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## Reply to “Comment on ‘Understanding first-order Raman spectra of boron carbides across the homogeneity range’ ”

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In response to Werheit’s Comment, we first discuss the following three points: (i) Attribution of the Raman bands with the help of calculations based on the density functional perturbation theory (DFPT), (ii) similarity of the Raman spectrum of boron carbide to the Raman spectrum of  $\alpha$  rhombohedral boron, and (iii) dependence of the experimental Raman spectrum on the frequency of the excitation laser. Central to the point at stake, we also present a Raman spectrum computed for the first time on a 405-atom unit-cell of boron carbide, where the simulation cell accounts for the substitutional disorder of the polar carbon atom in the six atomic positions that are equivalent in the trigonal symmetry. We thus obtain a *theoretical spectrum whose agreement with experiment is unprecedented in boron carbide*, all of the features being present, with however negligible intensities for the doublet at  $270/320\text{ cm}^{-1}$ . We argue that the doublet intensity seen in experiments is not purely vibrational—as computed at mechanical equilibrium—and that FT-Raman spectroscopy taken at  $1.06\ \mu\text{m}$  lacks the accuracy that is necessary to study vibrational modes of boron carbides.

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In this Reply we take the opportunity to extend and ascertain our previous study reported in the original paper [1]. Before doing this, we first discuss the following three points raised by the Comment: (i) Attribution of the Raman bands with the help of calculations based on the density functional perturbation theory (DFPT), (ii) similarity of the Raman spectrum of boron carbide to the Raman spectrum of  $\alpha$  rhombohedral boron, (iii) dependence of the experimental Raman spectrum on the frequency of the excitation laser.

Starting with the first point, we recall that our mode attribution to specific phonons displacements rests on a method whose reliability and accuracy is nowadays well established and has met great success in obtaining the phonon frequencies in the harmonic approximation [2], the Raman polarizability tensor [3], as well as the phonon homogeneous (anharmonic) linewidth [4,5] of various materials and nanostructures [6,7]. DFPT calculations are parameter-free, at variance with force-field models like the one cited in Ref. 19 of the Comment, and this is particularly important as bonding in boron carbide, with three-center bonds in the icosahedra due to the intrinsic electronic deficiency of  $\text{B}_{12}$  and  $\text{B}_{11}\text{C}$  icosahedra, may be not as simple as in some other semiconductors. The atomic

structure with nominal 20% at. C concentration,  $\text{B}_4\text{C}$ , has by far the lowest DFT formation energy value among a wealth of other atomic structures that have been systematically investigated so far [8], even if in experimentally available samples, probably due to sample preparation dependent quenched high temperature entropic effects not accounted for in DFT, the maximal carbon concentration amounts to 19.3% (Refs. 2 and 3 of the Comment). Phonon calculations performed on the  $\text{B}_4\text{C}$  DFT ground-state atomic structure yield in particular two modes at  $480$  and  $530\text{ cm}^{-1}$  whose phonon displacement patterns (PDP) are reported in Fig. 1 [panels (a)–(d)] and correspond to the so-called pseudorotation of chains [with, however, response of the icosahedra, panels (a) and (b)] and to the rotation/libration of the icosahedra [with tiny chain displacements, panels (c) and (d)], respectively. We stress that the libration mode is also found in  $\alpha$  boron [panels (e) and (f)], both in theory and in experiment [9], at variance with Ref. 19 of the Comment, thus confirming the predictive power of the DFPT calculations.

We now turn to the second point. To refute our attribution of the two  $480$  and  $530\text{ cm}^{-1}$  harmonic modes to bulk vibrational modes, Werheit invokes the absence of correlation of these modes with the Raman spectrum of  $\alpha$  boron and attributes them to surface-induced defect modes. However, the comparison of  $\text{B}_{4,3}\text{C}$  and  $\alpha\text{-B}_{12}$  spectra shown in Fig. 1

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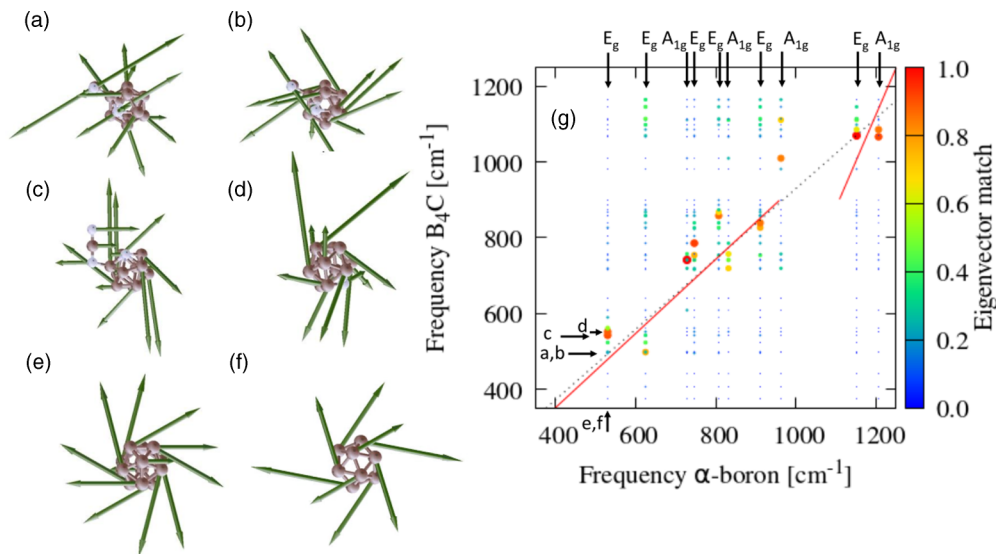


FIG. 1. Panels (a)–(d) Phonon displacement patterns (PDP) of the calculated modes at 498 and 543–550  $\text{cm}^{-1}$  of boron carbide, corresponding to the experimental ones at 480/530  $\text{cm}^{-1}$ . Panels (e) and (f): PDP corresponding to the two degenerate Raman active modes of  $\alpha$  boron at 531  $\text{cm}^{-1}$  (525  $\text{cm}^{-1}$  in experiment). (g) Each point is the projection of one of the computed PDP of boron carbide onto the Raman active ones of  $\alpha$  boron. PDP corresponding to panels (a)–(f) are indicated, as well as the symmetry of  $\alpha$  boron modes. The red line is the  $\alpha$ -boron/boron carbide frequency scaling chosen in the Comment; the dotted line corresponds to a frequency scaling as the cubic root of the ratio of the respective unit-cell equilibrium volumes.

of the Comment is somewhat biased. While a shift in the frequency scales of the two materials is announced as a way to compensate for different crystal fields, such a shift is not quantitatively justified and, moreover, in the right panel of the same figure, instead of a simple shift a considerable, unexplained, stretch of the scales is applied. The intensity ratio between the three curves has also been altered from one panel to the other in Fig. 1 of the Comment. It would have been more natural, in our opinion, to present the whole spectra in a single plot, applying a unique frequency stretch corresponding to a length ratio between the two materials, like the average bond length ratio (0.99) or the cubic root of the ratio of the unit volumes (0.93). The latter frequency scaling is represented by the dotted line in Fig. 1(g), while the frequency transformation adopted in the Comment is the red line. Whatever the chosen frequency relationship, a comparison of the vibrational spectra of two similar materials should rather be founded on the similarity of the PDP. In Fig. 1, we report the magnitude of the projection of the boron carbide icosahedral PDP onto those of  $\alpha$  boron [panel (g)]. One can see that while the high frequency modes ( $\geq 800 \text{ cm}^{-1}$ ) correspond well to one another with the proposed frequency scaling, the PDP having the lowest frequencies have comparable frequencies in  $\text{B}_4\text{C}$  and in  $\alpha$  boron. In particular, the two modes at 543–550  $\text{cm}^{-1}$  of  $\text{B}_4\text{C}$  are substantially projected onto the subspace spanned by the  $\alpha$  boron Raman active PDP at 531  $\text{cm}^{-1}$  that begets a doubly degenerate mode. This degenerate mode is the signature of the presence of icosahedra in the material and is located at, respectively, 535  $\text{cm}^{-1}$  and 525  $\text{cm}^{-1}$  in actual samples of  $\text{B}_4\text{C}$  and  $\alpha$  boron, respectively. Their absence in the FT-Raman spectra of the Comment, coming from Ref. [10], is thus intriguing, as discussed below. In all other experimental Raman spectra (including with 785 nm laser excitation), they are present and rather harmonic, which contrasts with

the broadening of the other bands. Consistently, the peak at 535  $\text{cm}^{-1}$  lowers in frequency with increasing boron content, while the one at 480  $\text{cm}^{-1}$  diminishes in intensity [11]. As expected the icosahedral displacements of the highest strongly Raman active mode of boron carbide, which is a chain mode (at 1112  $\text{cm}^{-1}$  in the calculation), has small overlap with high frequency  $\alpha$ -boron modes. Concerning the correspondence invoked in the Comment between the 925  $\text{cm}^{-1}$  of boron with the 867  $\text{cm}^{-1}$  of boron carbide, it is well confirmed by our PDP analysis, and well present both in the theoretical and experimental spectrum, simply the intensity in boron carbide is smaller than in  $\alpha$ -boron and, in the experimental spectrum, broadened.

Point (iii), which actually lies beside the main scope of our paper, concerns the dependence of the experimental Raman spectrum on the frequency of excitation laser, and the origin of a band with two peaks at 270 and 320  $\text{cm}^{-1}$  which is often, but not always, found in experiments. We find, as previously reported [12], no presence of the peaks at 270 and 320  $\text{cm}^{-1}$  in the calculations of ordered  $\text{B}_4\text{C}$ : They are therefore not phonon modes of pristine  $\text{B}_4\text{C}$  as modeled in the ground-state DFT atomic structure at mechanical equilibrium.

To ascertain our analysis, we now present in Fig. 2 a new result obtained since the publication of Ref. [1]. This result has been obtained in the same theoretical framework and with the same computational parameters as those of Ref. [1]. We have constructed a large  $3 \times 3 \times 3$  supercell composed of 27 C-B-C chains and 27  $\text{B}_{11}\text{C}^p$  icosahedra. The carbon atoms on the polar sites  $\text{C}^p$  have been placed such that the six polar atomic positions that would be equivalent by symmetry in the trigonal cell are, respectively, occupied four, four, four, five, five, and five times. These occupation numbers come from various constraints: (i) we limit the simulation cell to 27 elementary unit cells to limit the computational burden;

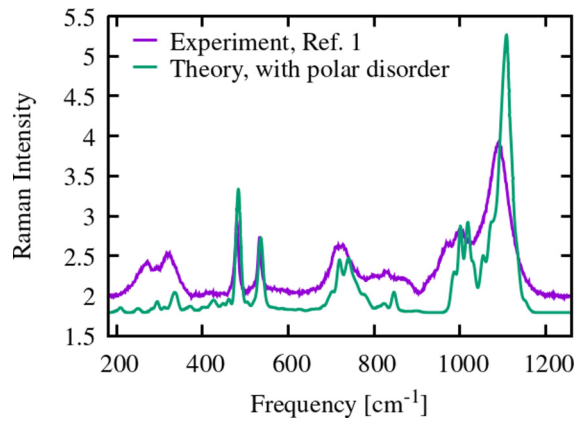


FIG. 2. Comparison of the experimental spectrum presented as Fig. 1 in Ref. [1] with a theoretical spectrum of  $(B_{11}C)C-B-C$  obtained by including disorder in the position of carbon on polar icosahedral sites. Each peak has been enlarged by a gaussian with a  $10\text{ cm}^{-1}$  full width at half minimum (the same broadening as used in Ref. [1]).

(ii) no intericosahedral C-C bonds are created, as such bonds are energetically costly [8]; (iii) no clusters of neighboring icosahedra with occupation of the same atomic position are created or, in other words, icosahedra with a carbon atom at the same polar atomic position are as far from one another as is authorized by the (large yet) limited size of the simulation cell. This atomic model has, on average, the trigonal symmetry that fits the experimental one observed by x-ray diffraction. We note that performing the Raman calculation on a 405-atom unit cell is a computational challenge. The experimental spectrum reported in the same figure has already been presented in Fig. 1 of our main paper [1] and has been acquired with a laser wavelength of 633 nm (1.96 eV). We believe that, up to now, no other theoretical Raman spectrum of boron carbide without empirical parameters has been in such good agreement with an experimental spectrum of boron carbide. One can even see the presence of weak intensity modes in the  $270\text{--}320\text{ cm}^{-1}$  frequency range. This implies that in principle, the disordered atomic structure can sustain low frequencies modes in this range, whose Raman polarizability tensor is however rather weak at the theoretical equilibrium, which rests on both negligible strain/stress and vanishing forces on atoms. Therefore, one has to look for the experimental reasons why, in some of the experiments, the  $270\text{--}320\text{ cm}^{-1}$  peaks have enhanced Raman intensities with respect to the other vibrational modes, and with respect to the theoretical intensities.

However, we note that the experimental context about the occurrence of the doublet has not been satisfactorily unified yet, which may be the signature of its sensitivity to the synthesis conditions. In experiments on carbon-rich single crystals illuminated at 514.5 nm (2.41 eV), this doublet is either absent [13], quasiabsent although it appears at high pressure [14], or has a very weak intensity when taken on single crystals with either the (223) or (111) plane orientation [15,16]; an exception to this being the experiment on a single crystal with the (210) orientation, where the doublet has a significant intensity [17]. The intensity becomes, however, large when single crystals are illuminated at 633 nm (1.959 eV) [15–17]

and very large with an unusual background when illuminated at 785 nm (1.579 eV) [16,17]. Experiments performed on polycrystals show moderate (as our work at 633 nm) to large intensities (as in Ref. [13] at 514.5 nm and Ref. [18] at 785 nm). All of the experiments performed at 785 nm present an unusual background [16–18]. We point out that in all of these experiments the two modes of pseudorotation of chains and of librations of the icosahedra have been observed.

In this context, the spectrum taken at  $1.06\text{ }\mu\text{m}$  (1.16 eV) by FT-Raman, discussed by Werheit in his Comment, has two prominent peaks at the doublet frequencies, but has no peaks corresponding to the pseudorotation of chains and of librations of the icosahedra, in wide contrast with all the other experiments. We attribute the absence of those vibrational peaks at low frequency in FT-Raman to three mechanisms that limit the efficiency of FT-Raman at this energy [19,20]: First, the mechanism of self-absorption by which scattered photons are absorbed by  $B_4C$ , leading to decreases in spectral intensities of the lattice vibrations. Second, as the scattering cross section evolves as inverse of the fourth power of the wavelength, the cross section for Raman scattering at the infrared excitation wavelength of  $1.06\text{ }\mu\text{m}$  is reduced by a factor of 16 with respect to that of the visible excitation wavelength of 514.5 nm, resulting in a considerable loss in sensitivity. Third, local heating of the sample by the infrared radiation. The fact that, in wide contrast, the doublet at  $270$  and  $320\text{ cm}^{-1}$  is prominent at  $1.06\text{ }\mu\text{m}$  leads us to conclude that the doublet intensities are definitively not determined solely by the scattering cross section at this wavelength and by the equilibrium Bose-Einstein distribution.

Instead of reaching this conclusion, Werheit questions the experimental Raman spectrum we present again in Fig. 2, asserting that it is not a bulk spectrum but a surface one. The reason for this would have to be found in the penetration depth of the laser which would be too small, or in effects of “*so far unknown other reasons*.” Although “effects of so far unknown other reasons” can never be excluded, they have no reason to be invoked when a very good agreement between theory and experiment is reached as shown in our present Fig. 2. We also strongly contest the assertion about the allegedly too small penetration depth of the laser we used with the following back-of-the-envelope calculation: even taking a more conservative estimate of the penetration depth  $\delta$  than Werheit himself in Ref. [21] by a factor of two and using penetration depth  $\delta = 1/[2\alpha(\lambda)]$  where  $\alpha(\lambda)$  is the absorption coefficient whose laser wavelength  $\lambda$  dependence is given in Ref. [22], we have for the laser we used  $\alpha(633\text{ nm}) \approx 2000\text{ cm}^{-1}$ , hence a penetration depth of  $\approx 2.5\text{ }\mu\text{m}$ . This value corresponds to more than 5000 layers of icosahedra, considering  $3\text{ \AA}$  as roughly the thickness of a layer of icosahedra. If the Raman spectrum is acquired on such a thickness of material, we think that we can safely speak of a bulk spectrum.

Additionally, it is mentioned in the Comment that the results by Fanchini *et al.* [18] and Domnich *et al.* [17], obtained with a 785 nm laser, can be considered as bulk spectra; but the absorption coefficient is practically constant between 1.5 and 2 eV ( $\lambda \approx 800$  and  $\approx 600\text{ nm}$ , respectively), so the same should apply to the penetration depth. Thus we contest that the spectra shown in our paper (obtained with a 633 nm laser) should be attributed to the surface while the one shown

in Refs. [17,18] would have, according to the Comment, “[...] obtained correct bulk Raman spectrum.”

In conclusion, we have shown that the account for substitutional disorder of the carbon atom on the polar site of the icosahedra yields a theoretical Raman spectrum that agrees with most of the experimental spectrum with unprecedented precision, all of the features being present, with however negligible intensities for the doublet at 270/320  $\text{cm}^{-1}$ . Our experimental spectrum reported in Ref. [1], acquired at 633 nm, agrees with previous experiments and illustrates

the *bulk* vibrational modes of boron carbides. We argue that the doublet intensity reported in the Comment is not purely vibrational—as computed at mechanical equilibrium—and that FT-Raman spectroscopy taken at 1.06  $\mu\text{m}$  in that experiment lacks the accuracy that is necessary to study bulk vibrational modes of boron carbides.

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