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Evidence of the Superposition of Drude Type and Hopping Type Transport in Boron-Rich Solids

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The dielectric function of the boron-rich solids in the FIR range is analyzed on the basis of their optical reflectivity spectra, which exhibit obviously typical, strongly increasing slopes with decreasing frequencies. It is shown that these slopes can be quantitatively described, when a superposition of Drude type and hopping type parts for the dynamical conductivity is assumed. The corresponding fits were simultaneously made for the real and imaginary parts of the dielectric function to achieve unambiguous parameters. The obtained results are consistent, e.g., with the DC conductivity of these semiconductors, and in particular in the case of β-rhombohedral boron with the known energy band scheme and the related electronic properties. The bipolaron hopping model of the electronic transport in boron carbide turns out to be inappropriate.

INTRODUCTION

Characteristic for all icosahedral boron-rich solids is a rapid rise of the optical reflectivity toward low frequencies in the FIR spectral range. Till now this has been qualitatively explained by a Drude type plasma edge related to strongly damped free carriers. Although the corresponding fits yielded qualitatively plausible results (1), they were quantitatively hardly satisfactory. The aim of this paper is to develop a quantitatively convincing description of the FIR optical spectra, which is based on the known features of conductivity mechanisms in the boron-rich solids and is thus consistent with their experimentally proved electronic properties. Below it will be shown that a simulation of the spectra is possible when a dynamical conductivity resulting from a superposition of hopping type and free carrier type charge transport is assumed. The model used is based on the dominating hopping mechanism of the DC conductivities, which was first demonstrated for β-rhombohedral boron (2) and has meanwhile been confirmed for this and many other boron-rich solids by various authors, on the hopping character of AC conductivity demonstrated in particular for boron carbide (3), and on experimental results of transport properties like, for example, magnetoresistance, whose interpretation requires the assumption of band-type free carriers.

SAMPLE MATERIAL

The solid solutions of transition metals in β-rhombohedral boron were prepared by arc-melting high purity ingredients and afterward were heat treated typically for 40 hours at 1200°C to guarantee homogeneity. For details of the vanadium and cobalt doped samples, see Ref. (4), and of the iron-doped samples see Refs. (5, 6). The boron carbide samples were prepared partly by melting and partly by hot pressing (for details of their properties see Refs. (7, 8). In the case of YB_{66} a cleaved single crystal surface was used (for more details see Refs. (9, 10).

EXPERIMENTAL

The FIR reflectivity spectra were obtained 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 YB_{66}. A liquid helium-cooled Ge-Bolometer was used in the FIR, and a liquid nitrogen-cooled MCT detector in the MIR range to achieve largely noise-free spectra. With respect to the topic to be discussed, only the FIR sections of the spectra will be presented. The specific complete spectra of the different boron-rich solids are discussed in separate papers in more detail; for vanadium- and cobalt-doped β-rhombohedral boron see Ref. (4), for Fe-doped β-rhombohedral boron see Refs. (5, 6), for boron carbide see Refs. (7, 8), and for YB_{66} Refs. (9, 10).

From the measured reflectivity spectra $R(\omega)$ the complex dielectric function was numerically calculated by Kramers-Kronig transformation (11, 12). For $\omega \rightarrow 0$ the reflectivity spectra were extrapolated according to the Hagen-Rubens relation. By a careful check it was proved that the method of extrapolations has no remarkable influence on the results in the spectral ranges measured and presented below.

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MODELS OF DYNAMICAL CONDUCTIVITY

On one hand, the electronic transport properties of the different boron-rich solids exhibit characteristics sometimes which can only be understood when carriers with considerable mobilities are assumed to exist. On the other hand, for example, the DC conductivities of the boron-rich solids quantitatively meet the theories of hopping conduction. This ambiguity of the electronic properties was our basis for describing the FIR optical spectra and the dielectric function of the boron-rich solids respectively by a linear superposition of classical band-type and hopping-type conductivity.

The dielectric function caused by the dynamical band-type conductivity is classically described by the Drude theory

$$\varepsilon_{\mathrm{Drude}}(\omega) = \varepsilon_{\mathrm{L}} - [\omega_{\mathrm{p}}^2/(\omega^2 + i\omega_{\mathrm{s}}^2)], \qquad [1]$$

where 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.

A suitable theory to describe hopping at very high frequencies is more difficult to find. 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 influence of resonant processes exist. On hopping conductivity based on relaxation processes several theories were developed (see e.g. (13–16) for reviews). However, most of them are restricted to AC and microwave frequencies ($\omega \leq 10^{10}\ \mathrm{s}^{-1}$) and do not hold in the FIR range ($\omega \sim 10^{11}...10^{12}\ \mathrm{s}^{-1}$) that interests us here.

The theory of Butcher and Morys (17) is based on a pair approximation with electronic tunneling as relaxation process; it holds in particular for the range of the high frequency limit. Although this theory is not immediately developed for transport mechanisms like those assumed for boron-rich solids, it seems to be applicable, because according to Dyre (18) hopping processes based on different relaxation mechanisms lead to at least qualitatively similar frequency dependences.

This theory yields the complex dynamical conductivity

$$\sigma(\omega) = A\int_0^\infty \frac{x^4}{e^x + i(\omega_\tau/\omega)}\,dx. \qquad [2]$$

Aside from some theoretical model parameters as factors, $A \propto n_{\mathrm{s}}^2 \cdot T$ (T, temperature) yields the density of hopping states n_{s}. ω_τ is the relaxation frequency, which depends on the specific relaxation processes. These are usually in the range of the phonon frequencies. The frequency dependence of the dielectric function

$$\mathrm{Re}(\varepsilon_{\mathrm{hopping}}) = \varepsilon_L + \frac{\mathrm{Im}(\sigma)}{\varepsilon_0\omega} \qquad \mathrm{Im}(\varepsilon_{\mathrm{hopping}}) = \frac{\mathrm{Re}(\sigma)}{\varepsilon_0\omega} \qquad [3]$$

comes from the frequency dependence of the electrical conductivity, which we describe as a superposition of both transport theories. The integral in Eq. [2] was solved numerically. From the apparently great number of model parameters only the plasma frequency ω_{p} of the Drude model and factor A of the hopping model turned out to be essential. For the scattering frequency of the Drude-type part $\omega_{\mathrm{s}} = 5\ \mathrm{cm}^{-1}$ ($\hat{=}9.4 \times 10^{11}\ \mathrm{s}^{-1}$) was used. For $T = 300$ K and $m^* = m_{\mathrm{e}}$ this value corresponds to a mean-free path of about 100 nm, which is rather high compared with other semiconductors. However it must be obeyed that this way only a very rough estimation is possible. 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 typical phonon frequencies were taken.

RESULTS

Some typical FIR reflectivity spectra of boron-rich solids are shown in Fig. 1. A reliable simulation of the experimental spectra based on an unambiguously defined set of parameters requires to fit real and imaginary parts of the dielectric function simultaneously. In most cases a superposition of hopping and band type conductivity were needed to fit the spectra satisfactorily. In no case could the dielectric functions of the boron-rich solids be satisfactorily

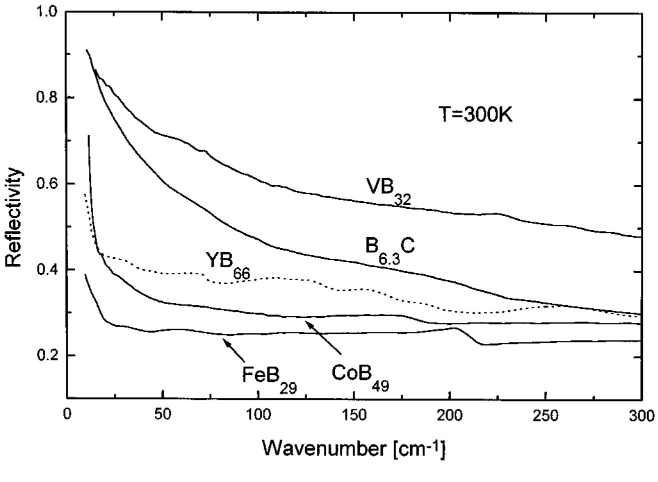

FIG. 1. Typical reflectivity spectra of some icosahedral boron-rich solids at 300 K in the FIR range. The estimated error of the spectra including influences of nonideal sample surfaces and influences of all possible uncertainties of the spectrometer and of the Fourier transformation is less than 5% relatively.

described with one Drude process only. Formally, in some cases 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 assumed for the second strongly damped Drude process were unrealistically high. Some spectra allowed a satisfactory fit with a hopping term alone. As will be shown below, this can be easily explained by a decreasing band type conduction shifting the plasma edge to small energies beyond the accessible spectral range in consequence of decreasing thermal excitation toward low temperatures or because of the change of chemical composition.

As an example of the temperature dependence real and imaginary parts of the dielectric function of the boron-rich boron carbide $B_{7.91}C$ are shown in Fig. 2. 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 yields a satisfactory fit. Obviously the band-type conductivity decreases toward decreasing temperatures so far that the plasma frequency is finally shifted to such small frequencies that contributions to the FIR spectra fall below the detection limit.

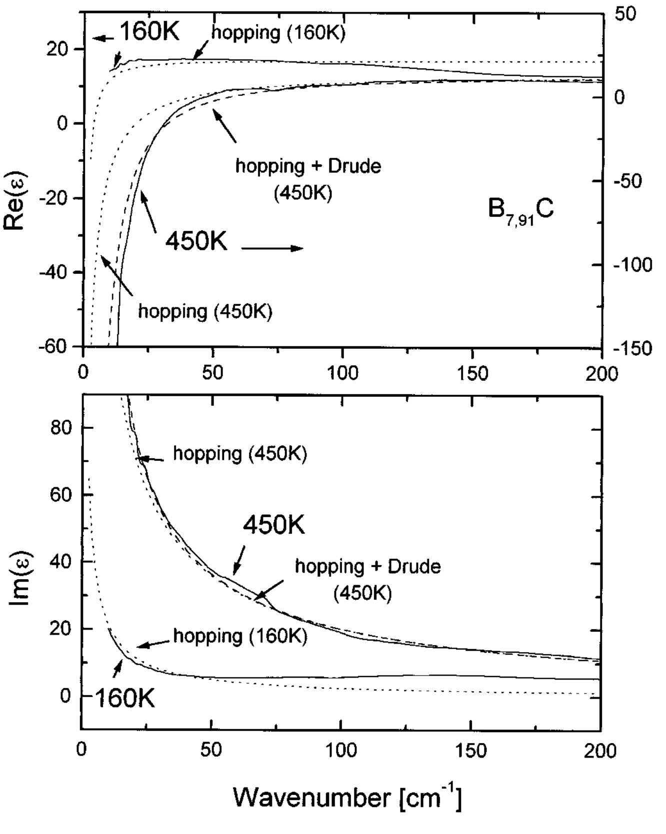

FIG. 2. Dielectric function of $B_{7.91}C$ in the FIR range for 160 and 450 K and the fitted model. The systematic deviation between fit and measured spectrum at 160 K increasing toward higher photon energies is attributed to resonance effects not considered in the theory used for fittings.

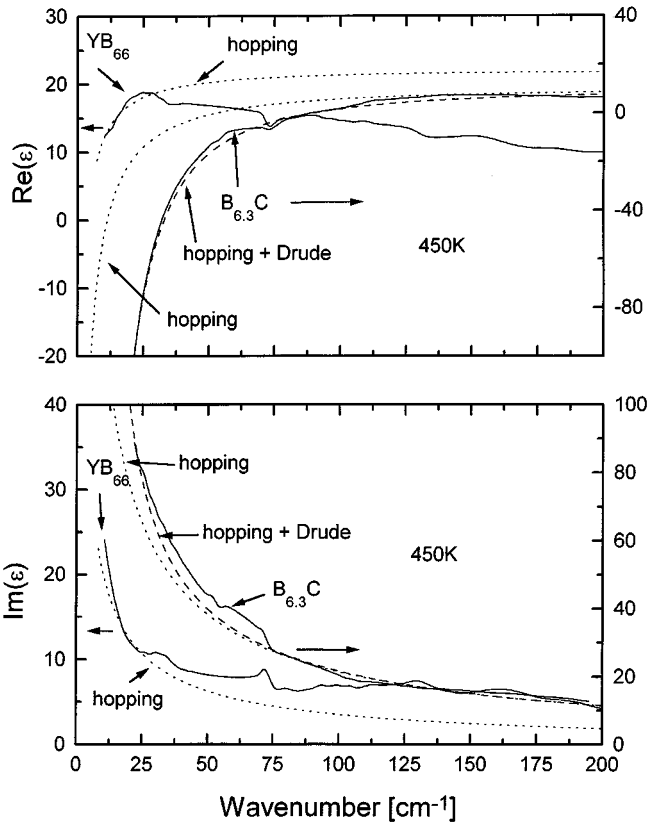

FIG. 3. Comparison between the dielectric function of $B_{6.3}C$ and YB_{66} at 450 K. The systematic deviation between fit and measured spectrum of YB_{66} is attributed to resonance effects not considered in the theory.

The representatives of two different structure families (boron carbide $B_{6.3}C$ and YB_{66}) are compared in Fig. 3. In the case of YB_{66} even at the highest sample temperature of 450 K no indication of a Drude-type conductivity was found. The systematic deviations between fits and experimental spectra of YB_{66} toward larger wavenumbers is attributed to a dispersive tail of absorption processes at higher photon energies, which remained out of consideration.

In Fig. 4 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. Contrary to B : Co, which remains p-type for all investigated metal concentrations, B : Fe and B : V in the compositions shown are n-type.

DISCUSSION

The parameters determined by fitting the optical spectra (for the complete set see (19)) are to be compared with other experimental results. At first, the squared plasma frequency ω_p^2, which is proportional to the density of Drude-type-free

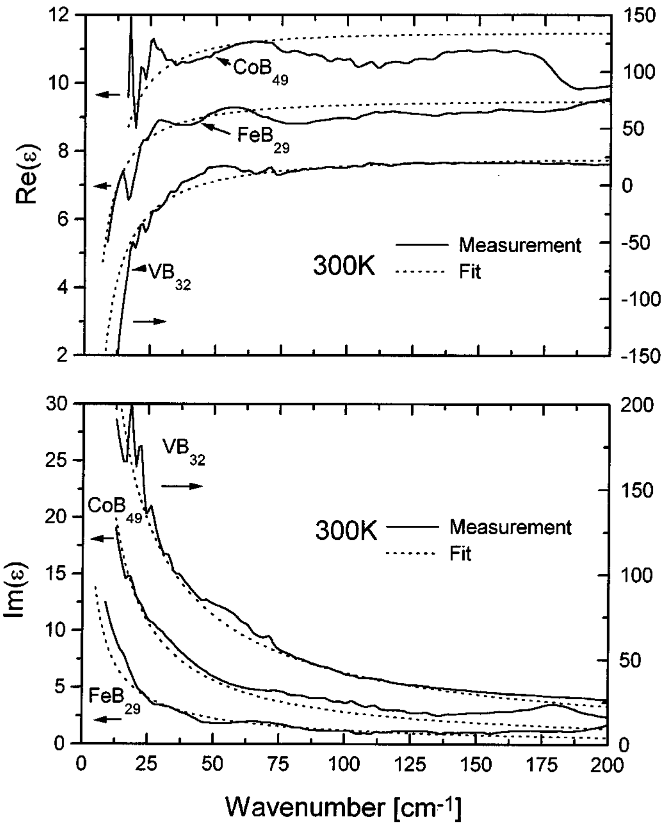

FIG. 4. Dielectric functions of β-rhombohedral boron largely saturated by interstitially doped Co, Fe, and V atoms. Full lines, experimental; broken lines, final fits.

carriers, is compared in Fig. 5 with the DC conductivity beeing proportional to the density of carriers as well. For the DC conductivity obtained on the same set of samples (20), the maxima coincide at about $B_{6.3}C$, while the maximum of the results of Wood (21) is shifted toward more boron-rich compositions. The maximum of the high temperature DC conductivity (20) is found at 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 (22, 23) suggest a smaller gradient near the maximum.

At fixed temperatures $\sqrt{A}$ is proportional to the density of hopping sites. In Fig. 6 these values obtained from the optical spectra are compared with the densities of states, which result from the parameters σ_0 and T_0 of the DC conductivities at 450 K according to Mott's theory for variable range hopping (20)

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \qquad [4]$$

Maxima of the satisfactorily agreeing slopes occur again at $B_{6.3}C$, which is known to be the chemical composition of boron carbide with the mostly distorted structure (7), thus explaining the minimum thermal conductivity (7, 24, 25). It is noteworthy that as proved in (7) in boron carbide at this composition the maximum concentration of B_{12} icosahedra ($\approx 42\%$) and the minimum concentration of $B_{11}C$ icosahedra ($\approx 58\%$) occur. Accordingly, the B_{12} icosahedra in boron carbide are preferably responsible for hopping and band-type conductivity both. Hence the hypothesis of other authors (26–29) assuming $B_{11}C$ icosahedra to be the essential hopping centers responsible for small bipolaron hopping is not confirmed. Moreover, the experimental Drude type contribution increases with increasing temperature, which is hence opposite to the small bipolaron hopping theory as presented by Emin (30). This describes a coherent motion of bipolarons, which would yield Drude-like spectra at very low temperatures only and would lead to a temperature dependence opposite to that experimentally found.

For boron carbide the Drude type dynamical conductivity which increases with increasing temperature suggests a thermally activated generation of the carriers. The accordingly determined activation energy $\Delta E = 0.14(2)$ eV is the same for the whole homogeneity range of boron carbide and is therefore 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 toward 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, but it cannot be explained at present.

For transition metal compounds of β-rhombohedral boron with interstitially accommodated V atoms the slope of the Drude-type carrier density (proportional to ω_p^2) agrees quite well with the DC conductivity (31) (see Fig. 7). In both cases saturation is approached for vanadium contents excceding about 1.5% V. For B:Co the density of Drude-type carriers has a decreasing tendency with increasing metal content at all investigated temperatures. Unfortunately in this case DC results are not yet available for comparison.

For V- and Co-doped boron both, the densities of hopping centers can be easily extrapolated to the same values for pure boron. While for B:V, which becomes n-type already at 0.5 at.%, the density increases monotonously with increasing metal content, for B:Co, which is p-type for all compounds investigated, a weak decrease is followed by a certain increase of the density. The results can be consistently interpreted within the band scheme of β-rhombohedral boron (32). 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 overlaps with intrinsic trapping states increases with increasing V content. The density of Drude-type electrons thermally

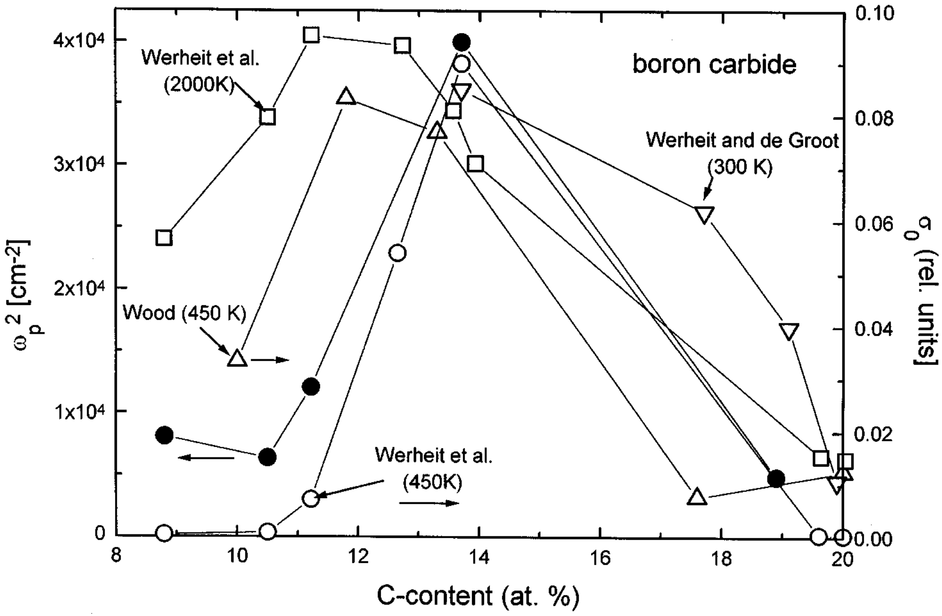

FIG. 5. DC conductivity of boron carbide vs C content compared with (●) ω_p^2 proportional to the density of Drude-type carriers at 450 K; (○) DC conductivity σ_0 at 450 K (20), (▽) DC conductivity σ_0 at 300 K (22, 23), (□) DC conductivity at 2000 K (20), and (△) DC conductivity at 450 K according to Wood (21).

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 assumed to be slightly above the valence band, electrons are transferred to the upper valence band accordingly reducing its density of hopping sites at first. Toward higher Co concentrations the Fermi level moves to the Co level, forming an increasing density of hopping sites within a new level. The Drude-type conductivity is reduced accordingly 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

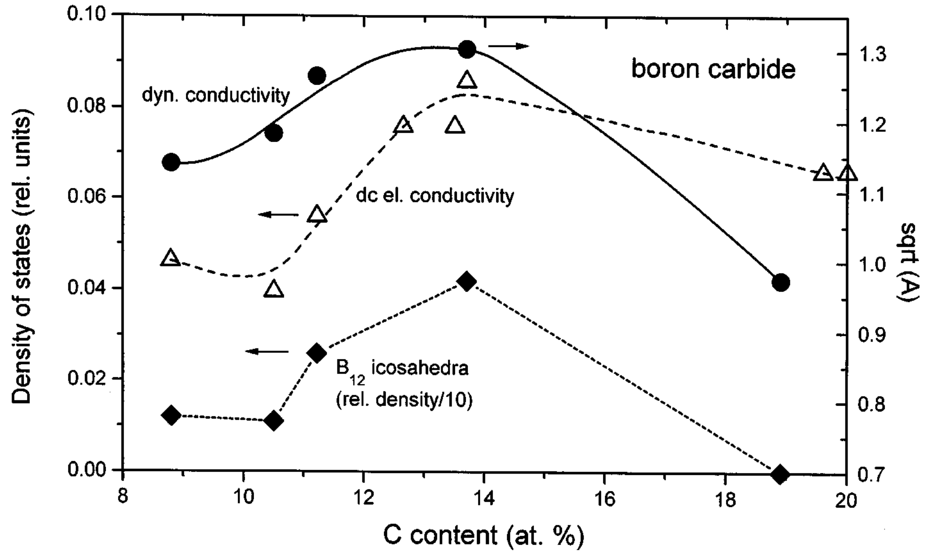

FIG. 6. Density of hopping sites of boron carbide vs C content compared with (◆) density of B_{12} icosahedra in boron carbide (percentage of unit cells with this structure element) (7). (●) $\sqrt{A}$ (FIR); (△) DC result derived according to Mott's law for variable range hopping (20).

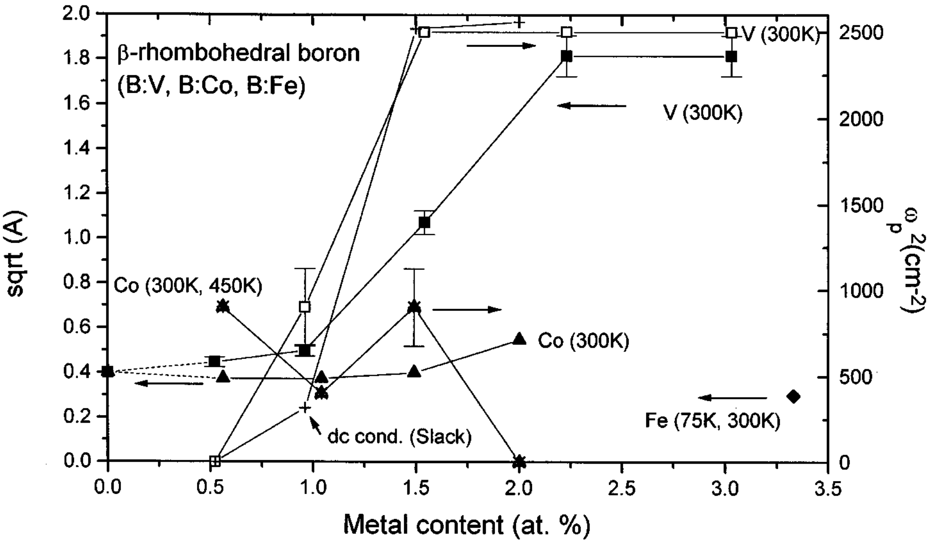

FIG. 7. Densites of Drude-type carriers and hopping sites in metal-doped β-rhombohedral boron vs metal content compared with some measerments of DC conductivity. B : V : (□) $\omega_p^2 \propto$ to Drude-type carrier density; (+) DC conductivity (rel. units) according to Slack *et al.* (31); (■) density of hopping sites. B : Co : (△, ×, ◇) $\omega_p^2 \propto$ to Drude-type carrier densities at 300, 450, and 77 K; (▲) density of hopping sites. B : Fe : (◆) density of hopping sites. The error is essentially determined by the accuracy of fits.

β-rhombohedral boron only the FIR spectrum of the largely saturated n-type compound FeB_{29} is available at present. Its DC conductivity, which is much lower than that of B : V, is consistent with the lower density of hopping sites and a Drude-type share, which is too low to be observable in the FIR.

For the dynamical conductivity of YB_{66} between 30 and 450 K hopping processes alone are sufficient for a satisfactory description of the optical spectra. No contribution of Drude-type-free carriers is detectable in the FIR range down to $10\,cm^{-1}$.

SUMMARY

The specific slope of the reflectivity rising toward low frequencies, which is typical for the boron-rich solids, is attributed to their dynamical conductivities and can be well described by a linear superposition of contributions by Drude-type-free carriers and hopping processes. This holds for p-type and n-type boron-rich solids both. These results are supported by their correspondence with the DC conductivities. With decreasing temperature and for suitable modifications of the chemical composition the Drude-type contribution can become small, and its effect on the dielectric function is shifted beyond the accessible FIR range limited at $10\,cm^{-1}$. For β-rhombohedral boron the results are consistent with the band scheme based on numerous optical and electrical results. Both conductivity mechanisms in boron carbide are correlated with the concentration of B_{12} icosahedra, and therefore the hypothesis for the explanation of the electronic transport in boron carbide based on bipolaron hopping between $B_{11}C$ icosahedra (26–29) turns out to be inappropriate.

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