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The Complete Optical Spectrum of β-Rhombohedral Boron

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To give a quantitative overview of the interaction between electromagnetic waves and icosahedral boron-rich solids, the reflectivity and absorption index spectra of β-rhombohedral boron between dc and about 250 eV are presented. They are put together from reliable results obtained from literature and new measurements partly with very high resolution. From a suitable combination of the experimental data the real and the imaginary parts of the dielectric function were calculated The interband transitions prove to be the strongest interaction in the whole spectrum.

INTRODUCTION

The icosahedral boron-rich solids cover a wide variety of structures extending from α-rhombohedral boron with 12 atoms per unit cell to YB_{66} with more than 1600. All of them are characterized by periodically arranged B_{12} icosahedra. These icosahedra essentially determine the electronic structures as well, therefore exhibiting closely related characteristics, which are to a considerable degree independent of the specific structural details.

Therefore the icosahedral boron-rich solids are to be distinguished from semiconductors with structures consisting of simply periodically arranged atoms and from amorphous semiconductors, too. Even amorphous boron (statistically) consists of icosahedra and therefore, apart from the narrow range order, it exhibits a medium-range order as well. Moreover, boron-rich solids are to be distinguished from molecular crystals, because the intericosahedral bonds are stronger than the intraicosahedral ones.

A considerable part of information on the boron-rich solids has been obtained by optical spectroscopy. In large spectral ranges this method is charaterized by a largely undisturbing interaction between the light beam acting as a weakly coupled probe and the investigated matter. Therefore the results obtained by this method are, if at all, only insignificantly influenced by deviations from the thermal equilibrium.

The investigations of optical spectroscopy have been largely restricted to more or less narrow and separated spectral ranges (for references in detail see (1–3)). To allow a complete quantitative overview of the entire electromagnetic spectrum, the most reliable results of optical spectroscopy are below put together and completed or amended by new results.

OPTICAL SPECTRA

Figure 1 contains the complete optical reflectivity and absorption spectrum in the electromagnetic spectrum as far as it is available at present. The following single results are included (for references on other papers, which are not included in Fig. 1, see (1, 3)).

A. Reflectivity

*R*0. $R(\omega = 0)$ calculated from the static dielectric constant ε_0 measured by Lagrenaudi (4).

*R*1. *R* calulated from interference patterns in transmission and reflectivity spectra obtained on plane-parallel samples in the range between 10 and 100 cm^{-1} by Binnenbruck and Werheit (5, 6).

*R*2. *R* calulated from interference patterns in transmission and reflectivity spectra obtained on plane-parallel samples in the range between 0.8 and 8.6 μm (7).

*R*3. *R* measured with a FTIR spectrometer, 5 cm^{-1} resolution (8) and 2 cm^{-1} resolution (9).

*R*4. *R* measured with a dispersive spectrometer (7).

*R*5. *R* measured with a dispersive spectrometer (0.86–3.2 μm, resolution about 3 nm) Ag mirror for reference (this work).

*R*6. *R* measured with a dispersive spectrometer (0.3–0.86 μm, resolution 2 nm) Ag mirror for reference (this work).

*R*7. Ellipsometric reflectivity measurement (13). It is known that in this method the reflectivity is underestimated.

*R*8. *R* directly measured by Sidorin *et al.* (10)

B. Absorption Coefficient

*k*1. Absorption index *k* calculated by Kramers–Kronig transformation form reflectivity spectra (160–1500 cm^{-1}, resolution 1 cm^{-1}) (9).

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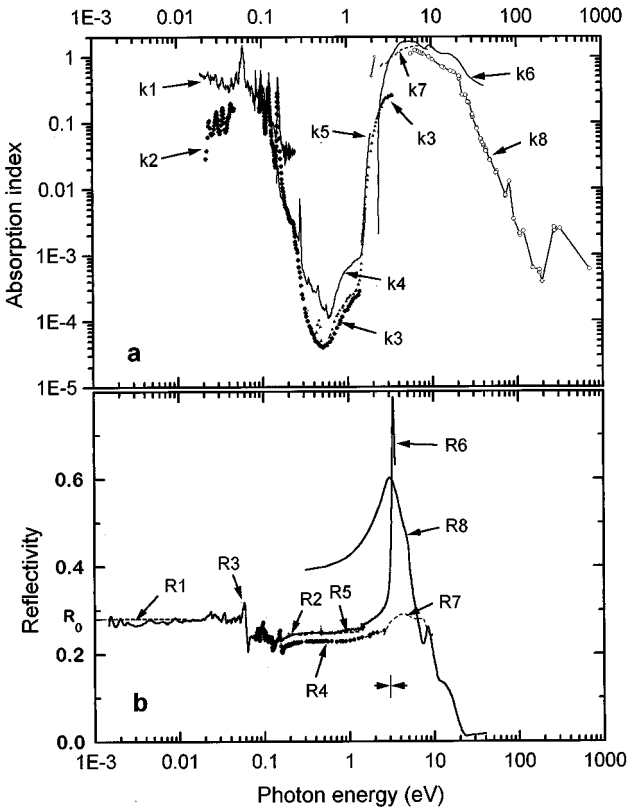

FIG. 1. Optical spectra of β-rhombohedral boron. (a) Absorption index, (b) Reflectivity. For references see text. The indicated spectral resolution in the reflectivity spectrum is referred to R6.

*k*2. *k* determined by transmission measurements with a FTIR spectrometer (5, 8).

*k*3. *k* derived from transmission measurements with a dispersive spectrometer (resolution better than 0.1 eV) (11).

*k*4. *k* derived form transmission measurements with a dispersive spectrometer (resolution 2 nm) by Werheit *et al.* (12).

*k*5. *k* derived form transmission measurements with a deispersive spectrometer (resolution 1 nm) (this work).

*k*6. *k* derived form reflectivity measurements by Sidorin *et al.* (10).

*k*7. *k* derived from ellipsometric reflectivity measurements (13).

*k*8. *k* calculated from transmission measurements by Labov *et al.* (14). For this caclulation the influence of reflectivity on the transmission is ignored. Taking the reflectivity spectrum measured by Sidorin *et al.* into account, this is largely correct for energies $\gtrsim 20$ eV; for smaller energies the real absorption index is smaller. However, based on the reflectivity spectra shown the maximum error at the low-energy limit at about 5 eV can be estimated to be not more than about 30%, which is not more than the difference between the results published by different authors.

From the different partial spectra of the absorption index shown in Fig. 1a the complete absorption index spectrum in Fig. 2a was determined partly by selecting the aparently most reliable results and partly by interpolating between different partial spectra. Then, taking the reflectivity spectrum into account, the refractive index spectrum (Fig. 2a) and the spectra of the real and the imaginary part of the dielectric function (Fig. 2b) were calculated. The measured reflectivity data end at about 40 eV. To extend the calculation to the limit of the absorption measurements at about 700 eV a specific assumption on the disperison in this range was necessary. After classical theory $\mathrm{Re}(\varepsilon)$ deceases toward high photon energies as $1/\omega^2$. However, it was not possible to fit such an extrapolation convincingly to the measured spectra. Therefore a dispersion-free behavior was assumed, which may influence the imaginary part of the dielectric function in this range only insignificantly. Indeed, the energy-independent real part of the dielectric function at high energies in Fig. 2b is not realistic.

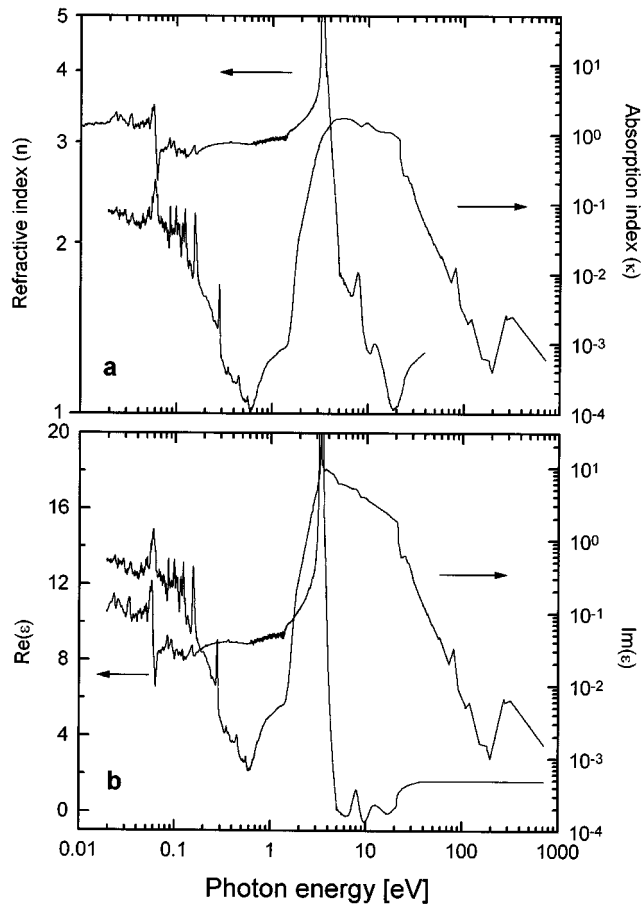

FIG. 2. (a) Complete spectrum of the absorption index derived from the experimental results shown in Fig. 1a and the refractive index calculated form absorption index and reflectivity. (b) Real and imaginary part of the dielectric function of β-rhombohedral boron (for the discussion of the reliability in the high energy range, see text).

DISCUSSION

In the electromagnetic spectrum of β-rhombohedral boron the ranges of electronic interband transitions and lattice vibrations are distinctly separated as usual in semiconductors. The highest absorption is due to the interband transitions. Some results seem to suggest that between about 2.5 and 5.5 eV the absorption coefficient is still higher than indicated by the experimental results presented. This is supported by the derivative of the dielectric function (13) and by the structure-modulated optical spectra (15) showing that in this spectral range there are several critical points with probably high combined densities of states.

Compared with ionic solids the absorption in the phonon range, which is essentially determined by intraicosahedral phonons, is rather weak. This is an inevitable indication that the ionicity in β-rhombohedral boron is weak and no strong transfer of charge between the different structural elements takes place. Hence the bonds are largely covalent.

In the low absorption range between interband transitions and phonons the absorption depends on the sample individuum and its impurities, in particular on its carbon content. For the high-purity samples, whose spectra are shown, the carbon contents varies only between 66 and 90 ppm.

In the low-energy range ($\lesssim 0.04$ eV) the absorption depends strongly on the individual sample properties as well. The reflectivity spectrum is shown for a sample, which is extremely pure more or less by chance, while the absorption index is presented for two nominally high-purity samples. For that with the highest purity (spectrum measured on the same sample as used for the reflectivity measurement) the absorption decreases below the phonon range, while that of the less pure sample increases because of the influence of the dynamical conductivity. For more details on this topic the reader is referred to (16, 17)

From the agreement between the dielectric function derived from interference patterns in the FIR range and the static dielectric constant follows that beyond the optical active lattice vibrations there are no essential dispersion oscillators.

As far as it is known from single investigations on other icosahedral boron-rich solids, their absolute and relative strengths of the absorption processes are qualitatively similar to those in β-rhombohedral boron.

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