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# Comment on "Understanding first-order Raman spectra of boron carbides across the homogeneity range"

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The Raman spectra of boron carbide presented by Roma *et al.* are severely impaired by surface excitations. The reason is the inappropriate energy of the laser used in their spectrometer. Thus, the claimed correlation between point defects in the structure and the resonance peaks in their Raman spectra is highly questionable.

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## I. COMMENTS

It is noteworthy that Roma *et al.* [1] acknowledge—for the first time in a theoretical study—$B_{4.2}C$ as a stable version of boron carbide, a fact which has long been proved experimentally. Already in 1990, Schwetz and Karduck [2,3] determined $B_{4.3(1)}C$ as the carbon-rich limit of the homogeneity range. Meanwhile, this result has been confirmed in various experimental studies (see Refs. [4,5] and references cited therein).

In Sec. III A of their paper [1], the authors claim that in Raman spectroscopy molecules in the gas phase are perfectly suited to randomly oriented grains of polycrystalline solids. In fact, there is a fundamental difference. Molecules in the gas phase are very small compared with the wavelength of the exciting laser ($\lesssim 1$ $\mu$m) and the optical properties of the container wall are usually ignored. In contrast, the size of crystalline grains is significantly larger (in Ref. [1], 10–50 $\mu$m). Accordingly, the interaction between laser radiation and grain surface, such as reflectivity must not be ignored. In the case of boron carbide, this is crucial (see Refs. [6,7] and references cited therein). The penetration depth of laser radiation $\gtrsim 2.4$ eV often used in Raman spectroscopy may be so small that Raman scattering occurs preferently in the surface range. Generally, in all cases preventing laser radiation from exciting bulk vibrations in the grains for whatever reasons, the random crystalline orientation has no effect on Raman scattering.

Bulk Raman spectra of boron carbide have been obtained by Nd-YAG laser excitation (1.07 $\mu$m = 1.16 eV; see Ref. [6] and references cited therein). Local heating by the exciting laser has no effect on the spectra [8]. Irrefutable proof for the bulk character of these Raman spectra is their correlation with the Raman spectrum of $\alpha$-rhombohedral boron [7,9]. The closely related structures differ only by the mostly three-atomic linear chain in boron carbide, which is missing in $\alpha$-rhombohedral boron. Accordingly, the icosahedral structures and related phonons are essentially the same only slightly shifted in frequency due to the different crystal fields [5,10]. This check verifies, for example, that Fanchini *et al.* [11] and Domnich *et al.* [12] obtained correct bulk Raman spectra using the excitation wavelength 780 nm (1.59 eV). So far, this is the highest excitation energy known yielding correct bulk Raman spectra of boron carbide.

The authors obtained Raman spectra with He-Ne Laser excitation (633 nm, 1.958 eV). Obviously, these do not withstand this scrutiny. In contrast, they are essentially determined by scattering of so far undefined surface states of boron carbide (see Ref. [6], and references cited therein). References [13,14] used by the authors for evidencing the bulk character of their Raman spectra are inappropriate as they refer to SiC whose optical properties [15] are significantly different from those of boron carbide.

At ambient conditions, the edge of fundamental absorption in single-crystal $B_{4.3}C$ boron carbide exhibits an absorption coefficient rapidly increasing above ~1 eV to extraordinary high values (see Ref. [16] and references cited therein). This feature changes drastically on rising pressure: Boron carbide becomes transparent in the visible range [17]. The band gap increases monotonically from ~2.1 to ~3.5 eV [17,18]. Accordingly, the penetration depth of exciting lasers with energies in the according range increases, and the Raman spectra change continuously from surface to bulk character on rising pressure.

This behavior of the absorption coefficient of boron carbide at high photon energies suggested the penetration depth of the exciting laser radiation to be reason for the difference in the Raman spectra. However, at excitation energies below ~2.1 eV small penetration depths seem to be incompatible with the absorption coefficient decreasing (see Ref. [17] and references cited therein). Therefore, effects of so far unknown other reasons preventing bulk excitation cannot be excluded. Hence, further investigation of this issue is desirable. In particular, the determination of surface phonon modes would be helpful.

In Fig. 1, bulk and surface Raman spectra of single-crystal $B_{4.3}C$ [9,19,20] are compared with that one of coarse-crystalline $\alpha$-rhombohedral B [9]. The scales of the wave number are shifted relative to one another, this way approximately compensating the effect of the different crystal fields on the phonon modes. So, related phonon modes in the different spectra are to be found in the diagram immediately about each other, thus, facilitating comparison and mutual

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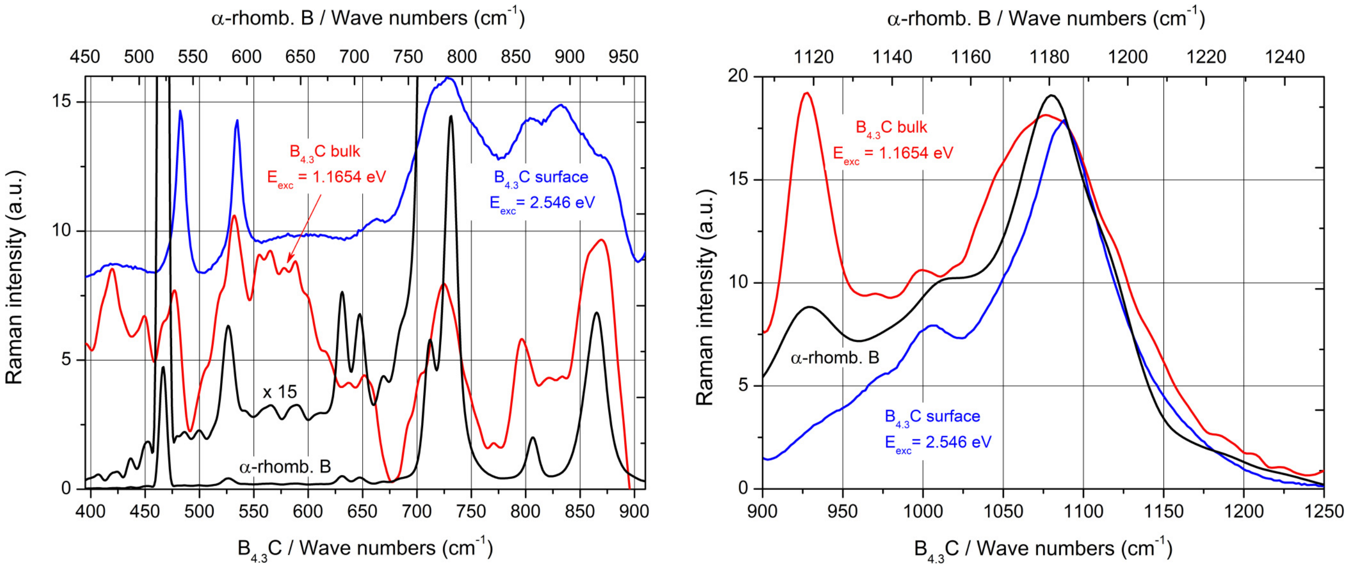

FIG. 1. Bulk and surface Raman spectra of single-crystal $B_{4.3}C$ boron carbide compared with that of coarse-crystalline $\alpha$-rhombohedral boron [9,19].

allocation. The result (confirming the conclusion in Ref. [7] in detail): Numerous Raman modes of bulk boron carbide (obviously those, which are related to the common icosahedral structure) are found in the spectrum of $\alpha$-rhombohedral boron as well, albeit in different intensities. At individual modes, the frequency shift varies slightly; apparently due to different impacts of the polar C atom in the $B_{11}C$ icosahedra on the specific modes. In contrast, in the surface spectrum, the strong modes at 867 and 925 $\text{cm}^{-1}$ and most of the weaker modes occurring in bulk boron carbide and $\alpha$-rhombohedral boron are missing. The strong modes around 725 and 835 $\text{cm}^{-1}$ are considerably broadened, possibly due to the relaxation of surface atoms.

The close relation between the Raman spectra of bulk boron carbide and the $\alpha$-rhombohedral boron allows using the thorough study of Beckel *et al.* [21] on the latter for attributing icosahedral phonons of boron carbide to specific atomic movements in the idealized basic structures. This gives rise to doubts to the authors approach attributing specific peaks in the surface Raman spectrum to structural defects in the bulk. In particular, this holds for the pair of rather strong very narrow lines at $\sim 480/535\,\text{cm}^{-1}$, a characteristic feature in the surface Raman spectra of boron carbide but lacking in the bulk spectrum. Probably, these Raman lines are due to the excitation of molecules adsorbed to the surface. Systematic studies on surface phonons and adsorbed molecules on the surface of boron carbide are missing so far.

Roma *et al.* [1] leave the most prominent feature in the Raman spectrum of bulk boron carbide unsolved: the strong phonon-doublet at $270/320\,\text{cm}^{-1}$. The absence of corresponding features in the spectrum of $\alpha$-rhombohedral boron makes evident that it is associated with the C-B-C chain in $B_{4.3}C$. In Ref. [10], we attributed this doublet to the $E_g$ phonon at $335\,\text{cm}^{-1}$ described by Shirai and Emura [22]. It represents a rotation of the CBC chain associated with a wagging icosahedron. The split is explained by the occupation of specific icosahedral sites by B and C atoms, respectively (for details, see Ref. [10]). The well-defined Raman shift being independent of excitation energy excludes attributing this doublet to electronic transitions.

Clear effects of structural defects in boron carbide have been proved in the case of the optical absorption. Ektarawong *et al.* [23] studied idealized $B_4C$ [structure formula $(B_{11}C)CBC$] distorted by differently distributed C atoms in $B_{11}C$ icosahedra. Rasim *et al.* [24] calculated the electronic density of states of $B_{4.3}C$ boron carbide distorted by chain-related defects. A comparison with experimental data suggests that the effect on the optical properties in the range of the absorption edge by defects in the icosahedra is predominant in comparison with chain-related defects [18].

## II. CONCLUSION

Boron carbide belongs to the structure group of $\alpha$-rhombohedral boron, whose rhombohedral unit cell is formed by one $B_{12}$ icosahedron on each vertex. The unit cell of boron carbide contains a mostly a three-atomic linear chain on the main diagonal additionally. Moreover, one of the six polar B atoms in the icosahedra is replaced by carbon. Consequently, phonons belonging to the common basic icosahedral structure of both solids must be closely related. As a result, comparison with the undoubted spectrum of $\alpha$-rhombohedral boron is a simple but powerful tool to ascertain whether a phonon spectrum can be assigned to the bulk structure of boron carbide or not. The Raman spectra presented by Roma *et al.* [1] fail this check. Hence, their assignment of peaks in such spectra to specific bulk properties of boron carbide is highly questionable.

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