Reply to "Comment on ’Understanding first order Raman spectra of boron carbides across the homogeneity range’’
Guido Roma, Antoine Jay, Nathalie Vast, Olivier Hardouin Duparc, Gaelle Gutierrez

To cite this version:

HAL Id: cea-03573786
https://hal-cea.archives-ouvertes.fr/cea-03573786
Submitted on 14 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Reply to “Comment on ‘Understanding first-order Raman spectra of boron carbides across the homogeneity range’ ”

Guido Roma*  
Université Paris-Saclay, CEA, Service de Recherches de Métallurgie Physique, 91191 Gif sur Yvette, France

Antoine Jay  
Laboratoire d’analyse et d’architecture des systèmes, CNRS, 31031 Toulouse cédex 4, France

Nathalie Vast and Olivier Hardouin Duparc  
Laboratoire des Solides Irradiés, CEA/DRF/IRAMIS, CNRS, École Polytechnique, Institut Polytechnique de Paris, 91120 Palaiseau, France

Gaëlle Gutierrez  
Université Paris-Saclay, CEA, Laboratoire Jannus, Service de Recherches de Métallurgie Physique, 91191 Gif sur Yvette, France

(Received 10 November 2021; accepted 21 December 2021; published 18 January 2022)

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 α 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 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 μm lacks the accuracy that is necessary to study vibrational modes of boron carbides.

DOI: 10.1103/PhysRevMaterials.6.016602

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 α 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 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 μm lacks the accuracy that is necessary to study vibrational modes of boron carbides.

DOI: 10.1103/PhysRevMaterials.6.016602

*guido.roma@cea.fr
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 B\(_4\)C and in \( \alpha \) boron. In particular, the two modes at 543–550 cm\(^{-1}\) of B\(_4\)C are substantially projected onto the subspace spanned by the \( \alpha \) boron Raman active PDP at 531 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 cm\(^{-1}\) and 525 cm\(^{-1}\) in actual samples of B\(_4\)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 cm\(^{-1}\) lowers in frequency with increasing boron content, while the one at 480 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 cm\(^{-1}\) in the calculation), has small overlap with high frequency \( \alpha \)-boron modes. Concerning the correspondence invoked in the Comment between the 925 cm\(^{-1}\) of boron with the 867 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 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 cm\(^{-1}\) in the calculations of ordered B\(_4\)C: They are therefore not phonon modes of pristine B\(_4\)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 B\(_{11}\)C\(^{9}\) icosahedra. The carbon atoms on the polar sites C\(^{9}\) 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;
single crystals are illuminated at 633 nm (1.959 eV) [15–17]. The intensity becomes, however, large when with the (210) orientation, where the doublet has a significant intensity 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 μm (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,C, 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 μm 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 cm$^{-1}$ is prominent at 1.06 μm 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 $\approx 2.5 \mu m$. This value corresponds to more than 5000 layers oficosahedra, considering 3 Å 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 $\approx 600$ 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.

![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 cm$^{-1}$ full width at half minimum (the same broadening as used in Ref. [1]).](image-url)
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 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 μm in that experiment lacks the accuracy that is necessary to study bulk vibrational modes of boron carbides.

This work was granted access to the HPC resources of IDRIS and TGCC under the allocations 22010 and 2020-A0090906018 made by GENCI.