Lattice Vibrations, MIR and FIR Optical Properties of Boron and Icosahedral Boron-Rich Borides
I. Alpha-Rhombohedral Structure Group

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General remarks on the structure and the lattice vibrations of the different structure groups of boron and icosahedral boron-rich borides are made. In detail, the lattice vibrations of the alpha-rhombohedral boron structure group are systematically investigated by group theory. Reflectivity spectra of boron-carbide of different chemical composition and preparation and of B_6O were measured in the MIR and FIR spectral range. These phonon spectra are analyzed in connection with previous experimental and theoretical results obtained by other authors. A proposal for the intercorrelation of the phonon spectra of this structure group is derived. The plasma resonance spectra of boron carbide and B_6O yield qualitative information on the dependence of electronic transport on material properties.

A) General Remarks

Introduction

The crystalline modifications of boron and of its boron-rich compounds exhibit a variety of inorganic complex crystal structures, which is not known from any other element. This variety extends from the alpha-rhombohedral modification of elementary boron with 12 B atoms to the structure type of YB_{66} with about 1600 B atoms per unit cell. Most of these structure types are related to one another. They contain nearly regular B_{12} icosahedra, whose high symmetry is characterized by 6 five-fold, 10 three-fold and 15 two-fold rotation axes as symmetry elements; alpha-rhombohedral boron contains one, the unit cell of YB_{66} 104 of them. These structures [1] characterized by B_{12} icosahedra are the object of the subsequent investigations, which means that e.g. hexaborides and dodecaborides will not be considered.

In spite of the obviously strong bonding within the icosahedra, the boron-type crystals are not at all molecular crystals: 26 electrons occupy the strongly bonding orbitals within the icosahedron and the remaining ten electrons are at the disposal of the linkage to other icosahedra or structure units [2]. This leads to a lack of two electrons per icosahedron. Nevertheless the ionic contribution to the bonding within these structures is rather low, which follows from the oscillator strengths of the lattice vibrations (see below). The intericosahedral bond strength is assumed to be even higher than the intraicosahedral one [3], which accounts for high melting points, small extension coefficients, great hardness and related mechanical properties. The contrast to molecular crystals can clearly be seen in the phonon spectra, where internal and external vibrations of the icosahedra are superimposed and not separated like in molecular crystals.

Besides the icosahedra, fragments of them and related condensed systems are found in these structures. Periodical arrangements of icosahedra or such related polyhedra in chains, layers or three-dimensional networks form the main structures of these crystals. Within these polyhedral boron networks remain voids beeing large enough to accommodate additional single boron or foreign atoms in periodical or statistical arrangements. Most borides and solid solutions can thus be attributed to the modifications of elementary boron, and hence an especially narrow relationship and systematic change of properties within these structure families can be expected.

Thus the modifications and compounds of boron offer favourable presuppositions to investigate the properties of complex crystal structures, the influence of the degree of complexity and the effects of substitutional and interstitial foreign atoms on the physical properties of such

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crystals. A rather immediate information on the structural properties of crystals and their relation to physical properties is obtained from the lattice vibrations, whose IR active branches determine the optical absorption and reflectivity spectra in the MIR and FIR spectral region. In the case of boron modifications and compounds, investigations of this kind were hithertoo confined to particular materials; sometimes even in these cases only incomplete spectra are reported. Therefore in a series of papers the lattice vibration spectra of the different structure families of boron and its boron-rich compounds with icosahedral structures will be investigated. Group theoretical determinations of the lattice vibrations were performed and will be discussed in relation to experimentally obtained reflectivity and absorption spectra in the MIR and FIR spectral range taking into account previous results.

Lattice Vibrations Obtained by Group Theory

The fundamental procedure to determine the normal vibrational modes of molecular and crystalline structures is described in the literature (cf. e.g. [4, 5, 6]). The expenditure increases with the number of atoms (in crystals the number of atoms per unit cell) to be considered, and hence in the case of boron and its boron-rich compounds it increases especially with the degree of complexity.

From structure analysis the atom positions and symmetry groups needed for the group theoretical investigations are known. Then the normal modes at $q = 0$ in the center of the Brillouin zone are classified according to the symmetry types of their symmetry group, which can be derived from stereo-chemical structure models.

The number of normal modes attributed to the i-th symmetry type is equal to the dimension of the irreducible subspace. U_i. These eigenfrequencies are k-fold degenerated, when the corresponding normal mode belongs to a k-dimensional symmetry type. Accordingly the number of symmetry types with different frequencies is

$$n_i = \mathrm{Dim}\, U_i/\chi_i(E)$$

with $\mathrm{Dim}\, U_i = h_i/h \sum_\sigma \chi_i(\sigma^{-1}) * \mathrm{trace}\,(\sigma)$;
h_i: Dimension of the i-th irreducible representation, h: order of the group, χ_i: i-th character of the group and $\mathrm{trace}\,(\sigma) = u(\sigma) * k(\sigma)$

$u(\sigma)$ = number of atoms undisplaced during the symmetry operation.

$k(\sigma)$ = trace of σ referring to one of the coordinate systems undisplaced during the symmetry operation σ (to be taken from tables in literature).

Accordingly, the main fundamental problem in performing the group theoretical analysis of lattice vibrations proves to be the determination of the number $u(\sigma)$ of atoms undisplaced during the symmetry operations σ.

The effect of the actual crystal field on the vibrations of structure elements (icosahedra or other subunits) incorporated in the structure is taken into consideration, whilst the irreducible representation of e.g. the icosahedral group is reduced e.g. in the rhombohedral lattice. From this procedure moreover result the initial vibrations of the structure elements from which the IR active vibrations of the final crystal structure originate.

From the vibrations derived in this way the translations are to be eliminated as spurious. According to Matossi [5], the rotational vibrations are interpreted as liberational vibrations of structure groups. Then, according to the selection rules the IR active and the Raman active vibrations result as well as their polarization. Of course idealized structures are assumed, which means that the icosahedra are taken as undistorted and the positions of the single atoms are assumed to be completely occupied.

Unfortunately, the group theory only yields the number of normal modes and their polarization but not their frequencies. Hereto detailed physical assumptions on the bonding forces acting in the actual structure are necessary. With respect to the boron-type structures, at present only more or less preliminary results are available [3, 7].

Experimental Procedure

The ionicity of the chemical bonding in the modifications and boron-rich compounds of boron is sufficient to cause considerable absorption of one-phonon processes. Therefore the direct determination of the absorption coefficient can only be performed on very thin samples or on powder pellets. But the preparation of very thin polished plane-parallel plates is rather difficult, and quantitative measurements on powder pellets

are problematic because the optical transmission depends on grain size and scattering.

For these reasons our optical investigations in the MIR and FIR spectral range were largely performed by reflectivity measurements, which require a comparably simple sample preparation (one polished plane surface only). They yield a complete access to the vibration parameters, although every reasonable absorption leads to the well-known dispersion behaviour in the reflectivity spectrum, which aggravates the precise quantitative evaluation to some extend, since all the oscillator parameters must be obtained by mathematical fitting.

Crystallographically oriented single crystals facilitate the association of the experimentally obtained phonons to the group theoretical results, when measured with polarized radiation. Unfortunately, we had single crystals at our disposal only in particular cases; thus most of the measurements were performed on polycrystals or unoriented single crystals, and the evaluation had partly to be limited to a qualitative interpretation.

The samples were mechanically ground and polished using boron carbide powders and diamond pastes (Elektroschmelzwerk Kempten) of subsequently reduced grain size.

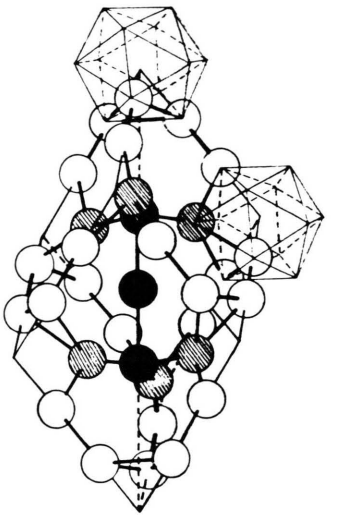

Fig. 1. Unit cell of the alpha-rhombohedral boron structure group.
○ atoms of the icosahedra located on the edges of the unit cell.
◍ equatorial atoms forming three-center bonds in alpha-rhombohedral boron. They are saturated by chain atoms in the borides.
● atoms located on the main diagonal of the unit cell (trigonal axis of the structure).

B) Alpha-Rhombohedral Structure Group

Structure

The members of this structure group are isostructural to the alpha-rhombohedral modification of elementary boron, the vertices of whose unit cell ($a = 0.5057$ nm, $\alpha = 58°\ 4'$) are occupied by one icosahedron, each, beeing insignificantly distorted in the direction of the trigonal axis. The icosahedral atoms on the edges of the rhombohedral unit cell are mainly covalently bonded to neighboured icosahedra, whereas the equatorial atoms of the icosahedra form three-center bonds. The structure may be considered as a slightly deformed cubic packing of icosahedra [8]. The space group is $R\bar{3}m$.

The unit cells of the isostructural borides contain additional atoms symmetrically arranged along its main diagonal (Figure 1). Such structures with one, two or three additional atoms are known (see Table 1). The main influence of these atoms on bonding is the saturation of the three-center bonds mentioned, which stiffens the structure and increases the hardness.

Isostructural boron carbide is reported to be existent in the large homogeneity range between B_4C and about $B_{10.6}C$ [23, 24, 25]. Structural details, especially with respect to the distribution of the C atoms are still under discussion. The most

Table 1. Structure group of alpha-rhombohedral boron.

Chemical formula		Structural formula	References
B (alpha-rhombohedral)		B_{12}	[9, 10]
$B_{12}X$	$B_{12}S$	$B_{12}S$	[11]
$B_{12}X_2$	$B_{3-4}Si$	$(B_{12-n}Si_n)Si_2$	[12]
	B_6P	$B_{12}P_2$	[9, 13 – 16]
	B_6As	$B_{12}As_2$	[9, 13 – 16]
	B_6O	$B_{12}O_2$	[17 – 19]
$B_{12}X_3$	$B_4C \ldots B_{10.6}C$	$(B_{12-n}C_n)C_2B$	(see [36] and ref. therein) [15 – 20]
	$B_{12}C_2Al$	$B_{12}C_2Al$	[14 – 19]
	$B_{12}C_2Si$	$B_{12}C_2Si$	[12, 15]
	B_4Si	$(B_{11}Si)Si_2B$	[21, 22]
	$B_{13}P_2$	$B_{12}P_2B$	[10, 13 – 16]
	$B_{13}As_2$	$B_{12}As_2B$	[10, 13 – 16]

Table 2. Number of undisplaced atoms $u(\sigma)$ in the symmetry elements of the alpha-rhombohedral boron structure group.

Structure type		E	$2C_3$	$3C_2'$	i	$2S_6$	$3\sigma_d$
B_{12}		12	0	0	0	0	4
$B_{12}X$		13	1	1	1	1	5
$B_{12}X_2$	$u(\sigma)$	14	2	0	0	0	6
$B_{12}X_3$		15	3	1	1	1	7
$B_{12}B_4$-1		20	2	2	0	0	6
$B_{12}B_4$-2		20	2	0	0	0	8

probable assumption for the carbon-rich limit of the homogeneity range seems to be a $B_{11}C$ icosahedron connected wtih a C – B – C chain. Towards the boron-rich limit a statistical replacement of the C – B – C chain by planary B_4 arrangements is proposed [26, 27].

Similar homogeneity ranges with variations of structural details are to be expected in the case of the other members of this structure group, too, even though not yet proved, perhaps apart from B – Si compounds [28, 29, 30].

Contrary to the $B_{12}X_3$ compounds, in some representatives of the $B_{12}X_2$ structures, as e.g. in B_6O, the distance between both X atoms seems to be too large to assume efficient bonding between them. Then these atoms may only be particularly linked to the icosahedral boron atoms and saturate the three-center bonds acting between them in the initial alpha-rhombohedral structure.

Group Theoretical Analysis

To perform the group theoretical analysis, idealized structures had to be assumed. This means especially that the slight distortions of the icosahedra obtained by structural investigations of the real structures were not taken into consideration.

The numbers of undisplaced atoms in the different symmetry operations are listed in Table 2, and those of the vibrations accordingly derived for the alpha-rhombohedral structure family in Table 3. From the transformation of the vibration species of the free icosahedron to those of the icosahedra incorporated into the actual alpha-rhombohedral structures one can conclude which original vibrations the IR-active vibrations originate from (Table 4). For the present interpretation of IR active vibrations, especially the A_{2u} mode ($E \| c$) and the E_u mode ($E \perp c$) are important. From Table 4 results that additionally to the IR active F_{1u} mode of the free icosahedron also IR inactive modes lead to IR active vibrations of the crystal structures.

It was especially problematic to adapt the structure proposal of Yakel [26, 27] for boron-rich borides to the symmetry requirements in group theory providing qualitative accordance to the experimental spectra. According to Yakel two atoms of a planar B_4 arrangement replace the terminal atoms of the C – B – C chain bridged by two boron atoms located on a twofold axis perpendicular to a vacant central atom site. In one variation of the different models proposed, the planar arrangement leads to a lowering of the space group of symmetry by elimination of mirrors (R 32) or twofold axes (R 3m).

For our group theoretical consideration we assumed these bridging atoms to be located on C_2' axes (model $B_{12}B_4$-1) or on the symmetry planes σ_d (model $B_{12}B_4$-2). To save the C_3 symmetry axes of the boron carbide structure, moreover the resulting

Table 3. Number of vibrations n_i in the alpha-rhombohedral structure group.

Symmetry type	Degeneracy	B_{12}	$B_{12}X$	$B_{12}X_2$	$B_{12}X_3$	$B_{12}B_4$-1	$B_{12}B_4$-2	Activity
A_{1g}	1	4	4	5	5	6	7	Raman
A_{2g}	1	1	1	1	1	3	2	
		1	1	1	1	1	1	(rotation)
E_g	2	5	5	6	6	9	9	Raman
		1	1	1	1	1	1	(rotation)
A_{1u}	1	2	2	2	2	3	3	
A_{2u}	1	3	4	4	5	6	6	IR
		1	1	1	1	1	1	(translat.)
E_u	2	5	6	6	7	9	9	IR
		1	1	1	1	1	1	(translat.)

Table 4. Transformation of the vibration species (symmetry types) of the icosahedron in the alpha-rhombohedral structure group.

Phonon frequencies [cm^{-1}]		Free icosahedron			Alpha-rhombohedral structure group		
theor. [7]	exp. [32]	IR-active	Raman-active	inactive	IR-active	Raman active	inactive
860.5				G_u	$A_{2u}+E_u$		A_{1u}
858.9			H_g			$A_{1g}+2E_g$	
805.1	750	F_{1u}			$A_{2u}+E_u$		
772.8			A_g			A_{1g}	
625.2				G_g		$A_{1g}+E_g$	A_{2g}
464.8				H_u	$2E_u$		A_{1u}
406.8				F_{2u}	$A_{2u}+E_u$		
355.8			H_g			$A_{1g}+2E_g$	
Rotation				(F_{1g})		(E_g)	(A_{2g})

three pairs of equivalent sites in both models were taken as completely occupied. This leads to a formal increase of the number of bridging atoms per unit cell to six, while in the real structure the equivalent sites of bridging atoms are statistically occupied with only two of such bridging atoms per unit cell. Table 3 shows that only the number of Raman active vibrations enables to decide between both models, while the number of IR active modes is the same.

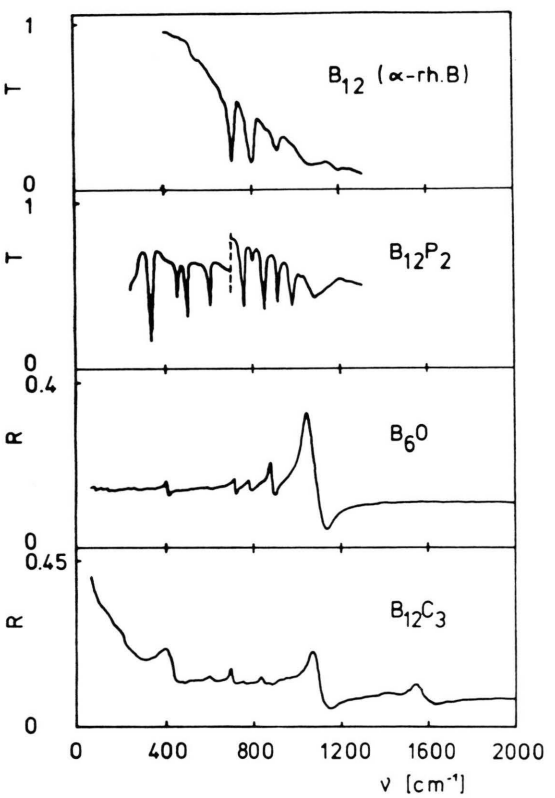

Fig. 2. MIR and FIR optical transmission and reflectivity spectra of representatives of the alpha-rhombohedral boron structure group. a) B_{12}: Transmission of alpha-rhombohedral boron (after Golikova et al. [31]. b) $B_{12}X_2$: 1. Transmission of $B_{12}P_2$ (after Becher and Thevenot [33]. 2. Reflectivity of B_6O. c) $B_{12}X_3$: Reflectivity of boron carbide ($B_{12}C_3$, coarse crystalline); for deviating results at low wavenumbers see Figure 6.

Experimental Results

Figure 2 shows the best available MIR and FIR optical spectra of the representatives of the alpha-rhombohedral structure group. Besides the new reflectivity spectra of B_6O (compact-grained, hot-pressed) and several boron carbide samples of different composition and preparation (approximately $B_{13}C_2$ and $B_{12}C_3$, coarse crystalline, molten; approximately $B_{12}C_3$, compact grained, sintered), for a better synopsis and comparison the transmission spectra of alpha-rhombohedral boron according to Golikova et al. [31] (earlier results of Becher [32] show fewer details) and $B_{12}P_2$ after Becher and Thevenot [33] are shown. Results on $B_{12}As_2$ are mentioned by Becher and Thevenot [33], but without publishing the spectrum.

Our reflectivity measurements were performed on mechanically ground and polished samples by using a Fourier transform spectrometer (Bruker, Karlsruhe, FRG). Since the surfaces were not ideally plane because of the sample consistency, due to intensity loss by surface scattering the absolute values fo the reflectivity may be uncertain by several percent. The relative accuracy is much higher, apart from noise in the FIR range.

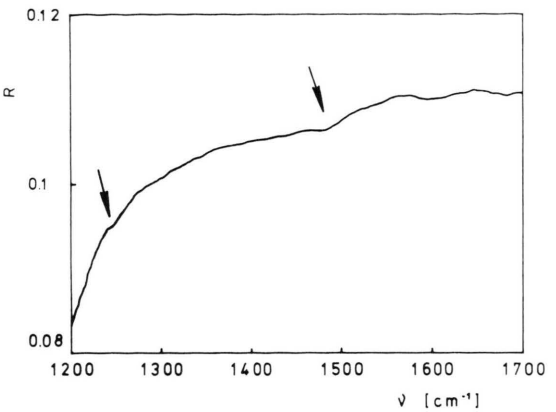

Fig. 3. Better resolved part of the reflectivity spectrum of B_6O showing the weak lattice vibrations at 1250 and 1400 cm^{-1}. The ribble at higher frequencies is caused by noise.

With respect to the strong vibrations, the results on $B_{12}O_2$ are consistent with the qualitative transmission measurements on powder pellets by Becher and Thevenot [33]. But a better resolution exhibits an additional weak band at about 1500 cm^{-1} (Figure 3).

For boron carbide the better resolution of weak bands compared with earlier measurements [34] is important. An additional weak band was discovered at 1400 cm^{-1}. The spectra of samples of different chemical composition and material preparation allow for a preliminary interpretation of the influence of such parameters on phonon spectra and free carriers. Some information on the polarization dependence of the phonons can be obtained from qualitative measurements on single crystals [34].

For $B_{12}O_2$ a dispersion analysis was performed by fitting the dielectric function by superimposed suitable oscillators (cf. e.g. [34]):

$$\varepsilon(\nu) = \varepsilon_\infty \sum_j \frac{\Delta\varepsilon_j}{1-(\nu/\nu_{j_0})^2 - i(\gamma/\nu_{j_0})(\nu/\nu_{j_0})},$$

ε_∞: optical dielectric constant (contribution of bonded electrons),
$\Delta\varepsilon_j$: oscillator strength (contribution of the j-th oscillator),
ν: frequency in wave numbers (in cm^{-1}),
ν_{j_0}: resonance frequency of the sustained oscillator,
γ: frequency independent damping constant.

Table 5. Fitting parameters of the dispersion analysis of B_6O.

a) Phonons: Resonance frequency [cm^{-1}]	Oscillator strength	Attenuation constant [cm^{-1}]	*b) Plasma vibrations*
1056	0.327	50	Plasma resonance frequency: $1.3 \cdot 10^{14}\ s^{-1}$
885	0.035	15	
784	0.012	12	
715	0.012	10	Collision frequency: $1 \cdot 10^{15}\ s^{-1}$
409	0.027	11	
			Optical dielectric constant: 4.35

The increase of reflectivity towards small wave numbers is attributed to strongly attenuated plasma oscillations and fitted by a Drude term (cf. e.g. [34]).

The fitting parameters for the B_6O reflectivity spectrum are listed in Table 5, and the accordingly calculated spectra of the refractive and absorption index are shown in Figure 4.

Interpretation of the Phonon Spectra

The lattice vibration spectra of the alpha-rhombohedral boron structure family are expected

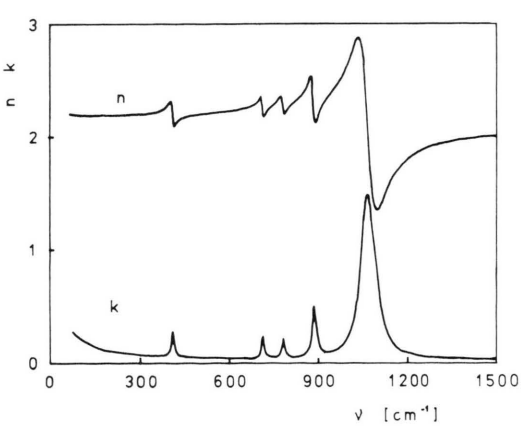

Fig. 4. B_6O: Refractive and absorption index, calculated by use of the fitting parameters listed in table 5 and obtained by a dispersion analysis of the reflectivity spectrum.

to be much simpler than those of the other structure families of boron insofar as the unit cells contain only one icosahedron and, besides of alpha-rhombohedral boron itself, only one additional structure element. Therefore no resonance splitting is to be expected but only systematic shifts of the resonance frequencies of the original vibrations of the icosahedron depending on the actual crystal structure. These frequency shifts may be anisotropic, but for symmetry reasons, in the idealized structure the vibrations of type A_{2u} ($E \| c$) are single while those of types E_u ($E \perp c$) are twofold degenerated and hence exhibit double intensity when measured with unpolarized light or on polycrystalline material. Polarization dependent results were obtained only in case of boron carbide [20] with limited accuracy because of the very small samples investigated. Nevertheless, these results yield valuable support for the subsequent interpretation of the spectra.

According to the group-theoretical analysis, in the alpha-rhombohedral boron structure family the following IR active phonon spectra are to be expexted:

- in alpha-rhombohedral boron itself, eight phonons arise, which are to be attributed to the icosahedron in the rhombohedral crystal structure.
- in the borides $B_{12}X$ and $B_{12}X_2$ the additional atoms arranged on the trigonal axis generate two additional phonons, one of types A_{2u} ($E \| c$) and E_u ($E \| c$), each.
- the borides $B_{12}X_3$ exhibit in comparison to alpha-rhombohedral boron two additional phonons of types A_{2u} and E_u, each,
- both versions of the structure $B_{12}B_4$ (planar B_4 arrangement in boron-rich boron carbide) lead to three additional phonons of type A_{2u} and of E_u.

Reference quantity of the IR active vibrations in the different structures is the fundamental IR active phonon frequency 750 cm^{-1} of the free icosahedron derived by Becher [32] from the absorption spectrum of the $(B_{12}H_{12})^{--}$ ion. This three-fold degenerated vibration was calculated by Beckel and Vaughan [7] somewhat deviating to 805.1 cm^{-1} by considering only nearest neighbours bonding represented by 30 identical Hooke's law springs. Nevertheless, this rather good agreement allows to consider the other vibration frequencies calculated by these authors and especially the sequence of these vibration frequencies within the subsequent interpretation of the spectra.

Besides the spectra of the further representatives of this structure group, already the transmission spectrum of alpha-rhombohedral boron experimentally obtained by Golikova et al. [31] exhibits six different absorption bands, which are to be interpreted according to the eight phonons group-theoretically expected. This means that vibrations originating from IR-inactive vibrations of the free icosahedron are strong enough to become experimentally detected, contrary to the assumption of Becher and Thevenot [33]. All vibrations which are important in connection with the interpretation of the optical phonon spectra are listed in Table 4.

The variation of the Raman active vibration frequencies with bond strength calculated by Weber and Thorpe [3] exhibits only few crossings. A similar behaviour should be expected for the IR-active phonon frequencies, too. Hence the sequence of frequencies derived in [7] for the free icosahedron should be essentially the same in the crystal structures of the alpha-rhombohedral structure group. Accordingly we attribute the strongest vibration at higher frequencies, which is found in all representatives of this structure group at nearly the same spectral position, to the initial F_{1u} mode.

An additional strong argument to attribute these vibrations to the F_{1u} mode of the free icosahedron is the MIR/FIR absorption spectrum of amorphous boron (see [34] and [36]), which is known to consist largely of B_{12} icosahedra statistically bonded to one another. The broad absorption band in the lattice vibration range of this disordered icosahedral structure peaks at 1080 cm^{-1}, i.e. exactly at the same frequency.

This mode splits according to Table 4 into one A_{2u} and one E_u mode. As was already shown, the spectra themselves respectively their dispersion analysis confirm the approximate degeneracy of this vibration. Moreover, the polarization dependent measurements on boron carbide single crystals [34] support this conclusion; the intensity relation 1 : 2 for A_{2u} : E_u corresponds to the one to be expected in case of degeneracy. For boron carbide it was shown in [35] that the parameters of this vibration depend on the chemical composition, which led to the conclusion that in carbon-rich boron carbide carbon atoms substitute boron sites within the icosahedron.

In the same way the lowest resonance frequency of considerable strength in the IR spectra of all representatives of this structure group is assumed to originate from the F_{2u} mode having the lowest frequency of the free icosahedron. Again the polarization dependent results of boron carbide [34] (A_{2u}: $E_u \approx 1:2$) confirm the degeneracy of this vibration.

After these main associations, as shown in Fig. 4 the remaining ones are more or less inevitable. Starting at low frequencies, there are two branches with nearly identical behaviour throughout the whole structure group, suggesting to attribute them to the same symmetry type, which is the H_u mode according to the order of frequencies of the icosahedron. At least in one of both branches, the E_u character accordingly demanded is in agreement with the polarization in boron carbide. The high absorption of these vibrations in alpha-rhombohedral boron, which led Becher and Thevenot [33] to attribute them to the F_{1u} mode, is striking. Moreover the considerably decreasing oscillator strength correlated with an adequate reduced resonance frequency within the branch is noteworthy. Apparently there is a considerable ionicity in the icosahedron introduced by the structure of alpha-rhombohedral boron, which determines the resonance frequencies and the oscillator strengths of these vibrations as well. This ionicity seems to remain approximately unchanged when two separated atoms, as in B_6O, saturate the three-center bond between the equatorial atoms of the icosahedra, but becomes considerably reduced by linear chains with inner bonding as in boron carbide and $B_{12}P_2$. Unfortunately it is not possible to localize this ionicity within the icosahedron because the atomic movement of this vibration is rather complicated [7].

To classify the remaining two sequences of vibrations experimentally obtained, there are only the two vibrations originating from the G_u mode left at disposal. This attribution demands the only crossing of states within this model. The type of the lower frequency sequence seems to be A_{2u}, when generalizing the polarization in boron carbide. This mode seems to split in the case of boron carbide and beyond that in $B_{12}P_2$. Since according to [7] rather small regions of the icosahedron vibrate against one another in this mode, it seems possible that local systematic substitution of foreign atoms therein, or systematic distortions of the icosahedron may cause these additional modes respectively this splitting. The upper branch contains only very weak vibrations, which are distinctly detected only in case of alpha-rhombohedral boron and boron carbide. Additionally there seems to be a corresponding very weak vibration at about 1250 cm^{-1} in B_6O. The spectrum of $B_{12}P_2$ [33] does not cover this spectral range.

Besides these sequencies of icosahedral vibrations there is a rather strong vibration of A_{2u} type in boron carbide. This vibration corresponds with a vibration in beta-rhombohedral boron, whose symmetry is closely related to that one of boron carbide [34, 36, 37]. In case of boron carbide this mode is to be attributed to the stretching vibration of the C – B – C chain. Hence for symmetry reasons, in case of B_6O and $B_{12}P_2$ this vibration should be absent. But the weak vibration in B_6O at about 1500 cm^{-1} indicates that there must be some disturbance of symmetry.

According to group theory, in case of carbon-rich boron carbide there are two vibrations of the chain. Besides the stretching vibration, an IR-active deformation mode is expected at low frequencies. But in the spectra there is no evidence of this mode.

As shown by group theory, for the $B_{12}B_4$ structure models of boron-rich boron carbide additional phonons are expected and the parameters of the chain vibrations should change. Within the part of the homogeneity range investigated ($B_{13}C_{12}$ to $B_{12}C_3$) we did not find distinct absorption bands, which could be assigned to the planary B_4 arrangement. Possibly samples which are nearer to the boron-rich limit of the homogeneity range, are more promising. Nevertheless, the oscillator strength of the 1580 cm^{-1} phonon decreasing with carbon content [36, 37] points towards a structural variation with respect to the C – B – C chain.

As shown above, there is some evidence in the lattice vibration spectra of the alpha-rhombohedral structure group to assume deviations from the idealized structures like deformations of structure elements or substitution of sites. Sterzel [38] has shown that such structural defects can cause the selection rules of lattice vibration modes to become violated. Hence it cannot be excluded that some weak vibrations in boron carbide and B_6O originate from Raman active or inactive vibra-

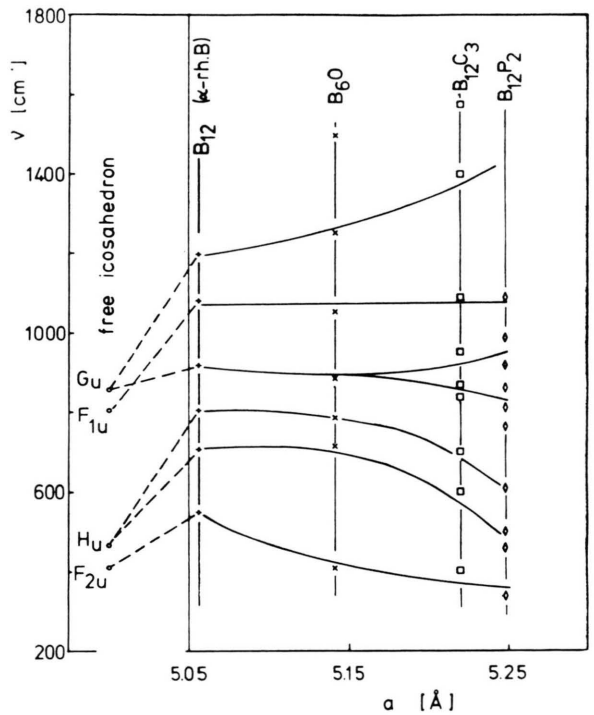

Fig. 5. Coordination of the phonons within the alpha-rhombohedral structure group and attribution to the vibrations of the free icosahedron. The phonon frequencies are plotted versus the lattice constant of the rhombohedral unit cells.

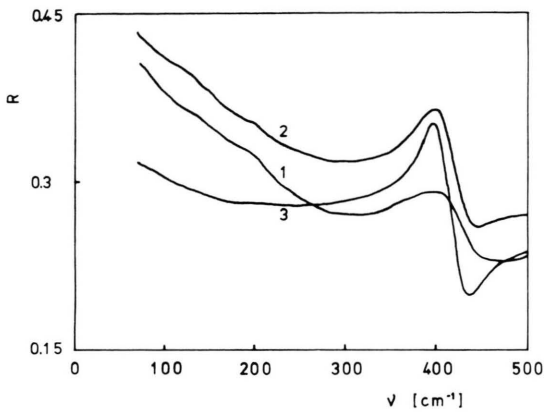

Fig. 6. Boron carbide: Reflectivity in the FIR spectral range (plasma edges). Sample properties: 1 composition $\approx B_{13}C_2$ (coarse crystalline); 2 composition $\approx B_{12}C_3$ (coarse crystalline); 3 composition $\approx B_{12}C_3$ (compact-grained, grain size ≤ 1 μm, sintered).

tions. Accordingly we assume that some vibrations in the Raman spectrum of boron carbide attributed to carbon contamination by Shelnutt et al. [39] are rather to be associated with the strong IR-active vibrations, which are at exactly the same frequencies.

Plasma Resonance

In Fig. 6 the FIR reflectivity spectra of boron carbide sample of different composition and preparation are shown. As already discussed in [34], the distinct increase of the reflectivity towards low frequencies can be attributed to plasma vibrations of free carriers in boron carbide. A similar behaviour is found in B_6O, too. The dependence of reflectivity on frequency can easily be adapted by the Drude theory. The results roughly agree with those reported in [34]. In spite of the low number of samples investigated, a qualitative systematic interrelation with the sample properties seems to be obvious:

The collision frequency of carriers in compact-grained boron carbide is considerably higher than in coarse crystalline material of the same chemical composition, while the carrier concentration decreases. Thus the electronic transport properties in compact-grained material (grain-size ≤ 1 μm) are not only determined by the volume properties but also by the grain size or by the grain boundaries, which conclusion agrees with the according comparison of static measurements of electronic transport [40, 41].

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