cells, i.e. in the case of boron carbide about 5 nm. This is a very small part of the penetration depth (here 1.7  $\mu\text{m}$ ). This has to be considered when discussing accordingly measured Raman spectra.

Subsequently, we present a systematic investigation of this problem by means of Raman spectroscopy, varying the penetration depths of the exciting laser radiation considerably.

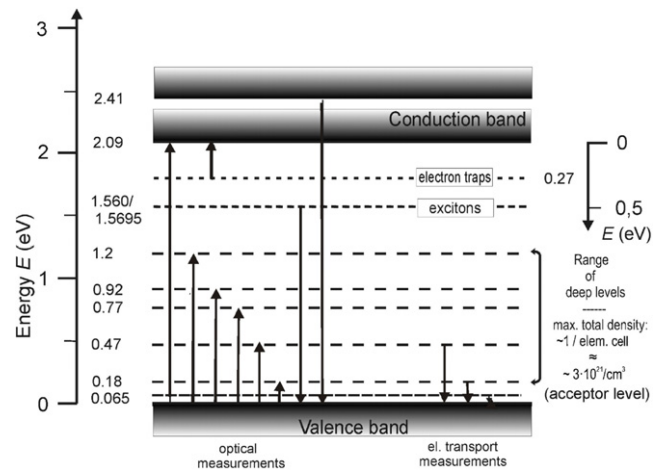
## 2. Experimental details

In an earlier Raman investigation of boron-rich compounds different methods of sample preparation were carefully checked [22]. Accordingly, in the present work we used freshly cleaved samples ensuring clean and undamaged surfaces. Indeed, in this way the crystallographic orientation of the samples was not controlled. However, this was rated as less important with respect to the aim of this project, because only the intensity and not the energetical position of Raman bands could be affected.

The main sample was taken from a section of a big, high quality boron carbide single crystal,  $\text{B}_{4,3}\text{C}$  ( $\varnothing \sim 7$  mm;  $l$ : 60 mm) prepared by Leithe-Jasper and Tanaka [23]. For some details of the preparation and properties, see [24]. Additionally, for checking the influence of isotope effects, spectra of polycrystalline  $^{11}\text{B}_{4,3}\text{C}$  were measured. For details of this material, see [25, 26].

The Raman spectra were obtained at ambient conditions with a Jobin–Yvon Labram spectrometer. Its spectral resolution is about  $1.5\text{ cm}^{-1}$ ; the attached microscope reduces the size of the laser focus to about  $5\ \mu\text{m}$ . The exciting laser lines were selected according to the requirements obtained from the actual band scheme for boron carbide (figure 1) [21]:

- (i) The blue line (488.0 nm) of the Ar ion laser yields the excitation energy of 2.546 eV, distinctly above the band edge of boron carbide (2.09 eV).
- (ii) The red HeNe laser (632.8 nm) has the excitation energy 1.963 eV, which is below the absorption edge but higher than the strong exciton absorption starting at 1.560 eV.
- (iii) These spectra are compared with those measured with a Bruker FT Raman spectrometer with a Nd:YAG laser (1064 nm, 1.165 eV), whose energy is below the range of interband transitions in boron carbide. The spectra



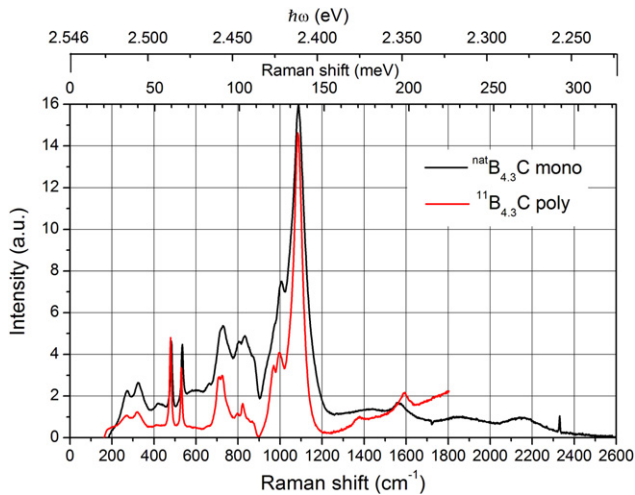
**Figure 1.** Band scheme of boron carbide; arrows indicate the direction of the measured transition. Compared with the version in [21], the band scheme is completed by the transition between valence band and upper conduction band according to the complex dielectric function [32], structure-modulated reflectivity [33, 34], photoluminescence [20], and possibly (Raman) luminescence (this work).

originate from a single-crystal  $^{nat}\text{B}_{4,3}\text{C}$  sample, cut from the same rod, close to that used in the present work [24], and from polycrystalline  $^{11}\text{B}_{4,3}\text{C}$  from the series of isotope-enriched boron carbides in [26]. The Raman-active modes in these spectra are in close agreement with those theoretically calculated by Shirai *et al* [27, 28].

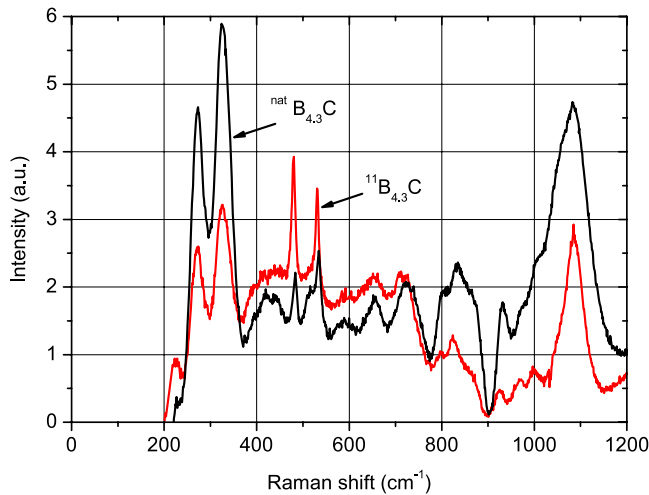
## 3. Results

The Stokes spectra of  $^{nat}\text{B}_{4,3}\text{C}$  and  $^{11}\text{B}_{4,3}\text{C}$  measured with Ar ion laser excitation at 2.546 eV and displayed in figure 2 confirm the significant difference from the bulk phonon Raman spectra obtained with Nd:YAG laser excitation (1.165 eV), reproduced in figure 4. Excitation at the intermediate energy 1.963 eV yields the spectra shown in figure 3. Obviously, they are a mixture of those in figures 2 and 4; indeed, the relative intensities of peaks are drastically different. These results confirm the conclusion [17] that the energies of exciting laser light, or to be precise the related penetration depths, are decisive for the differences of Raman spectra. Obviously, the contribution of bulk phonons to the Raman spectra systematically increases with the penetration depth of the exciting laser light increasing.

The spectra in figures 2 and 3 are obtained for samples with freshly cleaved surfaces, and hence without adsorbents or Beilby layers. Accordingly, the spectra in figure 2 essentially come from Raman scattering within a range close to the surface of  $<1.7\ \mu\text{m}$  thickness, estimated from the penetration depth of the exciting laser light. The most prominent bulk phonons at  $273/324\text{ cm}^{-1}$ , representing the rotating CBC and CBB chains and accompanying wagging icosahedra (see figure 4 and [26, 31]), are weak but clearly discernible. Comparing their relative intensities in figures 2 and 4 we estimate the contribution of bulk phonons to the spectrum in figure 2 to be



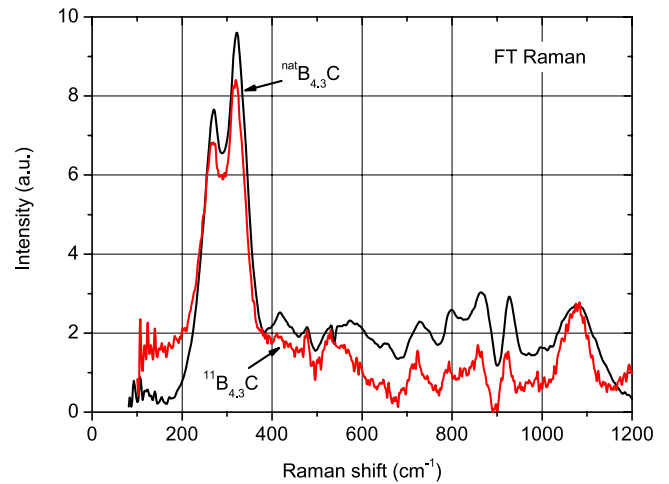
**Figure 2.** Raman spectra of  $^{nat}B_{4,3}C$  (single crystal) and  $^{11}B_{4,3}C$  (polycrystalline). Excitation: Ar ion laser, 488.0 nm (2.546 eV). The upper abscissa shows the relative Raman shift in meV and the absolute energy of the scattered radiation in eV.



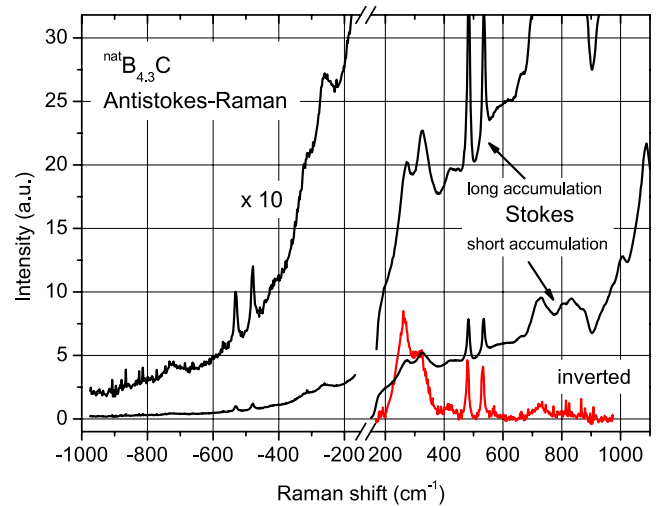
**Figure 3.** Raman spectra of  $^{nat}B_{4,3}C$  and  $^{11}B_{4,3}C$ . Excitation, He-Ne laser, 632, 82 nm, 1.963 eV.

not more than 10%. Accordingly no measurable contribution of other bulk phonons on the surface Raman spectrum is expected because their intensities are weaker by about one additional order of magnitude, i.e. <1%.

The Raman spectra of boron carbide in [1–13] were obtained at comparable excitation energies. There, the most prominent bulk phonons appear only weakly or not at all. Since there the information on sample preparation is usually missing, we suppose ground or otherwise mechanically treated surfaces. Such surfaces are strongly distorted within a Beilby layer, whose thickness depends on the hardness of material. The Mohs hardness of boron carbide (9.5+) is close to that of  $\beta$ -rhombohedral boron (9.3), and hence the thickness of the Beilby layer is similar ( $\sim 2 \mu\text{m}$  [29]). Within this layer, the intensity of the penetrating laser light is so strongly attenuated that its exponential tail remaining in the undistorted volume is not sufficient for a remarkable contribution of bulk phonons to the spectra.



**Figure 4.** FT Raman spectra of  $^{nat}B_{4,3}C$  and  $^{11}B_{4,3}C$ , reproduced from [24, 26]. Excitation, Nd:YAG laser, 1064 nm, 1.165 eV.



**Figure 5.** Anti-Stokes Raman spectrum of  $^{nat}B_{4,3}C$  (single crystal). Excitation: Ar laser, 488.0 nm (2.546 eV).

The simultaneous occurrence of modes in the Stokes and anti-Stokes spectrum is an irrefutable proof for Raman scattering. For higher Raman shifts this check is difficult because the scattering intensity decreases as  $\lambda^4$ . In the bulk Raman spectrum (figure 4), the phonons at 270 and 321  $\text{cm}^{-1}$  and the adjacent range were checked in this way [14, 15]. Electronic resonance processes are excluded, as the energy of the Nd:YAG laser is smaller than the band gap. For the surface Raman spectrum in figure 2 this check was performed for the range <1000  $\text{cm}^{-1}$  (figure 5). For realizing a discernible anti-Stokes spectrum the data accumulation exceeded the maximum storage limits of the spectrometer. Accordingly, the strong Stokes bands are cut at this upper limit. For better comparison, the enlarged difference of the anti-Stokes spectrum from an empirical baseline was inverted to the Stokes range. The Raman activity determined is noted in table 1 listing the peak positions of the spectra for facilitating the comparative study. Unfortunately, the  $\lambda^4$  law prevents checking the anti-Stokes occurrence of the strong 1087  $\text{cm}^{-1}$  peak in figure 2.

**Table 1.** Peak positions in the skin Raman spectra of figure 2. R, Raman activity evidenced by additional anti-Stokes emission; (R), indiscernible peaks in broad structures. Bulk phonon frequencies of  $^{nat}B_{4,3}C$ , in the sequence of occurrence in the spectrum, for comparison. **red** (bold in the printed version), significant phonon modes, attributed either to skin or to bulk.

No.	Skin Raman spectra ( $cm^{-1}$ )				Activity	Bulk Raman spectrum ( $cm^{-1}$ )	
	$^{nat}B_{4,3}C$	$^{11}B_{4,3}C$	Shift			$^{nat}B_{4,3}C$	Shift $B_{4,3}C$ bulk skin
1	273	269		4	R	<b>270</b>	-3
2	324	321		3	R	<b>321</b>	-3
3	420	416		4	R	418	-2
4	<b>482</b>	<b>478</b>		4	R	477	-5
5	<b>535</b>	<b>530</b>		5	R	530	-5
						550	
						573	
6	590	—				588	
						619	
7	663	656		7	(R?)	652	-11
8	—	708		10	(R)	—	
9	726	724		6	R	729	+3
10	805	795		10	(R)	798	-7
11	831	824		7	R	864	+33
12	870	865		5	(R)	—	
13	—	970			?	928	
14	1005	996		9	?	1001	-4
15	<b>1087</b>	<b>1085</b>		2	?	<b>1076</b>	-11

In conclusion, the Raman spectrum in figure 2 represents the properties of the surface region of boron carbide nearly exclusively. The only noticeable influence of bulk phonons comes from the very strong pair of bulk modes at  $273/324\text{ cm}^{-1}$ . All the other bulk modes are too weak to affect this spectrum remarkably ( $<1\%$  as estimated above). The FT Raman spectrum reproduced in figure 4 is nearly exclusively determined by bulk Raman modes. Obviously, it is not even affected by the strong peak with maximum at  $1087\text{ cm}^{-1}$  occurring in the surface Raman spectrum. Accordingly, it is concluded that the partial volume of the surface range is very small.

#### 4. Discussion

Irrespective of the hitherto unknown particular structural properties of the surface range in boron carbide and their effect on the Raman spectrum, the materials in both regions are fundamentally the same, and therefore only structural modifications may occur. If we neglect the trace of specific strong bulk phonons in the surface spectrum (see above), the variation of remaining Raman modes accounts for these modifications.

Three features in the surface Raman spectrum demonstrate its significant distinction from the bulk one:

- The absence of the  $270/321\text{ cm}^{-1}$  pair of modes, which are predominant in the bulk Raman spectrum (disregarding the relatively weak trace).
- The pair of untypically narrow peaks at  $482/535\text{ cm}^{-1}$  ( $^{nat}B_{4,3}C$ ) and  $478/530\text{ cm}^{-1}$  ( $^{11}B_{4,3}C$ ), which is completely missing in the bulk spectrum.
- The very strong Raman mode in the spectral range between about  $900$  and  $1200\text{ cm}^{-1}$  having no comparable counterpart in the bulk spectrum.

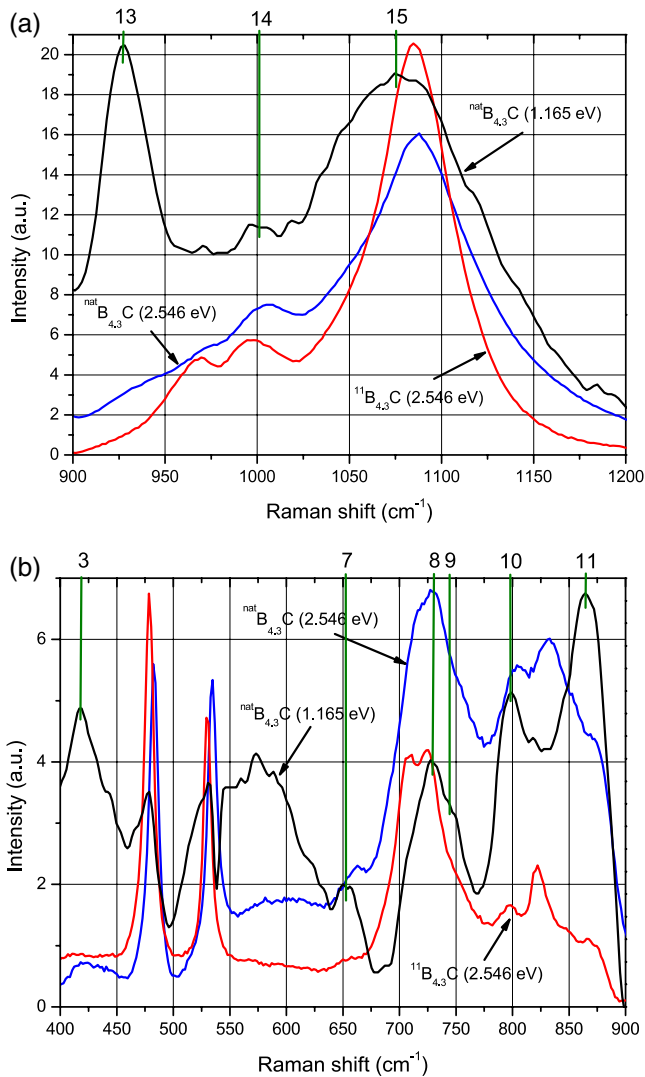
Some authors assigned the pair of narrow peaks at  $482/535\text{ cm}^{-1}$  ( $^{nat}B_{4,3}C$ ) to bulk phonons. However, these modes are completely missing in the bulk, and their intensity significantly decreases with increasing penetration depth of the exciting light (see figures 2–4). Hence their exclusive affiliation to the surface range is definitely proved. A further strong argument comes from the probable resonance absorption in the surface range (see below).

The split of this line pair is  $52\text{--}53\text{ cm}^{-1}$  fitting exactly to that of the rotating modes of the CBC and CBB chains in the bulk at  $270/321$  ( $^{nat}B_{4,3}C$ ). This could possibly indicate a relation to these bulk phonons, probably as phonons in the surface region.

This interpretation would be in accordance with an earlier observation. Gosh *et al* [20] and Dandekar *et al* [19] investigated the impact of high pressure on the boron carbide structure. From the disappearance of lines in Raman spectra obtained with lasers of high excitation energies they concluded an amorphization of the structure at high pressures. However, their x-ray diffraction patterns disprove an amorphization. This contradiction can be easily explained assuming that the modes essentially represent excitations in the surface region instead of bulk states. Thus their results suggest that the surface properties of boron carbide are strongly influenced by high pressure.

Otherwise, the average Raman shift of these lines ( $\sim 62\text{ meV}$ ) corresponds quite well to the  $65\text{ meV}$  distance of the acceptor level from the valence band edge (see figure 1). Therefore a Stokes and anti-Stokes resonance emission based on radiating transitions of excited electrons into the valence band and the adjacent acceptor level cannot be excluded.

For discussing the most prominent peak in the surface spectrum with a maximum at  $1087\text{ cm}^{-1}$ , the section of surface and bulk spectra between  $900$  and  $1200\text{ cm}^{-1}$  is displayed



**Figure 6.** Amplified display of sections of the Raman spectra of  ${}^{\text{nat}}\text{B}_{4.3}\text{C}$  (figures 2–4). The relative intensities are assimilated.  ${}^{\text{nat}}\text{B}_{4.3}\text{C}$ , bulk spectrum (1.156 eV excitation);  ${}^{\text{nat}}\text{B}_{4.3}\text{C}$ , surface spectrum (2.546 eV excitation);  ${}^{11}\text{B}_{4.3}\text{C}$ , surface spectrum (2.546 eV excitation). The peak numbers correspond to those in table 1. (a) spectral range 900–1200  $\text{cm}^{-1}$ ; (b) spectral range 400–900  $\text{cm}^{-1}$ .

in figure 6(a). On the basis of theoretical calculations by Beckel *et al* [30], the associated movements of atoms are described in [31]. Accordingly, this strong peak in the surface spectrum, which is obviously associated with the much weaker bulk mode No. 15 in table 1, is characterized by radial movement of triangle polar atoms of the icosahedra (accordingly threefold degenerate), meaning double stretching and double compression of the strong inter-icosahedral two-centered bonds. Mode No. 13 is a mix of two frequencies  $\omega_1$  and  $\omega_2$  of the  $\text{B}_{12}$  cluster. For  $\omega_1$  all six two-center bonds of the icosahedra are compressed simultaneously; for  $\omega_2$  (at a given instant) two of the six are compressed, two stretched, and two unstrained. The influence of  $\omega_1$  is prevailing.

Hence the modification of the structure in the surface region compared to the bulk evokes considerable strengthening of the inter-icosahedral two-center B–B bonds (or at least of the corresponding polarizability), while the simultaneous

movement of polar atoms in the icosahedra is entirely suppressed.

Figure 6(b) shows the range 400–900  $\text{cm}^{-1}$  in detail. Mode No. 11 (831  $\text{cm}^{-1}$ ) involves distortions of the polar triangles as well as of the equatorial hexagon of the icosahedra, where two of the six bonds are stretched. In the surface this mode is strongly reduced or possibly shifted towards lower frequencies (832  $\text{cm}^{-1}$ ).

Mode No. 10 is essentially an isolated icosahedral mode mainly stressing the equatorial and the slant bonds of the icosahedron. Therefore it is not surprising that it remains largely unchanged in the surface range.

Mode No. 8/9 is attributed to the external three-center bonds, being compressed at an instant, when two-centered bonds are stressed. Internally, the triangle and the vertical bonds are most strained. This mode seems to be somewhat strengthened in the surface range but remains essentially unchanged.

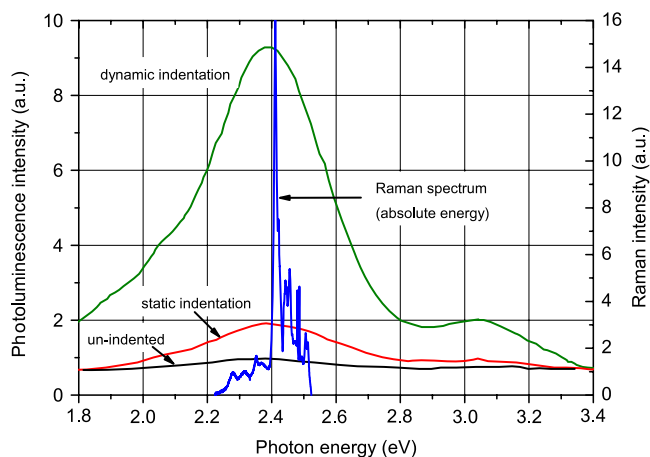
We guess that the negative narrow peak at 538  $\text{cm}^{-1}$  in the bulk spectrum is caused by resonance absorption of the 535  $\text{cm}^{-1}$  mode in the surface range, and in the case of the lower frequency resonance (482  $\text{cm}^{-1}$ ) that the resonance absorption occurs as well, but in this case partly masked by a steep edge in the bulk spectrum. Such resonance absorption would strongly support the attribution of the mode pairs at 482/535  $\text{cm}^{-1}$  ( ${}^{\text{nat}}\text{B}_{4.3}\text{C}$ ) and 478/530  $\text{cm}^{-1}$  ( ${}^{11}\text{B}_{4.3}\text{C}$ ) respectively to modes exclusively occurring in the surface region.

The bulk modes in the range 400–675  $\text{cm}^{-1}$ , whose nature is not identified, are considerably weakened in the surface range.

A different interpretation of the most prominent peak in the surface range spectrum (table 1, No. 15) should be discussed as well. This peak appears at absolute energy 2.4112 eV for  ${}^{\text{nat}}\text{B}_{4.3}\text{C}$  and 1085  $\text{cm}^{-1}$  (134.6 meV) or absolute energy 2.4114 eV for  ${}^{11}\text{B}_{4.3}\text{C}$ . This small shift is just at the resolution limit of the spectrometer and clearly falls below the  $\sim 0.8\%$  shift expected for phonon frequencies of  ${}^{\text{nat}}\text{B}$  and  ${}^{11}\text{B}$  arrangements respectively.

The absolute energy position of this peak (see figure 2) suggests that it could be evoked by electronic resonance absorption in connection with the interband transition close to 2.4 eV. This transition is proved (i) in the complex dielectric function [32], (ii) additionally in structure-modulated reflectivity spectra [33, 34], and (iii) moreover in photoluminescence spectra [20], all confirming an electron transition close to 2.4 eV. In figure 7 the photoluminescence spectra (reproduced from [20]) are compared with our Raman spectrum plotted versus absolute photon energy presuming its interpretation based on luminescence. The peak positions of both kinds of spectra agree very well. Unfortunately, in [20] the spectral resolution of the photoluminescence spectrum is missing.

However, some arguments speak against this interpretation. The Raman peak (half-width, 11 meV) is untypically narrow for an emission due to interband recombination, even for boron carbide with extraordinary narrow energy bands (see [34]). Figure 3 shows that this peak occurs at lower excitation energies as well, although with considerably reduced



**Figure 7.** Photoluminescence spectra of indented and unindented boron carbide [20], compared with the Raman spectrum (this work) plotted versus absolute photon energy according to the alternate interpretation based on luminescence.

intensity. Accordingly we prefer its attribution to phonons (see above). Anyway, three remaining different experimental methods yielding an interband transition at this energy justify its consideration in the band scheme (figure 1).

Some rather broad peaks occur at higher Raman shifts in the surface spectrum (figure 2). The peak at  $1568\text{ cm}^{-1}$  ( $^{\text{nat}}\text{B}_{4,3}\text{C}$ ) could correspond to the strong stretching mode of the three-atom chain in boron carbide ( $1568\text{ cm}^{-1}$  in  $^{\text{nat}}\text{B}_{4,3}\text{C}$  [35, 36];  $1580\text{ cm}^{-1}$  in  $^{11}\text{B}_{4,3}\text{C}$  [25]). Fundamentally, this mode is Raman-inactive, but it might be that in the surface range the bulk structure is distorted, thus slightly lifting the selection rules. However, the shift depending on isotopes is opposite to that expected (see figure 2). Moreover, the rotation mode of the three-atom chains is predominant in the bulk spectrum only. This suggests a considerable perturbation of the bonding of the three-atom chains in the surface range, and the occurrence of a related Raman-inactive vibration is therefore improbable.

The weak broad peaks in the spectrum at  $1440$ ,  $1850$  and  $2150\text{ cm}^{-1}$  ( $178$ ,  $229$ ,  $276\text{ meV}$ ) are separated from phonon modes for boron carbide. Therefore, we attribute them to luminescence processes in connection with states in the band gap (figure 1), where such energy differences between gap levels are found. Their position is known from optical absorption [24, 37].

## 5. Summary

The surface range of boron carbide exhibits structural deviations from the bulk properties, which are clearly detectable by adapted Raman spectroscopy. From the penetration depth of the exciting radiation the thickness of this range is estimated as  $<1.7\text{ }\mu\text{m}$ . Indeed, it seems more realistic assuming that these structural variations are restricted to a range of some lattice constants beneath the surface only, i.e. about  $5\text{ nm}$ . Indeed, this implies that the intensity of the modes excited in the surface range is very high. The solution of this experimental evidence requires further investigation.

Most significant features of the Raman spectrum of the surface range are the missing pair of  $270/321\text{ cm}^{-1}$  phonons, dominant in the bulk spectrum, the  $482/535\text{ cm}^{-1}$  pair, exclusively occurring in the surface range spectrum, and the considerable strengthening of the inter-icosahedral two-center B–B vibrations. The close agreement of the splits of the phonon pairs occurring in the bulk and the surface region suggests a correlation between them. Modifications of the other weaker features in the Raman spectra confirm structural changes in the surface range as well.

A surface range with modified structural properties is not restricted to boron carbide. Significant features, in particular the pair of narrow modes, determine the Raman spectrum of  $\text{B}_{12}\text{P}_2$  [5] as well. Like boron carbide, this compound belongs to the  $\alpha$ -rhombohedral boron structure group. For  $\beta$ -rhombohedral boron and  $\text{YB}_{66}$  the Raman spectra are largely independent of the exciting photon energy, and therefore no surface range could be verified [31], at least not by Raman spectroscopy. However, it cannot be excluded that the effect is only masked.

Further investigations are required for elucidating structural details and related processes in the surface region of boron carbide. The question of how far specific Raman-active phonons or electronic emission processes occur either within an distorted surface range beneath the boron carbide surface or even within the largely two-dimensional surface itself cannot be answered at present.

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