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On the electronic properties of β-rhombohedral boron interstitially doped with 3d transition metal atoms

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Abstract

The controlled modification of the p-type character of pure boron-rich solids to n-type by suitable doping is an essential prerequisite for technical applications. Interstitial doping of β-rhombohedral boron with V, Cr, Fe and Ni fulfils this requirement, while Cu and Co do not. Comparative investigations of the Seebeck coefficient, the DC electrical conductivity, the optical absorption and the dynamical conductivity of B–V, B–Co and B–Fe lead to the conclusion that donor levels positioned between the conduction band and the uppermost intrinsic electron trapping level and of sufficient density to overcompensate unoccupied valence and gap states are necessary for n-type conductivity. In contrast to Fe, the interstitial accommodation of V atoms seems to reduce the concentration of possible gap states.

1. Introduction

At present, β-rhombohedral boron is the model crystal of the boron-rich solids, whose structural and electronic properties are both essentially determined by B_{12} icosahedra. These icosahedra are mostly found in a slightly distorted form and sometimes as fragments or condensed systems. In all structures the influence of the icosahedra on the electronic structures of the boron-rich solids is more or less prevailing.

The distortion of the icosahedra is caused by the Jahn–Teller effect splitting the valence band, separating occupied and unoccupied electronic states by 0.188 eV thus being responsible for the exceptional semiconductor behaviour of the condensed boron systems composed of atoms with odd electron numbers [1–5]. The split-off valence band is partly occupied by electrons coming from non-icosahedral structural elements, which are the two B_{10} units on the trigonal axis and the single atoms in the center and at some weakly occupied sites of the unit cell [6]. Accordingly, p-type electronic transport by thermally activated holes in the lower valence band is superimposed by hopping processes within the split-off valence band. Apart from the great distance between the conduction band and the Fermi level positioned within the split-off valence band, the contribution of electrons to the electronic transport is moreover reduced by intrinsic electron traps generated by the interaction of electrons with specific intra-icosahedral phonons [7,8]. The energy band scheme of pure β-rhombohedral boron is shown in Fig. 1 [7,9].

Systematic and controlled n-doping of boron-rich solids is required for technical applications. Because of its excess electron compared with boron, carbon appears to be a suitable n-dopant, however, the substitution of carbon for boron atoms in the structure fails in this respect, because the deep-lying donor level of carbon coincides with the split-off valence

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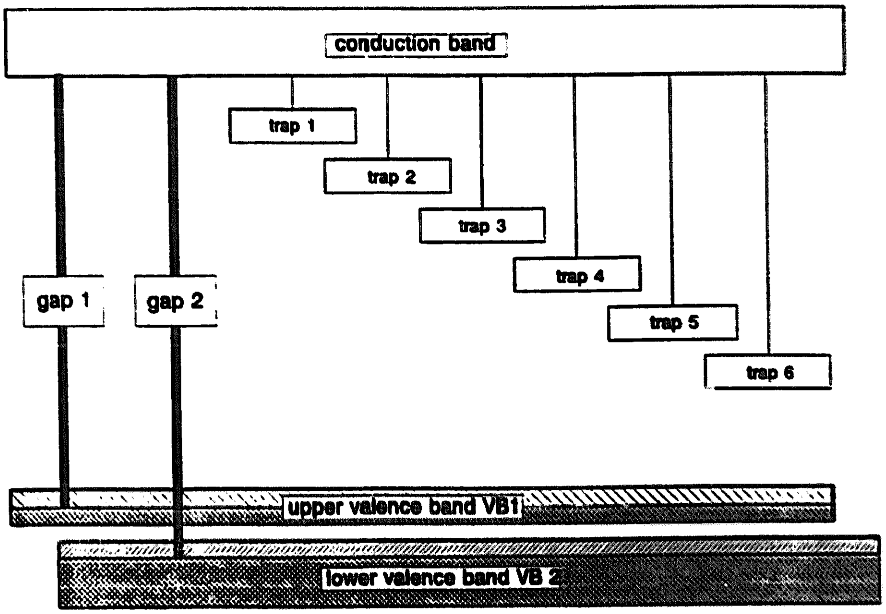

Fig. 1. Energy band scheme of pure β-rhombohedral boron; the vertical lines indicate the allowed transitions [7,9]. Gap 1: 1.32(1) eV (E||c), 1.29(1) eV (E ⊥ c); gap 2: 1.50(1) eV (E||c), 1.46(1) (E ⊥ c); the values correspond to extrapolations to $T = 0$ K. Positions of the electron traps: n-times 0.188 eV (n = 1–6) below the conduction band edge [9].

band. N-doping of β-rhombohedral boron is possible by the interstitial accommodation of certain 3d transition elements like V, Cr, Fe and Ni [10,6], while it remains p-type for example in the case of other interstitially accommodated transition elements like Co and Cu. For Li-doped β-rhombohedral boron the carrier type has not yet been experimentally determined, however, it is assumed to be n-type [11].

For most interstitial doping elements the electrical conductivity increases monotonically with increasing dopant concentration and approaches saturation. In contrast, for interstitial Li and Cu doping the conduc-

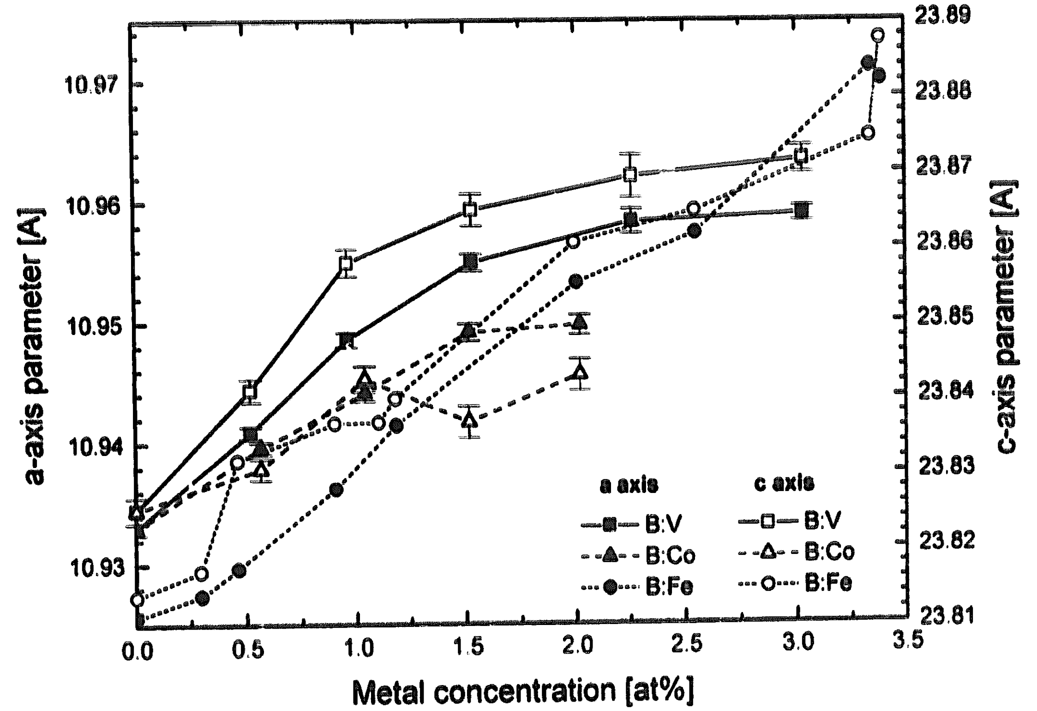

Fig. 2. Unit cell parameters of β-rhombohedral boron interstitially doped with V, Co and Fe atoms. The smaller starting values for B–Fe [15] compared with B–V and B–Co are caused by carbon impurities (see [9]).

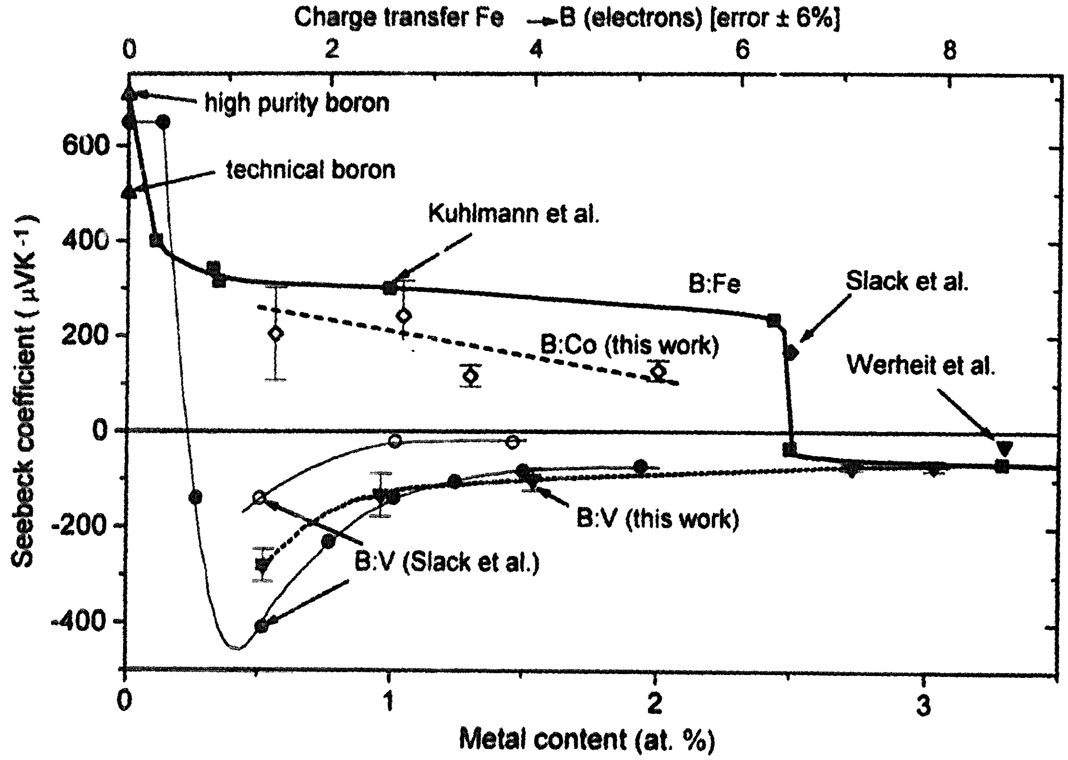

Fig. 3. Seebeck coefficient of β-rhombohedral boron interstitially doped with V, Fe and Co vs. metal content. Data obtained from the literature: Werheit et al. [10], Slack et al. [6] and Kuhlmann et al. [12].

tivities exhibit maxima at specific medium metal concentrations [6,11]. For B–Cu this exceptional behaviour is underlined by a correlated non-monotonic slope of the Seebeck coefficient [6]. Obviously the effect of the doping transition elements on the electronic structure is not uniform.

The distribution on the different interstitial sites in the β-rhombohedral boron structure is not uniform as well. For example, the Fe atoms are statistically distributed on the A and D interstitial sites in the structure irrespective of the metal content, merely their ionisation to Fe^{2+} and Fe^{3+} ions varies [12],

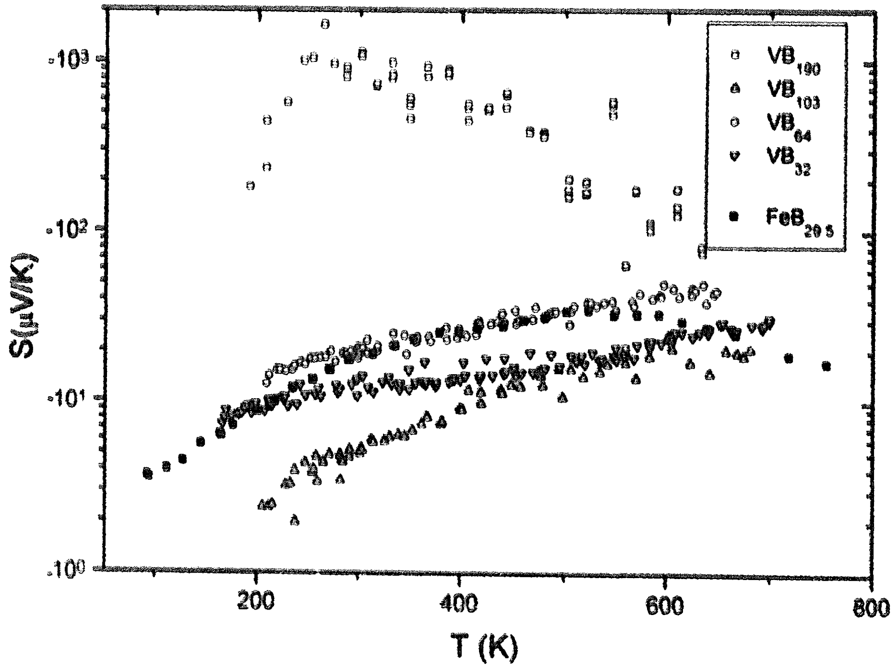

Fig. 4. Temperature dependence of the Seebeck coefficient of several B–V compounds and of $FeB_{29.5}$ [10]. For the B–V samples the absolute values are somewhat uncertain because of the experimental difficulties to measure the Seebeck coefficient on very small samples; however, the tendency of temperature dependence is reliable.

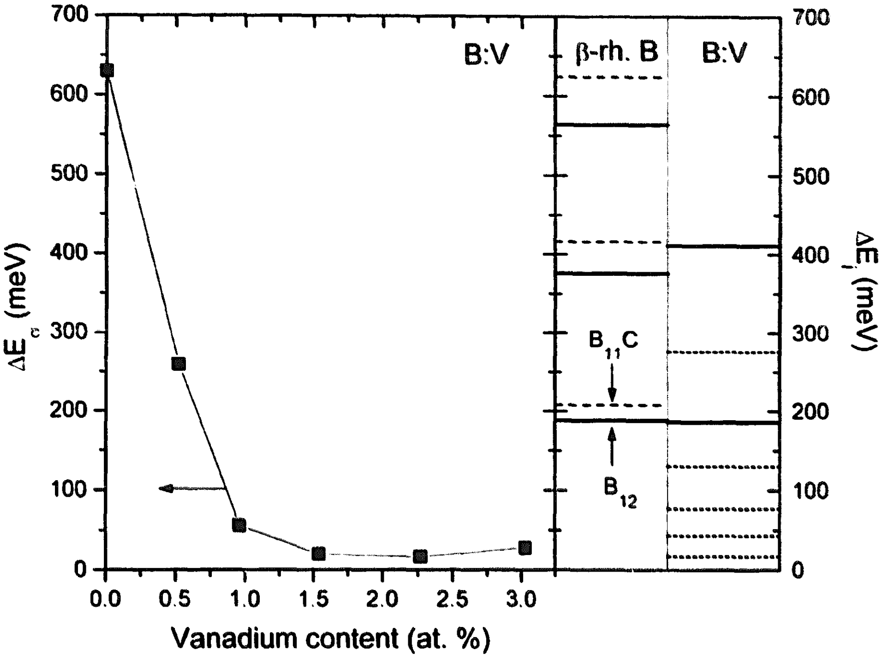

Fig. 5. Thermal activation energy of the high temperature electrical conductivity of B-V vs. V content (left) and ionization energies determined from optical absorption (right) compared with the energies of the intrinsic trapping levels [7,9].

whereas V atoms are preferably accommodated in A sites at lower concentrations and the occupancy of D sites becomes perceptible rather at higher V contents [6,13].

Little has become known about the electronic effects of the numerous interstitial dopants in β-rhombohedral boron (see [13] and references therein) and in particular on the energetical position of the doping levels of the different transition elements in the band gap. A comparative investigation of V, Fe and Co as doping elements depending on the metal content is presented below.

2. Sample material

The solid solutions of V, Fe and Co in β-rhombohedral boron were prepared by arc-melting high purity ingredients which are then heat treated typi-

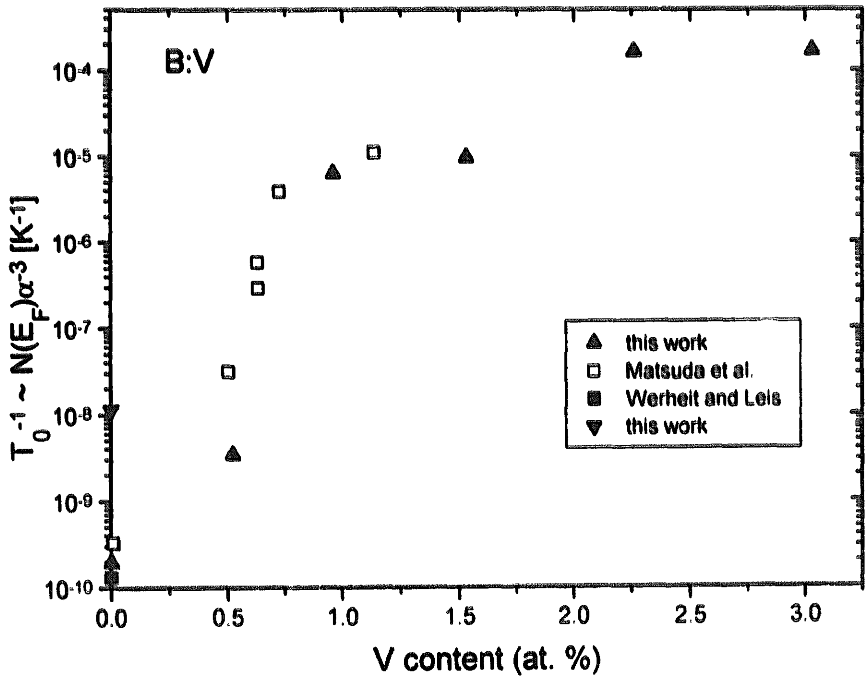

Fig. 6. Dependence of T_0^{-1} the product of the density of states at the Fermi level and of the localization volume on the V content. Data of Werheit and Leis [21] and Matsuda et al. [22] for comparison.

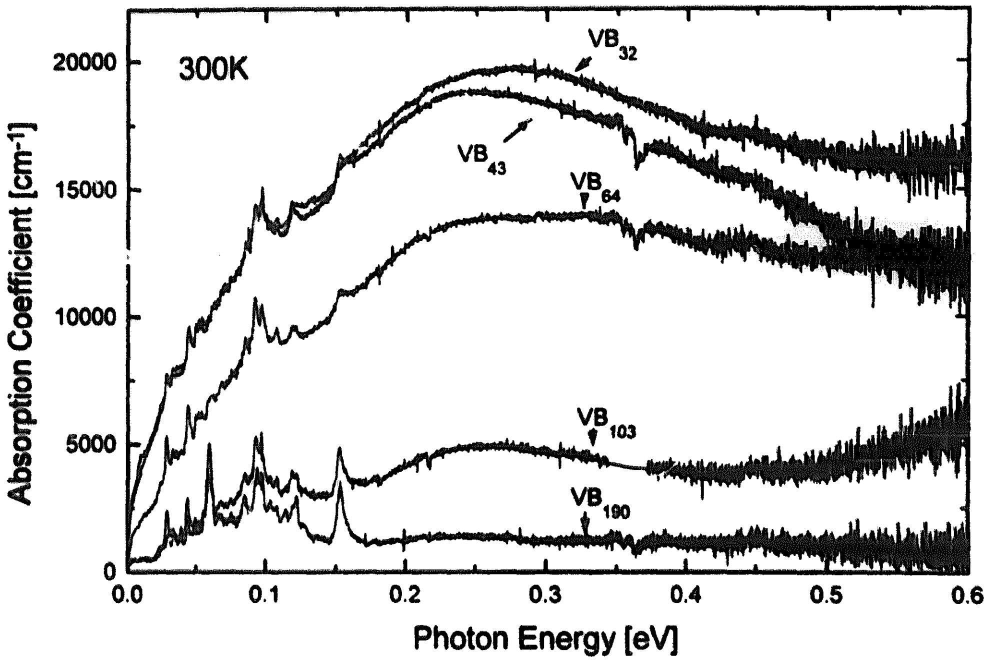

Fig. 7. Optical absorption of the B–V samples vs. photon energy. The narrow absorption peaks at energies below 0.16 eV belong to the characteristic phonon spectrum of β-rhombohedral boron.

cally for 40 h at 1200°C to guarantee homogeneity. For details of the vanadium and cobalt doped samples see reference [14] and for details of the iron-doped samples see references [12,15].

The samples are single-phase, excluding VB$_{32}$ and VB$_{43}$ containing small amounts of VB$_2$ and CoB$_{49}$ and CoB$_{66}$ containing traces of CoB. Fig. 2 shows the unit cell parameters depending on the metal content.

As is well known from other elements [16], the structure is widened by the interstitial accommodation of transition elements. However, while the unit cell parameters for B–Fe increase proportional to the metal content throughout the whole range, for B–V and B–Co they seem to indicate saturation (Fig. 2). The reason may be that the distribution of Fe atoms on the A and D sites (two Fe atoms maximum per

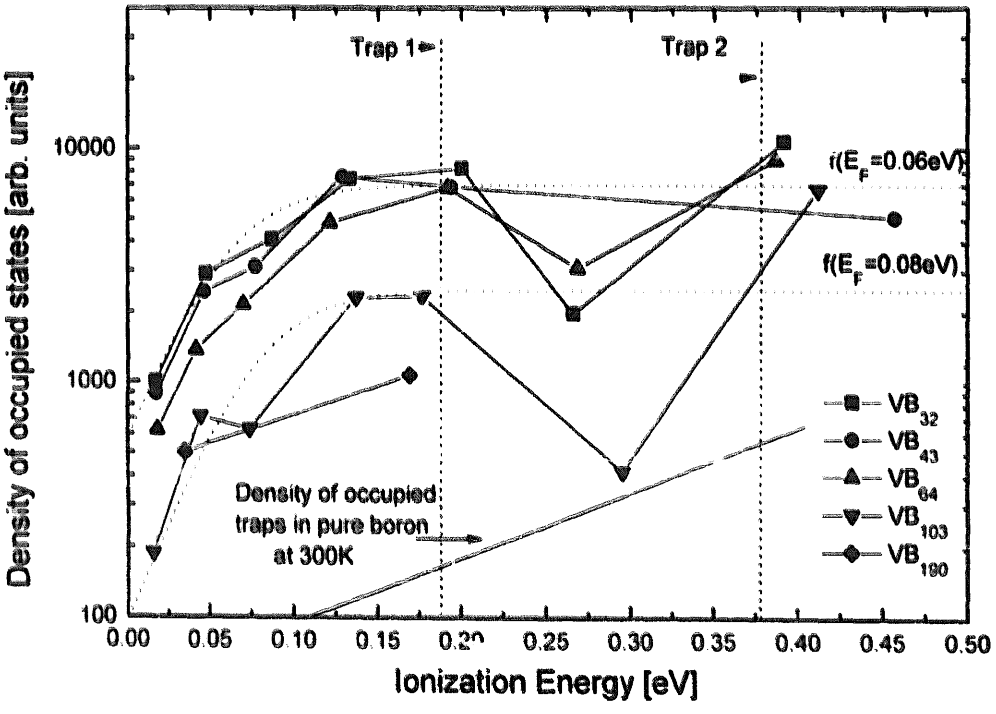

Fig. 8. Occupation densities of gap states in B–V derived from the optical absorption.

unit cell for A and D sites each) in the β-rhombohedral boron structure is statistical up to saturation [12], while for V the accommodation in A sites is preferred at lower contents and this is essential for the widening of the structure. The accommodation in D sites particularly at higher V contents (apparently 1 V atom maximum in D sites per unit cell) is assumed to have less effect on the structure.

3. Experimental data

3.1. Seebeck effect

For classical band-type conduction the sign of the Seebeck coefficient is determined by the sign of the prevailing type of mobile carriers, for hopping conduction it is determined by the gradient of the density of states at the Fermi level [17]. Therefore, irrespective of the specific transport mechanism, the Seebeck coefficient yields the information, whether the electronic transport takes place in a largely filled band, usually the valence band, or in a largely empty band, usually the conduction band.

Fig. 3 shows the Seebeck coefficient of β-rhombohedral boron interstitially doped with several transition elements depending on the metal content. For Fe-doped boron the transition from p-type to n-type takes place at a transfer of six electrons per unit cell from the Fe^{2+} and Fe^{3+} ions to the boron structure [12]. This corresponds to the sum of two unoccupied states in the valence band range and one intrinsic electron trap formed in each of the four B_{12} icosahedra in the unit cell. Accordingly, it was concluded that the uppermost donor level of Fe in β-rhombohedral boron is situated between the conduction band edge and intrinsic electron trap with the smallest binding energy.

Assuming the number of six electrons needed for n-type β-rhombohedral boron to be valid for V-doping as well, for which according to Fig. 3 the transition to n-type takes place at a metal content of only about 0.25 V atoms per unit cell, one would get a transfer of about 24 electrons per V atom to the boron structure. That is unrealistic for the V atom with 23 electrons in total. Therefore the doping mechanism of the V atoms in β-rhombohedral boron must be qualitatively different from that of the Fe atoms. This even holds, when according to calculations of DeLeo et al. [18] for interstitial transition metal impurities in silicon the uppermost occupied level of the V atoms is assumed to be within the conduction band of β-rhombohedral boron as well.

For B–Co the Seebeck coefficient does not change sign up to the saturation of the structure with these transition metal atoms.

The assumption of qualitatively different transport mechanisms at low and high V doping is supported by the tendencies of the temperature dependences of the Seebeck coefficient (Fig. 4). For low V contents the typical decrease in the Seebeck coefficient is found towards higher temperatures, which is due to the beginning influence of intrinsic conductivity, where finally the Seebeck coefficients of electrons and holes largely cancel each other. On the contrary, at high V

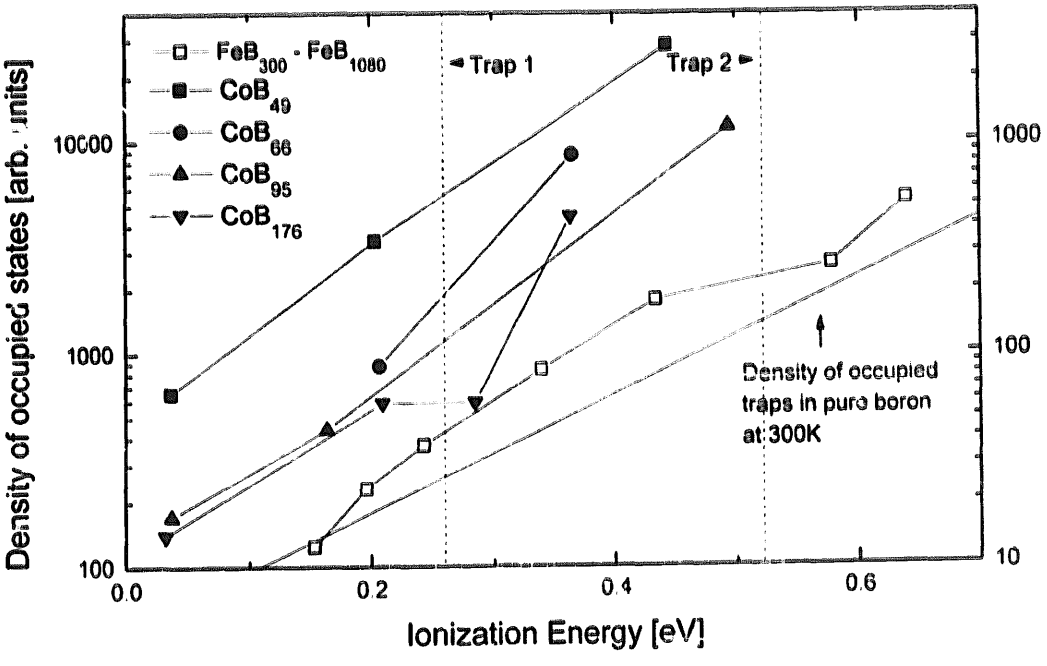

Fig. 9. Occupation densities of gap states in B–Co derived from the optical absorption. For B–Fe the according data are determined from the difference spectrum of FeB_{300} and FeB_{1080} [15] to eliminate unspecified absorption processes.

contents the negative Seebeck coefficients monotonically increase with temperature at least up to the limit of measurement at 700 K. This reminds us of p-type boron carbide, where the Fermi level is pinned even up to more than 2000 K within the split-off valence band overlapped by an occupied carbon level [19,20]. This behaviour is in contrast to B–Fe, where even close to saturation, S decreases towards high temperatures indicating an increasing contribution of holes [10].

3.2. DC conductivity

The DC conductivity of B–V increases with increasing V content and does not reach saturation within the investigated range of V content. For lower temperatures the temperature dependence of the electrical conductivity indicates a hopping type conductivity, while it seems to be thermally activated at high temperatures. These activation energies are plotted in Fig. 5 vs. V content. At a high V content they seem to approach a composition-independent value of 22(5) meV, which can be easily attributed to a high-density V level close to the conduction band. This supports the conclusion derived from the Seebeck effect that intrinsic behaviour is not reached up to approximately 800 K.

The temperature dependence of DC hopping conductivity can be described according to Mott [17] by $\sigma = \sigma_0\ [-(T_0/T)^{1/4}]$ with $T_0^{-1} \propto N(E_F)\ \alpha^{-3}$ (α^{-1}, localization length). For B–V T_0^{-1}, the product of the density of states at the Fermi level and the localization volume, increases monotonically with increasing V content (Fig. 6) [21,22] indicating that the density of states of the assumed V impurity band tends to saturate in the range of about three V atoms per unit cell. Taking the results of Slack et al. [6] into account, there are probably two of them accommodated in the isolated A sites and one in the space of six equivalent D sites around the central boron atom in the unit cell.

For nearly Fe-saturated $FeB_{29.5}$ the activation energy formally determined from the slope of the electrical conductivity decreases between 400 and 800 K from about 80 to 35 meV indicating a corresponding occupied donor level close to the conduction band edge [21]. However, compared with B–V the density of occupied states of the shallow level is much lower, because the Seebeck coefficient indicates a considerable contribution of holes to the electronic transport.

3.3. Optical absorption

The IR optical absorption of the B–V samples up to 0.6 eV (Fig. 7) is essentially due to excitations from gap states into the conduction band. The absorption was decomposed according to Lucovsky's theory on deep level-to-band transitions [23]. The determined ionization energies are presented in Fig. 6. The densities of states (Fig. 8) indicate that already at rather low V contents the Fermi level is shifted to a position close to the conduction band edge. On the contrary, for B–Co in general and B–Fe with a low Fe content the higher levels in the gap are obviously only occupied by the thermal activation of electrons from lev-

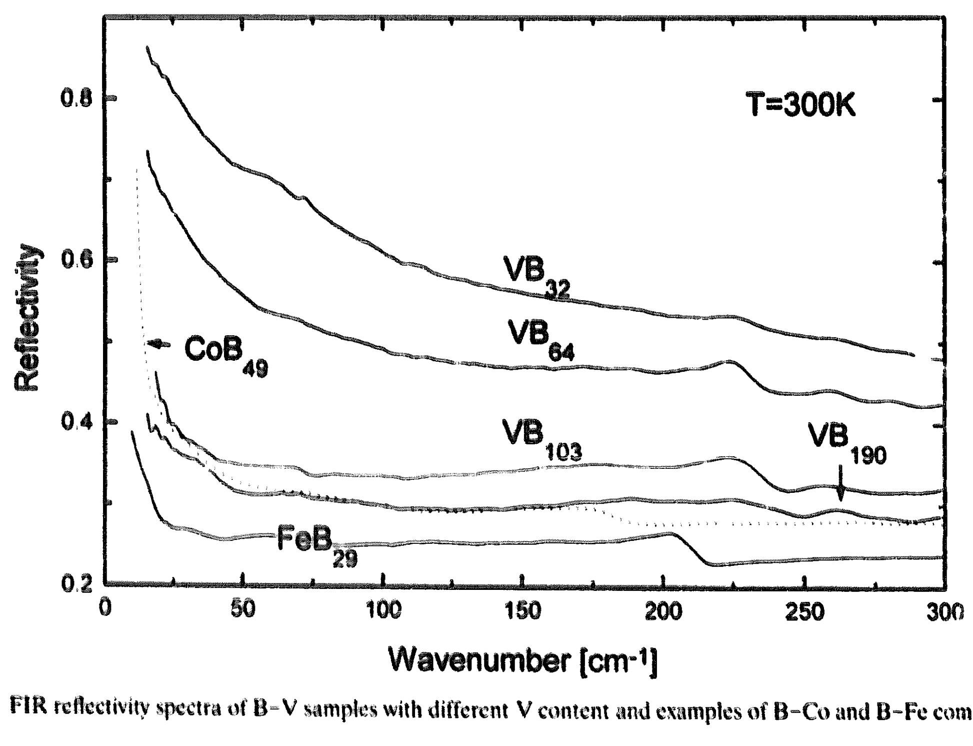

Fig. 10. FIR reflectivity spectra of B–V samples with different V content and examples of B–Co and B–Fe compounds.

els, which are close to the valence band (Fig. 9). The occupation densities increase with increasing metal content as expected.

3.4. Dynamical conductivity

Like in the case of most boron-rich solids, the FIR spectra of β-rhombohedral boron interstitially doped with V, Fe and Co show reflectivities which strongly increase towards lower frequencies (Fig. 10). The specific behaviour depends on the individual properties of the sample and are correlated with their DC conductivities as shown in Fig. 12. By analyzing the dielectric functions derived from the reflectivity spectra, it was shown that a satisfactory simulation of the experimentally obtained spectra is only possible when in general a superposition of Drude-type band conductivity and hopping conductivity is assumed [24]. Examples of such fits are shown in Fig. 11 (for details see reference [24]).

The fit to the Drude part of the dynamical conductivity yields the plasma frequency, whose squared value ω_p^2 is proportional to the free carrier density and the fit to the hopping part yields the parameter A, whose square root is proportional to the density of hopping states. The results are shown in Fig. 12. For the scattering frequency of the free carriers in B–V, $\omega_s = 5\ \mathrm{cm}^{-1}$ ($\cong 9.4 \times 10^{11}\ \mathrm{s}^{-1}$) was determined as the upper limit. This value is typical for semiconductors.

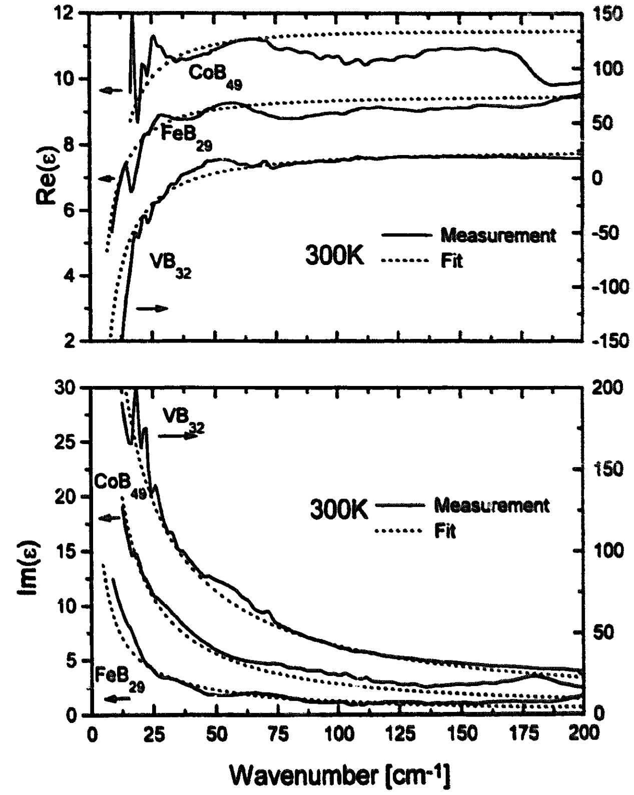

Fig. 11. Examples of the simulation of the FIR dielectric function of B–V, B–Fe and B–Co by assuming a superposition of Drude-type and hopping conduction. For details see reference [24].

4. Conclusion

Doping of β-rhombohedral boron to n-type by the interstitial accommodation of transition elements requires donor levels of sufficiently high densities between the uppermost intrinsic electron trapping level and the conduction band edge. Obviously it is necessary to transfer a sufficient number of electrons from the dopant to the boron framework to fill up the empty valence states and the intrinsic electron traps.

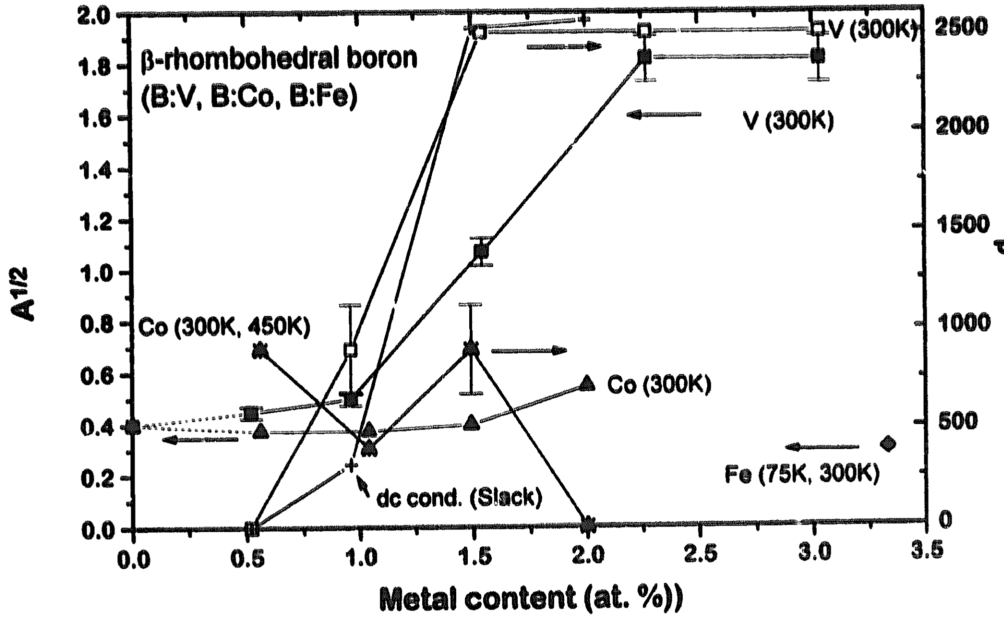

Fig. 12. Drude type carrier densities (ω_p^2) and hopping site densities ($\sqrt{A}$) in transition metal-doped β-rhombohedral boron, in the case of B–V compared with DC conductivity.

In principle this is the case for V and Fe atoms. In both cases optical absorption, electrical DC conductivity, dynamical conductivity and the Seebeck effect can be consistently described, when the generation of an impurity band closely below the conduction band is assumed. Hopping takes place within this partly occupied impurity band and band type electron transport is generated by the thermal activation of electrons from the impurity band into the conduction band. This situation is similar to the transport mechanism in p-type pure β-rhombohedral boron, where hopping takes place within the split-off valence band and band-type conduction by thermally activated holes in the lower valence band.

Indeed, this phenomenological description becomes unsatisfactory, if one looks on the details. While the number of the donor electrons of Fe atoms can be quantitatively correlated with the number of unoccupied valence and gap states in pure β-rhombohedral boron, this is not possible in the case of V atoms. The transition to n-type occurs already at such low V contents that an overcompensation of the intrinsic unoccupied valence and gap states of pure boron must be excluded. It seems that the interstitial accommodation of V atoms reduces the concentration of gap states considerably, however, not completely, because the optical absorption indicates the existence of levels at the trap positions in V doped material as well. Such effects of interstitial doping elements on the density of gap states could also be the reason for the uncommon behaviour of Li and Cu doped boron mentioned in the introduction.

Interstitial Co doping does not lead to n-type boron. In summary the results shown indicate that the donor level of Co is close to the valence band. Compared with V and Fe this is in qualitative agreement with the relative electron ionisation energies of the same interstitials in Si calculated by DeLeo et al. [18]. The free carrier densities and the densities of hopping states suggest that the Co donor by electrons coming from the increasing number of Co atoms. In consequence the density of hopping sites within the upper valence band decreases. However, when the density of Co atoms becomes sufficient to form an impurity band, it increases again. Contrarily, the density of mobile free carriers in the lower valence band decreases monotonically with increasing Co content, because their activation energy increases while the Fermi level moves from the upper valence band to the above lying Co level in the band gap.

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