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On the diffusion of free carriers in β-rhombohedral boron

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Abstract

To determine the diffusion of untrapped carriers in β-rhombohedral boron, we constructed a feedback pico-ammeter based on pulse integration technique. This enabled measuring deviations from the bias in a $10^9\,\Omega$ sample in the order of 1 nA with 0.7 ms time resolution. For the first time, we obtained the drift velocity of optically generated untrapped electron–hole pairs $106(20)\,cm\,s^{-1}$ yielding for the band-determined diffusion coefficient $D = 12(4)\,cm^2\,s^{-1}$ and for the carrier mobility $\mu_{ambipolar} = 565(120)\,cm^2\,V^{-1}\,s^{-1}$. Fitting Fick's second law to the measured trap-determined dispersion of carriers yields the ambipolar diffusion coefficient $D^* = 0.043(14)$ and $0.28(10)\,cm^2\,s^{-1}$ at 260 and 340 K, respectively. The thermal activation energy of 0.18 eV agrees with the well-known trapping levels in β-rhombohedral boron.
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Keywords: Boron; β-rhombohedral; Charge transport; Ambipolar diffusion; Carrier mobility

1. Introduction

Completing the idealized structure formula of β-rhombohedral boron ($(B_{12})_4(B_{28})_2B$ or $B_{84}(B_{10})_2B$) (see Ref. [1]) there are several additional atomic sites (B(16)–B(20)) with considerably reduced occupation densities leading to about 106.5 atoms per unit cell in total. The actual electronic band scheme [2–4] shows a gap of about 1.5 eV and numerous high-density gap states, which are at least partly correlated with structural defects [5]. The band gap is essentially determined by the Jahn–Teller splitting of the orbitals of the B_{12} icosahedron [6]. Charge transport by electrons and holes is usually determined by a superposition of band conduction and hopping processes. Depending on the actual conditions, one of these mechanisms can prevail. However, because of the extremely high trapping probability of electrons and holes the separation of band-type, that means untrapped free carriers failed till now. For example, in previously performed photoconductance (see Ref. [1] and references therein) [3,4,7] and drift experiments [8–11] the sensitivity was not sufficient to detect the very small contribution of untrapped free carriers. Object of the present work was a sufficiently sensitive equipment to close this gap.

2. Sample material and experimental setup

A prismatic sample ($1.6 \times 1.6 \times 10.5$ mm) was cut from a high-purity β-rhombohedral boron single crystal (Wacker, Munich; claimed purity 99.9999% except carbon (typically 60 ppm)) roughly parallel to the crystallographic c axis and immediately neighbored to the sample investigated in Ref. [11] and prepared according to [12]. On opposite places of the side faces of the prismatic sample, pairs of thin platinum wires (0.1 mm) were fixed by capacitor discharge as ohmic contacts.

After switching on, the radiation of a laser diode (Sharp LTO15MDO, $\lambda = 827$ nm, 30 mW) generated a time-independent concentration of electron–hole pairs at one end face of the prismatic sample within the penetration depth of 0.25 mm. The concentration gradient causes the ambipolar drift of electron–hole pairs thus increasing the local and time-dependent conductivity in the sample. As the optical excitation changed the dark current by less than 1%, the deviation from thermal equilibrium is negligible. The time-dependent conductivity was tapped at the ohmic probes mounted in different distances from the illuminated

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surface. A self-constructed feedback ammeter based on pulse integration measurements with the IC's INA116, IVC102 and OPA27 (Burr–Brown) and a digital storage oscilloscope (Tektronix 2430) as essential components allowed measuring photocurrents in the order of 10^{-9} A in a $10^{9}\,\Omega$ sample, with a time resolution of 0.7 ms. The principle of the method is as follows: After the equipment is initially triggered by the onset of the optical excitation, a capacitor is charged by an electric current passing the sample, whose conductance determines the charging process. In periods of 0.7 ms the capacitor is shortcut, and the charging process restarts. These cycles are stored in the oscilloscope, whose data are continuously transferred into a PC memory for evaluation. The sample temperature was controlled by a closed-cycle He cryostat and measured with a thermocouple fixed close to the sample. The basic circuit diagram (Fig. 1) allowed adjusting the bias before optical excitation. In the optimal setting, the arriving front of untrapped carriers changed the sign of the charging current of the capacitor (see Fig. 2).

The high density of traps and extremely long relaxation times of trapped carriers in β-rhombohedral boron ($\tau_{relax} \geqslant 2.5$ h at room temperature; see Refs. [1,11,13] and references therein) required careful precautions to realize thermal equilibrium: Before each measuring cycle, the sample was kept in complete darkness; at first for 6 h at 60 °C to empty the traps, then within about 2 h slowly cooled to the wanted temperature, where it finally remained for additional 14 h.

3. Results

Some examples of the steep front of drifting electron–hole pairs in 1.3 mm distance from the illuminated surface are displayed in Fig. 2. The front is obviously determined by untrapped electron–hole pairs. The derivative $\Delta I_{photo}/\Delta t$ obtained from the smoothed average of numerous spectra measured between 260 and 340 K and displayed in Fig. 3 is closely related to the spectra of classical time-of-flight measurements. The free carriers determining the sharp peak are followed by carriers delayed by trapping and multitrapping. The diagram yields the velocity $v_{drift} = 106(20)\,\mathrm{cm\,s^{-1}}$, and accordingly the ambipolar diffusion coefficient $D = xv = 14(3)\,\mathrm{cm^2\,s^{-1}}$. The Einstein

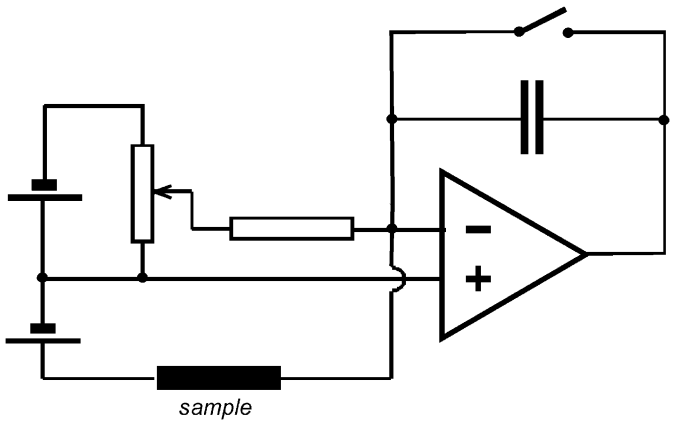

Fig. 1. Basic circuit diagram.

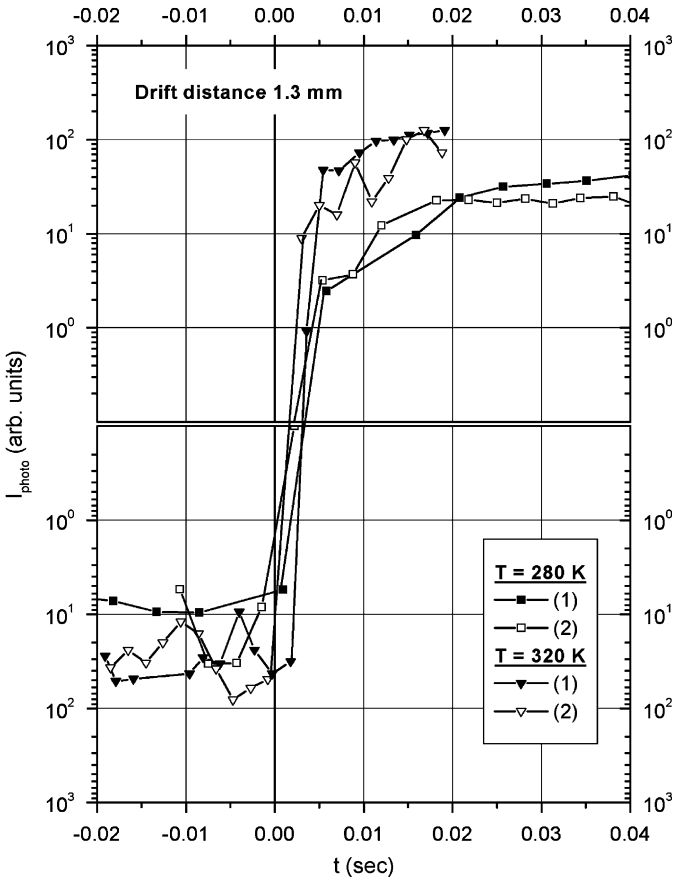

Fig. 2. Drift front of electron–hole pairs in 1.3 mm distance from the place of generation; photocurrent vs. time.

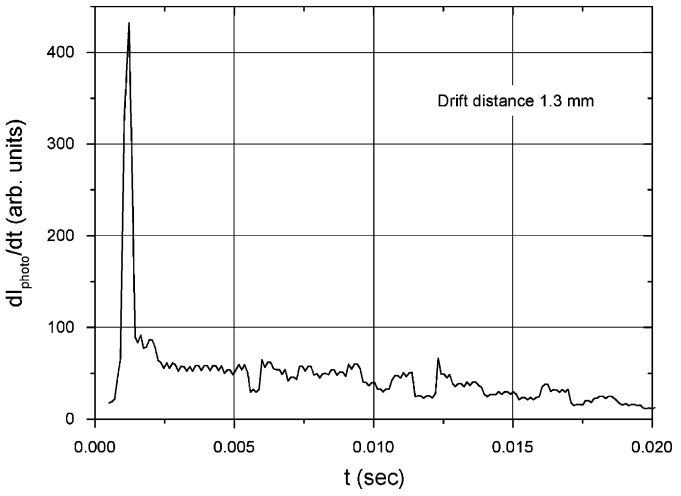

Fig. 3. Derivative of the average of numerous drift spectra measured at permanent optical excitation between 260 and 340 K. The result is closely related to the spectra of time-of-flight measurements, where electron–hole pairs are generated by pulsed optical excitation. The spectra obtained between 260 and 340 K were averaged because they agree within the accuracy of measurement.

relation $D/kT = \mu/e$ is undoubtedly valid and yields the average band-determined ambipolar mobility of electron–hole pairs in β-rhombohedral boron:

$$\mu_{\text{ambipolar}} = 565(120)\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}.$$

The time resolution of our equipment is not sufficient to determine the temperature dependence of the mobility. The error margin is estimated from the average fluctuation of the measurements and the uncertainty of the drift distance essentially due to the penetration depth of the exciting light. Since the height of the proceeding drift front is progressively reduced by recombination and multi-trapping, at the second pair of probes in 2 mm distance from the illuminated surface it is already below the detection limit.

For our measurements at longer drift times the high time resolution of the equipment is merely a disadvantage compared with previous investigations [11]. Therefore, the concerning results will be only shortly discussed. As examples, in Fig. 4 the time-dependent photocurrents at 298 K in 1.3 and 2.0 mm distance from the illuminated surface are displayed ($t = 0$, beginning of optical excitation). The required reduction of the sensitivity leads to the two gaps in the spectra near 1 and 100 s. The short integration time of 0.7 ms for each data point causes strongly scattered data covering details in the time dependence.

The boundary conditions of our experiments can be fitted to Fick' second law, which however neglects recombination and presumes diffusion without trapping. At least the latter condition is approximately met at the beginning and in the range of saturation of the diffusion spectra, indeed under somewhat different conditions. In spite of the high capture cross-section of empty traps there is a small probability for untrapped or at least not essentially delayed carriers forming the beginning of the

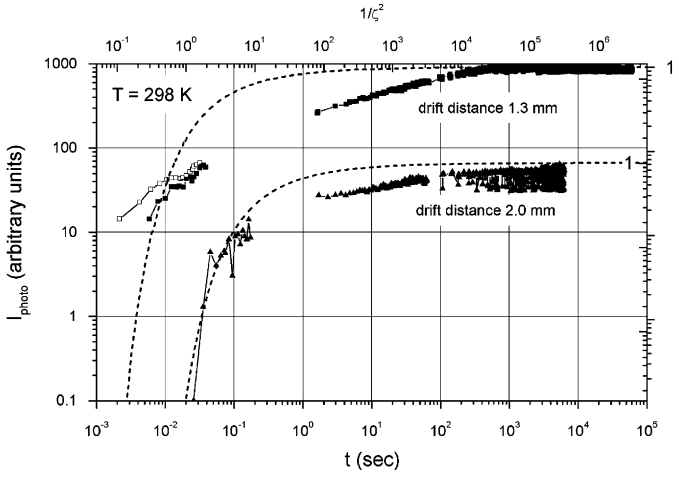

Fig. 4. Concentration of drifted electron–hole pairs vs. time in 1.3 and 2.0 mm distance from the place of generation at 298 K. Dashed lines, Fick's second law fitted to the experimental data (saturation equated to 1, see right ordinate).

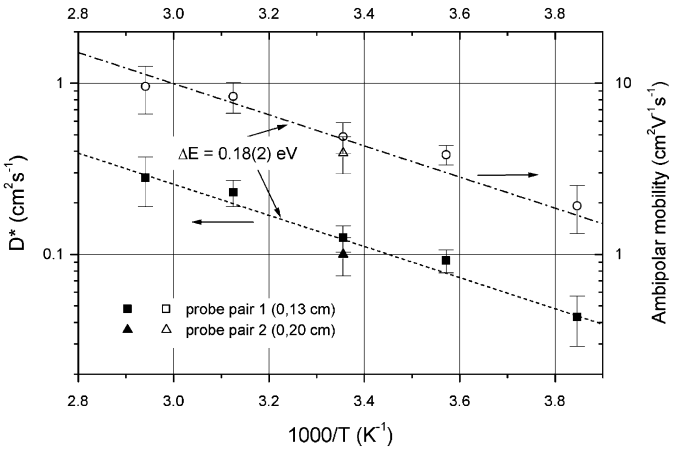

Fig. 5. Diffusion coefficient (full symbols) and ambipolar mobility (open symbols) of electron–hole pairs vs. inverse temperature.

dispersion spectrum. The range of saturation is determined by largely filled traps, whose capture cross section is accordingly reduced. For our boundary condition Fick's second law $\partial n/\partial t = -D^*q(\partial^2 n/\partial x^2)$ has the solution $n(t,x) = n_0(1 - \Psi(\xi))$ with the Gaussian error function $\Psi(\xi) = (2/\sqrt{2\pi})\int_0^{\xi} \exp(-u^2)\,\mathrm{d}u$, where $\xi = x/2\sqrt{D^*t}$. This equation is adapted to the measured dispersion curves in Fig. 1 by plotting in the form

$$\frac{1}{\xi^2} = \frac{4D^*}{x^2}\,t,$$

where the ambipolar diffusion constant D^* is the only fitting parameter.

As expected, the initial and the saturation range satisfactorily agree with the calculated time dependence. The considerable deviation in the middle range is due to multitrapping, and increases with decreasing temperature, as the thermal re-excitation from traps is delayed.

The ambipolar diffusion constant D^* as fitting parameter, and the ambipolar mobility—because of the strong influence of traps only formally derived using the Einstein relation—are displayed in Fig. 5. The thermal activation energy is $\Delta E = 0.18(2)$ eV corresponding to the position of electron and hole traps in the band scheme of β-rhombohedral boron [4]. These mobilities well agree with Hall mobilities obtained at high temperatures (see Ref. [1] and references therein), where the traps are assumed to be largely occupied by thermal excitation, and hence similar conditions for charge transport seem to exist like in the case of drifting carriers at trap saturation. This agreement supports the at first somewhat questionable evaluation based on Fick's law and Einstein relation.

4. Conclusion

We measured the diffusion of untrapped, band type carriers in β-rhombohedral boron for the first time. The diffusion coefficient and the ambipolar mobility of these

carriers correspond to values known from classical semiconductors, e.g. from holes in silicon. This definitely confirms the sometimes questioned assumption that β-rhombohedral boron, a semiconductor with a very complex crystal structure, has nevertheless typical energy bands, and that its unusual transport properties are essentially due to the high-density gap states proved in numerous experiments. At least for β-rhombohedral boron the amorphous concept [14] and similar assumptions (see, e.g. Ref. [15]) are definitely disproved. Accordingly, our experimental result is also not compatible with the theoretical hypothesis of bipolaron transport (see Refs. [16–22]). Indeed, at first this only holds for β-rhombohedral boron here investigated. However, numerous further experimental facts disproving the theoretical model of bipolaron transport suggest extending this conclusion to the icosahedral boron-rich solids in general, and to boron carbide in particular.

So the extraordinary weak Raman effect of all icosahedral boron-rich solids (see, e.g. Refs. [1,23] and references therein) indicates the very small polarizability of the structure elements hence disproving the formation of bipolarons or making it at least very improbable. Apart from the results of earlier drift investigations [10,11], the existence of band-type free carriers was proved in the high frequency and in the dynamical transport properties of icosahedral boron-rich solids [24–27]. The quantitative agreement between the concentrations of structural defects and electronic gap states in the icosahedral boron-rich structures [28,29] contradicts the existence of bipolaron states as well. Moreover, for boron carbide Hall effect and magnetoresistance in high magnetic fields [30] confirm the existence of band-type free carriers. The proved correlation between the density of hopping states and the concentration of B_{12} icosahedra in the whole homogeneity range of boron carbide refutes the bipolaron theory attributing the bipolarons to polarized $B_{11}C$ icosahedra [24,25].

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