TOPICAL REVIEW

Raman effect in icosahedral boron-rich solids

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Abstract

We present Raman spectra of numerous icosahedral boron-rich solids having the structure of α-rhombohedral, β-rhombohedral, α-tetragonal, β-tetragonal, YB₆₆, orthorhombic or amorphous boron. The spectra were newly measured and, in some cases, compared with reported data and discussed. We emphasize the importance of a high signal-to-noise ratio in the Raman spectra for detecting weak effects evoked by the modification of compounds, accommodation of interstitial atoms and other structural defects. Vibrations of the icosahedra, occurring in all the spectra, are interpreted using the description of modes in α-rhombohedral boron by Beckel et al. The Raman spectrum of boron carbide is largely clarified. Relative intra- and inter-icosahedral bonding forces are estimated for the different structural groups and for vanadium-doped β-rhombohedral boron. The validity of Badger’s rule is demonstrated for the force constants of inter-icosahedral B–B bonds, whereas the agreement is less satisfactory for the intra-icosahedral B–B bonds.

Keywords: Raman scattering, icosahedral boron-rich solids, α-rhombohedral boron, β-rhombohedral boron, α-tetragonal boron, β-tetragonal boron, orthorhombic boron structures, YB₆₆, amorphous boron

1. Introduction

Raman spectroscopy is a sensitive tool for investigating the phonon spectra of crystalline solids and their modification due to changes in the chemical composition or presence of structural imperfections. This is particularly important in the case of icosahedral boron-rich solids containing different types of such structural imperfections.

i. Natural boron consists of 18.83% isotope ¹⁰B and 81.17% ¹¹B, which have a considerable mass difference of 8.7%. Usually, these isotopes are assumed to be statistically distributed in the lattice, but a preferred occupation of specific sites might be conceivable as well.
ii. The $\text{B}_{12}$ icosahedra are slightly distorted owing to the Jahn–Teller effect, thus reducing their symmetry from $I_h$ to $D_{5d}$ in the rhombohedral structures.

iii. Most of these atomic arrangements exhibit intrinsic defects of unoccupied or partially occupied regular atomic sites.

iv. Carbon has a high affinity to boron. Therefore, carbon impurities are usually found in boron and boron compounds. In the icosahedra, carbon atoms preferably occupy polar sites. Therefore, they induce a specific distortion of the icosahedra, as revealed by the anisotropic changes in the structure of $\beta$-rhombohedral boron and boron carbide [1, 2].

Structural distortions are important for the electronic properties of icosahedral boron-rich solids. In some cases, they are even responsible for the semiconducting properties of these materials, in contrast to the metallic behavior of idealized structures predicted by theoretical calculations [3, 4].

Deviations from the ideal crystal structures lift the symmetry selection rules and induce the Raman activity of modes that are normally inactive. Attribution such Raman signals to vibrations of specific atoms or atomic arrangements may yield information on specific structural defects. However, defect-induced changes in the Raman spectra are relatively weak. Therefore, in this paper, we specifically emphasize the importance of a high signal-to-noise ratio for studying structural defects by Raman spectroscopy.

The periodicity of crystals is abruptly terminated at the surface. This modifies the bulk properties within a distorted layer of rearranged atoms. Therefore, when investigating bulk phonons, it must be ascertained that Raman scattering within this layer does not essentially contribute to the measured spectra. Beilby layers or adsorbed layers on the surface can aggravate this problem. As shown below, Raman spectra of boron carbide can be affected accordingly.

In this review, we present, compare and discuss the Raman spectra of numerous icosahedral boron-rich structures belonging to various structure groups. Such comparison requires spectra obtained under the same experimental conditions, including equipment, sample preparation, spectral resolution, excitation energy, etc. Therefore, most spectra shown in this review were newly reproduced often with improved spectral resolution and signal-to-noise ratio. A few Raman spectra of icosahedral boron-rich solids are taken from literature.

2. Experimental details

In an earlier Raman study of icosahedral boron-rich compounds, we have carefully tested different methods of sample preparation [5]. Accordingly, the Raman spectra in this study, as far as measured using the Jobin–Yvon Labram spectrometer, were obtained on freshly cleaved samples, ensuring clean and undamaged surfaces. However, the crystallographic orientation was not controlled and the relative intensity of Raman peaks can be slightly affected by polarization effects.

Most spectra were recorded under ambient conditions, using a Jobin–Yvon Labram spectrometer and the blue line of an Ar ion laser (487.987 nm, 2.546 eV). The spectral resolution was approximately 1.5 cm$^{-1}$ and the excitation power was about 15 mW. Some spectra were acquired using a Bruker Fourier-transform (FT) Raman spectrometer with Nd:YAG laser excitation (1064 nm, 1.1654 eV, power < 1.5 W) at a spectral resolution of approximately 2 cm$^{-1}$.

Both these acquisition methods can induce unwanted ancillary effects. The excitation energy of the Ar ion laser (2.546 eV) considerably exceeds the band gap energy in most icosahedral boron-rich solids. Because of the high absorption coefficient at 2.546 eV, the penetration depth of the exciting light can become so small that a narrow region below the surface of the sample is preferably excited. This experimental condition caused controversy in the past discussions of the Raman spectra of boron carbide. The problem of Raman excitation in the surface region in materials like boron carbide, where the interband transitions determine the penetration depth of the exciting laser light, can be avoided using a sufficiently low excitation energy, like that of the Nd:YAG laser in FT-Raman spectroscopy. This was demonstrated by Werheit et al [6] by applying different excitation energies to the very same sample and was further elaborated in a recent work [7].

A disadvantage of FT-Raman spectroscopy is the high excitation intensity of the Nd:YAG laser, which can raise the sample temperature. This might affect the spectra in such materials as $\beta$-rhombohedral boron, where phase transitions occur near room temperature.

The considerably different excitation energies and laser intensities in both methods may result in different interactions with electrons and electronic states. Therefore, electron-resonance effects and luminescence radiation cannot be excluded.

In this study, background radiation in the spectra was approximated by a straight line and subtracted from the measured spectra.

3. Results

3.1. Icosahedra

The high symmetry of the regular icosahedron shown in figure 1 is characterized by inversion and twofold, threefold and fivefold rotation axes. The fivefold rotation axis is incompatible with translation symmetry, and therefore, icosahedra are distorted in crystal structures. Franz and Werheit [8] demonstrated that the reason for this distortion is the Jahn–Teller effect. The latter reduces the icosahedral group $I_h$ to the subgroup $D_{5d}$, which corresponds to the space group $R3m$. This naturally explains the existence of $\alpha$-rhombohedral and $\beta$-rhombohedral boron structure groups with the space group $R3m$. In those structures, one of the three-fold rotation axes of the icosahedron coincides with the crystallographic c-axis.

The intra-icosahedral B–B distances summarized in table 1 suggest that the icosahedra are also distorted in other
Table 1. Intra- and inter-icosahedral B–B distances in the icosahedra of various icosahedral boron-rich solids.

| Bond                  | α-rh. B          | γ-rh. Bβ         | γ-B[14,15] | γ-AlB[16] |
|-----------------------|------------------|-----------------|-----------|-----------|
| Polar triangle        | 1.7237(5)        | 1.736–1.864     | 1.726     | 1.808     |
| Equatorial            | 1.741(4)         | 1.735–1.863     | 1.726     | 1.808     |
| Inter-icosahedral      | 1.7237(5)        | 1.736–1.864     | 1.726     | 1.808     |

The inter-icosahedral bond length is not explicitly given in [17,18]. However, the close similarity of the diffraction pattern with that of β-rhombohedral boron justifies using the value of this crystalline solid, in particular because the inter-icosahedral bond is preferably radially oriented along the fivefold rotation axis of the icosahedron. This value is used for model calculations in [19] as well.

Figure 1. Icosahedron; twofold, threefold and fivefold rotation axes are indicated.

groups of icosahedral boron-rich structures. The determining role of the Jahn–Teller effect and other structural distortions in the electronic properties of these solids was shown by Schmechel and Werheit [9] who considered the splitting of electronic states calculated by Fujimori and Kimura [10].

The electron density distributions in the icosahedra of α-rhombohedral boron and boron carbide are very similar as demonstrated by Hosoi et al. [23]. Therefore, bonds and vibration spectra are expected to be closely related (see figure 7 and the text below).

Vibrations of the isolated regular icosahedron were calculated by Beckel and Vaughan [24]. However, they can be considerably altered in crystal fields. For α-rhombohedral boron, the simplest icosahedral boron-rich solid, the phonon frequencies were determined by Beckel et al. [29], and in better agreement with the experimental Raman spectra reported by Vast et al. [35].

As parts of the Raman spectra of all icosahedral boron-rich solids are significantly determined by vibrations of the icosahedra, the variation of the bond distances summarized in table 1 will be used for the spectral analysis below.

3.2. α-rhombohedral boron structure group

3.2.1. α-rhombohedral boron. α-rhombohedral boron has the simplest crystal structure among icosahedral boron-rich solids [25]. One slightly distorted B12 icosahedron is positioned at each of the eight rhombohedral vertices of the rhombohedral unit cell (figure 2). The associated lattice parameters are 5.0643 Å and α = 58.0962°; or, in hexagonal description, a = 4.9179 and c = 12.5805 Å [26, 27]. There are two independent atomic positions: six equivalent polar atoms in the idealized structure (black circles in figure 2) form the upper and lower triangles of the icosahedron. In between, there are six equatorial atoms (bright circles in figure 2) arranged in a puckered hexagon. For B–B distances, see table 1.

According to group theory, 10 Raman-active modes (4 $A_{1g}$ singlets and 6 $E_{g}$ doublets) are expected for α-rhombohedral boron with $D_{3d}$ point symmetry [28, 29]. In total, 30 nonzero modes with 20 distinct crystal vibration frequencies (barring accidental degeneracy) are predicted [29].
The first experimental Raman spectrum of \( \alpha \)-rhombohedral boron, showing 12 peaks, was published by Richter and Ploog [30] and was subsequently confirmed by other authors [31–35]. Polarization-resolved measurements [33] provided information on the symmetry of the observed modes. FT-Raman spectra were also obtained [34].

Initial theoretical simulations of the Raman spectrum of \( \alpha \)-rhombohedral boron [29, 36] were not satisfactory. Later \textit{ab initio} lattice dynamics calculations by Vast \textit{et al} [35] yielded very good agreement between mode frequencies and measured Raman spectrum and an unambiguous assignment of all significant observed features. Finally, Shirai and Katayama-Yoshida [37] studied the phonon spectrum of \( \alpha \)-rhombohedral boron from the viewpoint of anharmonic effects. They calculated the phonon spectrum by evaluating the anharmonic force constants of individual bonds obtained from the pressure dependence of phonon frequencies. For the phonon dispersion curves, see [37].

In table 2, the frequencies of the experimentally determined Raman modes (figure 3) are compared with the theoretical results obtained by \textit{ab initio} calculation [35] and by preferably considering the anharmonicity of vibrations [37]. For most phonon modes, the agreement with the experimental data is slightly better for \textit{ab initio} results than for anharmonic calculations.

Despite these theoretical improvements, the initial calculations of Beckel \textit{et al} [29] remain important because they contain a detailed description of the specific movements of atoms and atomic groups in the different modes (see below).

Figure 3 shows the high-resolution (\( \sim 1.5\) cm\(^{-1} \)) Raman spectrum of \( \alpha \)-rhombohedral boron measured in this study. Long data accumulation resulted in a high signal-to-noise ratio and enabled the detection of weak spectral features. As a result, several weak Raman bands were found in addition to the well-known modes. Moreover, the second-order Raman spectrum of \( \alpha \)-rhombohedral boron was not reported before, to the best of our knowledge. The anti-Stokes spectrum measured for Raman shifts below 1000 cm\(^{-1} \) confirms the Stokes Raman peaks in this spectral range.

Assuming equivalent bonding of isotopes, the isotope-dependent shift of vibration modes corresponds to \( \sqrt{m^{(10)B}/m^{(11)B}} = 0.96 \). In particular, this holds for individual atoms. For larger atomic clusters, the mass difference of vibrating groups of atoms is reduced by the statistical distribution of isotopes. This effect is observed for the 527 cm\(^{-1} \) mode, which corresponds to the rotation of the rigid B\(_{12} \) icosahedra [29], and it explains the narrow width of this line. A detailed theoretical investigation of this problem by Shirai and Katayama-Yoshida [37, 38], ignoring the effect of isotope distribution, showed that among many factors, including anharmonicities, temperature is most important. As an essential new aspect concerning lattice dynamics of boron-rich structures, it was stated that the anharmonicities of individual bonding angles are rather large.

\( ^{10}\)B/\( ^{11}\)B isotope effects in form of split modes are mostly expected at high frequencies, which are associated with small assemblies of moving atoms. Figure 4 shows the highest-frequency region of the one-phonon Raman spectrum. Instead of the two \( \alpha \)-Raman-active phonons, as predicted theoretically [35], four strong peaks are clearly discernable (Nos 13–16 in table 2) and probably two very weak ones at 1094 and 1238 cm\(^{-1} \). Polarization-resolved measurements by Tallant \textit{et al} [33] assigned one of the main peaks to an \( E_g \) mode (doublet) and three others to \( A_{1g} \) (singlet) symmetry.

Beckel \textit{et al} [29] described the movement of atoms in these modes as follows. The \( E_g \) mode (No. 13) is a mixture of two vibration modes of the B\(_{12} \) cluster, having frequencies \( \omega_1 \) and \( \omega_2 \). For \( \omega_1 \), all six external two-center bonds of the icosahedra are compressed simultaneously. For \( \omega_2 \) (at a given moment) two of the six are compressed, two are stretched and two are unstrained. The effect of \( \omega_1 \) is prevalent. The \( A_{1g} \) modes predominantly originate from the radial movement of the polar atoms belonging to the triangles of the icosahedra, which induce double stress and double compression of the strong two-center bonds between the icosahedra. This movement is mixed with an intra-icosahedral vibration where the polar triangles move in opposite vertical directions, while the puckered hexagon breathes through a horizontal atomic displacement. Accordingly, the vertical movement of the polar triangle atoms is amplified and the motion of hexagon atoms is reduced. Therefore, there is little internal hexagon strain and external three-center bond strain in the vibration.

According to Beckel’s description, the triplets of polar atoms are essentially involved in the \( A_{1g} \) mode (No. 15, and 16). The radial movement of triangle atoms means double stretch and double compression of the strongest bonds, which are the inter-icosahedral two-centered bonds. Hence, triplets of boron atoms must be considered for explaining a possible isotope-dependent frequency shift of this mode. The frequency ratio of the peak maximum at 1187 cm\(^{-1} \) and the 1201 cm\(^{-1} \) shoulder, \( \omega_1 / \omega_2 = 0.988 \), agrees well with the value \( [(2m^{(10)B}+m^{(11)B})/(m^{(10)B}+2m^{(11)B})]^{1/2} = 0.986 \). This isotope distribution has a relatively high probability in comparison with that of a \( ^{10}\)B triplet vibrating against a \( ^{11}\)B triplet. Nevertheless, the shift to the very weak maximum at 1238 cm\(^{-1} \) with \( \omega_1 / \omega_2 = 0.9588 \) agrees well with the
value \((3m^{10}\text{B})/(3m^{11}\text{B})\))^{1/2} = 0.9592. Raman spectra of isotopically enriched \(\alpha\)-rhombohedral boron should be used to verify the above assignment. However, by anticipating the results for orthorhombic borides presented below, the attribution of the 1187/1201 cm\(^{-1}\) pair to the boron isotopes becomes questionable—they are shifted, but an accordingly separated pair of equally strong bands occurs, which contrasts to the abundance ratio \(^{10}\text{B}/^{11}\text{B} \approx 1/4\).

While the calculated \(A_{1g}\) mode (1192 cm\(^{-1}\)) is close to the experimental position (1187 cm\(^{-1}\)) there is a larger discrepancy for the \(E_g\) mode: 1138 and 1125 cm\(^{-1}\), respectively. The theoretical value 1138 cm\(^{-1}\) is in between the 1125 and 1160 cm\(^{-1}\) peaks. This suggests splitting of the \(E_g\) doublet, an assumption which is not supported by the polarization-resolved measurements [33].

Comparison of Raman and absorption spectra in figure 4 brings an alternative interpretation. The Raman peaks at 1201 and 1238 cm\(^{-1}\) coincide with absorption maxima and thus can be attributed to luminescence due to electronic transitions between gap states. The increasing absorption slope can well be fitted to Lucovsky's theory [39] of deep-level-to-band transitions, yielding 0.126 eV as the ionization energy of the deep level. Further investigation is required for deciding between these interpretations.

According to Beckel \textit{et al} [29], the 934 cm\(^{-1}\) mode (No. 11) involves distortions of the polar triangles as well as of the equatorial hexagon, where two of the six bonds are stretched. The 873 cm\(^{-1}\) line (No. 10) is essentially an isolated icosahedral mode, which mainly stresses the equatorial and the slant bonds of the icosahedron. The strongest peak at 795 cm\(^{-1}\) (No. 9) is attributed to the external three-centered bonds, which are compressed at an instant when two-centered bonds are stressed. Internally, the triangle and vertical bonds are most strained. The 694 cm\(^{-1}\) mode (No. 5) is assumed to be almost unaffected by the crystalline two- or three-centered forces, which explains its weakness. In this mode, the three northern-hemisphere ring atoms move south, and the southern atoms move north. In this movement, the slant bonds of the icosahedron. The strongest peak at 795 cm\(^{-1}\) (No. 9) is attributed to the external three-centered bonds, which are compressed at an instant when two-centered bonds are stressed. Internally, the triangle and vertical bonds are most strained. The 694 cm\(^{-1}\) mode (No. 5) is assumed to be almost unaffected by the crystalline two- or three-centered forces, which explains its weakness. In this mode, the three northern-hemisphere ring atoms move south, and the southern atoms move north. In this movement, the slant bonds are equally and simultaneously stretched. Strain of the three-centered bonds is assumed to be mostly responsible for
Figure 3. Raman spectrum of α-rhombohedral boron. Different colors correspond to different accumulation times. The signal is suppressed in the spectral range of the notch filter (−200 to +200 cm\(^{-1}\)). Inset shows a comparison of two-phonon Raman spectrum with calculated two-phonon density of states [37].

Figure 4. High-frequency range of one-phonon modes in α-rhombohedral boron. The black curve shows high-frequency first-order Raman spectrum. Symmetry classification is after Tallant et al [33] and theoretical mode positions are after Vast et al [35]. The red curve indicates IR absorption [34].

the 589 cm\(^{-1}\) peak (No. 4). There is a dissimilarity in the distance changes between one hexagon atom and each of the two bonded externally: one separation may increase at an instant, while the other is decreased from the equilibrium value. Vast et al [35] assign the 527 cm\(^{-1}\) mode (No. 2) to the librational mode of the entire icosahedron.

3.2.2. Boron carbide. Boron carbide belongs to the α-rhombohedral boron structure group. As shown in figure 5, its rhombohedral elementary cell additionally contains three- or two-atomic chains arranged on the main diagonal of the rhombohedron. The homogeneity range of the chemical composition extends from B\(_8\)C at the carbon-rich to about B\(_{11}\)C at the boron-rich limit (see [40]). The structure is
composed of nearly isomorphous elementary cells with varying microstructures. None of the compositions in the homogeneity range exhibits a well-defined unit cell representing the whole structure. The common elements here are the 12-atomic icosahedra, which are slightly distorted due to the Jahn–Teller effect and are located at each vertex, as well as three-atomic linear C–B–C or C–B–B chains (figure 5(a)) or BCB arrangements (figure 5(b), here, the symbol □ represents a vacancy) on the main diagonal parallel to the crystallographic c-axis. The B12 and B11C icosahedra and C–B–C, C–B–B, and B□B chains form differently composed, statistically distributed elementary cells. The resulting crystalline structure can be described using the formula (B12)α(B11C)1−α(CBC)q(CBB)p(B□B)1−p−q determined from the IR and Raman-active phonon spectra and other experimental results [41–45]. X-ray and nuclear magnetic resonance methods, which average over large sample volumes, fail in such cases. For an experimental and ab-initio study of the charge density in disordered boron carbide, see [46].

According to group theory, 11 Raman-active modes (5 \( A_{1g} \) singlets and 6 \( E_g \) doublets) are expected for each idealized boron structure (B12)X-Y-X and (B12)X-X. In real solids, these structures are mixed and modified by various other arrangements of icosahedra and chains. Therefore, a higher number of modes is expected in the experimental spectrum.

In this paper, we only show spectra of high-quality B4.3C single crystals [47, 48]. Figure 6 shows the fundamental problem of the Raman spectroscopy of boron carbide: the spectra are qualitatively different when excited by different laser energies. The problem is related to the extremely high absorption coefficient of boron carbide in the range of fundamental absorption [49, 50]. For these energies, the penetration depth of the exciting laser radiation (typically the 2.546 eV line of an Ar ion laser) is very shallow, and the bulk phonons do not contribute much to Raman scattering. Such Raman spectra are essentially determined by the near-surface region. In contrast, the penetration depth of the Nd:YAG laser light is deep enough to probe the bulk phonons [6, 7]. A discussion of the surface Raman spectrum of boron carbide is beyond the scope of this work and can be found in [7].

As mentioned, the electron density distributions in the icosahedra of \( \alpha \)-rhombohedral boron and B4.3C are very similar [23]. Therefore, a close similarity of their lattice vibration spectra is expected. This is indeed the case, as shown in figure 7, for the range of inter-icosahedral B–B vibrations, thus confirming the bulk nature of the FT-Raman spectrum. Compared with \( \alpha \)-rhombohedral boron, the Raman bands of boron carbide are broadened, as a consequence of the distorted structure. The distortion originates from the significant (20%) sharing of B11C icosahedra with carbon atoms in one of six polar sites, which corresponds to a displacement of 3.3% of the sites of the whole structure.

Table 2 attributes some boron carbide Raman modes to those of \( \alpha \)-rhombohedral boron (see also figure 29).

The librational mode of the entire icosahedron (No. 2) does not occur in boron carbide. There are two possibilities for this in observation, but neither of them is satisfactory: (i) In boron carbide, the polar boron atoms in the icosahedra are partly replaced by carbon atoms. However, this would only broaden the Raman line at most. (ii) The weak three-center bonds between the icosahedra in \( \alpha \)-rhombohedral boron are replaced in boron carbide by the rigid B–C or B–B bonds linking the equatorial icosahedral B atoms with the end atoms of the three-atomic C–B–B and C–B–C chains. The orientation of these bonds is nearly perpendicular to the rotational motion, and therefore, a rather weak effect is expected.

Line 4 in the spectrum of \( \alpha \)-rhombohedral boron is evoked by the inter-icosahedral three-center bonds, which are missing in boron carbide. Therefore, there is no corresponding peak in the boron carbide spectrum.

We attribute the strong Raman doublet at 321/270 cm\(^{-1}\) to the bending mode of the C–B–B and C–B–C chains of boron carbide, and therefore, there is no counterpart in the spectrum of \( \alpha \)-rhombohedral boron. This attribution is based on the average frequency ratio \( \sim 5.3 \) of the stretching and bending modes of three-atomic molecular chains [51]. In boron carbide, the IR-active stretching vibration of the C–B–B and C–B–C chains corresponds to the frequency \( \sim 1580 \text{ cm}^{-1} \) (see [40] and references therein), and thus, the 321/270 cm\(^{-1}\) doublet fits to the bending mode quite well. The previous attribution to ‘rotating C–B–C and C–B–B chains and accompanying wagging icosahedra’ [52] was based on theoretical calculations by Shirai and Emura [120]. The calculated frequency of that librational mode (170 cm\(^{-1}\)) was quite different from the experimental values. However, it is worth noting that the calculations in [35, 53] are adapted to specific Raman spectra, which do not represent bulk boron carbide (see [7] for details).

Interpretation of the surface spectrum (figure 6, red line) remains open. The bands in the range below \( \sim 1000 \text{ cm}^{-1} \) occur in the anti-Stokes spectrum as well, and therefore, their Raman origin is unambiguous [7]. However, it is unclear whether the spectrum is dominated by two-dimensional
Figure 6. Raman spectra of $\text{B}_4\text{C}$ boron carbide (single crystal). The black curve was recorded using an FTR spectrometer under 1.165 eV (bulk) excitation; the red curve corresponds to surface excitation (Ar laser, 2.546 eV).

Figure 7. Raman spectra of $\alpha$-rhombohedral boron and $\text{B}_4\text{C}$.

surface phonons or by distorted atomic arrangements in a certain range below the surface. As the spectrum in figure 6 is obtained with Ar laser excitation from a freshly cleaved surface, vibrations of adsorbents can be excluded in our spectra.

3.3. β-rhombohedral boron structure group

Figure 8 shows the idealized structure of β-rhombohedral boron: space group $R\overline{3}m$, structure formula $(\text{B}_{12})_2(\text{B}_{28})_2\text{B}$. The idealized rhombohedral unit cell contains 105 atoms in the sites $\text{B}(1)$–$\text{B}(15)$ with 82 Raman-active vibrational modes ($31 A_{1g}$ and $51 E_g$).

In the real structure, the occupation of site $\text{B}(13)$ is only 74.5(6)%%. However, there are additional sites $\text{B}(16)$–$\text{B}(20)$ with low occupancies (3.7, 6.8, 6.6, 8.5 and 27.2%, respectively) leading to about 106.5 atoms per unit cell (figure 9) $[73, 74]$. Accordingly, a larger number of phonons is expected.

Ogitsu et al $[54, 55]$ describe the partial occupancies of the sites $\text{B}(13)$ and $\text{B}(17)$–$\text{B}(20)$ on the basis of the
Figure 8. β-rhombohedral boron—idealized structure 
(B₁₂)(B₂₈)₂B; all sites B(1)–B(15) are assumed to be completely occupied; there are 105 atoms per rhombohedral unit cell.

development of the slightly lower nominal resolution of the equipment: 2 cm⁻¹ compared with 1.5 cm⁻¹ for excitation with the Ar laser. We suppose that the Nd:YAG laser warms the sample thus inducing the fast relaxation of optically excited electrons. At room temperature, ambient light evokes a considerable photo-effect with a very long relaxation time, which evokes certain structural distortions [56].

Carbon atoms in β-rhombohedral boron preferably substitute for boron atoms in the polar sites of the icosahedra [57]. Electron diffraction experiments on molecular structures showed that the carbon atoms are shifted towards the center of the icosahedron by about 5% [58]. Theoretical calculations by Howard et al, based on

| x       | y       | z       | Pos. | Site | Occupancy |
|---------|---------|---------|------|------|-----------|
| 0.0546  | 0.1092  | 0.1176  | 18h  | B(16)| 27.2(7)%  |
| 0.0833  | 0.1666  | 0.4760  | 18h  | B(17)| 8.5(9)%   |
| 0.1440  | 0.2880  | 0.5239  | 18h  | B(19)| 6.6(6)%   |
| 0.1805  | 0.3610  | 0.5347  | 18h  | B(19)| 6.8(6)%   |
| 0.2067  | 0.2280  | 0.0711  | 36i  | B(20)| 3.7(4)%   |
According to figure 10(a), the effect of carbon doping on the Raman spectrum of \( \beta \)-rhombohedral boron is small. The phonons at 239 and 1223 cm\(^{-1} \) vanish with increasing carbon concentration, and the features in the range 250–420 cm\(^{-1} \) and at 986 cm\(^{-1} \) weaken. At higher wave numbers (lower absolute photon energy), a luminescence peak develops with the maximum at about 1400 cm\(^{-1} \).

The spectra in figure 10 might still indicate some effect of the laser energy (see table 3). In figure 10(a) (Nd:YAG laser excitation), the intensities of the 986 and 1223 cm\(^{-1} \) phonon bands strongly decrease with increasing carbon content, while this is not observed in figure 10(b) (Ar laser excitation). Two effects of the laser excitation are possible: (i) electronic excitations induced by different laser energies and intensities and (ii) sample heating caused by the high intensity of the Nd:YAG laser, which is known to considerably affect electrical conductivity (see [25, 63] and references therein).
Doping of $\beta$-rhombohedral boron is possible by accommodating metal atoms into specific interstitial sites (see figure 11, [25] and references therein, [65–67]). N-type boron is achieved, for example, by doping with iron and vanadium atoms occupying A and D sites (see [68, 69, 74] and references therein). Comparison of figures 8 and 9 reveals that some interstitial sites are close to the partly occupied regular sites B(13) and B(16)–B(20) or even coincide with them. Accordingly, a simultaneous occupation can be excluded. This means a twofold effect of interstitial doping: (i) feeding additional electrons from the doping elements and (ii) modification of the basic electronic structure by removing regular boron atoms responsible for electronic states in the band gap [9].

Both A sites in the unit cell are symmetrically arranged on the $c$-axis close to the $B_{12}$ icosahedra, whereas the six D sites form a hexagon, which is arranged perpendicularly to the $c$-axis around the central B atom (figures 8, 9 and 11). Looking at the whole structure, the hexagon of D sites is surrounded by a larger hexagon of the six A sites in the adjacent unit cells, all together forming puckered planes [70].

Some occupancies of vanadium atoms in the A and D sites are taken from literature (table 4). The size of vanadium atoms does not allow for independent occupation of the six D sites. Therefore, it seems useful to compare the occupancy of a single A site with that of the assembly of six D sites. As shown in table 4, the occupancy ratio is about 2, implying that the hexagon of six D sites is already saturated with one vanadium atom.

The Raman spectra of $\beta$-rhombohedral boron containing 0.56, 1.03, 1.66 and 3.33 vanadium atoms per unit cell are shown in figure 12. A strong spectral variation with increasing

### Table 3. Raman-active phonons of high-purity and C-doped $\beta$-rhombohedral boron measured by different methods using Ar laser (2.546 eV) and Nd:YAG laser (1.1654 eV) excitation. Symmetry types are after Richter et al [64]. Phonon frequencies in curly brackets denote very weak peaks and are less precise, and uncertainties in the frequencies are given in brackets.

| Symmetry | Laser | High purity $\beta$-rh. B | 0.11 at.% C | 0.43 at.% C | 1.1 at.% C |
|----------|-------|--------------------------|-------------|-------------|-----------|
| $A_{ig} + E_g$ | Ar | 135 | 197 | | |
| | Nd:YAG | 219 | 222 | 239 | |
| | Nd:YAG | 282 | 291 | 309 | 313 |
| | Nd:YAG | 341(5) | 343 | 340 | |
| $A_{ig}$ | Ar | 357 | 353 | | |
| | Nd:YAG | 376 | 367 | | |
| $A_{ig} + E_g$ | Ar | 456 | 457 | 480 | 480 |
| | Nd:YAG | 492(5) | 492(5) | | |
| | Nd:YAG | [512] | [512] | | |
| | Nd:YAG | 565 | 563 | 561 | 594 |
| | Nd:YAG | [575] | [575] | 587 | 600 |
| $A_{ig}$ | Ar | 630 | 627 | 660(5) | 677 |
| | Nd:YAG | 685 | 691 | [685] | [693] |
| | Nd:YAG | 710 | 705 | 703 | |
| | Nd:YAG | 725 | 726 | 723 | |
| | Nd:YAG | 752 | 749 | 748 | 773 |
| | Nd:YAG | [797] | [797] | 783 | 795 |
| $A_{ig}$ | Ar | 813 | 814 | 841 | 858 |
| | Nd:YAG | [859] | | |
| $?A_{ig} + E_g$ | Ar | 885 | 887 | 924 | 891 |
| $?A_{ig} + E_g$ | Nd:YAG | | | 991 | |
| $A_{ig} + E_g$ | Ar | 987 | 986 | 1040 | 1084 |
| | Nd:YAG | 983(10) | 990(10) | 990(10) | 1085 |
| | Nd:YAG | [1049] | [999] | [991] | |
| $A_{ig} + E_g$ | Ar | 1097 | 1113 | 1207 | 1217 |
| | Nd:YAG | 1106 | [1109] | [1108] | 1208 |
| $A_{ig} + E_g$ | Ar | 1217 | 1223 | 1234 |
vanadium content is clear. The total range of inter-icosahedral vibrations (<500 cm\(^{-1}\)) is significantly changed; in the range of intra-icosahedral vibrations (500–1150 cm\(^{-1}\)), the intensity of some peaks is modified; a strong peak develops at about 1060 cm\(^{-1}\); and the peak at about 1100 cm\(^{-1}\) splits.

The peak at 1223 cm\(^{-1}\), representing the vibration of the central boron atom, considerably weakens. It seems possible that the occupation of the A sites surrounding the central B(15) atom in the unit cell changes the occupancy of either the B(15) or the neighboring, partly occupied B(16)–B(20) sites. This would in turn alter the polarizability, which is relevant to the Raman effect. The interaction between interstitial doping and occupancy of the partly occupied B sites has recently been confirmed experimentally \[71\]. Unfortunately, no theoretical calculation is available, which would allow the attribution of phonons to specific atomic movements.

Preliminary theoretical analysis of the B\(_{65}\)V structure by Widom \[72\] led to an optimal structure with 104 boron atoms and 2 vanadium atoms per rhombohedral primitive cell. The vanadium atoms fully occupy the A site (experimental occupation 64%), whereas the D site is empty (experimental occupation ~5%). The partly occupied B(13) boron site of the type ‘18h’ favored the accommodation of 5 atoms to the 6 available positions, that is, 83% occupancy (experimental value 75%). According to the total energies, this structure should be thermodynamically stable at \(T = 0\) K. That is, its energy lies 7 meV atom\(^{-1}\) below the tie-line from elemental boron to B\(_2\)V. This energy difference is sufficient for the structure to be stable.

Charges on atoms and charge transfer related to vanadium doping were also considered by Widom \[72\]. Since elemental boron contains inequivalent sites, even undoped boron has charged atoms. For example, the cell-center B(15) atom of Wyckoff type ‘3b’ has a net charge of 0.24 electrons according to density functional theory. Upon vanadium doping, each V atom donates 0.58 electrons and the nearby B atoms gain about 0.06 electrons each.

Four Raman peaks at 223, 287, 317 and 363 cm\(^{-1}\) develop upon doping, which are not present in the pure material. Therefore, they can probably be attributed to the interstitial, weakly bound and relatively heavy vanadium atoms (\(m_V = 50.9\) g) in the A and D sites. However, there is no explanation at present why there are four vibration frequencies for V atoms in two different interstitial sites—anisotropy of the structure and different ionizations of the V atoms are possible reasons for that. The signal at 437 cm\(^{-1}\) is possibly a shifted 458 cm\(^{-1}\) peak of the pure material.

A certain effect of V doping on the structure of \(\beta\)-rhombohedral boron was demonstrated in an x-ray study by Slack \etal \[74\]. The average occupation of the partly occupied B(16) site is reduced from 4.8 in pure boron to about 2.8 when two V atoms are accommodated in the A sites of the unit cell. Vanadium atoms in the D sites displace the partly occupied boron sites B(13), B(16), B(17) and B(18) or change their occupancy. No displacement of icosahedral boron atoms is observed. However, the electron density in the inter-icosahedral B–B bonds is modified. For intra- and inter-icosahedral force constants derived from the Raman spectra, see section 4. A correlation between inter-icosahedral force constant and Seebeck coefficient is revealed as well.
Table 4. Occupancies of $A$ and $D$ sites by V atoms in $\beta$-rhombohedral boron.

| Reference V atoms/unit cell | Occupancy % Occupancy % Rel. occupancy |
|-----------------------------|----------------------------------------|
|                            | $A$ (2A/unit cell) $D$ (6D/unit cell) |
|                            | (A/6D)                                 |
| $\text{VB}_{65}$ [73]      | 0.65 31.6 2.3 2.29                      |
| $\text{VB}_{65}$ [69]      | 1.64 64 5.3 2.01                       |

Figure 12. Raman spectra of high-purity and interstitially V-doped $\beta$-rhombohedral boron ($\text{VB}_{190}$, $\text{VB}_{103}$, $\text{VB}_{64}$, $\text{VB}_{32}$) recorded under Ar ion laser excitation (2.546 eV).

3.4. Orthorhombic icosahedral boron structures

Orthorhombic borides of MeAlB$_{14}$ type are well known. In contrast, a corresponding boron allotrope, which was synthesized in 1965 by Wentorf [75] upon subjecting $\beta$-rhombohedral or amorphous boron to high pressures, has been ignored until Oganov et al [14, 15, 76] and Zarechnaya et al [16] have recently confirmed the existence of this structure and investigated some of its properties.

3.4.1. $\gamma$-B$_{28}$ boron. This densest boron phase (2.52 g cm$^{-3}$) was synthesized under pressures above 9 GPa and at temperatures up to 1800°C by Oganov et al [14, 15, 76] and Zarechnaya et al [16]. The boron phase diagram, calculated for temperatures up to 3500 K and pressures up to 150 GPa [14], indicates that this phase is stable between 19 and 89 GPa and can be quenched to ambient conditions. Its crystalline structure (figure 13) contains 28 atoms in the unit cell and consists of icosahedral B$_{12}$ clusters and B$_2$ pairs arranged in orthorhombic symmetry (space group $Pnm$, No. 58). The lattice parameters are $a = 5.0563$, $b = 5.6126(5)$, $c = 6.9710(7)$ Å and $V = 197.83(3)$ Å$^3$. For intra- and inter-icosahedral B–B distances [14, 16], see table 1.

The Raman spectrum recorded by Zarechnaya et al [16] is displayed in figure 15 for comparison with the spectra of orthorhombic boron compounds of the MeAlB$_{14}$ type. The narrow line width reveals low lattice distortion. Empirical correlations of the Raman peaks in $\gamma$-B$_{28}$ with those of the MeAlB$_{14}$-type compounds are marked in figure 15.

We attribute the mode at $\sim 1121$ cm$^{-1}$ with a weak satellite at $\sim 1161$ cm$^{-1}$ to the inter-icosahedral B–B vibrations according to modes 13–16 of $\alpha$-rhombohedral boron (1125–1200 cm$^{-1}$), and accordingly, the 885 cm$^{-1}$ mode to the intra-icosahedral B–B vibrations (No 11 of $\alpha$-rhombohedral boron, 834 cm$^{-1}$).
The pair of modes at 651 and 591 cm\(^{-1}\) has its counterparts in the less distorted LiAlB\(_{14}\) spectrum. It is accordingly attributed to the librational mode of the rigid icosahedron (No. 2, 527 cm\(^{-1}\) in \(\alpha\)-rhombohedral boron), which is split because of the structural anisotropy.

3.4.2. Orthorhombic MeAlB\(_{14}\)-type borides. The unit cell of the orthorhombic borides (structure formula (B\(_{12}\))\(_4\)Me(1)\(_4\)Me(2)\(_4\)B\(_8\); space group \(\text{Imam}\)) consists of four B\(_{12}\) icosahedra, eight more individual B atoms and up to eight metal atoms, i.e., 64 atoms per unit cell (figure 14(b)). The structure is characterized by a predominantly covalent boron network, which is formed by chains of icosahedra arranged parallel to the \(c\)-axis and the (110) direction. Some of the external bonds of the icosahedra are directly inter-icosahedral and some are indirectly inter-icosahedral via the isolated boron or metal atoms. The metal sites are outside the icosahedra, in the large holes of the boron framework. In most compounds, they are only partly occupied [77–88]. For a summary of lattice parameters, see [89, 90].

The structural parameters of the crystals investigated in this paper are listed in table 5. A comparative investigation of some optical and electronic properties of LiAlB\(_{14}\), MgAlB\(_{14}\) and ErAlB\(_{14}\) is reported in [89, 90]. The first-order Raman spectra of these compounds and of HoAlB\(_{14}\) [84] are shown in figure 15.

The similarity of the Raman spectra in figure 15 confirms the attribution of the corresponding materials to the same structure group. Nevertheless, there are distinct differences in the frequencies and intensities of the Raman modes, which reveal the effect of bonding in those compounds.

The narrow Raman lines in the spectrum of LiAlB\(_{14}\) show that its lattice is relatively undistorted, as compared with the other orthorhombic compounds. This conclusion is underlined by the clear second-order Raman spectrum shown in figure 16. The reason for the low distortion may be that the metal sites are almost occupied in LiAlB\(_{14}\), whereas the occupancy is much lower in other crystals (see table 5).

The librational mode of the rigid icosahedron in \(\alpha\)-rhombohedral boron (527 cm\(^{-1}\)) occurs in LiAlB\(_{14}\) as well; however, it is apparently split into a very strong line at 566 and a weaker one at 482 cm\(^{-1}\). The reason for this splitting is probably the anisotropy of the structure. In the spectra of the other members of this group, the main line is slightly shifted to higher energies, and the line splitting is weaker, if present at all.

The modes representing the inter-icosahedral two-center bonds (Nos. 13–16 in \(\alpha\)-rhombohedral boron) are distinctly separated from each other in the orthorhombic structures, particularly in LiAlB\(_{14}\). The reason for this might be the structural anisotropy and the different inter-icosahedral bonding as compared with the rhombohedral structures.

The weak and narrow bands at low frequencies are probably due to the individual metal atoms. The peaks occurring at 325, 331, 335 and 338 cm\(^{-1}\) for Li, Mg, Er and Ho compounds, respectively, may be due to the Al atoms, which are present in all these materials.

Figure 16 shows the second-order Raman spectrum of LiAlB\(_{14}\). The absorption spectrum related to the stretching modes of individual atoms in this structure [90] is also plotted for comparison. Obviously, there is no correlation between the absorption and Raman spectra. Hence, the high-frequency stretching vibrations of individual atoms in this structure are not Raman-active, as is well known from molecular M-X-M structures. The ratio \(\omega(\text{^{11}B})/\omega(\text{^{10}B}) = 1.034\) of the peak frequencies attributed to the boron isotopes fits quite well to the value \((m(\text{^{11}B})/m(\text{^{10}B}))^{1/2} = 1.042\), thereby justifying these assignments. For the peaks assigned to the Li isotopes,
Figure 15. Raman spectra of orthorhombic icosahedral boron structures. Bottom: $\gamma$-B$_{28}$ [16]; top: MgAlB$_{14}$-type borides; excitation: Ar ion laser (2.546 eV).

Table 5. Structural details of MeAlB$_{14}$ crystals.

|       | $a$       | $b$       | $c$       | Me occupancy (%) | Al | Reference |
|-------|-----------|-----------|-----------|------------------|----|-----------|
| LiAlB$_{14}$ | 5.8469(9) | 8.1429(8) | 10.3542(6) | 100              | 95.6 | [91]      |
| MgAlB$_{14}$ | 5.848(1)  | 8.112(1)  | 10.312(1) | 78               | 75  | [92]      |
| HoAlB$_{14}$ | 5.841(5)  | 8.188(5)  | 10.410(6) | 63.3             | 74.04 | [93]     |
| ErAlB$_{14}$ | 5.8157(2) | 8.1816(3) | 10.3956(4) | (62)             | (75) | [90, 84] |

Occupancies in brackets were taken from a nearly equivalent ErAlB$_{14}$ crystal ($a = 5.8200(1)$, $b = 10.3950(4)$ and $c = 8.1825(3)$ [84]).
the corresponding relations are $\omega^{-1}({}^6\text{Li})/\omega^{-1}({}^7\text{Li}) = 1.058$ and $(m({}^6\text{Li})/m({}^7\text{Li}))^{1/2} = 1.080$. The peak at lower frequencies can possibly be attributed to Al, the remaining interstitial atom.

The bending vibrations of such arrangements are Raman-active and are expected at much lower frequencies. For boron carbide, the reduction factor is $\sim$5.3 (see [51] and table 2). Accordingly, the singlet peaks in the spectra of the orthorhombic compounds between 200 and 400 cm$^{-1}$ are probably due to the bending modes associated with individual atoms.

3.5. Amorphous boron

The basic structural element of amorphous boron is the $\text{B}_{12}$ icosahedron. According to neutron diffraction studies, the icosahedral units are essentially intact and disorder occurs in the linking between the icosahedra. A medium-range order similar to crystalline $\beta$-rhombohedral boron was shown to exist, suggesting that the icosahedra are more or less statistically arranged, and their external bonds are covalently saturated [17, 94].

Figure 17 shows the FT-Raman spectrum of amorphous boron (H.C. Starck, Goslar) [95]. X-ray diffraction measurements revealed that the sample contains less than 0.5–1% crystalline phases. As these values are within the detection limit, the sample is assumed to be completely amorphous. As expected for a disordered solid, the Raman spectrum does not contain narrow lines. There are two broad bands with maxima at 1166 and 827 cm$^{-1}$. We attribute them, respectively, to inter-icosahedral B–B vibrations (corresponding to modes 13–16 of $\alpha$-rhombohedral boron) and to the intra-icosahedral B–B vibrations (corresponding to mode 11 of $\alpha$-rhombohedral boron).

Ignoring a frequency shift, there is a clear similarity between the amorphous boron spectrum and the part of the YB$_{36}$ structure spectra representing their inter- and high-frequency intra-icosahedral vibrations (see below). Of course, spectral features are broadened for amorphous boron.

The Raman spectrum calculated by Shirai and Thorpe [96] confirms the attribution of the 1200 cm$^{-1}$ mode to the inter-icosahedral vibrations. The broad range of calculated intra-icosahedral vibrations, which strongly increase towards low frequencies, agrees with the experiment only for the peak close to 900 cm$^{-1}$. The absolute maximum of the theoretical curve, near 400 cm$^{-1}$, is barely discernible as a weak shoulder in the experimental spectrum.

3.6. Tetragonal boron structures

Initially, tetragonal boron allotropes were assumed to be alternatives to the rhombohedral modifications, but later investigations on high-purity boron led to the conclusion that foreign atoms are required to stabilize the structures. Therefore, in solid form, these structures occur in boron compounds only. Tetragonal boron phases have attracted attention recently, because they were found in pure boron-rich nanobelts [97–100].

3.6.1. $\alpha$-tetragonal boron structure group. The 50 atoms of the idealized unit cell of $\alpha$-tetragonal boron (figure 18) are distributed between four $\text{B}_{12}$ icosahedra at 4c positions and two boron atoms in 2b positions (Wyckoff notation). In the isostructural borides, the 2b positions and an additional interstitial void position 2a are completely or partly occupied by foreign, preferably metal atoms [101]. $\text{B}_{38}\text{Al}_3\text{C}_2$ (lattice parameters $a = 12.390(3)$, $b = 12.637(3)$ and $c = 10.136(4)$ Å) belongs to this structure group; its Raman
Figure 17. Measured (black curve [95]) and calculated (red curve [96]) FT-Raman spectra of amorphous boron.

Figure 18. Schematic structure of $\alpha$-tetragonal B.

3.6.2. $\beta$-tetragonal boron structure group. $\alpha$-AlB$_{12}$ is the prominent representative of the $\beta$-tetragonal boron structure group (figure 20). Its structure formula is (B$_{12}$)$_2$B$_{20}$Al$_{13.33}$ and the space group is $P4_12_12$ or $P4_32_12$. The structure formula of $\gamma$-AlB$_{12}$ is (B$_{12}$)$_4$B$_{20}$B$_{20}$Al$_{6.66}$ and its space group is $P2_12_12_1$. The $\text{B}_{20}$ structure elements consisting of two incomplete, fused $\text{B}_{12}$ icosahedra are different in both structures. One of them, called $\text{B}_{20}$-(C$_2$), occurs in both structures; another one, called $\text{B}_{20}$-(C$_3$), was found in $\gamma$-AlB$_{12}$ only (for more details, see [104–106]). The close relationship between these two structures is demonstrated by describing $\alpha$-AlB$_{12}$ in the pseudo-orthorhombic presentation. Then, the unit cell of $\gamma$-AlB$_{12}$ is two-thirds of the pseudo-orthorhombic cell of $\alpha$-AlB$_{12}$ [106]. This relation between the two structures was confirmed using IR phonon spectra and other optical properties [107].

In this paper, we present the Raman spectra of the following compounds:

**$\alpha$-AlB$_{12}$ structures**
- $\alpha$-AlB$_{12}$ (Higashi) [20, 108]
- $\alpha$-AlB$_{12}$:Er (Gurin and Korsukova) [110]
- Al$_{1.2}$Be$_{0.5}$B$_{22}$ (Higashi) [20]
- Al$_{1.0}$Be$_{0.97}$B$_{22}$ (Gurin and Korsukova) [110]
- $\alpha$-AlB$_{12}$:Eu (Al$_{1.09}$Be$_{0.44}$ Eu$_{0.022}$ B$_{22}$) (Gurin and Korsukova) [110]

**$\gamma$-AlB$_{12}$ structures**
- $\gamma$-AlB$_{12}$ (Gurin and Korsukova) [109, 110]
- $\gamma$-AlB$_{12}$:Si(Al$_{1.0}$B$_{15}$Si$_{0.7}$) (Gurin and Korsukova) [109, 110]
Figure 19. FT-Raman spectrum of B_{48}Al_{3}C_{2} [102].

Figure 20. β-tetragonal boron structure. (a) chains of B_{12} icosahedra that run along the x- and y-axes. (b) helical connection of condensed double-icosahedra along the z-axis.

γ-AlB_{12}:Ho (Gurin and Korsukova)  
Al_{1.44}Be_{0.65}B_{22} (Higashi) [21]

The Raman spectra are shown in figures 21 and 22 and the Raman frequencies are listed in table 6. The spectra of the α-AlB_{12} and γ-AlB_{12} groups are so similar that it is hardly reasonable to assume different structures.

The positions and intensities of specific Raman modes change for different compositions within one structure group. One reason for that is the different occupancies of the metal sites, and those for α-AlB_{12} and Al_{1.7}Be_{0.5}B_{22} [110] are listed in table 7. The associated changes in the Raman spectra are remarkable. This is in contrast to α-AlB_{12}:Er where the spectrum is not essentially different from that of the pure compound.

The spectra of the γ-AlB_{12}-type compounds distinctly change when Al atoms are partly replaced by Mg, as shown for Al_{1.44}Mg_{0.55}B_{22} [111]. Otherwise, there is no significant difference in the spectra of γ-AlB_{12}:Si (compound Al_{1.8}B_{15.6}Si_{0.7}; 0.1 wt.% Si) [110] and γ-AlB_{12}:Ho (Ho content unknown). The reason may be that the content of foreign atoms is relatively low, or they are accommodated in interstitial holes with weak bonding to the boron framework.
Figure 21. Raman spectra of $\alpha$-AlB$_{12}$ and of the related compounds Al$_{1.2}$Be$_{0.5}$B$_{22}$ [20, 108] and $\alpha$-AlB$_{12}$ : Er [110].

Figure 22. Raman spectra of $\gamma$-AlB$_{12}$ and some related compounds. $\gamma$-AlB$_{12}$ : Si (Al$_{1.0}$B$_{15.6}$Si$_{0.7}$; 0.1 wt. % Si) [110], $\gamma$-AlB$_{12}$ : Ho [109, 110], and Al$_{1.44}$Mg$_{0.55}$B$_{22}$ [21]. Ar ion laser excitation (2.546 eV).

Figure 23 shows two spectra of other compounds attributed to the $\alpha$-AlB$_{12}$ structure by Gurin and Korsukova [110]. However, they are significantly different from the spectra shown in figure 22 and between each other. At most, there is some similarity between the spectra of Al$_{1.0}$Be$_{0.97}$B$_{22}$ and $\gamma$-AlB$_{12}$-type Al$_{1.44}$Mg$_{0.55}$B$_{22}$. We assume that these structures are different from $\alpha$-AlB$_{12}$. Further investigations are required to solve this discrepancy.

3.7. $YB_{66}$ structure group

The $YB_{66}$ structure group is the most complex among the icosahedral boron-rich solids. Its boron framework is composed of B$_{12}$(B$_{12}$)$_{12}$ giant icosahedra consisting of a central icosahedron, 12 surrounding B$_{12}$ icosahedra and B$_{80}$ clusters, in which 80 sites are statistically occupied by 42 boron atoms (figure 24). In total, this model contains 1584 boron atoms per unit cell. The yttrium sites enclose the B$_{80}$ clusters in octahedral arrangements; there are eight such octahedral Y arrangements per unit cell. However, the Y sites are not completely occupied as well; the actual composition is determined by the occupancy of the Y sites, for example, 0.5 for YB$_{66}$ [22, 112].

The experiment, however, suggests more than 1584 boron atoms in the unit cell. The corresponding data for some
Table 6. Raman frequencies of $\alpha$-AlB$_{12}$ and $\gamma$-AlB$_{12}$.

| Raman frequencies (cm$^{-1}$) | $\alpha$-AlB$_{12}$ | $\gamma$-AlB$_{12}$ |
|-------------------------------|----------------------|----------------------|
| 1                            | 1248                 | 1252                 |
| 2                            | 1219                 | 1223                 |
| 3                            | 1139                 | 1136                 |
| 4                            | 1125                 | 1125                 |
| 5                            | 1058                 | 1058                 |
| 6                            | 1039                 | 1035                 |
| 7                            | 927                  | 932                  |
| 8                            | 906                  | 905                  |
| 9                            | 866                  | 867                  |
| 10                           | 844                  | 844                  |
| 11                           | 804                  | 805                  |
| 12                           | 711                  | 709                  |
| 13                           | 680                  | 680                  |
| 14                           | 663                  | 656                  |
| 15                           | 632                  | 633                  |
| 16                           | 615                  | 615                  |
| 17                           | 581                  | 578                  |
| 18                           | 561                  | 562                  |
| 19                           | 516                  | 516                  |
| 20                           | 495                  | 495                  |
| 21                           | 472                  | 476                  |
| 22                           | 416                  | 414                  |
| 23                           | 357                  | 357                  |
| 24                           | 336                  | 346                  |
| 25                           | 294                  | 294                  |
| 26                           | 265                  | 265                  |
| 27                           | 230                  | 230                  |
| 28                           | 217                  | 218                  |
| 29                           | 195                  | 196                  |

Table 7. Occupancies of metal sites in $\alpha$-AlB$_{12}$ and Al$_{12}$Be$_{0.5}$B$_{22}$ [20, 108].

| Me site | $\alpha$-AlB$_{12}$ | Al$_{12}$Be$_{0.5}$B$_{22}$ |
|---------|---------------------|---------------------------|
| Al(1)   | 0.717(7)            | 0.390(2)                  |
| Al(2)   | 0.491(3)            | 0.341(2)                  |
| Al(3)   | 0.240(6)            | 0.477(2)                  |
| Al(4)   | 0.150(3)            |                           |
| Al(5)   | 0.021(5)            | 0.021(1)                  |
| Be(1)   | 0.33(1)             |                           |
| Be(2)   | 0.19(1)             |                           |
| Be(3)   | 0.05(1)             |                           |

YB$_{66}$-type structures are listed in table 8. Some properties of YB$_{66}$-type crystals were reported in [113].

The Raman spectra of these compounds, shown in figure 25, largely agree. Obviously, the spectra are essentially determined by vibrations of the boron framework. Apart from the spectral resolution, there is no essential difference between conventional and FT-Raman spectra (inset in figure 25) [113], and thus, the penetration depth of the Ar laser is sufficient for exciting the bulk phonons. The intra- and inter-icosahedral B–B distances vary considerably. Because of this variation and the structural distortions due to incomplete cluster occupation, broadening is expected for the Raman peaks, and it is observed experimentally.

Raman spectra of the following YB$_{66}$-type compounds were measured in this work: YB$_{66}$ (Tanaka) [112, 113], GdB$_{66}$ (Tanaka) [112, 113] and YB$_{66}$ (IPMS Kiev).

According to the phonon spectra of other icosahedral boron structures, the spectral range between about 500 and 1200 cm$^{-1}$ can be attributed to vibrations of the icosahedra, while peaks at lower frequencies may be due to inter-cluster vibrations. Above 200 cm$^{-1}$ (the limit determined by the notch filter in our equipment), there is no effect of the metal atoms on the Raman spectra, which should be easily discernible because of the large difference in atomic masses (88.9 for Y and 157.25 for Gd). The peaks at frequencies above 1200 cm$^{-1}$ are due to luminescence related to gap states.

It seems natural to assign the strong band around 1050 cm$^{-1}$ to mode 15 in $\alpha$-rhombohedral boron. According to Beckel, this mode originates from the radial movement of the boron atoms in the polar triangles. Of course, in YB$_{66}$, this mode is expected at the upper end of the spectrum as well. In mode 13 (1125 cm$^{-1}$ in $\alpha$-rhombohedral boron), the radial external bonds of the icosahedra are stressed. Another strong band in $\alpha$-rhombohedral boron at 934 cm$^{-1}$ (mode 11) involves distortions of the polar triangles and of the equatorial hexagon. This is expected to appear in YB$_{66}$ as well. We attribute the 817 cm$^{-1}$ peak to this mode.

4. Force constants

Force constants, which determine atomic vibrations in some icosahedral boron-rich solids, were calculated by Weber and Thorpe [36], Beckel et al [116, 117] and Shirai et al [118, 119]. Values derived by Kuhlmann and Werheit [116] from the Raman spectra of boron carbide were based on assumptions, which are different from those of the present work; see table 9 for comparison.

As shown above, the Raman modes 13–16 and mode 11 in $\alpha$-rhombohedral boron and the corresponding modes in the other icosahedral structures can be attributed to essentially the same type of inter-icosahedral and intra-icosahedral B–B vibrations. Accordingly, they are the basis for estimating the related force constants. We presume that the nature of vibrating atomic configurations is largely independent of the individual structure. Relative to $\alpha$-rhombohedral boron, we particularly expect this for boron carbide, Be$_{2}$As, and $\beta$-rhombohedral boron (black symbols in figures 26(a) and (b)), probably somewhat less for amorphous boron, YB$_{66}$, $\alpha$-AlB$_{12}$, and $\gamma$-AlB$_{12}$ (green symbols), and even lesser for $\gamma$-B$_{28}$ and the other orthorhombic borides like LiAlB$_{14}$ (red symbols). The data for Be$_{2}$As are taken from [120] (spectrum) and [11] (B–B distances).

The relative $k$ values for the icosahedral boron-rich solids are related to $\alpha$-rhombohedral boron using the formulas $\omega = \sqrt{k/\mu}$ and $\mu = m_A m_B / (m_A + m_B)$, thus avoiding the problem of unknown masses. The results are displayed in figure 26(a) for inter- and in figure 26(b) for intra-icosahedral B–B vibrations.

After Badger [122], the force constant $k$ in equation $\omega = \sqrt{k/\mu}$ is quite accurately related to the distance $d_0$ between the vibrating atoms as

$$k^{1/3} = a_{ij}(d_0 - b_{ij}),$$
Figure 23. Raman spectra of Al$_{1.0}$Be$_{0.97}$B$_{22}$ and Al$_{1.09}$Be$_{0.44}$Eu$_{0.022}$B$_{22}$ (Eu, 1.43 wt.%). Ar ion laser excitation (2.546 eV).

where the parameters $a_{ij}$ and $b_{ij}$ depend on the nature of the vibrating atoms. Badger initially proved the validity of this relation for two-atomic molecules with equal parameters for all atoms belonging to the same row of the periodic system of elements. Later, the applicability of this relation was verified for vibrations in solids as well (see [122]). In figure 26(a), this is confirmed for the relative force constant of the inter-icosahedral two-center bond. Badger’s rule fits well to the experimental data with the parameters listed in table 1.0.

For the intra-icosahedral B–B bonds (figure 26(b)), Badger’s rule seems less satisfactory, although it remains within the margins of possible B–B distances. These distances are considerably spread, and it is unknown which value is most relevant for the Raman-active mode. It is possible that Badger’s rule is not entirely valid for the boron atoms incorporated into the icosahedra as compared with a real two-center bond.

In general, the force constants are smaller in the more complex icosahedral boron structures than in $\alpha$-rhombohedral boron. For boron carbide, the relative shifts satisfactorily agree with those predicted theoretically (see table 9).

The Raman-active phonons selected for the preceding determination of relative force constants are attributed to specific intra- and inter-icosahedral B–B vibrations. Therefore, the absolute force constants can be roughly estimated by simply taking individual boron atoms for determining the reduced mass in $\omega = \sqrt{k/\mu}$. The resulting force constants included in table 10 are higher than those predicted theoretically. However, it must be considered that the theoretically determined $k$ values describe the spring-like force constant in the specific bond between two adjacent atoms, while $\omega = \sqrt{k/\mu}$ yields an effective force parameter, which is active in the phonon frequency $\omega$; thus taking the complete bonding between the vibrating atomic assemblies into account. Therefore a close agreement can not be expected.

As shown in figure 12, the Raman modes of the B–B vibrations spectra of $\beta$-rhombohedral boron exhibit strong and complex splitting when vanadium atoms are accommodated into interstitial sites. The relative modification of the force constants depending on the vanadium content is shown in figure 27. The split and shift of the Raman lines suggest an anisotropic distortion of the icosahedra or an
Table 8. Experimentally determined parameters of some YB$_{66}$-type structures compared with structure analysis by Richards and Kasper [22].

| Chemical composition | $a$ (nm) | Density (g cm$^{-3}$) | N(B) (unit cell$^{-1}$) | N(Y) (unit cell$^{-1}$) | N(Tr) (unit cell$^{-1}$) | Reference |
|----------------------|----------|----------------------|------------------------|------------------------|------------------------|----------|
| YB$_{66}$            | 2.3440   | 2.52                 | 1610                   | 24.4                   | –                      | [22]     |
| YB$_{63.75}$         | 2.3445   | 2.5687               | 1628                   | 26.4                   | –                      | [114]    |
| YB$_{62}$            | 2.34364  | 2.5662               | 1624                   | 26.2                   | –                      | [115]    |
| YB$_{56}$            | 2.34600  | 2.5927               | 1626                   | 29.0                   | –                      | [115]    |
| YMn$_{2.2}$ B$_{62.4}$ | 2.34258  | 2.64                 | 1628                   | 26.1                   | 5.3                    | [115]    |
| YMo$_{0.2}$ B$_{63.5}$ | 2.34300  | 2.6344               | 1634                   | 25.7                   | 2.4                    | [115]    |
| YP$_{0.096}$ B$_{63.3}$ | 2.34223  | 2.6355               | 1630                   | 25.7                   | 2.5                    | [115]    |
| YP$_{0.14}$ B$_{62.0}$ | 2.34055  | 2.6762               | 1629                   | 26.3                   | 3.7                    | [115]    |

Figure 25. Raman spectra of YB$_{66}$ (Ar laser) [112, 113], YB$_{66}$ (IPMS Kiev), and GdB$_{66}$ [112, 113] measured under Ar ion laser excitation (2.546 eV). Inset shows FT-Raman spectrum of YB$_{66}$ measured under 1.165 eV excitation [113].

Table 9. Intra- and inter-icosahedral force constants in $\alpha$-rhombohedral boron and boron carbide; for further discussion see [23].

| Force constants | This work (mdyne Å$^{-1}$) | This work (rel. units) | This work (mdyne Å$^{-1}$) |
|-----------------|-----------------------------|------------------------|-----------------------------|
| B–B             |                             |                        |                             |
| intra-icos.     | 1.3                         | 1.2                    | 0.64                        | 1                          | 2.78       |
| inter-icos.     | 3.0                         | 3.1                    | 1.3                         | 1                          | 4.48       |
| B–C             | 0.7                         | 1.0                    | 1.1                         | 0.4                        | 2.39       |
| inter-icos.     | 1.8                         | 2.4                    | 2.4                         | 0.71                       | 3.18       |

inhomogeneous distribution of the charge transferred from the vanadium atoms to the icosahedra in the boron framework.

Intra- and inter-icosahedral force constants behave differently. The intra-icosahedral force constant splits when the vanadium content exceeds one atom per unit cell. The inter-icosahedral force constant abruptly splits into three branches of different intensities already at very low vanadium contents. For low vanadium content, the center of gravity of the inter-icosahedral force constant is essentially determined using the central branch, but at higher doping level, it decreases and falls even below the value for high-purity boron.

As shown by Widom [72] (see section 3.3), most of the charge donated by the vanadium atoms is transferred to the nearby boron atoms. The split of intra- and inter-icosahedral vibrations seems to indicate that the charge transferred from the vanadium atom in the A site is not homogeneously distributed over the icosahedron. Moreover, as proved for
Figure 26. Relative force constants of the inter-icosahedral (a) and intra-icosahedral (b) B–B vibrations in the icosahedral boron-rich structures versus B–B distances (table 2). Symbols present averaged experimental data, and their color is explained in the text. The error margins show maximum deviation. These data correspond to the minimum B–B distances in table 1 and to the maximum extensions of the associated spectral ranges. The solid line represents Badger’s rule (parameters in table 10).

Fe-doped boron [70], the ionization of the V atoms in the A site could depend on concentration.

The strong effect of vanadium doping on the electronic properties of β-rhombohedral boron is demonstrated by the Seebeck coefficient plotted in figure 26 [68, 123], which even changes sign at V contents below 0.5 atoms per unit cell. Obviously, this effect takes place in non-icosahedral structure elements, because only the inter-icosahedral force constant is affected, while the intra-icosahedral ones remain unchanged in this doping range.

The electronic properties of 3d-metal-doped β-rhombohedral boron exhibit extraordinary features, which cannot be explained by conventional charge transfer from the dopant to the host. Werheit [125] discussed the electronic properties assuming a strong Kondo-related correlation between the diluted 3d atoms. The reason

| Table 10. Parameters for fitting Badger’s rule to the relative intra- and inter-icosahedral force constants in figures 26(a) and (b) \((f_{\text{B-rhom}} = 1)\). |
|-----------------|-----------------|-----------------|
| B–B vibrations | \(a_{ij}\) | \(b_{ij}\) |
| Intra-icosahedral | 4.76 | 1.563 Å |
| Inter-icosahedral | 1.28 | 0.89 Å |
Figure 27. Relative change in the force constants of intra-icosahedral and inter-icosahedral B–B vibrations versus V content in β-rhombohedral vanadium-doped boron. Black symbols and lines represent the force constants determined from the maxima of single peaks or shoulders in the Raman spectra; red symbols represent the visually determined center of all Raman peaks associated with the inter-icosahedral B–B vibrations.

Figure 28. Seebeck coefficient versus V content in β-rhombohedral boron. Experimental data are taken from Werheit et al [68] (solid squares) and Slack et al [124] (open squares).

5. Conclusions

The Raman-active vibrations of the icosahedra in icosahedral boron structures were previously described for α-rhombohedral boron by Beckel et al [29]. They were identified in all icosahedral boron-rich solids in this study. As an example, figure 29 presents a correlation between the Raman lines of α-rhombohedral boron with those of boron carbide and LiAlB₁₄.
As shown, the spectra of some compounds distinctly deviate from the reference spectra, even though these compounds have been attributed to the same structure group. Such discrepancies require further investigation.

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Figure 29. Correlation of the Raman peak positions in α-rhombohedral boron, B₄.₃C boron carbide and LiAlB₁₄. The linewidths roughly indicate the intensities of the Raman lines.

The absence of specific lines in the spectra can usually be explained on the basis of structural details. For example, the librational mode of the rigid icosahedron occurring in the spectrum of α-rhombohedral boron is missing for boron carbide. One reason is that the weak inter-icosahedral three-center bonds between equatorial atoms of adjacent icosahedra are replaced in boron carbide by strong two-center bonds to the end atoms of the three-atomic chains. Accordingly, this vibration is suppressed in boron carbide. In contrast, it occurs in the LiAlB₁₄ spectrum and is split because of the considerable structural anisotropy.

It is demonstrated that Raman spectroscopy is a very sensitive tool for detecting different types of modification of crystalline structures. Measurable changes in the Raman spectra are also induced, for example, by slightly lifting the selection rules or by modifying the polarizability of atoms or atomic groups as a consequence of electron transfer. Reliable attribution of Raman modes to structural elements and their movement is required for a detailed interpretation of such effects. The shift or modification of Raman modes also yields immediate information on the change of force constants.

For all the studied icosahedral boron-rich structures, the force constant of inter-icosahedral B–B bonds can well be fitted using Badger’s rule. The agreement is less satisfactory for intra-icosahedral B–B bonds.
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