SOME OPTICAL PROPERTIES OF CRISTALLINE LaB_6

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The ultraviolet reflectivity and the plasma reflection edge in cristalline samples of LaB_6 were investigated. The spectral dependences of the optical constants were calculated in the region 1.1 to 6.0 eV, using Kramers-Kronig method. The dielectric constant and carrier concentration to the effective mass ratio N/m^* were evaluated by application of the Drude's theory.

I. Introduction

All rare-earth and alkaline metals form with boron hexaborides of general structure MB_6. The electronic structure of these compounds was investigated theoretically (1) by the tight-binding approximation. From these calculations it follows, that if M is a bivalent metal the crystal should exhibit semiconducting properties, but if M has the valency greater than two the crystal should exhibit metallic behaviour. LaB_6 is one of these compounds for which these theoretical calculations forecast mettalic properties. Some electrical properties of LaB_6 were described in papers [2], [6] and [7], for the samples produced by pressing powder of pure LaB_6. From these papers it follows that resistivity of this compound is very low $57\times10^{-6}\Omega$ cm [7] $15\times10^{-6}\Omega$ cm [6] and its value increases with the temperature likewise for metals. Also the low value of carrier mobility 32 cm^2V sek and 33.1 cm^2/V sek [2] comparable with the carrier mobility of metals was found. The carrier concentration in LaB_6 obtained by Hall measurements is about 10^{22} cm^{-3} [2], [6].

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The reflectivity of the sintered samples of LaB_6 in the visibile and near infrared region was described in [2]. An analysis of the observed plasma reflection edge [2] near 2.0 eV was carried out using simple Drude's theory and assuming that extinction coefficient k can be neglected in comparison to the refractive index n. From these calculation the dielectric constant $\varepsilon = 15.6$ and the effective mass $m^* = 0.32\ m_0$ was obtained.

The present paper describes the spectral dependence of the reflectivity of crystalline samples LaB_6 in the visibile and ultraviolet region up to 6.0 eV. Our analysis of the reflection curve was carried out exactly, using values of n and k evaluated by the Kramers-Kronig dispersion relation.

II. Theoretical analysis

Assuming the solution of the Maxwell equation in the form:

$$\boldsymbol{E} = \boldsymbol{E}_0 \exp i\omega \left(t - \frac{\boldsymbol{Kr}}{c}\right) \tag{1}$$

one can obtain the following equation for the complex refractive index:

$$(\boldsymbol{KK})E - (\boldsymbol{K}E)\boldsymbol{K} + \frac{4\pi i}{\omega}\,\check{\sigma}(\omega)\boldsymbol{E} - \varepsilon\boldsymbol{E} = 0 \tag{2}$$

Where $\hat{\sigma}$ is a conductivity tensor, ε is the lattice dielectric constant and $\mathcal{N}$ is a propagation vector which is related to the optical constants: the refractive index n and extinction coefficient k by the expression

$$\mathcal{N} = n - ik \tag{3}$$

These above optical constants depend on the circular frequency of the electromagnetic wave and are characteristic of the medium.

On the other hand one can express the propagation vector by the components on the free carrier conductivity tensor [11]. In the absence of an external fields all non diagonal components vanishes and all diagonal components are the same and have the form:

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \frac{N}{m^*}\,\frac{q^2\tau}{1 + i\omega\tau} \tag{4}$$

where N is the carrier concentration and m^* is the effective mass.
Making use of Eq. (2) and (4) the following solution for N can be found:

$$\mathcal{N}^2 = \varepsilon - \frac{4\pi i}{\omega}\,\frac{N}{m^*}\,\frac{q^2\tau}{1 + i\omega\tau} \tag{5}$$

Comparing the right hand sides of Eqs (3) and (5) one can obtain

$$(n - ik)^2 = \varepsilon - \frac{4\pi i}{\omega}\,\frac{N}{m^*}\,\frac{q^2\tau}{1 + i\omega\tau} = \mathcal{N}^2 \tag{6}$$

From Eq. (6) it follows that

$$n^2-k^2 = \mathrm{Re}\,\mathcal{N}^2 \tag{7a}$$

$$2nk = -\mathrm{Im}\,\mathcal{N}^2 \tag{7b}$$

In the case when absorption is very small and the medium is essentially dispersive we have $k^2 \ll n^2$. Aussming $\omega\tau \gg 1$ and making use of Eq. (6)

We obtain:

$$n^2 = \varepsilon\left(1 - \frac{\omega_p^2}{\omega^2}\right) \tag{8}$$

Where $\omega_p^2 = \dfrac{4\pi q^2 N}{\varepsilon m^*}$ is the plasma frequency. The reflectivity of the electromagnetic wave normal to the boundary between the vacuum and conducting medium is described by the well known expression:

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \tag{9}$$

In the region where $n^2 \gg k^2$ and for frequencies $\omega^2 \gg \omega^2$ the refractive index is constant and according to (7) it is:

$$n^2 = \varepsilon \tag{10}$$

Thus the reflection coefficient has also the constant value

$$R = \frac{(\sqrt{\varepsilon}-1)^2}{(\sqrt{\varepsilon}+1)^2} \tag{11}$$

As the frequency is decreased from large ω a point is reached where $n \to 1$ for which case $R \to 0$. One can see from (8) this occurs for

$$\omega_{\min} = \omega_p\left(\frac{\varepsilon}{\varepsilon-1}\right)^{1/2} \tag{12}$$

For a relatively small further decrease of frequency, R goes repidly to unity as $\omega \to \omega_p$. The minimum of reflection coefficient is called the "plasma minimum" and this sharp rise of reflection coefficient is called the "plasma reflection edge".

This characteristic course of the reflectivity is typical for the metals in the visibile region [10] and for degenerate semincoductors in the infrared region [8], [9]. In the whole spectral region $n(\omega)$, $k(\omega)$ and $R(\omega)$ are mutually dependent and related by the Fresnel equation for reflection at the normal incidence

$$r = \frac{n-ik-1}{n-ik+1} = |r|\,e^{i\varphi} \tag{13}$$

and Kramers–Kronig integral

$$\varphi(\omega_0) = \frac{1}{\pi}\int_0^\infty \frac{d\ln|r(\omega)|}{d\omega}\ln\frac{|\omega+\omega_0|}{|\omega-\omega_0|}\,d\omega \tag{14}$$

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 5

It follows from Eq. (13) that if both amplitude $|r| = \sqrt{R}$ (where R was defined by Eq. (9)) and phase φ are known, n and k can be solved in the form:

$$n = \frac{1-|r|^2}{1+|r|^2-2|r|\cos\varphi} \tag{15}$$

$$k = \frac{2|r|\sin\varphi}{1+|r|^2-2|r|\cos\varphi} \tag{16}$$

The reflectivity measurements determines $R(\omega)$ and therefore $|r(\omega)|$, thus φ at any frequency ω_0 can be obtained by Eq. (13). Since in practice it is not possible to measure $R(\omega)$ for all frequencies, an explicit assumption for extrapolation to higher frequencies is necessary. The evidence that extrapolation is done correctly is fact that the evaluated by this method k and thus α is the same in the region were α could be meassured directly.

These theoretical assumptions will be applied to interpretation of the spectral dependence of the reflectivity of LaB_6.

II. Experimental results and discussion

The crystalline samples of LaB_6 we have used in experiment were prepared by the method described in [3]. The material obtained in this manner was of high purity (the total quantity of impurities was smaller than $10^{-4}\%$). In reflection measurements we used only mechanically polished samples, because we do not know any polishing solution for this compounds.

The experimental equipment used for the measurements of the reflection coefficient, was such that the incident and reflected beams were compared, and therefore the measurements reported here are "absolute". The monochromatic light was obtained by SPM-1 Zeiss monochromator with the glass and quartz prisms. In the visible region a tungstan lamp and in ultraviolet region a Xenon arc were used as a light sources. The light was detected by Zeiss photomultipliers with glass or quartz windows and the resulting signal was measured by Digital Voltmeter.

The measurements were made at room temperature under practically normal incidence of light.

The spectral dependence of the reflectance of LaB_6 is shown in Fig. 1. In the course of the reflectivity curve one can see low minimum at 2.10 eV and a sharp rise of reflectivity towards the lower energy. As we obtained the same shape of the spectral dependence of the reflectivity, which was forecasted for the influence of the electromagnetic wave on the free carriers, we thus suppose that we observed the plasma reflection edge. The weak structure observed at 4.90 eV and 5.40 eV like in pure B_6 is probably associated with the interband transitions. We can not tell exactly if 4.90 eV is the lowest energy gap in LaB_6 because according to the "critical point theory" [12] not all interband transitions are observed as a maxima of reflectivity.

Taking the experimental values of R presented in Fig. 2 and making use of integral (14) the optical constants n, k and α were computed.

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 5

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 5

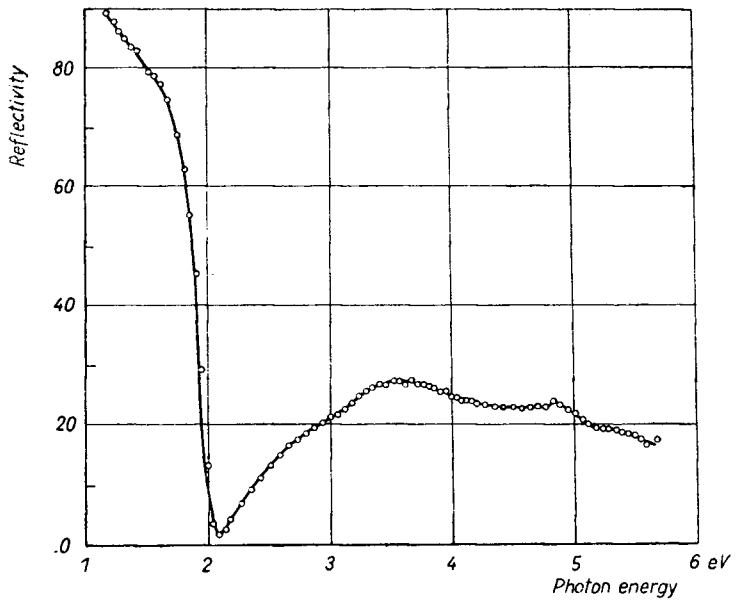

Fig. 1. The reflectivity of LaB_6 *versus* the photon energy

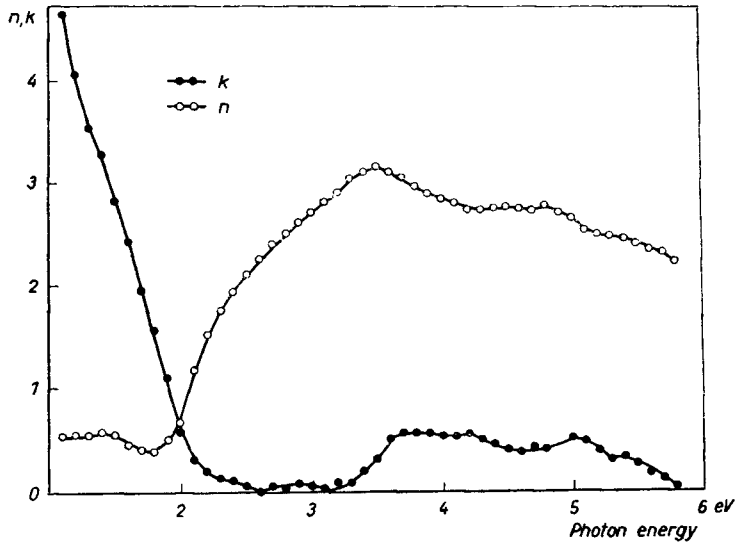

Fig. 2. The spectral dependence of refractive index n (open circles) and extinction coefficient k (full circles)

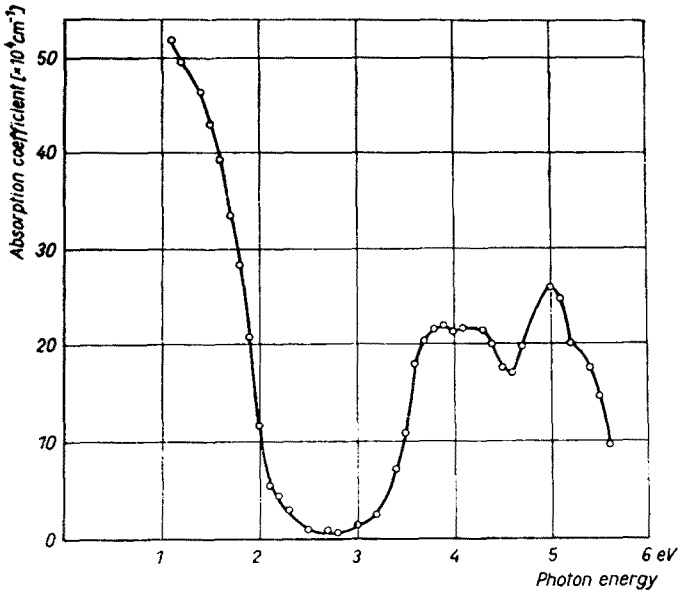

Fig. 3. The evaluated absorption coefficient α *versus* the photon energy

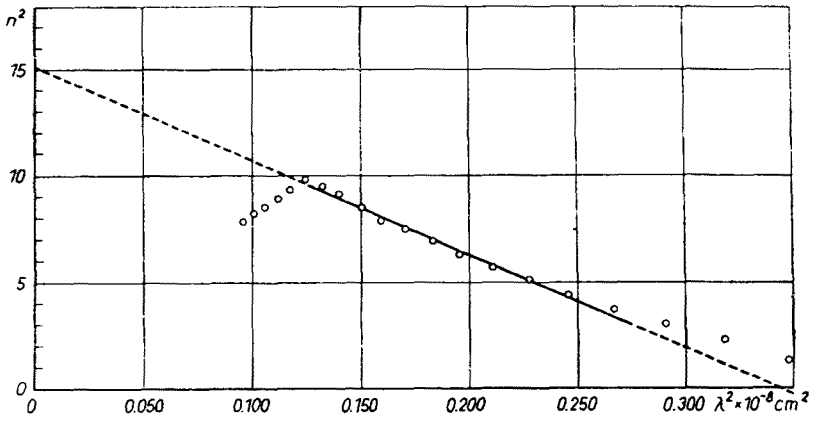

Fig. 4. The square of refractive index *versus* the square wavelengths

The integral (14) was computed by the method described in [5]. The reflectivity curve was approximated by 11 stright line segments assuming that the reflectivity is constant and equal 0.93 for the photon energy < 1 eV, and that the reflectivity decreasses logharitmically to 0.1 eV for the photon energy 100 eV. These conditions give the absorption coefficien about $10^4 cm^{-1}$ in the region of the minimum reflectivity which is in agreement with experimental data of α in this region. Numerical calculations were performed on computer "Odra 1013". The evaluated spectral dependences of the refractive index n and extinction coefficient k are shown in Figs 2 and 3.

The results for n and k derived by Kramers–Kronig method were analysed to obtain the lattice dielectric constant and carrier concentration to the effective mass ratio.

After some transformations of Eq. (8) one can obtain:

$$n^2 = \varepsilon - \frac{q^2}{\pi c^2} \frac{N}{m^*} \cdot \lambda^2 \tag{18}$$

Thus n^2 plotted versus λ^2 gives a stright line the slope of which determines $\frac{N}{m^*}$ and whose intersection with the ordinary determines ε. It is evident from Fig. 3 that in the region 2.2–3.5 eV k^2 can be negligible towards n^2, thus the relation (18) may be applied in this region. Fig. 4 shows the results of this analysis. We thus determined $\varepsilon = 15.1$ and the carrier concentration to the effective mass ratio (in free electron mass units) $m_0 \frac{N}{m^*} = 4.93 \times 10^{22}$ cm^{-3}. These values are in a good agreement with data of Kauer who gives $\varepsilon = 15.6$, $N = 1.42 \times 10^{22}$ cm^{-3}, $m^* = 0.32\, m_0$. Taking his value for m^* the carrier concentration in our samples can be calculated as $N = 1.58 \times 10^{22}$ cm^{-3}. The deviation between our results and those published by Kauer, observed in Fig. 4 in the high energy region, we suppose is due to the fact, that in this region we can not apply the Drude's theory. As follows from our calculation for higher energies some structure in K and thus in absorption cofficient is observed. This structure is probably conected with interband absorption.

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