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Non-ohmic electrical conductivity of β-rhombohedral boron in high electric fields

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Abstract

The low-field conductivity of β-rhombohedral boron follows Mott's law of variable-range hopping. Recent improvements in the energy band scheme attribute the hopping centers to specific, partly occupied states in the band gap, evoked by structural defects, in particular unoccupied B(13) sites. Band type conductivity is also possible, after valence electrons have been excited into unoccupied gap states. An experimental tool to gain an insight into the transport mechanism of semiconductors is the field-dependence of the electrical conductivity. For the interpretation of such experiments various theories are at disposal: the classical model of hot electrons, the Poole-Frenkel model, models of non-thermally activated hopping by Mott and Shklovskii, the Model of the field-dependence of small polarons mobility, the model of space-charge-limited currents. New measurements of the electrical conductivity in the temperature range 187–303 K at field strength up to 8 k V cm^{-1} are presented and discussed according to the above-mentioned theories together with a critical review of the previous measurements of other authors. Three ranges are to be distinguished. (i) Up to about 200 V cm^{-1}: ohmic behavior; (ii) between about 200 V cm^{-1} and about 20 kV cm^{-1}: non-ohmic behavior with a temperature-dependent field-dependence; (iii) above the "electrical breakdown" at about 20 kV cm^{-1}: non-ohmic behavior with $I{:}E^2$ independent of temperature.

Keywords: Boron; Electrical conductivity; High-field conductivity

1. Introduction

It is well known that the low-field electronic transport mechanism in β-rhombohedral boron follows Mott's law of variable-range hopping ($\sigma \propto (T/T_0)^{-1/4}$ (see Ref. [1] and references therein). Recent improvements in the energy band scheme attribute the hopping processes to partly occupied states in the band gap at about 0.18–0.3 eV above the valence band edge with occupation densities of about 75% in thermal equilibrium. These states are due to structural defects, in particular unoccupied B(13) sites [2,3]. For free holes in the valence band, the occupied gap states act as traps with high density. Depending for example on temperature, preceding optical excitation or conditions of measurement a superposition of hopping conductivity and band-type conductivity occurs or one of these transport mechanisms prevails.

An experimental tool to gain an insight into the transport mechanism of semiconductors is the field-dependence of their electrical conductivity. For the interpretation of such experiments various theories are at disposal:

(i) The classic model of hot electrons [4]. The average temperature of the charge carriers T_e is higher than the lattice temperature T_L because the carriers are accelerated by the high field while moving between their impact processes. The coefficient β in the field-dependence $\sigma = \sigma_0(1 + \beta E^2)$ yields information on the scattering mechanism of free carriers: assuming that the carrier concentration is independent of field strength, the sign of β is positive in the case of ionized impurities scattering, however, negative in the case of scattering by phonons or neutral defects.
(ii) The Poole-Frenkel model [5,6] assuming trapping centers with Coulomb potential partly screened by

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free carriers [5,6] (see also Refs. [7–9]). Because of the reduction of the potential energy of trapped carriers in the electric field, the concentration of carriers is expected to increase $\propto E^{1/2}$.

(iii) Specific models of non-thermally activated hopping of carriers after Mott [10,11] and Shklovskii [12]. A review of the different models is found in Ref. [13].

(iv) Model of the field-dependence of the mobility of small polarons [14].

(v) Model of space-charge-limited currents [15,16].

New measurements of the electrical conductivity in the temperature range 187–303 K at field strength up to $8\,\mathrm{kV\,cm^{-1}}$ are presented and discussed according to the above-mentioned theories and in context with a critical review of the previous measurements of high-field conductivity by Klein [17], Prudenziati et al. [15], and Berezin et al. [18,19].

2. Previous experimental results

Only few investigations of the field-dependence of the electrical conductivity in β-rhombohedral boron have become known. Klein [17] found a breakdown of the voltage at field strengths between 15 and $25\,\mathrm{kV\,cm^{-1}}$ indicating a rapidly increasing conductivity. Simultaneously the spin density, which he attributed to the carrier density, increased by not more than factor of 10.5. Therefore, Klein concluded that the carrier mobility, which he estimated to be $0.1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in the ohmic region, drastically increases during breakdown.

Prudenziati et al. [15] performed measurements up to field strengths of about $100\,\mathrm{kV\,cm^{-1}}$ and described the field-dependence with the space charge limited currents (SCLC) theories [20–23]. Accordingly, the ohmic region is characterized by negligible deviations from thermal equilibrium, and the Fermi level remains unchanged. Towards higher field strengths, in a p-type conductor with one hole trap of bond energy E_0 the current J can be described by the modified Child's law [20]

$$J = \frac{9\varepsilon\varepsilon_0 V^2 \mu_{0h}}{8W^3}\delta \quad \text{with} \quad \delta = (N_V/N_t)\exp(-E_0/kT). \quad (1)$$

The electric field is assumed to depend on position. The reason is that injected carriers completely fill the traps in a certain volume adjacent to the electrode. In this limited range the carrier transport is no more impeded by trapping processes, and the Fermi level is shifted into the band. With increasing applied voltage, the carrier injection increases as well, and the range with completely filled traps extends towards the opposite electrode. The location-dependent Fermi level is accordingly changed.

At sufficiently high voltages ($V > V_{TFL}$; TFL = traps filled limit)

$$V_{TFL} \cong \frac{2}{3}\frac{eW^2 N_t}{\varepsilon\varepsilon_0}.$$

The traps in the whole range between both electrodes are completely filled by injection and in the whole volume the Fermi level is within the band. Then the electric current is only limited by the space-charge of the injected carriers. This situation is described by "Child's law" with $\delta = 1$ in Eq. (1). Prudentiati et al. determined from their results the trap energy $E_0 = 0.23\,\mathrm{eV}$ and the trap density $N_t = 5 \times 10^{19}\,\mathrm{cm^{-3}}$.

Berezin et al. [18,24] performed their DC measurements up to field strengths of $60\,\mathrm{kV\,cm^{-1}}$. Depending on temperature, a qualitative change of the conductivity mechanism occurs between about 3 and $20\,\mathrm{kV\,cm^{-1}}$. In these results the authors assume that at temperatures below 300 K the resistance of their samples is sufficient to exclude Joule heating, which is problematic. Contrary, in the present work we found out that even in high-purity boron (purity 99.9999%, except C mit typically 30–80 ppm) already at 300 K and field strengths of about $1.5\,\mathrm{kV\,cm^{-1}}$ the samples are remarkably heated. A further problem in all previous measurements of this kind, performed in two-probe technique only, are possibly the probes. Klein and Prudentiati used evaporated gold probes. The symmetry of the probes mentioned by Prudentiati seems to indicate ohmic behavior. Berezin et al. used unspecified silver probes without any hint, whether ohmic behavior was tested or not. Berezin et al. [18] show that their results at 77 and 113 K for field strengths $> 10\,\mathrm{kV\,cm^{-1}}$ can be well described by the Poole-Frenkel law for scattering of carriers by centers with Coulomb-like potentials:

$$(\sigma/\sigma_0)^{1/2} lg(\sigma/\sigma_0) \propto E.$$

They estimate from their results the following transport parameters: carrier mobility at 77 and 113 K, respectively, 3×10^{-9} and $3 \times 10^{-8}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$; activation energy of the carrier mobility, 0.05–0.08 eV, $N_c/N_{tr} = 2-8$, $N_{tr} = 10^{17}-10^{18}\,\mathrm{cm^{-3}}$.

Assuming hopping conductivity that has been proved for β-rhombohedral boron, Berezin et al. evaluate their results obtained at 77 and 113 K also using the theories of Mott [10,11] and Shklovskii [12]. They assume that the charge transport in sufficiently high electric fields takes place in a series of consecutive hopping events combined with phonon emission only and without phonon absorption. For field strengths $> 10\,\mathrm{kV\,cm^{-1}}$ the experimental results follow both theories, namely

$$\sigma(E) \propto \exp[-(E_0/E)^{1/3}] \text{ (Mott)}$$

and

$$\sigma(E) \propto \exp[-(E_0/E)^{1/4}] \quad \text{(Shklovskii)}$$

satisfactorily. The derived transport parameters are the concentration of hopping states $N_h \approx (10^{22}-3\times 10^{23})\,cm^{-3}$ (Mott) and $N_h \approx (10^{21}-3\times 10^{22})\,cm^{-3}$ (Shklovskii), respectively, when in both cases the broadness of the hopping level is assumed as 0.04 eV. These concentrations correspond with that of the elementary cells in β-rhombohedral boron ($\sim 10^{22}\,cm^{-3}$).

Berezin et al. largely exclude the applicability of the classic polaron model for β-rhombohedral boron, because the parameters that are to be used for a satisfactory fit to the experimental results do not seem realistic.

In Fig. 1 the results obtained by Prudentiati et al. [15] and Berezin et al. [18] between 77 and 171 K are displayed. At least at high fields they agree satisfactorily. The range of "electrical breakdown" assumed by Klein [17] is marked as well. However, according to Lampert [20] in such cases the assumption of an electrical breakdown is usually incorrect, because only the transport mechanism changes. This is confirmed for β-rhombohedral as well. In particular, the results of Prudentiati show the change of the transport mechanism in this range indicated by the changed slope of the $I(E)$ results.

It is obvious that at lower field strengths the currents obtained by Berezin start at relatively higher levels than those reported by Prudentiati. This seems to indicate

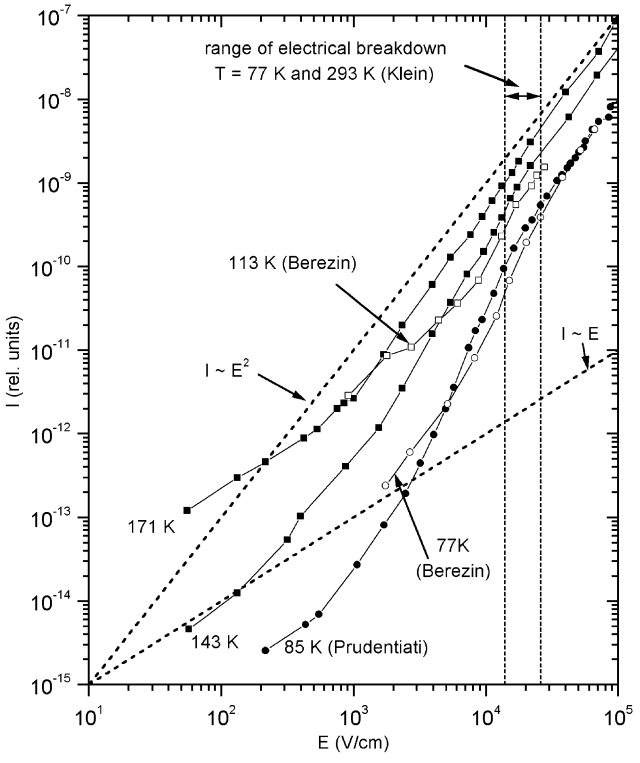

Fig. 1. Survey of the previous results on the electrical conduction of β-rhombohedral boron at high electric fields [Prudentiati, Berezin, Klein]. The slopes I–E and I–E^2 are marked.

that the samples of Berezin are less pure or not in thermal equilibrium and therefore contain frozen-in carriers.

Obviously, three ranges of different field-dependences are to be distinguished:

1. Below about 200 V cm^{-1}: Ohmic behavior.
2. Between about 200 V cm^{-1} and 20 kV cm^{-1}: Non-ohmic behavior with a field-dependence varying with temperature.
3. Above about 20 kV cm^{-1}: Unified non-ohmic behavior I:E^2 independent of temperature.

In the ohmic region the field-dependence of the conductivity allows conclusions on the transport mechanism only via temperature dependence (see above).

Based on the specific theoretical models, which were used by the authors to interpret their experimental results, the behavior at field strengths exceeding the "electrical breakdown" can be described in different ways:

The validity of "Child's law" could be explained by the assumption that the gap states become emptied by the injection of holes and therefore the charge transport takes place in the valence band. Then the electric current is limited by the space charge evoked by the injected holes, and the unoccupied gap states act as scattering centers of high concentration. This description agrees with the Poole-Frenkel model.

The model after Mott and Shklovskii presumes hopping even at these high field strengths, that means the charge transport takes place preferably within the gap states. This assumption seems to be supported by the spin density measured by Klein, which only insignificantly increases during the transition into "electrical breakdown". Hence the transport mechanism should be similar as well. Indeed, it cannot be excluded that like in low fields both transport mechanisms are superimposed. From the experiments none of the models can be excluded because the field-dependence is the same in both cases.

3. Sample and measuring equipment

A high-purity single crystal of β-rhombohedral boron provided by Wacker Chemistry, Munich, (purity 99.9999%, apart from C with typically 30–80 ppm) was used. The cylindrical sample (25 mm length, 5.08 mm diameter) was suitably etched [24] to avoid the influences of surface layers. For the four-probe measurements Pt wires of 0.1 mm thickness were attached as current probes to the end faces and as potential probes in 17.9 mm distance parallel to the cylinder axis. Accordingly, the probes were in sufficient distance to avoid mutual influencing. The ohmic behavior of such probes is well known from previous

experiments. Nevertheless, it was specifically proved for the used sample by the agreement of the conductivity obtained by two-probe and four-probe measurements. The deviation between the sample axis and crystallographic c-axis is about 12°. Therefore the measured results largely correspond to those parallel to the crystallographic c-axis.

A thermocouple, immediately attached to the sample, was used to control the temperature during the whole cycle. The sample was accommodated in the evacuated recipient of a closed-cycle helium refrigerator equipped with an additional electric heater. Drift voltages up to 12 kV were possible. Actually, DC measurements up to field strengths of 8 kV cm^{-1} were performed.

The long relaxation time of the conductivity in β-rhombohedral boron is well known. To guarantee reproducible conditions, the sample was kept in complete darkness for about 6 h at 60°C. Then, using the PID control of the refrigerator, the sample was cooled to the final temperature within about 2 h, where it was kept for at least 16 h, before the real measurement was started. Therefore thermal equilibrium can largely be assumed.

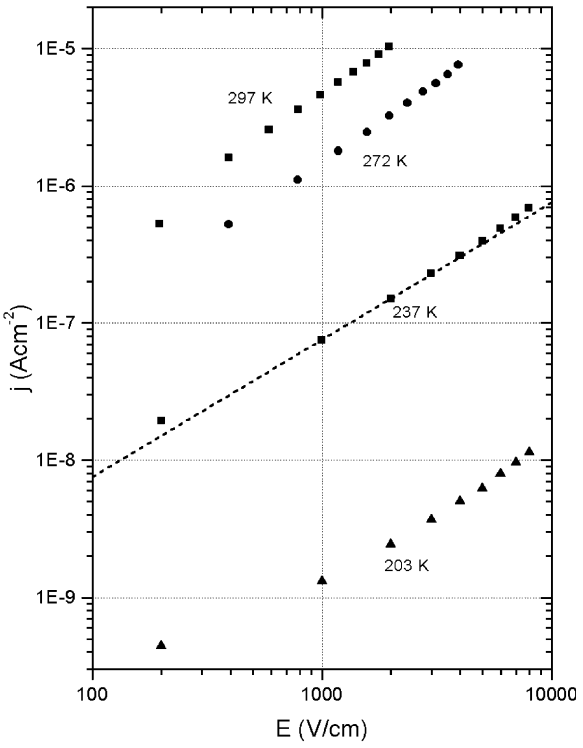

Fig. 2. Current density of β-rhombohedral boron vs. field strength for different temperatures.

4. Results

The new measurements confirm ohmic behavior up to field strengths of about 200–400 V cm^{-1} (Fig. 2) in agreement with the results of Prudentiati [15]. At higher fields there are deviations from the ohmic behavior varying as E^2 (example in Fig. 3). This behavior corresponds to the classical model and to Child's law as well. However, it must be considered that in a first approximation any weak deviation from Ohm's law can be described by a quadratic term. Therefore from the experimental results one cannot inevitably conclude that one of these theories is valid. Nevertheless, the assumption of scattering by charged defects is certainly compatible with the band scheme of β-rhombohedral boron. However, hopping is the prevailing transport mechanism in this temperature range, and this is not covered by the classical model. Anyway, the results definitely exclude the Poole-Frenkel-Modell ($j \sim E^{1/2}$).

Following the above-mentioned theory of space-charge-limited currents by Lampert [20], the transport mechanism in this temperature range is essentially determined by the situation that in the essential part of the current path between the electrodes ohmic behavior is expected and in a limited range close to the injecting electrode a behavior according to the "modified Chield's law". Therefore it seems admissible to separate in a first approximation this transport mechanism by subtracting the ohmic behavior after extrapolation from the low-field range. As already

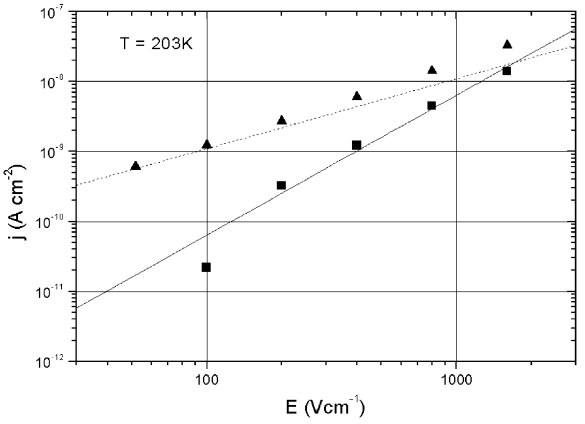

Fig. 3. Current density of β-rhombohedral boron vs. field strength at 203 K. Separation of linear (ohmic) and quadratic (non-ohmic) terms.

shown in Fig. 3 the theoretically expected dependence $\sim E^2$ is fulfilled.

For $E = 1000$ V cm^{-1}, Fig. 4 shows the non-ohmic share of the current density plotted vs. inversed temperature. According to the theory of space-charge-limited currents the temperature dependence can formally be described by an activation energy. However, the value of 0.37 eV obtained from Fig. 4 considerably exceeds the real distance of hole traps from the valence band of about 0.18–0.3 eV. The value of = 0.23 eV obtained by Prudentiati et al. [15] is not confirmed by the present results. Obviously, this theory is not suitable

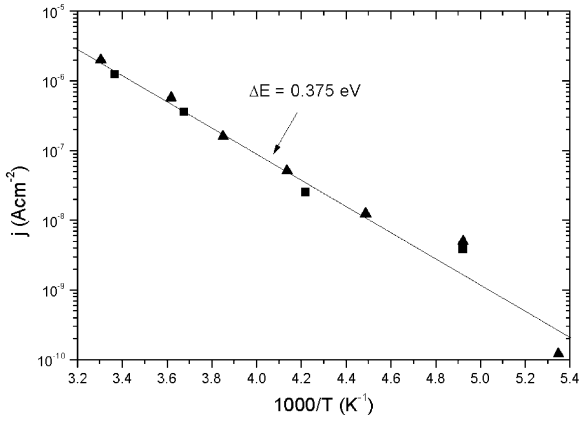

Fig. 4. Non-ohmic share of the current density plotted vs. reciprocal temperature. Electric field strength $E = 1000\,\mathrm{V\,cm^{-1}}$.

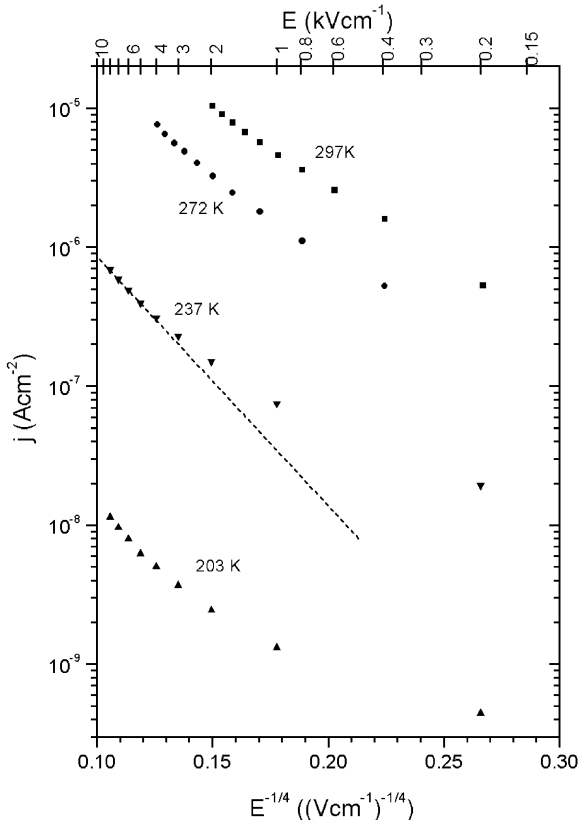

Fig. 5. Non-ohmic share of the current density at 203, 237, 272 and 297 K plotted vs. $E^{-1/4}$.

to describe the situation in β-rhombohedral boron quantitatively. The inset in Fig. 4 shows that the non-ohmic share is also compatible with Mott's law for variable-range hopping ($\sigma \sim \exp[(T_0/T)^{1/4}]$). For hopping the field-dependence $j \sim \exp(A/E^{1/4})$ is expected (see Ref. [13]). This relation has been confirmed in some papers on percolation as well. At higher fields, the present results satisfactorily agree with this law (Fig. 5). Other theoretical works based on percolation (see

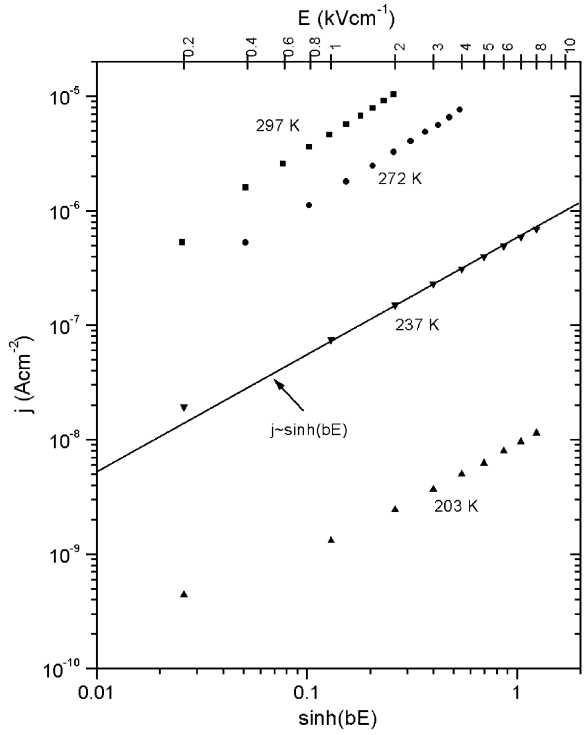

Fig. 6. Non-ohmic share of the current density at 203, 237, 272 and 297 K plotted vs. $\sinh(bE)$ with the empirically determined parameter $b = 1.3 \times 10^{-4}\,\mathrm{cm\,V^{-1}}$.

Ref. [13]) and papers assuming hopping processes were combined with phonon emission [25,26] or the transfer of excess energy to neighbouring centers [27,28], except for moderate electrical fields the relation $j \sim \sinh(bE)$. Using the empirical parameter $b = 1.3 \times 10^{-4}\,\mathrm{cm\,V^{-1}}$ the present results agree with this relation quite well (Fig. 6).

In conclusion, the present results confirm hopping as the prevailing transport mechanism in β-rhombohedral boron, and this up to field strengths of about $E = 8\,\mathrm{kV\,cm^{-1}}$. However, the fit of the experimental data to the available theories on the electronic transport in high electric fields is so good in all cases that it is not possible to decide as to which theory is the best compatible one for the complicated electronic structure of β-rhombohedral boron.

5. Conclusion

The low-field conductivity of β-rhombohedral boron follows Mott's law of variable-range hopping in partly occupied states in the band gap, evoked by structural defects, in particular unoccupied B(13) sites. Band type conductivity is also possible, after valence electrons have been excited into unoccupied gap states. Various theories were verified to describe the field-dependence of the electrical conductivity measured in the present

work combined with a critical review of the results obtained by other authors. Three ranges can be distinguished. (i) Up to about $200\,V\,cm^{-1}$: ohmic behavior; (ii) between about $200\,V\,cm^{-1}$ and about $20\,kV\,cm^{-1}$: non-ohmic behavior with a temperature-dependent field-dependence; (iii) above the "electrical breakdown" at about $20\,kV\,cm^{-1}$: non-ohmic behavior with $I{:}E^2$ independent of temperature.

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