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On the dynamical conductivity in icosahedral boron-rich solids

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Abstract. The FIR spectra of boron-rich solids measured down to 10 cm^{-1} exhibit strongly increasing reflectivities towards lower frequencies. These spectra are well described when a superposition of Drude-type and hopping-type dynamical conductivity is assumed. The corresponding fits were simultaneously made for the real and the imaginary part of the dielectric function to achieve unambiguous parameters. The results obtained can be described consistently, for example, with DC conductivity measurements, and moreover in the case of β -rhombohedral boron, with the known energy band scheme. The bipolaron hopping model of the electronic transport in boron carbide is proved to be inappropriate.

1. Introduction

The crystal and electronic structures of boron-rich solids are both essentially determined by B_{12} icosahedra, which are mostly found in a slightly distorted form and less frequently as fragments or condensed systems. They are bonded either directly by largely covalent inter-icosahedral B–B bonds or indirectly via single boron or foreign atoms, thus determining the different structural families ranging from α -rhombohedral boron with 12 atoms per unit cell to YB_{66} with more than 1600 atoms per unit cell. Doping is possible by substitution or by accommodation of foreign atoms in specific interstitial sites [1–5]. Moreover the electronic properties can be modified by changing the chemical composition within sometimes large homogeneity ranges for specific compounds. The semiconductor character of the icosahedral boron-rich solids is exceptional for condensed systems of atoms with odd electron numbers, and results from the Jahn–Teller effect distorting the icosahedra and splitting the electronic orbitals so that occupied and unoccupied states are separated [6–8].

The actual energy band scheme of pure β -rhombohedral boron (structure formula $(B_{12})_4(B_{28})_2B$), which is currently the model substance for the boron-rich solids, is consistent for numerous optical, electrical and thermal experiments (figure 1) [9]. The valence band range is characterized by a low-density split-off band (VB1) generated by a static Jahn–Teller effect distorting the icosahedra at the vertex of the unit cell. VB1 consists of localized states and is partly filled by electrons coming from other structural elements. Accordingly in thermal equilibrium two transport mechanisms are possible: (i) hopping within the split-off band VB1, and (ii) free-hole transport in the extended states of the lower valence band VB2, which depends on the density of holes generated by thermal excitation of electrons into the unoccupied sites of VB1. This free-hole transport is impeded by the occupied sites in VB1 acting as hole traps [10]. Depending on the actual conditions, one of these mechanisms

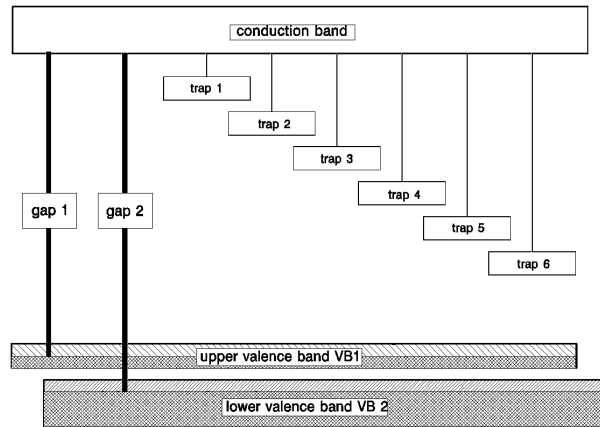


Figure 1. The energy band scheme of pure β -rhombohedral boron (gap 1: 1.32(1) eV ($E \parallel c$), 1.29(1) eV ($E \perp c$); gap 2: 1.50(1) eV ($E \parallel c$), 1.46(1) eV ($E \perp c$)); the values are obtained from extrapolation to $T = 0$ K. Position of electron traps: n times 0.188(2) eV ($n = 1$ to 6) below the conduction band edge [9].

may predominate; in most cases however a superposition of the two processes makes the interpretation of transport experiments difficult. In pure materials even at high temperatures hole transport remains prevailing because the excited electrons are captured in a series of intrinsic traps. Accordingly, doping to n-type requires a donor level between the uppermost electron trapping level and the conduction band edge. Six electrons per unit cell are needed to change β -rhombohedral boron to n-type [11]. The high density of states of the doping level suggests a superposition of impurity band hopping and band-type conduction for the electrons as well. Similar features of charge transport seem to hold for the other icosahedral boron-rich solids as well.

Competing approaches for explaining the transport properties of boron-rich solids are the ‘amorphous concept’ mainly established by Golikova [12, 13] and the bipolaron hopping model developed for boron carbide by Howard, Beckel and Emin [14–16]. The amorphous concept attributes to the icosahedral boron structures a continuous variation from crystalline to amorphous semiconductors depending on the complexity of the specific structure. The complexity is defined in terms of the number of atoms per unit cell. However, several crucial experimental results are in contradiction to this model; boron carbide with 15 atoms per unit cell for example does not fit at all. The small-bipolaron-hopping model theory is essentially based on the experimental fact that the spin density in boron carbide is lower by two orders of magnitude compared with the carrier density estimated from transport properties. It allows one to describe some aspects of the electronic transport of boron carbide satisfactorily [17]. However, it ignores the fact that other much simpler reasons, for example strong damping of the ESR, can be used to explain the discrepancy between spin and carrier density as well. Likewise some other essential properties of boron carbide such as, e.g., the low ionicity and the low polarizability of the structure, have not been considered. Moreover, some essential experimental results are contradictory to this theory, for example (i) the conclusion from experiments on β -rhombohedral boron that one excess-electron maximum can interact with intra-icosahedral phonons, and (ii) in boron carbide the coincidence of the density-of-states minimum of $B_{11}C$ icosahedra, which are assumed in

this theory to be the hopping sites, with the electrical conductivity maximum.

Characteristic for all icosahedral boron-rich solids is a rapid rise of the reflectivity towards low frequencies in the FIR spectral range, which reminds one of plasma edges due to strongly damped Drude-type carriers in semiconductors. Corresponding fits yielded qualitatively plausible results [7]; however, the fits were quantitatively not satisfactory. Below it will be shown that a convincing simulation of these spectra is possible if a superposition of hopping-type and free-carrier-type charge transport is assumed. The dominating hopping mechanism of the DC conductivity was first demonstrated for β -rhombohedral boron [18] and has meanwhile been confirmed for this and many other boron-rich solids by various authors; the hopping character of the AC conductivity was proved in particular for boron carbide [19].

2. Sample material

The metal-doped β -rhombohedral boron samples were obtained by arc-melting high-purity ingredients that were afterwards heat treated typically for 40 hours at 1200 °C to guarantee homogeneity. For details of the vanadium- and cobalt-doped samples see [20], and for those of the iron-doped samples see [11, 21]. The boron carbide samples were prepared partly by melting and partly by hot pressing (for details of properties see [22, 23]). For YB₆₆ a cleaved surface of a large single crystal was used (for more details see [24, 25]).

3. Experimental details

The reflectivity spectra were measured with a FTIR spectrometer IFS 113v (Bruker, Karlsruhe) in the spectral range between 10 and 5000 cm⁻¹ at temperatures between 77 and 450 K for doped β -rhombohedral boron and between 30 and 450 K for boron carbide and YB₆₆. For low noise levels a liquid-helium-cooled Ge bolometer was used as the FIR detector, and a liquid-nitrogen-cooled MCT detector was used for the MIR range. With respect to the topic to be discussed, only the FIR sections of the spectra will be presented; for the complete spectra and for detailed material-specific discussions the reader is referred for vanadium- and cobalt-doped β -rhombohedral boron to [18, 19], for Fe-doped β -rhombohedral boron to [11, 21], for boron carbide to [22, 26], and for YB₆₆ to [24, 25].

From the measured reflectivity spectra $R(\omega)$ the phase angle $\Theta(\omega)$ was numerically calculated by use of the specific Kramers–Kronig integral [27, 28]:

$$\theta(\omega) = \frac{1}{2\pi} \int_0^\infty \frac{d \ln(R(\omega'))}{d\omega'} \ln \left| \frac{\omega + \omega'}{\omega' - \omega} \right| d\omega' \quad (1)$$

whose validity is discussed in detail in [28] and references therein. Towards high frequencies the integration was limited to the largely dispersion-free range at the high-frequency boundary of the measured spectra (5000 cm⁻¹), where the integral converges quickly because the first derivative of $\ln(R(\omega'))$ determines the integrand. For $\omega \rightarrow 0$ the reflectivity spectra were extrapolated according to the Hagen–Rubens relation, after a careful check proved that the way in which the extrapolations are performed has no remarkable influence on the results in the spectral range actually measured and presented. From $\Theta(\omega)$ and $R(\omega)$ the complex dielectric function was computed.

4. Models of dynamical conductivity

The model of electronic transport outlined in the introduction suggests explaining the FIR optical spectra and the dielectric function of the boron-rich solids respectively in terms of a linear superposition of classical band-type conductivity and hopping-type conductivity.

The dynamical band-type conductivity can be classically described by the Drude equation:

$$\varepsilon_{\text{Drude}}(\omega) = \varepsilon_L - [\omega_p^2/(\omega^2 + i\omega_s^2)] \quad (2)$$

ε_L is the lattice contribution to the real part of the dielectric function, ω_p the plasma frequency of the free carriers and ω_s the scattering frequency.

To select a suitable theory to describe hopping at very high frequencies is more complicated. At higher temperatures resonant absorption can be excluded, since the thermal energy of the carriers exceeds the photon energy. Only in the spectra at 30 and 77 K could a certain degree of influence of resonant processes exist. Many theories were developed on hopping conductivity via relaxation processes (for reviews see, e.g., [29–32]). However, most of them are restricted to AC and microwave frequencies ($\omega \leq 10^{10} \text{ s}^{-1}$) and do not hold in the frequency range ($\omega \sim 10^{11}$ – 10^{12} s^{-1}) of interest here.

Butcher and Morys [33] solved the AC hopping conductivity problem for pair approximation with electronic tunnelling as the relaxation process; this theory holds in particular for the region of the high-frequency limit. Though this theory was not actually developed for transport mechanisms like that assumed for boron-rich solids, it seems to be applicable, because according to Dyre [34], hopping processes based on different relaxation mechanisms lead to at least qualitatively similar frequency dependences.

The theory of Butcher and Morys yields the complex dynamical conductivity

$$\sigma(\omega) = A \int_0^\infty \frac{x^4}{e^x + i(\omega_\tau/\omega)} dx. \quad (3)$$

Aside from some theoretical model parameters as factors, $\sqrt{A/T}$ (T , temperature) contains the density of hopping states. ω_τ is the relaxation frequency depending on the specific relaxation process and is usually expected in the range of the phonon frequencies. The dielectric function is

$$\text{Re}(\varepsilon_{\text{hopping}}) = \varepsilon_L + \frac{\text{Im}(\sigma)}{\varepsilon_0\omega} \quad \text{Im}(\varepsilon_{\text{hopping}}) = \frac{\text{Re}(\sigma)}{\varepsilon_0\omega}. \quad (4)$$

For the fit of a superposition of the two theories to the experimentally obtained spectra, the integral in equation (3) was solved numerically. From the apparently great number of model parameters only the plasma frequency ω_p of the Drude model and the factor A of the hopping model turned out to be essential. For the scattering frequency ω_s of the Drude-type part $\omega_s = 5 \text{ cm}^{-1}$ ($\simeq 9.4 \times 10^{11} \text{ s}^{-1}$) was chosen; this value is typical for semiconductors. Smaller scattering frequencies would not substantially improve the fit, and therefore this value is to be taken as an upper limit for the boron-rich solids. The influence of the relaxation frequency ω_τ on the hopping part is small; according to the features of the theory for ω_τ the frequencies of strong phonons were obtained from the IR spectra.

5. Results

Figure 2 shows a selection of typical reflectivity spectra of boron-rich solids in the spectral region $<300 \text{ cm}^{-1}$. A reliable simulation of the experimental spectra based on an unambiguously defined set of parameters is possible only if the real and imaginary

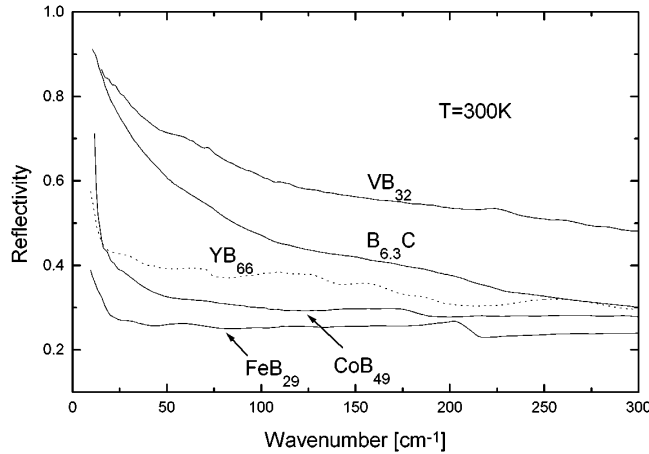


Figure 2. FIR reflectivity spectra of some boron-rich solids.

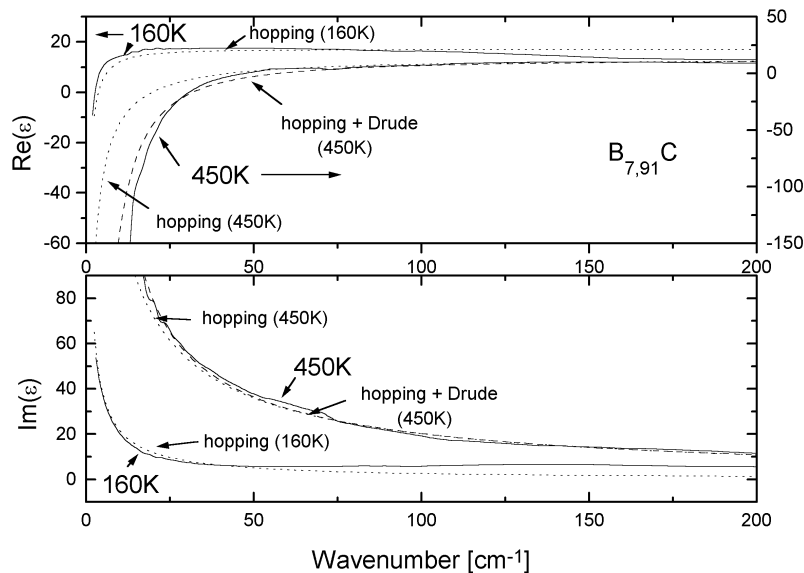


Figure 3. The dielectric function of $B_{7.91}C$ in the FIR range for 160 and 450 K and simulation. The systematic deviation between the fit and the measured spectrum at 160 K increasing towards higher wavenumbers is attributed to resonance effects not considered in the theory.

parts of the dielectric function are both considered. In most cases a superposition of hopping and band-type conductivity is needed to fit the spectra satisfactorily. In no case could the dielectric functions of the boron-rich solids be satisfactorily described with one Drude process alone. Formally, sometimes a superposition of two Drude processes allowed satisfactory fits as well; however, this explanation was excluded for physical reasons, because the scattering frequencies to be used for the second strongly damped Drude process were unrealistically high. Some of the measured spectra allowed a satisfactory fit with a hopping term alone. As will be shown below, this can be easily explained in terms

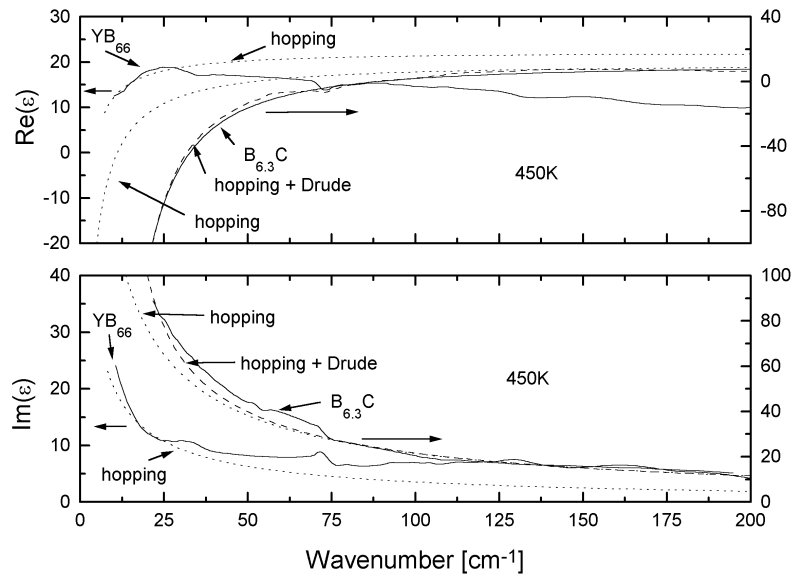


Figure 4. The dielectric function of $B_{6.3}C$ and YB_{66} at 450 K. The systematic deviation between the fit and the measured spectrum of YB_{66} is attributed to resonance effects not considered in the theory used for the fit.

of a decreasing band-type conduction shifting the plasma edge to small energies beyond the accessible spectral range in consequence of decreasing thermal excitation towards low temperatures or in consequence of the change of chemical composition.

As an example of the temperature dependence, the real and imaginary parts of the dielectric function of boron carbide with composition $B_{7.91}C$ are shown in figure 3. While at 450 K a superposition of a Drude and a hopping mechanism is needed to simulate the spectra, at 160 K the hopping mechanism alone is sufficient for a satisfactory fit.

The representatives of two different structure families (boron carbide $B_{6.3}C$ and YB_{66}) are compared in figure 4. Even at the highest selected temperature (450 K), in the case of YB_{66} no indication of a Drude-type conductivity was found in the FIR spectra. The systematic deviations between fits and experimental spectra for YB_{66} towards larger wavenumbers is attributed to a dispersive tail of the absorption processes at higher photon energies, which are not considered in the transport theories used for the fit.

In figure 5 spectra and final fits of the dielectric function of selected β -rhombohedral boron compounds interstitially saturated by Fe, Co and V are shown for 300 K. The effect in vanadium-doped β -rhombohedral boron is the strongest one by far. Unlike B:Co, which is p-type for all of the metal concentrations investigated, B:Fe and B:V in the compositions shown are n-type.

The parameters obtained by simulating the experimental spectra of all materials investigated and for all temperatures are collected together in table 1.

6. Discussion

The squared plasma frequency ω_p^2 , which is proportional to the density of Drude-type free carriers, is plotted in figure 6 versus the carbon content of boron carbide and compared

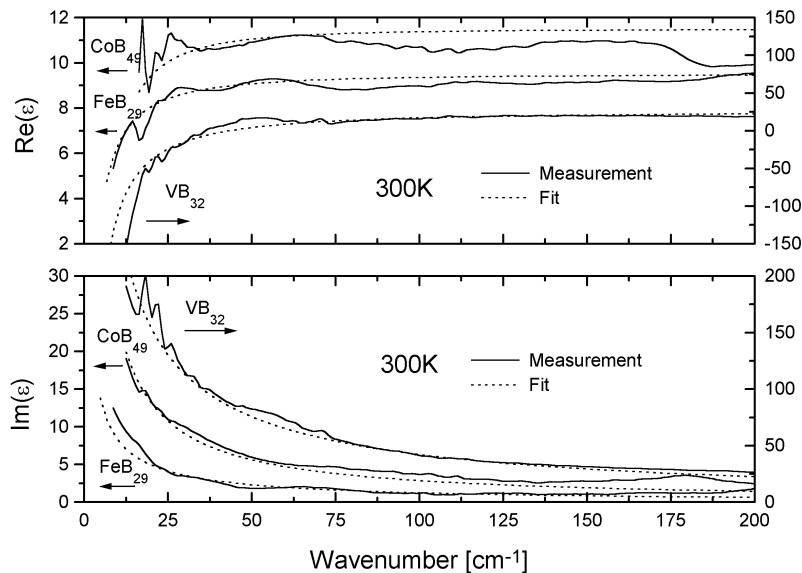


Figure 5. Dielectric functions of β -rhombohedral boron largely saturated by interstitially accommodated Co, Fe and V atoms. Full lines: experimental results; broken lines: final fits. For the fitting parameters see table 1.

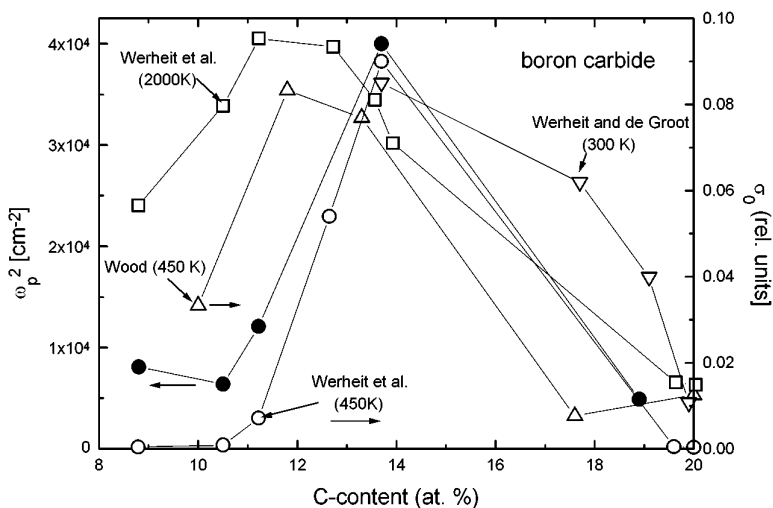


Figure 6. Electrical conductivity of boron carbide versus C content. ●, $\omega_p^2 \propto$ the density of Drude-type carriers at 450 K; ○, DC conductivity σ_0 at 450 K [35]; ▽, DC conductivity σ_0 at 300 K [37, 38]; □, DC conductivity at 2000 K [35]; △, DC conductivity at 450 K according to Wood [36].

with DC conductivity results. For those obtained on the same set of samples [35], the maxima coincide at about $B_{6.3}C$, while the maximum of the DC results of Wood [36] is

Table 1. Electronic transport parameters used to simulate the dielectric functions: A , the parameter in $\sqrt{A/T}$ (T , temperature), which is proportional to the density of hopping states; ω_τ , the scattering frequency; and ω_p , the plasma frequency of Drude-type charge carriers.

Temperature	450 K			300 K		
	A ($\Omega^{-1}\text{cm}^{-1}$)	ω_τ (cm^{-1})	ω_p (cm^{-1})	A ($\Omega^{-1}\text{cm}^{-1}$)	ω_τ (cm^{-1})	ω_p (cm^{-1})
B _{10.37} C	1.3	1100	90	0.65	150	—
B _{8.52} C	1.4	1100	80	0.5	1100	30
B _{7.91} C	1.6	1100	110	0.75	1100	40
B _{6.3} C	1.7	1100	200	1.5	1100	90
B _{4.3} C	0.95	1100	70	0.4	150	—
		450 K			300 K	
VB ₁₉₀	0.2	500	—	0.2	500	—
VB ₁₀₃	0.3	1000	30	0.25	500	30
VB ₆₄	1.6	1000	50	1.15	500	50
VB ₄₃	3.6	1000	120	3.3	1000	50
VB ₃₂	3.6	1000	120	3.3	1000	50
		450 K			300 K	
CoB ₁₇₆	0.16	150	30	0.14	150	30
CoB ₉₅	0.13	150	20	0.14	150	20
CoB ₆₆	0.18	150	30	0.16	150	30
CoB ₄₉	0.3	150	—	0.3	150	—
		450 K			300 K	
FeB ₂₉	0.11	500	—	0.09	500	—
		450 K			300 K	
YB ₆₆	0.28	1100	—	0.35	1100	—

shifted towards more boron-rich compositions. The maximum of the high-temperature DC conductivity [35] is found for more boron-rich boron carbides as well. DC results obtained from a closer sequence of compositions near the carbon-rich limit of the homogeneity range of boron carbide [37, 38] suggest a smaller gradient near the maximum.

For $T = 450$ K, as a measure of the density of hopping sites \sqrt{A} is plotted in figure 7 versus the carbon content of boron carbide and compared with the density of states derived from the parameters σ_0 and T_0 of the DC conductivity according to Mott's theory for variable-range hopping [35]:

$$\sigma = \sigma \exp[-(T_0/T)^{1/4}]. \quad (5)$$

Maxima of the satisfactorily agreeing slopes occur again at B_{6.3}C, which is known to be the composition with the most distorted structure [22], thus explaining the minimum thermal conductivity [22, 39, 40]. It is noteworthy that in boron carbide (structure formula (B₁₂) _{x} (B₁₁C)_{1- x} (CBC) _{y} (CBB) _{z} with $Y + Z \leq 1$) at this composition the maximum concentration of B₁₂ icosahedra ($\approx 42\%$) and the minimum concentration of B₁₁C icosahedra ($\approx 58\%$) are found [22]. Accordingly, the B₁₂ icosahedra in boron carbide are most likely to be responsible for both hopping and band-type conductivity. Hence the hypothesis of Emin *et al* [14–17], assuming B₁₁C icosahedra to be the essential hopping centres responsible for small-bipolaron hopping is not confirmed. Moreover, the experimental Drude-type

Table 1. (Continued)

Temperature	160 K			30 K		
	A ($\Omega^{-1}\text{cm}^{-1}$)	ω_τ (cm^{-1})	ω_p (cm^{-1})	A ($\Omega^{-1}\text{cm}^{-1}$)	ω_τ (cm^{-1})	ω_p (cm^{-1})
$\text{B}_{10,37}\text{C}$	0.2	150	—	0.09	150	—
$\text{B}_{8,52}\text{C}$	0.13	150	—	0.28	50	—
$\text{B}_{7,91}\text{C}$	0.18	150	—	0.15	50	—
$\text{B}_{6,3}\text{C}$	0.9	1100	—	—	—	—
$\text{B}_{4,3}\text{C}$	0.15	150	—	—	—	—
		75 K			30 K	
VB_{190}	0.22	500	—	—	—	—
VB_{103}	0.28	500	—	—	—	—
VB_{64}	0.8	500	40	—	—	—
VB_{43}	2.4	1000	—	—	—	—
VB_{32}	2.4	1000	—	—	—	—
		75 K			30 K	
CoB_{176}	0.16	50	50	—	—	—
CoB_{95}	0.19	150	30	—	—	—
CoB_{66}	0.16	150	40	—	—	—
CoB_{49}	0.23	250	—	—	—	—
		75 K			30 K	
FeB_{29}	0.09	150	—	—	—	—
		160 K			30 K	
YB_{66}	0.33	1100	—	0.11	150	—

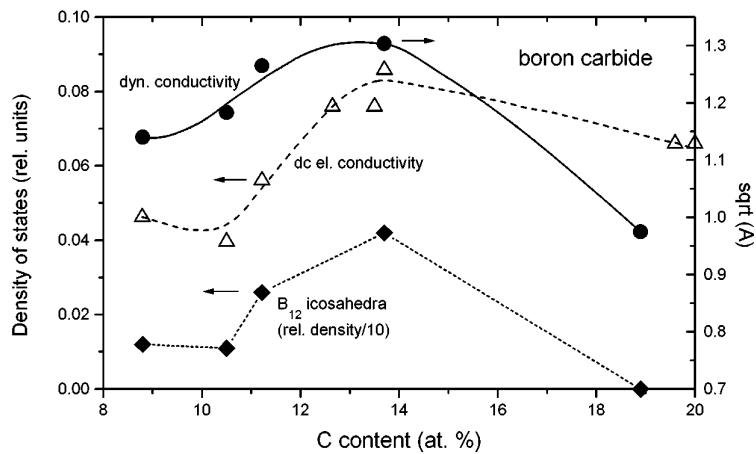


Figure 7. The density of hopping sites of boron carbide versus C content. ●, \sqrt{A} (FIR); Δ , DC result, derived according to Mott's law for variable-range hopping [35]; \blacklozenge , density of B_{12} icosahedra in boron carbide (percentage of unit cells with this structure element) [22].

contribution increases with increasing temperature and contradicts Emin's theory [41]. This describes a coherent motion of bipolarons, which would yield Drude-like spectra at very

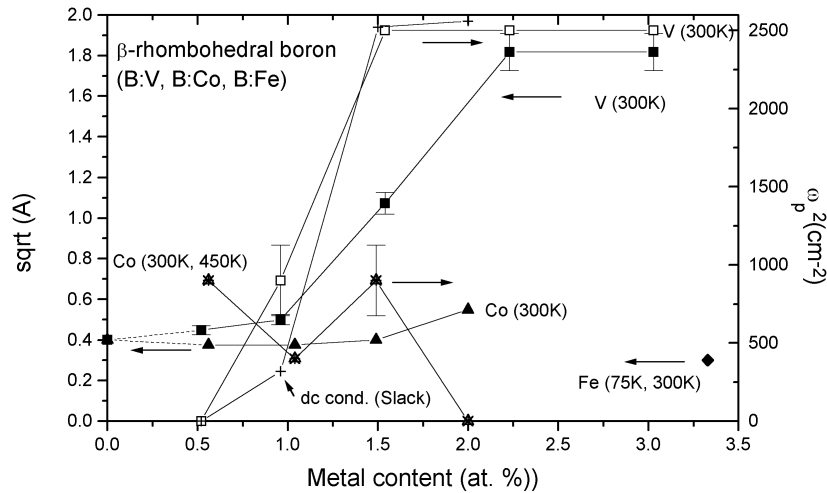


Figure 8. Densities of Drude-type carriers and hopping sites in metal-doped β -rhombohedral boron versus metal content. B:V: \square , $\omega_p^2 \propto$ Drude-type carrier density; +, DC conductivity (relative units) according to Slack *et al* [4]; \blacksquare , density of hopping sites. B:Co: \triangle , \times , \diamond , $\omega_p^2 \propto$ Drude-type carrier densities at 300, 450 and 77 K; \blacktriangle , density of hopping sites. B:Fe: \blacklozenge , density of hopping sites. The error is essentially determined by the accuracy of the fits.

low temperatures only and would lead to a temperature dependence opposite to that found experimentally.

The Drude-type dynamical conductivity increasing with increasing temperature (table 1) suggests a thermally activated generation of the carriers. The activation energy $\Delta E = 0.14(2)$ eV determined accordingly agrees for all of the compositions of boron carbide that were investigated and is obviously specific for this material irrespective of the chemical composition.

At lower temperatures, $\sqrt{A/T}$ —the density of hopping sites in boron carbide—is largely constant. A slight increase towards higher temperatures can be roughly described by an activation energy of 0.12(4) eV for all compounds apart from $B_{6.3}C$, whose density of hopping sites decreases slightly with increasing temperature. This deviation of $B_{6.3}C$ is beyond the experimental error.

For transition metal compounds of β -rhombohedral boron with interstitially accommodated V atoms the slope of the Drude-type carrier density ($\propto \omega_p^2$) agrees quite well with the DC conductivity [4] (figure 8). In both cases saturation is reached at about 1.5% V content. For B:Co the density of Drude-type carriers has a decreasing tendency with increasing metal content at all of the temperatures that were investigated. In this case DC results are not yet available.

For V- and Co-doped boron both of the densities of hopping centres can be easily extrapolated to the same values at zero metal content. While for B:V, which has become n-type already at 0.5 at.%, the density increases monotonically with increasing metal content, for B:Co, remaining p-type over the whole range, a weak decrease is followed by a certain increase of the density. The results can be consistently interpreted within the band scheme in figure 1. When the doping level of V in β -rhombohedral boron is close to the conduction band edge, the density of hopping sites within this level, probably overlapping with intrinsic trapping states, increases with increasing V content. The density of Drude-type electrons

thermally excited from the vanadium level into the conduction band increases as well with increasing V content and increasing temperature. From the doping level of Co positioned slightly above the valence band, electrons are transferred to the upper valence band VB1, accordingly reducing its density of hopping sites at first. Towards higher Co concentrations the Fermi level moves to the Co level, forming an increasing density of new hopping sites. The Drude-type conductivity is accordingly reduced because the increasing distance of the Fermi level from the extended states of the lower valence band reduces the density of thermally excited free holes in the lower valence band VB2. For Fe-doped β -rhombohedral boron only the FIR spectrum of the largely saturated n-type compound FeB₂₉ is available at present. The much lower DC conductivity compared with that of B:V is consistent with the lower density of hopping sites and a Drude-type share not observable in the FIR. For a more detailed discussion see [20].

For YB₆₆ the dynamical conductivity between 30 and 450 K can be well described by hopping processes alone. No contribution of Drude-type free carriers is detectable in the FIR range down to 10 cm⁻¹.

An alternative theory on the electronic transport in compensated semiconductors, which was earlier attributed to hopping, was developed by Pistoulet *et al* [42] taking the occurrence of potential fluctuations into account, which affect the local probability of the ionization of deep levels and influence the frequency and temperature dependence of the conductivity due to carriers in the bands. Since some essential conditions for this theory seem to have their counterparts in the boron-rich solids, investigations are in progress to find out whether this theory is applicable to the density of hopping sites of the electronic transport in these materials as well.

7. Summary

The dynamical conductivities of the boron-rich solids, as far as they are detectable in the FIR reflectivity spectra, can be well described by a linear superposition of contributions from Drude-type free carriers and hopping processes. This holds for both p-type and n-type boron-rich solids. The results obtained are consistent with the DC conductivities. With decreasing temperature and for suitable chemical composition the Drude-type contribution can become small and the effect on the dielectric function is shifted beyond the accessible FIR range ($\gtrsim 10$ cm⁻¹). For β -rhombohedral boron the results are consistent with the band scheme based on numerous optical and electrical results. The hypothesis for the explanation of the electronic transport in boron carbide, which is based on bipolaron hopping between B₁₁C icosahedra [14–17], is proved not to be supported.

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