Lattice Vibrations, MIR and FIR Optical Properties of Boron and Icosahedral Boron-Rich Borides

II. β-Rhombohedral Structure Group

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The lattice vibrations of the β-rhombohedral boron structure group are investigated in detail by group theory. IR spectra of pure β-rhombohedral boron as well as of B: Mn, B: Fe, B: Cu, and B: Cu/Al are presented and discussed. In comparison with boron carbide most of the absorption bands can be associated with certain vibrations. The vibration frequencies are determined by application of the phenomenological theory of Waser and Pauling, which thus yields a reliable estimation of the restoring forces ion these solides.

Introduction

After the α-rhombohedral boron structure group was treated in the first part of this series [1] (below cited as I), the β-rhombohedral boron structure group is discussed in the present paper. Some supplementary results to I developed from comparing discussions of both structure groups are included.

β-rhombohedral boron is the thermodynamically stable polymorph of this elementary semiconductor. Contrary to the other modifications, which can only be obtained at lower temperatures under special restricted conditions [2], the β-rhombohedral modification developes generally when the melt is cooled down. Therefore it is possible to grow single crystals from the melt according to the usual or related methods. The best, purest and largest single crystals were produced by the Wacker-Chemie, Munich [3], but these crystals, too, are not completely free of certain impurities, especially carbon, and of structural defects, especially twins and stacking faults [4], which seem to be caused by a rather low energy of disorder [5]. In spite of these crystals thus having not reached the high quality of e.g. single crystalline silicon, they have been the prerequisite that at present the β-rhombohedral modification is by far the best investigated polymorph of boron (cp. e.g. [6]).

Structure

The first description of the crystal structure of pure β-rhombohedral boron is due to Hoard et al. [7]. It was confirmed by Geist et al. [8] and determined by Callmer with high precision [9]. The most recent structural investigations were performed by Slack et al. [10–13].

According to the model of Hoard et al., the unit cell (rhombohedral description: $a = 10.145(15)$ Å, $\alpha = 75^\circ\, 17(8)'$; hexagonal description: $a = 10.944$ Å; $c = 23.811$ Å; space group R $\bar{3}$m) consists of 105 boron atoms occupying 16 independent positions, two of which are not completely occupied. Slack et al. [11] found four additional partly occupied boron positions raising the number of B atoms per unit cell to 106.7. Then the X-ray density agrees with the pycnometric density. Some of these positions were already known: in solid solutions of Ni [14] or Ge [15] the same sites are determined to be occupied by these atoms.

In a simple description of the unit cell, B_{12} icosahedra occupy the vertices and the medium points of the edges of the rhombohedral unit cell. Additionally, on the principal cell diagonal coinciding with the c axis in

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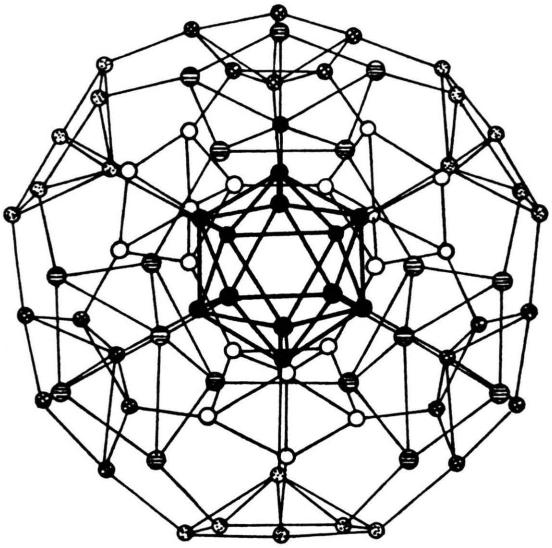

Fig. 1 a. B_{84}-subunit of β-rhombohedral boron.

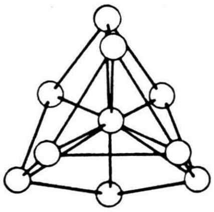

Fig. 2 b. B_{10}-subunit of β-rhombohedral boron.

the hexagonal description of the structure, two aggregates consisting of three intergrown icosahedra, each, are symmetrically arranged relatively to a single atom in the center of the unit cell [16].

For symmetry and group theoretical considerations a different description is more useful. A B_{84} giant unit of icosahedral symmetry is attributed to the vertices of the unit cell. It is formed by the central B_{12} icosahedron being linked to 12 half-icosahedra radially arranged on its six five-fold rotation axes (Figure 1 a). The large octahedral holes remaining in this distorted close cubic packing of B_{84} icosahedra contain two B_{10} units consisting of three condensed caps of icosahedra (Figure 1 b). Together with the central single B atom in the unit cell they form a B_{10}-B-B_{10} chain on the principal cell diagonal of the unit cell. This $B_{84}(B_{10}BB_{10})$ arrangement exhibits the close symmetry relation to the B_{12}(CBC) boron carbide structure.

A somewhat different description is sometimes preferred: A B_{48} unit consists of the central B_{12} icosahedron and only those six pentagonal B_6 half-icosahedra on these five-fold axes which are determined by the polar atoms of the icosahedra and coincide with the edges of the rhombohedral unit cell. The remaining atoms are attributed to a symmetric B_{28}-B-B_{28} chain. These B_{28} groups consist of three condensed icosahedra, each, sharing one face and one common vertex with the both other ones.

It must be kept in mind, however, that the B(13) sites in the B_{10} respectively B_{28} units are only occupied with a probability of about 70%, and that there are several interstitial boron sites. $B_{12}(B_{12})_3B_{28}BB_{28}$ is a more precise presentation from the crystallographic view point, because the icosahedron at the origin of the rhombohedral unit cell is crystallographically different from those three icosahedra located at the centers of the edges.

Investigating the phase transition from the α-rhombohedral polymorph, Runow [17] has shown that the β-rhombohedral unit cell can be approximately imagined to have been developed from eight α-rhombohedral unit cells. Indeed the resulting unit cell contains only 96 atoms, but in spite of the deficiency of nine atoms the lattice spacings agree with perfect β-rhombohedral boron. Especially there are no irregularities with respect to the B_{84} subunit.

In all these structure descriptions the icosahedra are assumed to be regular. But in reality they are distorted in consequence of the Jahn-Teller effect reducing the symmetry of the icosahedral group I_h to the subgroup D_{3d}, which corresponds to the space group $\bar{3}$m [18, 19]. Obviously this is the fundamental reason for the formation of the rhombohedral structures with space group R$\bar{3}$m.

The borides, which are isostructural to β-rhombohedral boron, form solid solutions by interstitial doping, which is sometimes accompanied by the substitution of certain B atoms in the outer shell of the B_{84} unit (Table 1). A previously assumed systematical substitution of boron atoms within the interior subunits of the unit cell by Al and Si atoms [20–23] seems not to be confirmed by the recent more accurate structure investigations.

Besides, it can be expected that a substitutional or interstitial doping with carbon atoms exists in most of the crystals available at present, because removing of carbon by the usual purification processes is very difficult and of low success in case of boron. The reason is that the solubility coefficients in the liquid and in the solid phase are nearly the same.

Table 1. Solid solutions of β-rhombohedral boron and occupancy of the interstitial sites obtained from the references cited.

Solid solution	Occupation of interstitial sites[a] (%)								B sites			Ref.
									partially occupied		substituted	
	6c A(1) Me(1)	18h A(2)	18h (D) Me(2)			6c (E) Me(3)	18g	36i	18h B(13)	18h B(16)	36i	
β-rh. B.									73.4	24.8		9
Dopant												
Mg	H			L		L						10
Al	L											10
AlB_{31}	Al(1) 86		Al2-2[b] 4	Al2-1 11	Al2-3[b] 4				68.2			43
Ga	X			X								10
Si	X	X										10
$SiB_{\approx 36}$	Si(1) 46.4	Si(2) 4.8							73.9		Si ↔ B(1) 13.3% Si	27
Ge												
$GeB_{\approx 90}$	Ge(1) 20.9	Ge(2) 0.46	Ge(4) 1.87		Ge(5) 1.03		Ge(6) 1.16	Ge(7) 0.42	71.6		Ge ↔ B(1) 3.38% Ge	15
Cu	H			L		M						10
CuB_{23}	Cu(1) 8		Cu(2′) 22		Cu(2″)[b] 12	Cu(3) 61			69	13		28
$CuB_{\approx 28}$	6.1		22		10.5	50.5			61	21		25
Cu/Al	H		L[b]	M	L[b]							42
$Cu_2Al_{2.7}B_{104}$	42			25								32
Sc	H			M		L						10
$ScB_{\approx 28}$				Sc(2) 31.4		Sc(3) 72.7			61		Sc ↔ B(4) 6% Sc	30
Ti	X			X								10
Zr	H			L		M						10
$ZrB_{\approx 51}$					Zr(2) 27.9	Zr(3) 18.1			53	14.5		31
Hf	H			L		M						10
V	L	H		H								10
$VB_{\approx 65}$	V(1) 64.0			V(2) 5.3					74.6			13
$VB_{\approx 165}$	31.6			<2.3					76.3	14.7		13
Nb	H			L								10
Ta	H			L								10
Cr	L			H								10
$CrB_{\approx 41}$	Cr(1) 71.9			Cr(2) 18.0					72			26
Mn	L			L		H						10
$MnB_{\approx 23}$	Mn(1) 25.6			Mn(2) 43.1		Mn(3) 66.2			65			25
Fe	L			H								10
$FeB_{\approx 49}$	Fe(1) 50.7			Fe(2) 18.5					73			35
Co	X			X								10
Ni	H			L								10
$NiB_{48.5}$	Ni(1) 44.67		Ni(3) 1.78		Ni(2)[b] 8.99			Ni(4) 0.58	67.1	18		14

[a] X: Occupied; L: Occupied at Low Concentration; M: Occupied at Medium Concentration; H: Occupied at High Concentration.

[b] Position 36i.

Table 2. Voids in the crystal structure of β-rhombohedral boron. Positions, coordinates, numbers and distances of neighbouring boron atoms in the case of $CrB_{\approx 41}$ [26].

Hole	Wyckoff-Position	Hexagonal coordinates			Number of boron neighbours and distances			
A(1), Me(1)	6(c)	0,	0,	0.135	12 B,	2.15–2.19 Å		
A(2)	18(h)	0.108,	0.216,	0.100	12 B,	2.06–2.14 Å		
A(3)	36(i)	0.279,	0.248,	0.046	12 B,	1.91–2.20 Å		
D, Me(2)	18(h)	0.205,	0.411,	0.174	1 B,	2.01 Å;	14 B,	2.28–2.45 Å
E, Me(3)	6(c)	0,	0,	0.245	15 B,	2.28–2.45 Å		
F(1)	18(h)	0.065,	0.130,	0.245	7 B,	1.95–2.18 Å;	2 B,	2.79 Å
F(2)	18(h)	0.117,	0.233,	0.252	3 B,	2.12 Å;	13 B,	2.39–2.66 Å
G	18(h)	0.055,	0.109,	0.117	8 B,	1.79–1.85 Å;	6 B,	2.54–2.62 Å

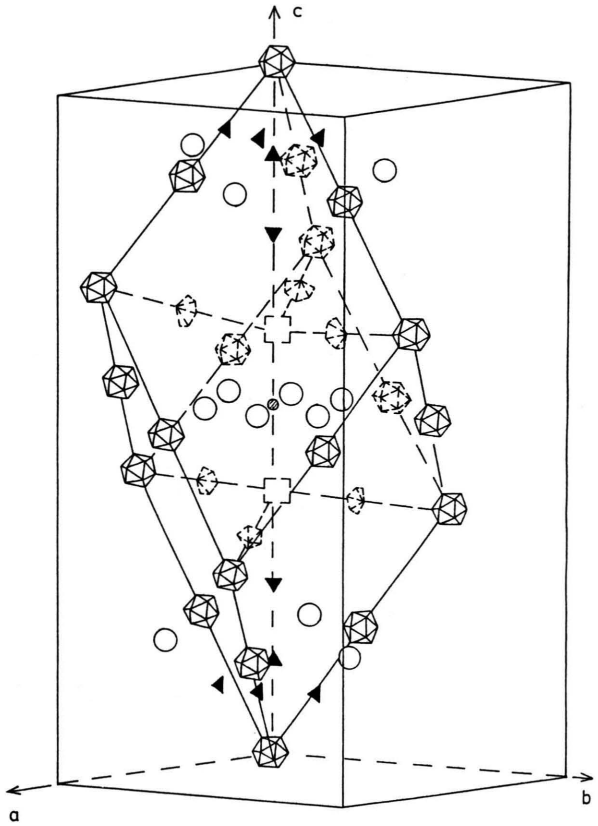

Fig. 2. Unit cell of β-rhombohedral boron with B_{12}-, B_6- and B_{10}-subunits and A(1) (Me 1), D Me(2), E Me(3) and Si(2) positions.

	Coordinates			Atoms	Pos.
▲	0;	0;	0.135	A(1) Me(1)	6c
○	0.245;	0.41;	0.17	D Me(2)	36i
▼	0;	0;	0.245	E Me(3)	6c
◀	0.11;	0.89;	0.10	Si(2)	18h
▨	0;	0;	0.5	B(15)	3b

A characteristic feature of the crystalline boron structures, essentially consisting of three-dimensionally linked icosahedra is the rather open structure, which in the case of β-rhombohedral boron is filled up by B atoms at only 36% ($r_B = 0.88$ Å) [24]. Hence the boron framework contains several voids, which are large enough to accomodate foreign atoms thus forming the solid solutions with various elements [10–13, 25–35, 42, 43].

These voids at different positions in the unit cell (cp. Fig. 2 and Table 2) are different with respect to their size, shape, symmetry and to the number of the adjoining boron atoms. Besides, in a manner not yet clarified systematically, the occupancies depend on size, bonding properties and concentration of the built-in atoms. Some more detailed knowledge is available on the most frequently occupied centers A(1)(Me 1), D(Me 2), and E(Me 3). The occupancy of these voids is not independent of the remaining structure; metal atoms in the D(Me 2) void dislodge B atoms from the B(13) site, and the occupancies of the A(1)(Me 1) and the adjacent E(Me 3) voids exclude on another. The D(Me 2) hole is very ill-defined, i.e. atoms have different possible coordinates. Sometimes they are situated on the mirror plane, sometimes the position is split into two further holes, and in AlB_{31} there are one non-split and two split positions. In the Figs. 3 and 4 the distances are indicated and exclude a simultaneous occupancy in the same unit cell. On the other hand it can be obtained from these figures that the distances are appreciable, and this accordingly represents a region of local disorder. The Ge(6) and Ge(7) atoms are at 0.78 Å from each other, and it is not clear if they should be denoted as the same hole, although a simultaneous occupancy in the same unit cell is excluded. Their distances from the D hole atom Ge(4) are 1.369 and 1.12 Å, respectively. For more details see e.g. [24]. Table 1 shows the collected data on intersti-

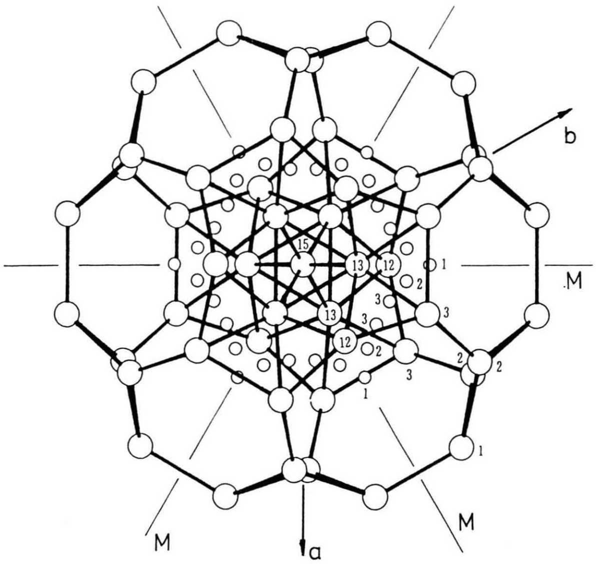

Fig. 3. Structural surrounding of the B(15) atom as seen along the hexagonal *c* axis. The larger circles represent boron atoms, and the small circles designated by 1, 2 and 3 indicate the three-fold splitted D Me(2) position designated by Al(2-1), Al(2-2) and Al(2-3) atoms, respectively. The B(15) atom lies in the inversion center on the threefold axis [43].

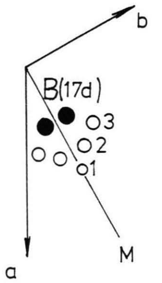

Fig. 4. Splitting of the D-hole as it was found in the case of AlB_{31} (cp. Fig. 3). Additionally the B(17d) position partially occupied at 8.5(9)% in pure crystals [11] is marked by full circles.

tially doping atoms and occupied sites taken from the literature.

The following formal models of solid solutions will be considered below:

MB_x-1: only A(1)(Me 1) occupied or only E(Me 3) occupied.

MB_x-2: only D(Me 2) occupied.

MB_x-3: A(1)(Me 1) + D(Me 2) occupied or D(Me 2) + E(Me 3) occupied.

MB_x-4: A(1)(Me 1) + D(Me 2) + E(Me 3) occupied.

Since the sites A(1)(Me 1) and E(Me 3) are both positioned on the c-axis, each symmetrically to the central B atom in the unit cell, their symmetry properties and their influence on the number of lattice vibrations is the same. Of course, this does not mean that the vibration frequencies, too, coincide.

Group Theoretical Analysis

For the group theoretical analysis it was necessary to idealize the basic crystal structure of β-rhombohedral boron:

- Distortions of the icosahedra were neglected. As already mentioned the icosahedron is distorted in principle by the Jahn-Teller effect. But since the reduction in symmetry corresponds to the space group $R\bar{3}m$ of the α- and β-rhombohedral structure group, it is assumed that at least in first approximation this distortion can be neglected with respect to the lattice vibrations. This holds especially with respect to group theory, which only yields the number of vibrations and not their resonance frequencies.
- All the 16 independent B sites were assumed to be entirely occupied. This is incorrect with respect to B(13) (occupancy 74.5(6)%) and B(16) (27.2(7)%).
- The occupancy of the four recently detected B sites [10] (3.7 to 8.5%) was not considered in pure boron.
- These idealisations lead to 105 B atoms per unit cell of pure β-rhombohedral boron.

In case of the isostructural borides (Table 1) the precise knowledge of the differently occupied sites would be needed for the group theoretical determination of the lattice vibrations. As shown in Table 1, the voids A(1) (Me 1), D (Me 2) and E (Me 3) are the mostly preferred ones for accomodating foreign atoms. There are 2 A(1), 6 D, and 2 E equivalent crystallographic positions in the rhombohedral unit cell. The occupancy does not reach 100% in any case, which means that the sites are only statistically occupied, and that the occupations of different sites may not be independent from one another. For the symmetry considerations in group theory, it was therefore necessary to assume complete occupation. This means of course that the number of atoms per unit cell used for this calculation increases to values, which are not in agreement with the real structure. Nevertheless this incorrectness is expected to be of minor importance than to use the correct number of introduced atoms at statistically occupied positions. Such a procedure would influence the long-range order of the structure essentially, and the symmetry of the complete unit cell would be strongly reduced. Hence the number of vibrations of the whole structure would become very small in contrast to the experimental results. Our procedure corresponds merely to a perturbation of the ideal structure, and the maximum number of the additionally induced vibrations is obtained. Possibly not all of these vibrations will be found in the spectra, because the oscillator strengths of the vibrations depend e.g. on the number of vibrating centers, which is low in case of low occupancy.

The numbers of vibration species, which are to be expected in the main representative structures, were calculated according to the procedure described in I and [36]. The first essential step is to determinate the atoms, which remain undisplaced during the different symmetry operations (Table 3). The accordingly derived numbers of vibrations in the β-rhombohedral structure group are listed in Table 4.

It is obvious that an essential part of the vibration spectrum is determined by the B_{84} unit. Therefore, to facilitate the interpretation of the spectra, in Table 5 the splitting of the corresponding vibration modes in the crystal field of the rhombohedral lattice is indicated in detail and compared with the vibrations of the B_{12} icosahedron. The complex movements of the vibrating atoms in the different modes of the B_{12} icosahedron are described in [37]. The symmetry in the B_{84} unit is the same, and hence the vibrations of the central B_{12} icosahedron can be transferred to the B_{84} unit. Group theoretically, 8 IR active F_{1u} modes are expected to split into 8 twofold degenerated E_u modes ($E \perp c$) and 8 A_{2u} modes ($E \parallel c$).

For the interpretation of the phonon spectra it is useful to distinguish between inner and outer vibrations of the structure groups in the unit cell. The outer vibrations are obtained according to the procedure described above, with the only difference that instead of the number of undisplaced atoms the number of undisplaced structure groups is determined. Such structure groups are B_{12}, B, and C in case of boron carbide and B_{84}, B_{10}, B respectively B_{48}, B_{28}, B in case of β-rhombohedral boron. The results for the related structures are listed in Table 6. While the results for translational motions are the same, the number of rotational vibrations of polyatomic structure units in β-rhombohedral boron exceeds that one of boron carbide. The reason is obviously the three-dimensional size of the B_{10} respectively B_{28} arrangements.

Table 3. Number of undisplaced atoms $u(\sigma)$ in the symmetry elements of the β-rhombohedral structure group.

Structure type	E	$2C_3$	$3C'_2$	i	$2S_6$	$3\sigma_d$
B_{48}	48	0	0	0	0	8
B_{28}-B-B_{28}	57	3	1	1	1	13
B_{84}	84	0	0	0	0	12
B_{10}-B-B_{10}	21	3	1	1	1	9
B_{105}	105	3	1	1	1	21
$MB_x - 1$	107	3	1	1	1	21
$MB_x - 2$	111	3	1	1	1	23
$MB_x - 3$	113	5	1	1	1	25
$MB_x - 4$	115	7	1	1	1	27

The group theoretical consideration of the solid solutions in the preceding section is based on the assumption of modified fundamental structures. An essentially different description would be to consider the metal atoms as weakly bonded single atoms in voids. In this case local vibration modes would arise, whose intensity depends on the number of occupied sites, and whose vibration frequencies are determined by the strength and the ionicity of bonding. Their anisotropy would depend on the voids and not on R $\bar{3}$ m. To decide this question, a quantitative interpretation of the spectra is necessary.

Specimens

1. Single crystal β-rhombohedral boron: the samples were cut from "hyper-pure" single crystals (Wacker-Chemie, Munich) claimed impurity 4N5. Typical impurity analysis according to the producer: C: 50 to 100 ppm; Si, Ca, Cu, Mg: < 1 ppm (cf. [38]). Split reflexes of Laue patterns obtained for orientation of the samples and electron microscope investigations lead to the assumption of stacking faults and twins [4]. The sample preparation was performed according to [4].

2. B: Mn: The specimens with the nominal chemical compositions MnB_{3330}, MnB_{713}, MnB_{307}, MnB_{116}, MnB_{55}, MnB_{22} were prepared by arc melting Wacker boron and freshly sublimated manganese (Highways, Baarn, The Netherlands; claimed purity 4N; Fe: < 1 ppm) and subsequent heat treating for 20 h at 1470 K in BN crucibles in a high vacuum furnace. The compositions were determined as the averages of microprobe results and unit cell determinations (linear dependence of unit cell volume on Mn content assumed between non-doped Wacker boron ($V = 24\,671.2$ Å^3) and MnB_{23} ($V = 2508.6$ Å^3) (for details, see [25, 39]).

3. B: Fe ($FeB_{29.5}$): This compound was the first n-type β-rhombohedral boron obtained by definite doping [40], which result is of especial importance for the application of boron in semiconductor technology. The specimens are the same as investigated there. They were prepared from boron (Wacker-Chemie, Munich, see above and iron (Johnson-Matthey Co., specpure) by arc melting under purified argon atmo-

Table 4. Number of vibrations in the β-rhombohedral structure group.

Symmetry type	Degeneracy	B_{48}	B_{84}	B_{105}	$MB_x - 1$	$MB_x - 2$	$MB_x - 3$	$MB_x - 4$	Activity
A_{1g}	1	15	24	31	32	33	34	35	Raman
A_{2g}	1	8 1	17 1	20 1	20 1	21 1	21 1	21 1	 (rotation)
E_g	2	23 1	41 1	51 1	52 1	54 1	55 1	56 1	Raman (rotation)
A_{1u}	1	9	18	21	21	22	22	22	
A_{2u}	1	14 1	23 1	31 1	32 1	33 1	34 1	35 1	IR (translation)
E_u	2	23 1	41 1	52 1	53 1	55 1	56 1	57 1	IR (translation)

Table 5. Number of vibration species of the icosahedral B_{12} and B_{84} units and splitting of the icosahedral symmetry types in the rhombohedral lattice.

I_h (isolated)									D_{3d} (rhombohedral lattice)		
Symmetry typ	Degeneracy	Vibrations				Activity			Activity		
		B_{12}			B_{84}						
		Number	Frequency [cm^{-1}]		Number	Ir	Raman	inactiv	Ir	Raman	inactiv
			theor. [37]	exp. [51]							
A_g	1	1	772.8		4		A_g			A_{1g}	
F_{1g}	3	0 (1)			4 (1)			F_{1g} (rotation)		E_g (rotation)	A_{2g}
F_{2g}	3	0			4			F_{2g}		E_g	A_{2g}
G_g	4	1	625.2		8			G_g		$A_{1g}+E_g$	A_{2g}
H_g	5	2	858.8 355.8		12		Hg			$A_{1g}+2E_g$	
A_u	1	0			1			A_u			A_{1u}
F_{1u}	3	1 (1)	805.1	750	8 (1)	F_{1u} (translation)			$A_{2u}+E_u$ (translation)		
F_{2u}	3	1	406.8		7			F_{2u}	$A_{2u}+E_u$		
G_u	4	1	860.5		8			G_u	$A_{2u}+E_u$		A_{1u}
H_u	5	1	464.8		9			H_u	$2E_u$		A_{1u}

Table 6. Number of translational ($n_{j(\mathrm{trans})}$) and rotational ($n_{j(\mathrm{rot})}$) lattice vibrationes of β-rhombohedral boron ($B_{84}(B_{10})B(B_{10})$ or $B_{48}(B_{28})B(B_{28})$) in comparison with boron carbide ($B_{12}CBC$).

Symmetry type	$n_{j(\mathrm{trans})}$ B_4C	β-rh.B	$n_{j(\mathrm{rot})}$ B_4C	β-rh. B	Activity
A_{1g}	1	1	0	0	Raman
A_{2g}	0	0	1	2	
E_g	1	1	1	2	Raman
A_{1u}	0	0	0	1	
A_{2u}	2	2	0	0	IR
E_u	2	2	0	1	IR

sphere and subsequent heat treatment at 1300 °C for 48 h in a BN crucible under ultrapure argon. For structure data, see [35].

4. B: Cu ($CuB_{41.2}$): The specimen was prepared by arc-melting crystalline boron (Borax Consolidated, claimed purity 99.8%) and copper (Johnson-Matthey & Co, claimed purity 99.9%) under an atmosphere of purified argon (for details and structure determination see [24, 25, 28].

5. B: Cu, Al ($Al_{2.6}Cu_{1.9}B_{105}$): The specimens were obtained by a solution-growth technique [41–43]. Ac-

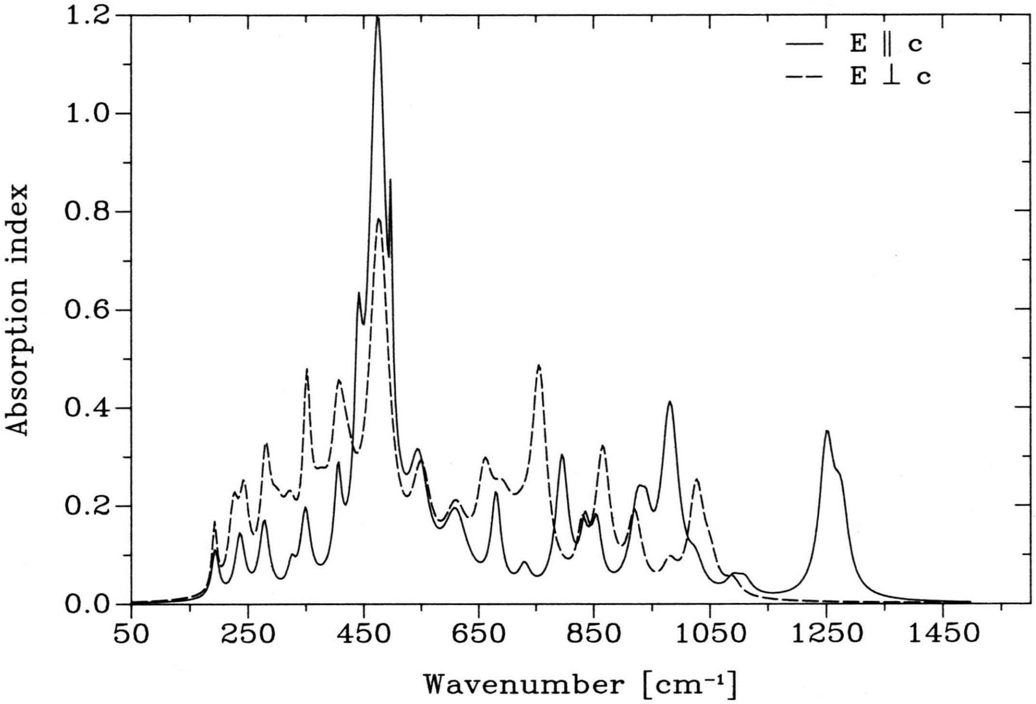

Fig. 5. Absorption index of β-rhombohedral boron in the spectral range of lattice vibrations [28].

cording to preliminary X-ray diffraction results the phase is assumed to have the same structure as $Cu_2Al_{2.7}B_{105}$ synthetized by Mattes et al. [32]. But the metal atoms are considered to be mixed in the A(1) (Me 1) and the D(Me 2) sites. The E(Me 3) site remains empty.

Experimental Results

For the optical measurements an IFS 113v Fourier transform spectrometer (Bruker, Karlsruhe, FRG) was used ranging from about 15000 to 4 cm^{-1} with maximum resolution of 0.03 cm^{-1}. Because of the high absorption in the lattice vibration range only the reflectivity spectra could be obtained directly, while the absorption spectra were derived from them by Kramers-Kronig transformation using the according spectrometer software program.

All the spectra presented in this paper correspond to the natural isotope distribution (B_{10}:B_{11} = 19:81). In isotope-enriched β-rhombohedral boron the phonon frequencies are shifted without essential change of the oscillator strength and the attenuation [44].

In Fig. 5 the polarisation dependent spectra of IR-active optical phonons in pure single crystals [36] are presented as standards for the subsequent comparison with doped material.

Figure 6 shows the series of spectra of Mn doped β-rhombohedral boron. In the Mn concentration range from pure β-rhombohedral boron up to MnB_{116} only some gradual change of the spectrum is found. At higher concentrations the band at 470 cm^{-1} is reduced while two additional bands develope at about 340 and between 130 and 230 cm^{-1}.

The spectra of $FeB_{29.5}$ (Fig. 7) seem to indicate a certain similarity of the influence of Fe and Mn on the IR phonon spectra. Again the 470 cm^{-1} band nearly vanishes and two additional bands at 340 and 208 cm^{-1} arise; but these absorption bands are distinctly sharper than in MnB_x with comparable metal content.

As can be taken from Fig. 8, the influence of Cu atoms and of a Cu/Al mixture occupying voids in β-rhombohedral boron leads to distinctly different influences on the IR phonon spectra. Indeed, contrary to the Mn and Fe compounds the intensity of the absorption band near 470 cm^{-1} remains comparable

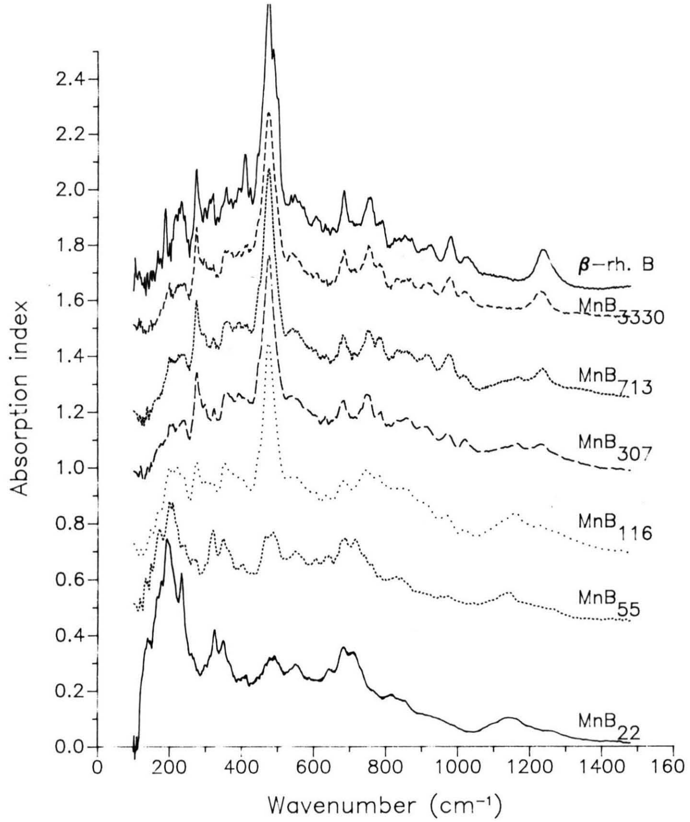

Fig. 6. Absorption index of **B**:**Mn** versus wavenumber; pure β-rhombohedral boron for comparison. For clarity the spectra are vertically shifted relative to one another.

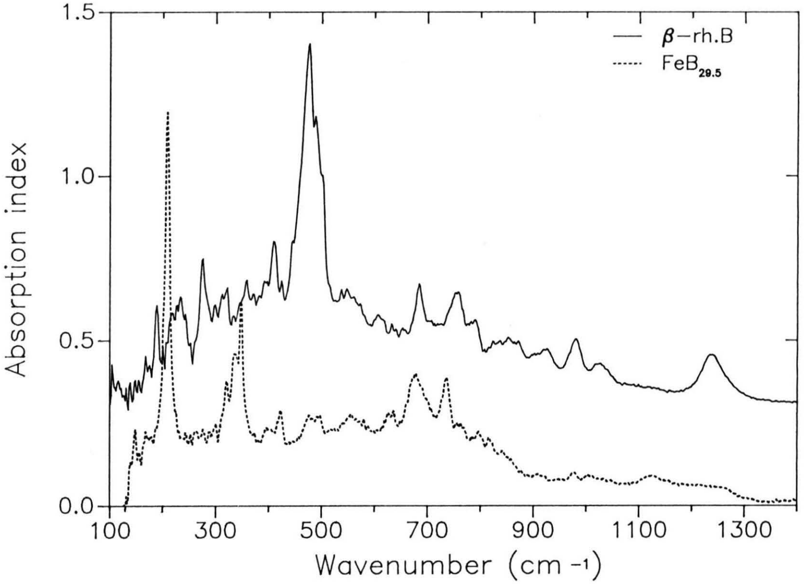

Fig. 7. Absorption index of **B**:**Fe** ($FeB_{29.5}$) versus wavenumber; pure β-rhombohedral boron for comparison. For clarity the spectra are vertically shifted relative to one another.

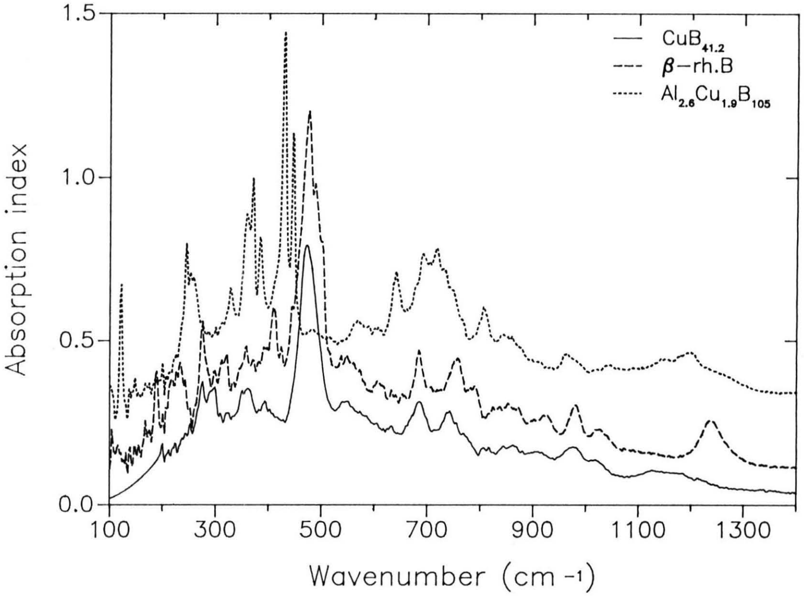

Fig. 8. Absorption index of **B**:**Cu** ($CuB_{41.2}$) and **B**:**Cu**/**Al** ($Al_{2.6}Cu_{1.9}B_{105}$) versus wavenumber; pure β-rhombohedral boron for comparison. For clarity the spectra are vertically shifted relative to one another.

to pure boron, but in the case of interstitial Cu atoms the attenuation increases while in case of the Cu/Al mixture the attenuation decreases significantly and a splitting into two sharp bands is observed.

In all the compounds investigated a distinct modification of the phonon spectrum in the range of the strong E_u phonon near 1240 cm^{-1} is observed. In case of the MnB_x series the variation of the absorption in this spectral range indicates that this absorption can be taken easily as a high-sensitive indicator of interstitial doping.

Discussion of the Spectra

a) Pure β-Rhombohedral Boron

According to Table 4, in case of pure β-rhombohedral boron 31 IR-active phonons of the type A_{2u} and 52 of the twofold degenerated type E_u are to be expected. 23 respectively 43 of them are attributed to the B_{84} unit and the remaining ones to the B_{10}-B-B_{10} structure unit.

As already shown in [36] the number of experimentally found distinctly discernable vibrations is considerably lower (about 24 A_{2u} and 25 E_u), which could be caused by different reasons:

1. Accidental degeneracy
2. Essentially different oscillator strengths.

Although in the case of such a great number of vibrations in a limited spectral range the first point cannot be excluded, it is supposed that especially the second one is decisive.

Since the inter- and the intraicosahedral restoring forces are not significantly different as in molecular crystals the inter- and intraicosahedral vibrations overlap in the spectrum and cannot be simply distinguished according to evidently separated spectral positions like in molecular crystals. Only the well-known 8 μm absorption band can be clearly attributed to the stretching vibration of the central B atom in the B_{10}-B-B_{10} chain in β-rhombohedral boron analogously to the C-B-C chain in boron carbide. Because of the low vibrating mass, in both cases the vibrations are distinctly shifted towards higher frequencies. It was already shown in [36] that in the dispersion analysis this absorption band cannot be described by a single vibration, but must be attributed to a double band. After in [44] the dependence of the phonon frequencies of the mass of isotopes was determined, it is possible to attribute both phonons to the ^{10}B and ^{11}B isotopes, respectively:

Attributing the main maximum of the 8 μm band (at 123 K: 7.98 μ = 1253 cm^{-1} [45]) to ^{11}B and the high frequency satellite maximum (at 123 K: 765 μm = 1307 cm^{-1} to ^{10}B [45]), the ratio of the absorption in both separated bands meets the isotope distribution 19:81 quite well, and the frequency shift

$$\nu(^{10}\mathrm{B}) : \nu(^{11}\mathrm{B}) = 1.044(4)$$

agrees with the general isotope shift of phonon frequencies obtained in [44] (misprint in [44]: correct 1.043 instead of 1.0043).

Moreover the spectral position of these vibrations can be estimated by using a bond theoretical consideration analogous to 3-atomic linear molecules [46]. After Waser and Pauling [47] the Badger rule of the relation between force constant and interatomic distance in diatomic molecules [48] holds in solids also, where in case of elements of one row in the periodic table universal interaction constants are valid. When this conception is applied to boron carbide and β-rhombohedral boron, from

$$k^{-1/3} = a_{ij}(d_0 - b_{ij}) \quad (a_{ij} = 2.89;\ b_{ij} = 1.13\ \text{Å})$$

the restoring forces k can be calculated phenomenonically using the nearest-neighbour distances in the crystals (B_4C: (C-B-C chain): $d_0 = 1.436$ Å [49]; β-rhomb. B (B_{10}-B-B_{10} chain): d_0 (B(15)/B(13)) = 1.686 Å [9]):

$$k(\text{C-B-C in } \mathrm{B_4C}) = 1.45 \cdot 10^3\ \mathrm{kg\,s^{-2}},$$

$$k(\mathrm{B_{10}\text{-}B\text{-}B_{10}} \text{ in } \beta\text{-rh. B}) = 0.241 \cdot 10^3\ \mathrm{kg\,s^{-2}}.$$

If approximately it is assumed that only the central atoms of the chains move, the stretching vibrations (A_{2u}) are obtained from

$$\nu = 1/2\pi\sqrt{k/m_B}\,.$$

For this vibration results in the case of B_4C: $\nu = 4.51 \cdot 10^{13}\ s^{-1}$; $\lambda = 6.65$ μm; $\tilde{\nu} = 1503\ cm^{-1}$, which value deviates from the real spectral spectral position 6.33 μm ≙ 1580 cm^{-1} by only 5%.

In β-rhombohedral boron it must be taken into account that the central atom B(15) is octahedrally surrounded by 6 B(13) atoms. If this is considered by tripling the restoring force,

$$\nu = 3.19 \cdot 10^{13}\ \mathrm{s^{-1}}; \quad \lambda = 9.41\ \mu\mathrm{m}; \quad \tilde{\nu} = 1063\ \mathrm{cm^{-1}}$$

is obtained, which deviates from the experiment (at room temperature 8.10 μm ≙ 1234 cm^{-1}) by 16%. Nevertheless, this result, too, is rather satisfactory with respect to the roughly estimated restoring force and the considerable deviation from linear central forces, on which the theory is based.

Additionally to this stretching mode (A_{2u}) of the central atom an IR-active bending mode (E_u) is predicted by group theroy. In this case the restoring force is assumed to be essentially determined by deformation of the bond angles. The according results on Y-X-Y molecules ([46], p. 172 ff) yield for the ratio of restoring forces the average value

$$k_\delta/l^2\,(\text{bending}):k\,(\text{stretching}) \approx 27(3)\,.$$

Hence after [46] (equations 196, 197) the vibration frequencies are related by

$$\tilde{\nu}_{\text{bending}} \approx \sqrt{2/27}\,\tilde{\nu}_{\text{stretching}} = 0.27\,\tilde{\nu}_{\text{stretching}}.$$

Applying this value to our materials, from the experimentally obtained stretching vibration frequencies can be estimated:

$$\tilde{\nu}_{\text{bending}}(B_4C) \approx 426\ \text{cm}^{-1},$$

$$\tilde{\nu}_{\text{bending}}(\beta\text{-rh. B}) \approx 333\ \text{cm}^{-1}.$$

In boron carbide, accordingly the 410 cm^{-1} phonon (recent precise determination) can be attributed to this bending vibration of the C-B-C chain respectively of its central atom. The predominant E_u character of this vibration was already stated in [36] (spectral positions there less precisely assumed at 390 cm^{-1}).

In B_6O (see I, Figs. 2 and 3 or [50], Fig. 9), where, owing to the lacking central atom in the chain, the IR active bending vibration is missing, only a vibration with low oscillator strength, which in I was attributed to the F_{2u} mode of the icosahedron, is found at the corresponding spectral position. Therefore we assume that in boron carbide the F_{2u} of the icosahedron and the bending mode of the central atom of the chain are accidentially degenerated.

Because of the octahedral surrounding of the central atom in β-rhombohedral boron, the stretching component acting on bonding in this formally named bending vibration is not neglectable. Therefore the difference between both vibration frequencies must be expected to be distinctly smaller than estimated above. Accordingly we attribute at least a portion of the E_u component of the 475 cm^{-1} phonon to this bending vibration.

Now we try to apply these considerations to the vibrations of the icosahedron. The F_{1u} vibration mode, which is the only IR-active one of the isolated icosahedron, can largely be described by the antisymmetric breathing of two half-icosahedra vibrating against one another [37], which leads to a reduced mass of $3\,m_B$. Since in the B_4C crystal the bonding between the equatorial atoms and the intericosahedral bonding along the vertices of the rhombohedral unit cell are the essentially stressed ones, the corresponding averaged atomic distance 1.744 Å is obtained from [49]. Using this value, according to the procedure described above, we obtain

$$k = 0.179 \cdot 10^3\ \text{kg}\,\text{s}^{-2};$$

$$\nu = 3.01 \cdot 10^{13}\ \text{s}^{-1};\quad \lambda = 9.97\ \mu\text{m};\quad \tilde{\nu} = 1003\ \text{cm}^{-1}.$$

In spite of the rough estimation, this result deviates only by about 7.7% from the 1075 cm^{-1} phonon attributed to the F_{1u} mode of boron carbide in I.

When in β-rhombohedral boron the overall averaged B-B distance of 1.803 Å [9] is used, the corresponding results of the F_{1u} vibration are

$$k = 0.135 \cdot 10^3\ \text{kg}\,\text{s}^{-2},$$

$$\nu = 2.612 \cdot 10^{13}\ \text{s}^{-1};\quad \lambda = 11.48\ \mu\text{m};\quad \tilde{\nu} = 871\ \text{cm}^{-1}.$$

To compare this value with the experimental spectra, one has to consider that contrary to boron carbide, which contains only one icosahedron per unit cell, in β-rhombohedral boron several icosahedra per unit cell are coupled.

According to Table 5 only 8 phonons of type A_{2u} respectively E_u result from the F_{1u} vibration mode, the only IR active one of the free icosahedron, while the remaining phonons develope from initially not IR-active modes by inserting the icosahedron in the crystal field of the rhombohedral structure. Therefore it seems not to be devious to expect that the vibrations originating from F_{1u} exhibit significantly higher oscillator strengths than the other ones and that the frequency splitting induced by reduction of symmetry ($I_h \rightarrow \bar{3}m$) leads essentially to pairs of A_{2u}/E_u modes. Since the anisotropy of physical properties in β-rhombohedral boron is known to be rather low, it is expected that the pairs are not significantly separated in the spectrum.

Taking the simplified structure model used by Runow [17] into account, which attributes approximately 8 unit cells of α-rhombohedral boron to the unit cell of β-rhombohedral boron, one gets 8 icosahedra per unit cell and hence by resonance (Davydov) splitting eight modes A_{2u} and E_u, each, in agreement with group theory, when the vibrations of the B_{84} unit are considered. Indeed in this comparison is neglected

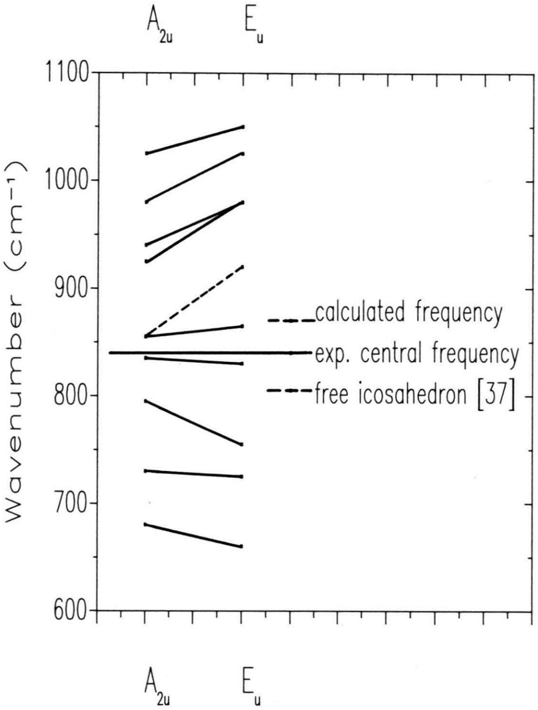

Fig. 9. Splitted IR active inner vibrations of the B_{12} icosahedra in β-rhombohedral boron.

that the B_{84} unit consists of seven icosahedra only. Since the foregoing calculation of the vibration frequency 871 cm^{-1} of the F_{1u} mode in β-rhombohedral boron neglected the coupling of the icosahedra, this value should be near the center of the Davydov-splitted F_{1u} modes. Besides, this value is in accordance with results of Becher [51] as well as of Weber and Thorpe [52], who attributed the spectral range from about 500 to 1100 cm^{-1} to these vibrations.

When this range is actually limited to about 650 to 1100 cm^{-1}, 8 more or less distinct vibrations of A_{2u} respectively E_u type are found allowing a largely certain correlation to one another, which is shown in Figure 9.

From the anisotropy of the absorption edge [38] can be obtained that bonding $\perp c$ is slightly stronger than $\parallel c$. This coincides with the E_u vibration modes originating from F_{1u} being more displaced relative to a certain center value than the A_{2u} modes. This center can be located at about 840 cm^{-1}, which deviates only by 3.7% from the medium frequency 871 cm^{-1} derived above using the mean B-B distance. According to weaker bonding, this value is shifted less than the corresponding mode in boron carbide from 805.1 cm^{-1}, which value was calculated by Beckel and Vaughan [37] for the free icosahedron. Hence we allocate the medium frequency of the F_{1u} mode in β-rhombohedral boron at 840 cm^{-1}. Resonance (Davydov) splitting and anisotropy splitting of this mode can be obtained from Figure 9.

According to this explanation it must be assumed that all the inner vibrations of the B_{12} icosahedron not originating from F_{1u} may only contribute to the integral absorption in this spectral range, but cannot be singly distinguished in the spectrum. This conception is supported by the results obtained in isotope-enriched β-rhombohedral boron [44]. The phonon frequencies shift in a certain dependence of the average isotope mass, while oscillator strengths and attenuation remain largely unaltered. Hence these vibrations must be attributed to arrangements containing greater numbers of atoms, because only in such cases a medium atomic mass can realistically be employed for a statistical isotope distribution. For the inner vibrations of the icosahedron, according to the results of Beckel and Vaughan [37] this assumption is only realistic for the F_{1u} mode, while in case of vibrating single atoms or small atomic groups in the other modes the individual distribution of atom masses leads to spreaded vibration frequencies. As was shown, in case of the central atom of the unit cell they are even discernibly splitted.

In spite of this quite good qualitative and largely even quantitative agreement between the measured phonon spectra and the vibration behaviour estimated by using the simplified Runow model of the unit cell, one must not overlook that the real structure is more complicated. This may be at least one reason of the different size of the absorption bands attributed to F_{1u} and a certain splitting of bands, respectively of some phonons not considered in this explanation.

In spite of a number of arguments supporting the preceding interpretation a different explanation of the spectrum of the inner vibrations of the icosahedron cannot be excluded at present. Besides the Jahn-Teller effect, a further reduction of symmetry could be caused e.g. by a statistical substitution of boron sites by C atoms. In this case the vibrations of the icosahedron (3 A_{2u}, 5 E_u; see Table 5) could become IR active in both orientations leading to the two times eight vibrations experimentally found in this spectral range.

In the spectral range between 180 and 650 cm^{-1} it is striking that the spectra $\parallel c(A_{2u})$ and $\perp c(E_u)$ are very similar. Apart from the strong absorption band

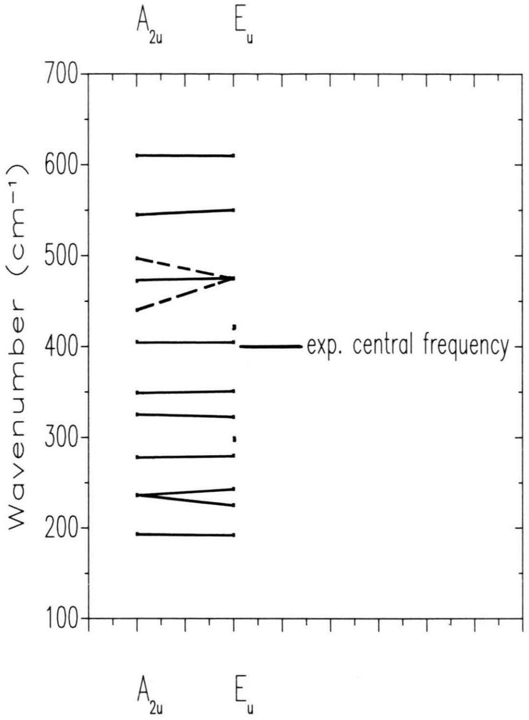

Fig. 10. Outer vibrations of the B_{12} icosahedra in β-rhombohedral boron.

apparently splitted with maxima $\parallel c$ at 440, 472 and 497 cm^{-1} (A_{2u}) and $\perp c$ at 497 cm^{-1} (E_u) there are essentially 8 phonons, whose resonance frequencies agree exactly for both orientations (only the 236 cm^{-1} phonon splits symmetrically into 235 and 243 cm^{-1}) (Figure 10). As in the case of the splitted F_{1u} mode (Fig. 9) this number corresponds with the number of icosahedra in the simplified Runow model of the unit cell containing essentially 8 B_{12} icosahedra.

Estimating the vibration frequency of the complete B_{12} icosahedron against the rigid remaining structure, one obtains according to the previous procedure

$$\nu = 1.306 \cdot 10^{13}\,\mathrm{s}^{-1}; \quad \lambda = 22.96\,\mu\mathrm{m}; \quad \tilde{\nu} = 436\,\mathrm{cm}^{-1},$$

which agrees satisfactorily with the center of these vibrations at 400 cm^{-1}.

Hence it seems reasonable that these vibrations are to be attributed to vibration modes of bigger structure units, especially of the B_{12} icosahedra splitted by resonance in the crystal field. Indeed our group theoretical consideration based on the description of the unit cell in T_d symmetry according to [53] confirms that there exist IR active vibrations of the rigid B_{12} icosahedron in the rhombohedral structure, and this vibration is splitted according to the number of icosahedra in the unit cell. Because of the great number of differently directed bondings contributing to the restoring force the anyhow low anisotropy becomes averaged.

The magnitude of the strong absorption with center at 477 cm^{-1} (A_{2u}) and the corresponding single band absorption at 477 cm^{-1} (E_u) reminds of the strong absorption in boron carbide at 400 cm^{-1}. As was already shown, certain arguments support to attribute the E_u portion of this band to the bending mode of the central B(15) atom. In Table 6 was shown that 2 A_{2u} and 3 E_u modes result from the B_{10}-B-B_{10} arrangement. Considering the stretching and the bending mode of the B(15) atom, 1 A_{2u} and 2 E_u remain, which should be detectable in the spectrum because of the rather strong ionicity of the B_{10}-B-B_{10} (respectively B_{28}-B-B_{28}) chain. We are convinced that this strong absorption band is essentially caused by this subunit of the structure, but neither can the threefold splitted A_{2u} portion convincingly be explained by the results of group theory, nor seems a degeneration of the remaining vibrations with the bending mode of the B(15) atom very probable. As will be shown below, this absorption band is significantly influenced by certain interstitial doping, but the results in the present paper are not sufficient for a final interpretation. Also the damping of this band apparently decreasing with decreasing averaged isotope mass [44] needs a careful verification.

For a final decision with respect to this absorption band and for the interpretation of details of the spectrum further investigations are necessary.

b) Solid Solutions

The statistical occupation of lattice sites in crystal structures by foreign atoms disturbs the translation symmetry of the structure. This enlarges the phonon scattering and hence the damping of lattice vibrations, which can be obtained from the absorption bands being broadened. The same consequence is obtained by assuming the $q = 0$ selection rules to become relaxed and the light being able to interact with vibration modes of approximate symmetry [54].

In the solid solutions of β-rhombohedral boron only definite interstitial sites are occupied by foreign atoms. Nevertheless the same tendency of the increasing damping can be observed more or less distinctly in their lattice vibration spectra, too (Figs. 5–7).

By group theoretical calculations was shown that additional phonons are to be expected, when these interstitial sites are assumed to be completely occupied (cp. Table 4). The question arises, in how far these vibrations can be described by a modification of the initial crystal structure or merely by localized phonons caused by the metal atoms essentially vibrating against the more or less rigid remaining structure.

When the initial structure is modified by interstitial metal atoms, on principle the following effects on the phonon spectrum are possible:

1. The increase of the lattice spacing is correlated with an increase of the bonding distances and correspondingly with a shift of the phonon frequencies to lower values.
2. The metal atoms can be assumed to be bonded in the voids of the structure by saturating dangling or multiple-center bonds of boron atoms. By the charge transfer related dipole moments between the metal atoms and the boron structure are induced leading to the localized phonons mentioned. Depending on the atomic surrounding, these bonding forces may be distinctly anisotropic (cp. [24]) with a corresponding anisotropy of the vibrations. Besides, this charge transfer may modify the charge distribution in the boron framework and the restoring forces as well, which leads to a frequency shift of phonons.
3. Very strong influences are to be expected, when in case of high interstitial doping a direct or indirect exchange interaction between these atoms arises. Such clusters were found by magnetical investigations on B:Mn and B:Fe [39, 55].

Only a small number of the solid solutions listed in Table 1 were at our disposal for the measurement of phonon spectra. Therefore the subsequent interpretation must be largely restricted to some characteristic tendencies and qualitative agreements, for which purpose the compounds are filed according to different aspects:

1. The series of Mn doped samples reaches from 0.03 to 4.35 at.% Mn. Hence information on the systematic changes depending on the metal content is expected.
2. At high doping levels Mn and Fe in Me(1) and Me(2) sites form magnetic clusters. The influence on the phonon spectra should be comparable. But it must be considered that the clusters are different in size and distribution, from which can be expected that the influence of clustering in B:Fe will appear at distinctly higher metal concentrations than in B:Mn [39, 55].
3. Mn and Cu both occupy all of the three positions A(1) (Me 1), D (Me 2) and E (Me 3), but the occupation density of Cu in A(1) (Me 1) is distinctly lower than that of Mn, while the occupation of the other sites is comparable, when the splitted Cu(2) position is summarized. Hence the influence of the occupation of the Me 1 site may be obtained from the spectra. Clustering, which is evident in B:Mn, seems to be possible in B:Cu, too, if Cu^{2+} or Cu^{3+} states are formed, but anyway it is expected to be appreciably weaker.
4. In the solid solutions with Fe and Cu/Al the A(1)(Me 1) and D Me(2) sites are both occupied at a comparable degree, while the E(Me 3) site remains empty. Hence in comparison with B:Mn and B:Cu the influence of this site on the spectra may be discernable.

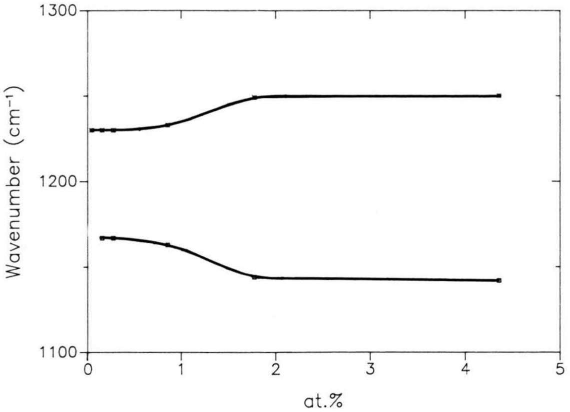

Fig. 11. Frequency shift of the stretching mode of the central atom B(15) in β-rhombohedral boron, depending on Mn content.

Generally can be stated that the splitted vibrations of the icosahedron are progressively damped with increasing metal content. Figure 11 shows the change of the stretching mode of the central B(15) atom. Already at very low Mn concentrations a small shift of the phonon frequency was found. But moreover, particularly shifted by about 60 cm^{-1}, towards lower frequencies, a second vibration developes, whose oscillator strenghts increases with Mn concentration, while the initial one decreases.

Obviously in unit cells, in which the D (Me 2) position is occupied, the vibration frequency is reduced, while it, besides of a certain shift caused by the increased lattice spacing, remains unchanged in unit cells, where this site remains unoccupied. The occupation of the A(1)(Me 1) position is assumed to be ineffective, because its distance from the B(15) atom seems to be too large. According to the results of ESR and magnetic susceptibility [39, 55], clusters between A(1)(Me 1) and D(Me 2) holes are formed already in the MnB_{3330} composition. Hence the intensity of the vibration at 1166 cm^{-1} seems to be immediately correlated with the number of clusters of this local type.

An additional distinct change is seen between 0.8 and 1.8 at.% Mn. Approximately symmetrically the initial vibration is shifted towards higher, the Mn induced vibration towards lower frequencies. Obviously this change coincides with the inter-cluster interaction [39, 55] infringing the whole structure, which means the unit cells with local clusters and those without clusters as well. This seems to be induced merely by a charge transfer than by a change of the bonding distances.

In any way can be seen that the bonding conditions of the B(15) atom are of different kind, when the D(Me 2) position in a certain unit cell is occupied by Mn or not. The bonding conditions are additionally modified, when intercluster interactions take place. Hence the X-ray determination of atomic positions in such solid solutions must be assumed to have yielded average values of unit cells with occupied and unoccupied voids, and the real structure deformation in the unit cells with occupied sites may be stronger than reported [39, 55].

The measurements were performed on polycrystals and therefore the polarization dependence of the second band could not be determined, but since the summarized absorption of both vibrations remains essentially unchanged, we assume it to be of A_{2u} type, too, and accordingly a strong bonding of $B(15) \perp c$ can largely be excluded.

Considering that the vibrations of pure β-rhombohedral boron are damped in the case of high occupation densities of the voids, one expects that in such cases the local phonons of the metal atoms determine essentially the spectrum. Indeed according to Table 5 in case of B:Mn 4 A_{2u} and 5 E_u modes are expected, but since three interstitial sites are occupied, the local phonons should be represented essentially by three anisotropic vibrations.

In the spectrum of MnB_{22} the absorption bands at 484 and 551 cm^{-1} are probably due to the bending modes of the central atom, and we take them as a confirmation of the corresponding interpretation in pure boron. As was shown, the absorption bands between 600 and 900 cm^{-1} can be attributed to certain less damped long wave vibrations of the icosahedron. Hence we attribute the distinct absorption bands in the spectral range $< 400\ cm^{-1}$ to vibrations of the metal atoms.

A different possibility is e.g. to attribute the threefold absorption band (644, 685, $\approx 710\ cm^{-1}$) to the stretching mode and the broad band between 100 and 250 cm^{-1} to the bending modes of the metal atoms. For a final attribution series of other solid solutions are necessary, especially those, in which the different voids are distinctly differently occupied. From such measurements probably the contribution of the single occupied voids can be derived.

Comparing the spectra of B:Mn and B:Cu at comparable concentrations, one sees that the damping of phonons in the spectral range between 650 and 1100 cm^{-1} is much stronger in case of B:Mn, where the A(1) (Me 1) site is occupied at a distinctly higher degree. Since this site is immediately neighboured to the B_{12} icosahedron at the vertex of the unit cell, the attribution of these vibrations to splitted F_{1u} modes is confirmed. The strong band at 470 cm^{-1} vanishes in case of B:Mn, while it remains essentially unchanged in case of B:Cu at a comparable metal content. This effect may also be caused by the significantly different occupation of the Me(1) site. But in B:Fe with comparable metal concentration the band vanishes, too, and therefore in the same way the formation of magnetic clusters could be the reason.

A certain common behaviour was observed depending on the occupation of the E(Me 3) site. This is empty in case of B:Fe and B:Cu, Al, which obviously leads to weakly damped absorption bands of local phonons, while it is occupied in B:Mn and B:Cu, where the phonon bands are broad with several peaks. Thus it seems that the occupation of the E(Me 3) site causes a stronger coupling of the different elements of the structure, which leads to splitted vibrations. This conclusion agrees with the existence of cluster and intercluster interactions in B:Mn. A more precise knowledge of the occupation densities of the voids in B:Cu, Al would help to ensure this consideration.

According to the present results the following preliminary attribution of absorption bands to metal atoms in certain voids seems possible. In B:Fe and B:Cu, Al two distinctly separated groups of vibrations are seen at lower frequencies:

B:Fe: 208 and 328–350 cm^{-1},
B:Cu, Al: 245–260 and 350–390 cm^{-1}.

The distinct splitting of these vibrations in B:Cu, Al seems to be caused by the variety of sites which are available for the Al atoms.

In B:Cu, where the Me(1) site is only weakly occupied, the corresponding ranges are

B:Cu: 270–300 and 350–395 cm^{-1}.

The second range contains only a comparably weak absorption, which could correspond to the Me(1) site in B:Cu being weakly occupied. Therefore it seems possible to attribute this absorption range to the Me(1) site and the range at lower frequencies to the Me(2) site. Moreover this is in a rough agreement with the relative bonding distances because of the larger size of the Me(2) void compared with Me(1) (cp. Table 2).

The bonding distances of the M(2) and the Me(3) sites are nearly the same (Table 2). This should cause that the corresponding vibration frequencies are close to one another, which would explain the broad absorption band from 130–230 cm^{-1} in MnB_{22}, where both sites are occupied at a high degree.

Further investigations of series of interstitially doped β-rhombohedral boron will give more reliable and more detailed insight into the influence of the different atoms on bonding. The X-ray determination of the vibration ellipsoids like in [11] would support the interpretation of the local phonons of interstitial atoms and their relation to the bonding forces.

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[1] H. Werheit and H. Haupt, Z. Naturforsch. **42a,** 925 (1987).
[2] E. Amberger and W. Stumpf, in Gmelin Handbook of Inorganic Chemistry, Supplement Vol. 2; Editor K.-C. Buschbeck, Springer, Berlin 1981.
[3] W. Borchert, W. Dietz, and H. Kölker, Z. Ang. Phys. **29,** 277 (1970).
[4] H. Binnenbruck, A. Hausen, P. Runow, and H. Werheit, Z. Naturforsch. **25a,** 1431 (1970).
[5] E. Amberger, W. Dietze, J. Jaumann, and P. Runow, Phys. Stat. Sol. a **2,** K 59 (1970).
[6] H. Werheit: Boron. In: Landoldt-Börnstein, New Series, Vol. III/17e; Ed. O. Madelung, M. Schulz, and H. Weiss; Springer, Berlin 1983, p. 9. H. Werheit: Optical Properties of the Crystalline Modifications of Boron and Boron-Rich borides. In: Prog. Crystal Growth and Charact. **16,** 179 (1988).
[7] J. L. Hoard, D. B. Sullenger, C. H. L. Kennard, and R. E. Hughes, J. Solid-State Chem. **1,** 268 (1970).
[8] D. Geist, R. Kloss, and H. Follner, Acta Crystallogr. Sect. B **26,** 1800 (1970).
[9] Callmer, B., Acta Crystallogr. Sect. B. **33,** 1951 (1977).
[10] G. A. Slack, J. H. Rosolowski, C. Hejna, M. Garbauskas, and J. S. Kasper, Proc. 9th Int. Symp. Boron, Borides and Related Compounds, Duisburg 1987, Ed. H. Werheit, p. 132.
[11] G. A. Slack, C. I. Hejna, M. F. Garbauskas, and J. S. Kasper, J. Solid State Chem. **76,** 52 (1988).
[12] G. A. Slack, C. I. Hejna, M. F. Garbauskas, and J. S. Kasper, J. Solid State Chem. **76,** 64 (1988).
[13] M. F. Garbauskas, J. S. Kasper, and G. A. Slack, J. Solid State Chem. **63,** 424 (1986).
[14] T. Lundström, L. E. Tergenius, and I. Higashi, Z. Krist. **167,** 235 (1984).
[15] T. Lundström and L. E. Tergenius, J. Less-Common Met. **82,** 341 (1981).
[16] B. Sullenger and Ch. L. Kennard, Sci. Amer. **215,** No. 7, (1966).
[17] P. Runow, J. Mat. Sci. **7,** 499 (1972).
[18] R. Franz and H. Werheit, Europhys. Lett. **9,** 145 (1989).
[19] H. Werheit: On the Electronic Transport Properties of Boron Carbide. In: R. Freer (Editor), The Physics and Chemistry of Carbides, Nitrides, and Borides; Kluwer Acad. Publ., Dordrecht, The Netherlands (in press).
[20] V. I. Matkovich, J. Economy. In Boron and Refractory Borides; Ed., V. I. Matkovich, Springer, Berlin 1977, p. 96.
[21] J. R. Giese, R. F. Economy, and V. I. Matkovich, Z. Kristallogr. **122,** 144 (1965).
[22] E. Lugscheider, R. Reimann, and W.-J. Quaddakers, Ber. Dt. Keram. Ges. **56,** No. 10, 301 (1979).
[23] P. Ettmayer, H. C. Horn, and K. A. Schwetz, Microchim. Acta, Suppl. IV, 87 (1970).
[24] T. Lundström. The Structure and Bonding of Solid solutions of Transition and p Elements in β-rhombohedral boron; in Boron-Rich Solids; Eds.: D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Wood; Albuquerque 1986, p. 19.
[25] S. Andersson and B. Callmer, J. Solid-State Chem. **10,** 219 (1974).
[26] S. Andersson and T. Lundström, J. Solid-State Chem. **2,** 603 (1970).
[27] M. Vlasse and J. C. Viala, J. Solid-State Chem. **37,** 181 (1981).

[28] I. Higashi, T. Sakurai, and T. Atoda, J. Less-Common Met. **45,** 283 (1976).
[29] I. Higashi, Y. Takahashi, and T. Atoda, J. Less-Common Met. **37,** 199 (1974).
[30] B. Callmer, J. Solid-State Chem. **23,** 391 (1978).
[31] B. Callmer, L. E. Tergenius, and J. O. Thomas, J. Solid-State Chem. **26,** 275 (1978).
[32] R. Mattes, C. Marosi, and H. Neidhard, J. Less-Common Met. **20,** 233 (1970).
[33] R. Telle and E. D. Franz, see [9], p. 451.
[34] I. Higashi, unpublished result.
[35] B. Callmer and T. Lundström, J. Solid State Chem. **17,** 165 (1976).
[36] H. Binnenbruck and H. Werheit, Z. Naturforsch. **34a,** 787 (1979).
[37] C. L. Beckel and J. P. Vaughan. Vibrations of Regular Boron Icosahedra. In Boron-Rich Solids, Eds. D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, AIP Conference Proceedings 140, Albuquerque, New Mexico, USA 1986, p. 305.
[38] H. Werheit, A. Hausen, and H. Binnenbruck, phys. stat. sol. (b) **51,** 115 (1972).
[39] G. P. Tsiskarishvili, T. Lundström, L. Lundgren, G. V. Tsagareishvili, D. N. Tsikaridze, and F. N. Tavadze, J. less-common met. **147,** 41 (1989).
[40] H. Werheit, K. de Groot, W. Malkemper, and T. Lundström, J. less-common Met. **82,** 163 (1981).
[41] I. Higashi and Y. Takahashi, J. less-common Met. **81,** 135 (1981).
[42] S. Okada, I. Higashi, Y. Takahashi, L. E. Tergenius, and T. Lundström, J. Ceram. Soc. Japan (Int. Ed.) **96,** 654 (1988).
[43] I. Higashi, H. Iwasaki, I. Ito, T. Lundström, S. Okada, and L.-E. Tergenius, J. Solid State Chem. (in press).
[44] H. Haupt, H. Werheit, M. E. Antadze, G. V. Tsagareishvili, G. P. Tsiskarishvili, and F. N. Tavadze, in Proc. 9th Int. Symp. Boron, Borides and Rel. Comp., Duisburg, 1987, Ed. H. Werheit, p. 279.
[45] J. Jaumann and H. Werheit, phys. stat. sol. **33,** 587 (1969).
[46] G. Herzberg. Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules; van Nostrand Reinhold Co., New York 1945, p. 172.
[47] J. Waser and L. Pauling, J. Chem. Phys. **18,** 747 (1950).
[48] R. M. Badger, J. Chem. Phys. **2,** 128 (1934); **3,** 710 (1935).
[49] B. Morosin, A. W. Mullendore, and D. Emin, A Slack, in: see [29] p. 70.
[50] H. Werheit. Optical Properties of Boron-Rich Solids with Icosahedral Structure. In: see [19].
[51] H. J. Becher, Z. Anorg. Allg. Chem. **15a,** 217 (1963).
[52] W. Weber and M. F. Thorpe, J. Phys. Chem. Solids **36,** 967 (1975).
[53] I. Higashi, Structure and Electron density distribution of icosahedral B_{12} compounds. In: see [10] p. 41.
[54] H. Böttger, phys. stat. sol. (b) **49,** 795 (1972).
[55] G. P. Tsiskarishvili, T. Lundström, L. Lundgren, G. V. Tsagareishvili, O. A. Tsagareishvili, and F. N. Tavadze, J. less-common Met. **142,** 91 (1988).