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Photoluminescence and Steady-State Interband Photoconductivity of High-Purity β-Rhombohedral Boron

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Photoluminescence and interband photoconductivity of high-purity β-rhombohedral boron were measured at different temperatures up to steady-state conditions. To consistently describe the results in relation to one another and with respect to previous results, the energy band scheme was improved. An essential improvement is the replacement of the previously called "upper valence band" by two closely neighbored levels S1 and S2 with localized states. According to the proved correlation between structural defects and electronic properties they are attributed to vacancies in the structure, probably preferably in B(13) sites. The photoluminescence yields the energy positions of the unoccupied gap states, and those are the prerequisites for the interpretation of nonradiating cascade-like recombination of electrons via the series of intrinsic trapping levels. Depending on temperature this recombination path is in competition with the radiating recombination related to the transition of electrons into the defect levels near the valence band edge. The luminescence intensity decreases with increasing time and only partly recovers even in long dark periods. © 2000 Academic Press

INTRODUCTION

The hitherto used energy band schema of β-rhombohedral boron is characterized by an indirect band gap of about 1.5 eV, a split-off upper valence band of 0.19 eV distance and six electron trapping levels off the conduction band edge, whose ionization energies are multiples of 0.19 eV. It was proposed by Werheit *et al.* (1, 2) and makes it possible to interpret optical absorption, photoabsorption, photoconductivity, electrical conductivity, and numerous other experimental results largely consistently. Recent results (3) led to the conclusion that the valence band level previously interpreted as split-off is in reality due to acceptor-like defect states in the band gap. This new interpretation solved a remaining inconsistency with respect to this level: Its interpretation by indirect interband transitions required the assumption of extended states, while the transport properties required the assumption of localized states. It will be shown below in some detail that a reinterpretation of the previously assumed indirect-allowed interband transitions by nondirect transitions is possible without problems because their energy and temperature dependencies well agree with the experimental results.

However, irrespective of the kind of states, all the experimental results mentioned are based on occupied levels only, and because of the well-known strong electron–phonon interaction a considerable difference between the energy positions of unoccupied and occupied levels must be expected. In particular because of the numerous electronic levels in the band gap, optical and thermal transitions between the occupied and unoccupied states cannot be excluded, and hence for the final understanding of the electronic processes a detailed knowledge of the unoccupied states and their energy relaxation after occupation is required.

A suitable experimental method for determining unoccupied electronic states is photoluminescence. Unfortunately this effect on β-rhombohedral boron is very small, and therefore only few experimental results have become available (4, 5), and those have not yet been satisfactorily explained within the band scheme. Below, new measurements of photoluminescence are presented and discussed in correlation with the likewise measured time-dependent interband photoconductivity.

EXPERIMENTAL

The measurements were performed on high-purity boron (Wacker, claimed purity 99.9999% except carbon, which is typically 60 ppm).

Photoluminescence was measured with the modified Raman unit of a Fourier transform spectrometer IFS 113v (Bruker, Karlsruhe) using a low-noise liquid nitrogen-cooled Ge detector. The interband excitation was generated by a GaAs laser diode ($\hbar\omega = 1.52$ eV, 0.25 W); a monitor diode controlled the optical power during the measurement.

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The time-dependent photoconductivity was measured on a 90-μm-thick sample using a two-probe method. As contacts, platinum wires were attached by a capacitor discharge, which guarantees ohmic contacts. Using a 22-V battery the current was determined by an electrometer (Keithley) and recorded with a computer.

RESULTS

Photoluminescence (spectrum at 90 K in Fig. 1) was measurable below ~180 K only (Fig. 2). Within the experimental error the spectral distribution is independent of temperature. The intensity decreases with increasing time, for example, at 90 K to about 50% after 30 min. (Fig. 3). After the excitation is stopped, the photoluminescence only partly recovers; for example, at 90 K after a dark period of about 3 min. the intensity has reincreased by 60% only, and no further recovery was observed, even after long dark periods.

Excitation with photon energies $\lesssim 1.2$ eV (lower than gap energy) has no effect on the recovery. However, when the temperature is raised during the dark period, the luminescence reincreases with an amount that depends on the temperature (Fig. 4). This thermally induced recovery is maximum at about 200 K. A second increase at temperatures $\gtrsim 300$ K is obviously due to the thermal interband excitation.

At low temperatures the inset of the photoconductivity is considerably delayed, after the interband excitation has been started (Figs. 3 and 5a). The time dependence of the photoluminescence and of the photoconductivity are complementary to one another (for 90 K, as an example, see Fig. 5b), indicating that both processes are closely related to one another.

In the whole investigated temperature range the steady-state photoconductivity is thermally activated (Fig. 6); below 250 K the activation energy is about 17 meV and above 250 K about 200 meV.

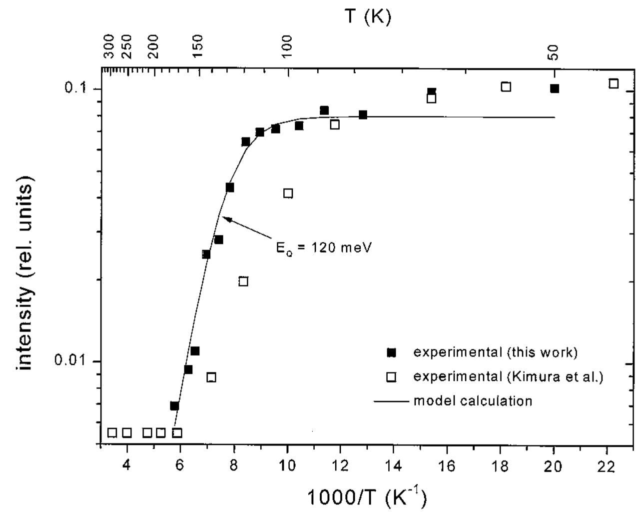


FIG. 2. Photoluminescence intensity (closed squares) vs reciprocal temperature compared with a model calculation based on the Franck–Condon model (solid line). Experimental results of Kimura *et al.* (4) (open squares) are provided for comparison.

INTERPRETATION AND DISCUSSION

(a) Photoluminescence

The spectral distribution of the photoluminescence can be well described by the superposition of three emission bands of Gaussian type (see Fig. 1). Two of them agree quite well with those reported in (5). This spectral distribution indicates that localized states with strong electron–phonon interactions are involved in the luminescence process. Since specific theoretical models are missing, the Franck–Condon model (6, 7) is used for the description. According to this

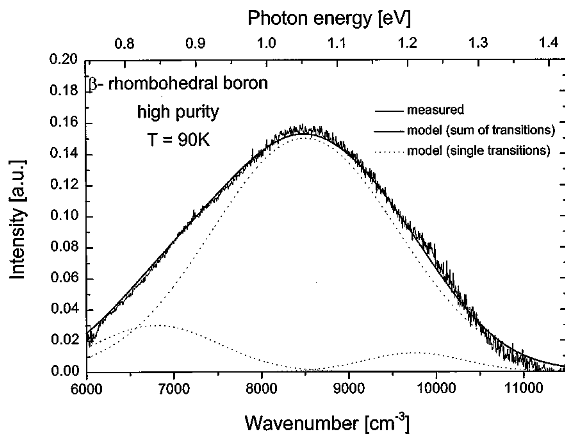


FIG. 1. Photoluminescence spectrum of pure β-rhombohedral boron at 90 K and decomposition into three separate Gaussian distributions.

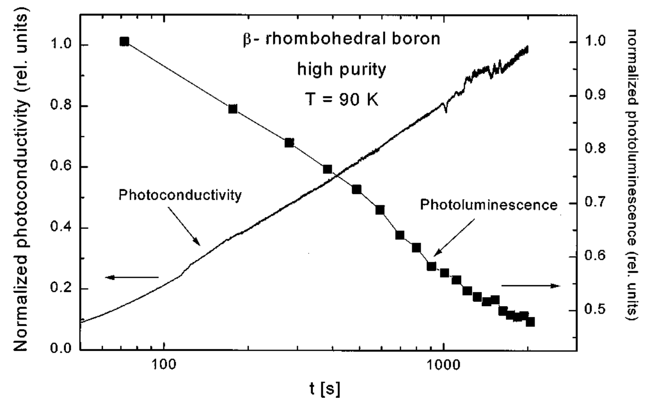


FIG. 3. Photoluminescence intensity and photoconductance of high-purity β-rhombohedral boron at 90 K vs time after the beginning of the optical interband excitation (1.5 eV).

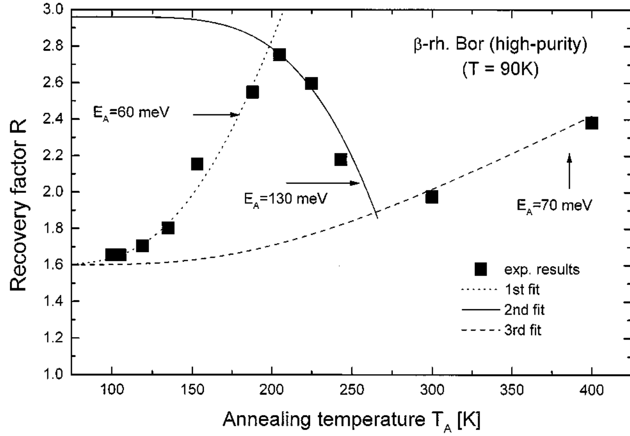


FIG. 4. Recovery of the photoluminescence at 90 K by annealing. After the steady-state condition of reduced luminescence was reached, the sample was heated (heating rate 7 K/min) to the annealing temperature T_A, kept at T_A for exactly 15 min., and then recooled to 90 K (cooling rate 30 K/min.). The recovery factor R is the relation between the luminescence intensities after and before this annealing process. If the temperature dependence of R is attributed to the thermal excitation of electrons into a higher level or to surmounting a potential barrier, the thermal activation energy can be estimated from the slope. The corresponding to fits for the different temperature ranges are indicated by the solid, broken, and dotted lines. Indeed, these fits are somewhat problematic, since because of the different times of heating and cooling, the annealing process is not exactly comparable for the different annealing temperatures.

model, the efficiency of the luminescence η (ratio of radiating transitions P_L to total transitions P_T) is

$$\eta = P_L/(P_L + P_T) = 1/[1 + (P_0/P_L)\exp(-E_Q/k_BT)], \quad [1]$$

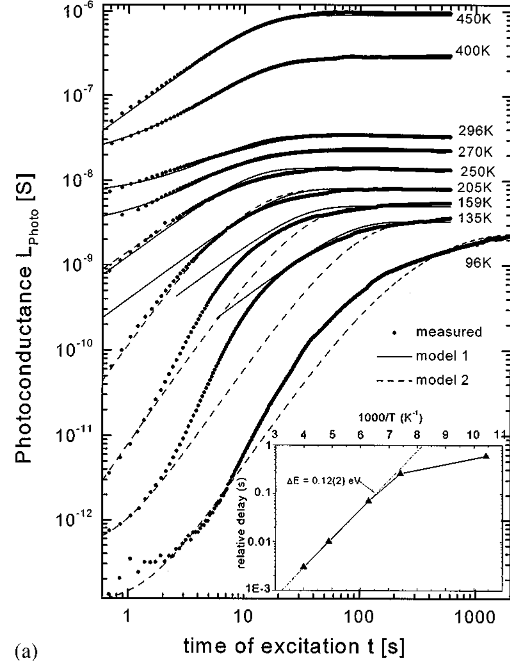
where P_T describes the thermally activated nonradiating transitions

$$P_T = P_0 \exp(-E_Q/k_BT) \quad [2]$$

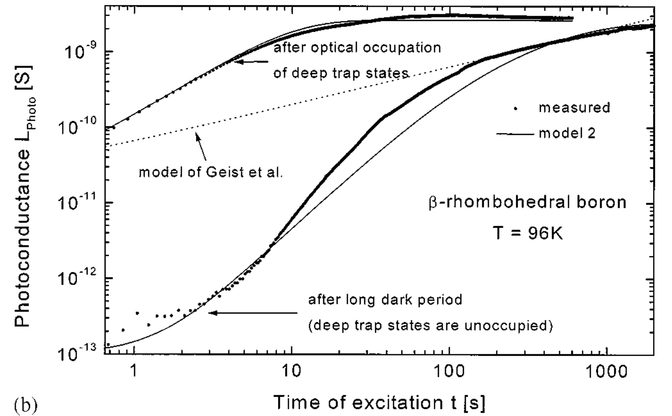
with the activation energy E_Q. In Fig. 2 it is shown that Eq. [1] quite well describes the observed temperature dependence of the photoluminescence, when for the nonradiating transitions a thermal activation energy $E_Q = 120$ meV is assumed.

That the recombination of free electrons with free holes is below the detection limit can be easily explained in accordance with the band scheme: The lifetime of free carriers is drastically reduced by electron traps and by occupied gap states near the valence band acting as hole traps respectively, both with very large capture cross sections. The observed luminescence must be attributed to the radiating transitions of electrons from the conduction band edge into empty localized gap states. These transitions are quantum mechanically allowed as is well known from absorption, photoabsorption, and photoconductivity investigations (1, 2, 8). However, it must be taken into account that the energies of the empty states, which are relevant for the luminescence, are different from those of the occupied states because of the relaxation after occupation, in consequence of the strong electron–phonon interaction.

Accordingly, we attribute the energetically highest emission process ($\sim$1.2 eV) to the absorption process at 1.37/1.34 eV ($E//c$ and $E\perp c$, respectively) (1, 2). The strong



(a)



(b)

FIG. 5. Photoconductance of high-purity β-rhombohedral boron after the beginning of the optical interband excitation (1.5 eV). (a) Results for different temperatures: symbols, experimental data; solid lines, model 1 calculation; broken lines, model 2 calculation (see text). (Inset) Relative delay times vs reciprocal temperature. The relative delay times were estimated by the extrapolation of the experimental data in the quasi-linear range in the double-logarithmic presentation on the time axis at 10^{-14} s. (b) Results for 96 K for different antecedents of the sample. Symbols, experimental data obtained after the sample had been in complete darkness for more than 12 h and after strong optical preexcitation; solid lines, model 2 calculations; broken line, model calculation according to Geist (5).

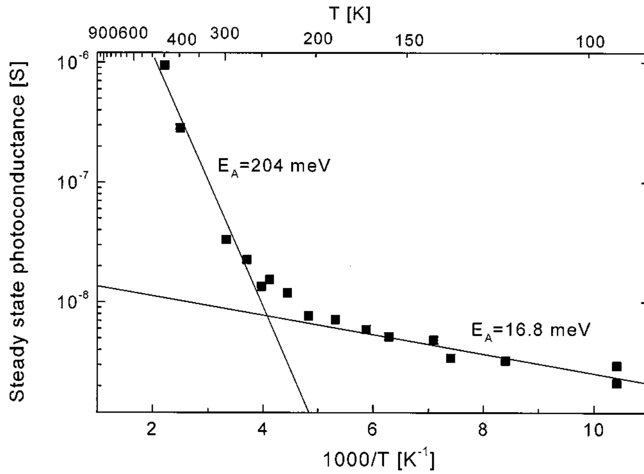


FIG. 6. Steady-state photoconductance vs reciprocal temperature.

absorption, even at low temperatures, indicates a highly occupied state. Accordingly, the radiating transition into this state is rather improbable. In contrast, the strong luminescence transition at about 1.05 eV is related to the weak absorption at 1.27/1.23 eV. Accordingly, the related states are assumed to be empty at low temperatures and to become occupied toward higher temperatures by thermally excited electrons.

According to their energy and temperature dependencies, those absorption processes were attributed to indirect band transitions with phonon emission and phonon absorption, respectively (1, 2), requiring the assumption of extended states in some contrast to the hopping transport, indicating a localized character of these states (9). The measured luminescence strongly supports the assumption of localized states, which no k-selection rules hold for. Accordingly they should be interpreted as non-direct transitions like those known from amorphous semiconductors (10). This is no contradiction to the optical absorption because nondirect and indirect optical transitions exhibit the same energy dependence and a very similar variation with temperature (11). Therefore, in consistency with luminescence and transport properties, we conclude that the optical transition energies at 1.37/1.34 eV and 1.27/1.23 eV, respectively, are nondirect transitions from two different localized states in the band gap.

The remaining luminescence transition at about 0.816 eV is attributed to the radiating transitions of electrons into a deep electron trapping level (trap 6) that moves to 1.15 eV after occupation and is known accordingly from absorption measurements.

Based on these considerations, the band scheme of β-rhombohedral boron must be revised with respect to the level above the valence band edge and completed with respect to the levels of the unoccupied electron traps (Fig. 7). Unfortunately, luminescence by electron transitions into the upper electron traps was not measured because these energies were outside the accessible range of the used spectrometer. However, Werheit *et al.* (1, 12). suggested a uniform formation mechanism for all six trapping levels that explains their nearly equidistant energies. Then the relaxation of these traps should be similar as well, and accordingly, the relaxation derived above from experiment for trap 6 was assumed to hold for the other traps (1–5) too.

The completed band scheme makes it possible to understand the mechanism of several experimental results: (i) The levels of the unoccupied traps 1 and 2 are in the conduction band. Therefore, as known from numerous experiments, the occupation of these traps requires the excitation of electrons into the conduction band. (ii) The energy difference between occupied trap n and unoccupied trap $n+1$ is about 130...140 meV. If this barrier is surmounted by thermal excitation, a cascade-like transition of trapped electrons into the valence band becomes possible. This easily explains the thermal activation energy 0.12 eV of the nonradiating transitions in Fig. 2 ($T \sim 125$–180 K), and of the temperature-dependent decrease of the 12-Hz-modulated photoconductivity based on trapped electrons (0.11 eV for $T \sim 160$–210 K) (8). (iii) The rather high relaxation energy of the traps makes hopping between occupied and unoccupied traps improbable in agreement with the experimental findings.

(b) Photoconductivity

The different activation energies of the steady-state photoconductivity (Fig. 6) indicate different transport mechanisms in different ranges of temperature. However, the prevailing p-type character is well known from the sign of the Seebeck coefficient (see (13)).

To analyze the observed photoconductivity at higher temperatures, a simplified energy band scheme was used (Fig. 8). Only two states are assumed in the band gap, an

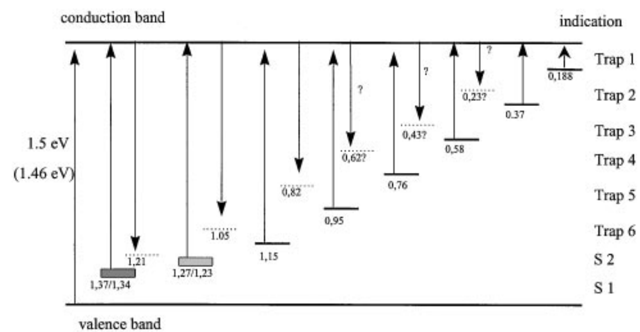


FIG. 7. Improved energy band scheme of pure β-rhombohedral boron. Arrows, allowed optical transitions; question marks indicate assumed transtions that have not yet been experimentally confirmed because they were outside the accessible spectral range of the spectrometer used.

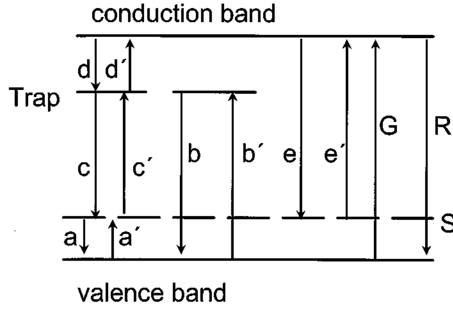


FIG. 8. Simplified energy band scheme of β-rhombohedral boron used for the model 1 calculations. The allowed transitions assumed for the model are indicated by arrows.

electron trapping level near the conduction band edge and a level S near the valence band edge, both in quasi-thermal equilibrium with the adjacent energy bands. Since the concentrations of electrons in the conduction band and the holes in the valence band are low compared to the concentration of occupied traps N^-_{Trap} and unoccupied S states N^+_{S}, the neutrality condition is approximately $N^-_{\mathrm{Trap}} = N^+_{\mathrm{S}}$. Then the time-dependent hole concentration in the valence band $p(t)$ can be calculated for different recombination paths. Independently, the recombination path holds

$$p(t) = p_{\max} \cdot \frac{\exp((t - t_0)/\tau) - 1}{\exp((t - t_0)/\tau) + 1} \qquad [3]$$

(for details see (14)). $p_{\max}$ is the steady-state hole concentration, τ the relaxation time, and t_0 the start time.

The temperature dependencies of $p_{\max}$ and τ depend on the dominating recombination path:

(a) direct recombination between the valence and conduction bands:

$$p_{\max} \propto \exp(\,-[(E_{\mathrm{S}} - E_{\mathrm{V}}) - (E_{\mathrm{C}} - E_{\mathrm{Trap}})]/2k_{\mathrm{B}}T)$$

$$1/\tau \propto \exp(-[(E_{\mathrm{C}} - E_{\mathrm{Trap}}) - (E_{\mathrm{S}} - E_{\mathrm{V}})]/2k_{\mathrm{B}}T);$$

(b) recombination via the trapping level:

$$p_{\max} \propto \exp(-(E_{\mathrm{S}} - E_{\mathrm{V}})/2k_{\mathrm{B}}T)$$

$$1/\tau \propto \exp((E_{\mathrm{S}} - E_{\mathrm{V}})/2k_{\mathrm{B}}T);$$

(c) recombination between state S and the conduction band:

$$p_{\max} \propto \exp([(E_{\mathrm{C}} - E_{\mathrm{Trap}})/2k_{\mathrm{B}}T] - [(E_{\mathrm{S}} - E_{\mathrm{V}})/k_{\mathrm{B}}T)]$$

$$1/\tau \propto \exp(-(E_{\mathrm{C}} - E_{\mathrm{Trap}})/2k_{\mathrm{B}}T);$$

(d) recombination between the valence and conduction bands via the trap and state S:

$$p_{\max} \propto \exp(-(E_{\mathrm{S}} - E_{\mathrm{V}})/k_{\mathrm{B}}T)$$

$$1/\tau = \text{const.}$$

From optical investigations the energy differences $E_{\mathrm{S}} - E_{\mathrm{V}}$ and $E_{\mathrm{C}} - E_{\mathrm{Trap}}$ are known to be about 200 meV. The steady-state photoconductivity (correlated to $p_{\max}$) is thermally activated with an energy of about 200 meV (Fig. 6). Such an activation energy is compatible with case (d) only. The estimated relaxation time τ has only a small activation energy (on the order of about 16 meV). The nearly temperature-independent relaxation time and the activation energy for the steady-state photoconductivity of about 200 meV both make the recombination path (d) the most probable one.

For β-rhombohedral boron with several gap states of the types assumed (see Fig. 7) this means that a cascade-like recombination over all states in the gap is the most probable. The lacking photoluminescence in this temperature range confirms that this recombination is nonradiating. Indeed, Eq. [3] with $p_{\max}$ according to model (d) satisfactorily describes the measured photoconductivity down to about 250 K (model 1 in Fig. 5a). Obviously, for lower temperatures this model is not suitable.

Below about 250 K the photoconductivity mechanism is different, and luminescence by radiating transitions becomes appreciable. Characteristic of the steady-state photoconductivity in this temperature range is the delay between optical excitation and inset of photoconductivity (Fig. 5). Accordingly, at least in the beginning, the charge carriers are not immediately but indirectly generated. A secondary process is presupposed that is thermally activated with an activation energy of 0.12 eV (see inset in Fig. 5). This value agrees with the assumed activation energy of the cascade-like recombination used to explain the photoluminescence, and it suggests that the temperature-dependent shift of the inset of the S-state-related photoconductivity is caused by this cascade-like recombination of electrons optically excited into the conduction band

The diffusion of carriers from the illuminated surface into the bulk can be largely excluded as the reason for this delay. In the 90-μm-thick sample (α(1.5 eV) $\sim$ 40 cm^{-1}) the excitation in the center is only 30% lower than that at the illuminated surface. Thus diffusion seems not to be significant.

In principle, in this range of temperature the following charge transport mechanisms possibly contribute to the steady-state photoconductivity. It must be acknowledged that photon energies that are sufficient to generate electron-hole pairs are also able to ionize gap states:

(i) Electron-hole pairs are generated by interband excitation. Because of the high densities of traps, the lifetime of the free carriers is assumed to be very small.

(ii) Excitation of trapped electrons into the conduction band. The existence of this effect with small relaxation time is proved by modulated photoconductivity (8). Because of the comparably small combined density of states we assume this contribution to be small compared with the interband transitions. Thermal excitations of trapped electrons into the conduction band can be largely excluded at those temperatures because of the value of the ionization energies of the traps.

(iii) States S1 and S2 are only partly occupied, and therefore a transport between them seems possible. Based on the energy band scheme in Fig. 7, this contribution to the photoconductivity can be described as follows: The absorbed light generates holes in the valence band and the fully occupied S1 state, respectively, and electrons in the conduction band. According to the luminescence results a certain portion of the free electrons recombines into the S states by radiating transitions. The remaining carriers in the conduction band and those in the valence are rapidly trapped and hardly contribute to the photoconductivity. Unoccupied and occupied S1 states are separated by about 150 meV due to the strong electron–phonon relaxation, and this makes hopping between them rather improbable. However, depending on temperature, via radiative transitions from the conduction band or via the cascade-like recombination, electrons occupy previously unoccupied S2 states. After relaxation these are expected to be about 20–60 meV below the unoccupied S1 states, and then hopping between occupied S2 and unoccupied S1 states becomes possible. We attribute the observed thermal activation energy of the steady-state photoconductivity at low temperatures of about 20 meV to the energy distance between occupied S2 and empty S1 states. This model makes it possible to explain the decreasing photoluminescence after initiation: According to the measured energy of the luminescence the main intensity comes from transitions between the conduction band and the initially empty S2 states, which become occupied with increasing time as described. Accordingly, the transition probability for radiating recombination decreases.

Because of the obviously considerable delay of the photoconductivity in S1/S2 in consequence of the indirect occupation of the S2 level, this transport was not detected by the modulated photoconductivity in (8), because the conductivity difference between dark and light chopping period (0.083 s at 12 Hz) is too small.

To test how far this model is able to describe the experimental results, a simplified mathematical description is used that is based on the simplified energy band scheme in Fig. 9. The rate equation for the electron density in state S2 is

$$dn_{S2}/dt = e(t) - C_f p_{S1} n_{S2}. \quad [4]$$

The generation rate $e(t)$ is proportional to the electron concentration in the conduction band. Their time depend-

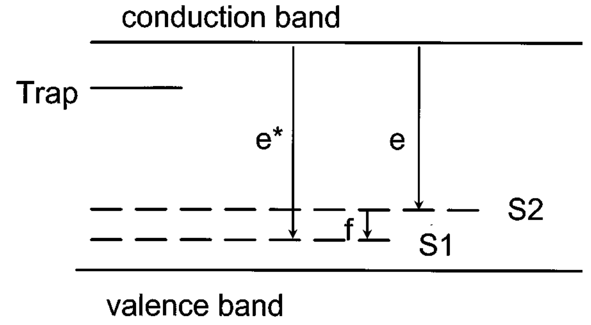


FIG. 9. Simplified energy band scheme of β-rhombohedral boron used for the model 2 calculations. The allowed transitions assumed for the model are indicated by arrows.

ence can be described in analogy to Eq. [1], but to simplify the problem as much as possible, $e(t)$ is assumed to vary as

$$e(t) \approx A(1 - \exp[-(t - t_0)/\tau]). \quad [5]$$

As a second strongly simplifying assumption the hole concentration in level S1 (p_{S1}) in Eq. [4] is set constant. This seems to be justified by the fact that the increase of n_{S2} is strongly delayed, such that the relative change of p_{S1} becomes low.

With this assumption Eq. [2] has the solution

$$n_{S2}(t) = a_0(1 - [\tau/(\tau - \tau_{S2})]\exp(-(t - t_0/\tau))) + b_0\exp(-t/\tau_{S2}) \quad [6]$$

with the parameters

$$a_0 = A\tau_{S2},$$
$$b_0 = n_0 - a_0[1 - [\tau/(\tau - \tau_{S2})]\exp(t_0/\tau)] \quad [7]$$
$$1/\tau_{S2} = C_f p_{S1}.$$

Simplified model 2 satisfactorily fits to experimental results below 250 K (Fig. 5a). Only in the middle range, in particular at low temperatures, is the calculated increase too slow. The reason may be that the influence of the different traps on the electron concentration in the conduction band is insufficiently covered by only one mean time-independent relaxation time τ in Eq. [6] because the deeper traps are not in a quasi-thermal equilibrium with the conduction band. However, their influence can be largely excluded when most of them are filled by a strong optical preexcitation. This was experimentally checked. As shown in Fig. 5b, if via this method the delaying influence of the unoccupied deep traps on the recombination of further electrons is strongly reduced, model 2 describes the time dependence quite well.

Geist (15) proposed for the photoconductivity at low temperatures a hopping-like transport of localized charge carriers near the valence band. However, he neglected the strong relaxation of the localized states separating occupied and unoccupied states. As is shown in Fig. 5b, his model yielding the time dependence

$$\sigma_{\text{Photo}} \propto \sqrt{1 + at} \qquad [8]$$

is not able to describe the observed strong delay of the photoconductivity.

SUMMARY

Photoluminescence and steady-state photoconductivity are consistently described within the improved energy band scheme of β-rhombohedral boron. An essential improvement is the new attribution of the previously called "upper valence band" to localized states in two neighbored levels S1 and S2, which according to results in (3) are attributed to vacancies in the structure, probably of the B(13) sites. The photoluminescence yields the energy positions of the unoccupied gap states, and those are the prerequisites for the interpretation of the nonradiating cascade-like recombination via a series of intrinsic trapping levels. Depending on temperature this recombination path works in competition with the radiating recombination related to the transition of electrons from the conduction band into the S_1 and S_2 states.

Simplified models 1 and 2 are not suitable to satisfactorily describe the recovery of the photoluminescence (Fig. 4). Model 1 is designed for high temperatures only, where the splitting into S1 and S2 can be neglected and a quasi-thermal equilibrium between S and the neighbored band edge can be assumed. Therefore a nonequilibrium state, that is required for a time-dependent decrease, and recovery of the photoluminescence is outside the scope of this model.

Indeed, model 2 for low temperatures does not contain this restriction, and a transition probability C_f in Eq. [4], which depends on time and temperature, would make it possible to describe such processes. However, the real conditions are expected to be much more complicated: It must be considered that a reoccupation of S2 by electrons thermally released from traps or excited from the valence band reduces the recovery process. The related transition probabilities, which are required to quantitatively describe the complete process, are not known at present. Moreover, a temperature-dependent structural relaxation possibly additionally complicates the process. Such a relaxation is indicated by internal friction maxima at 150 K in pure (16) and at 100–150 K and 200–250 K in metal-doped β-rhombohedral boron (17). Their correlation with optically induced electronic transitions (18, 19) is obvious, but has not yet been cleared up in detail. It cannot be excluded that the thermal recovery process of the photoluminescence with maximum at about 210 K in Fig. 4 is correlated with this structural relaxation. However, the activation energy of 130 meV (see Fig. 4) agrees with the determined activation energy of the cascade-like electronic process assumed above. Therefore, additional specific investigations are required to elucidate the recovery process of the photoluminescence.

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