F5
Birefringence of CdS and CdSe crystals.

The objective of the present experiment is to measure the birefringent response of CdS and CdSe through optical interference. The results of the experiment shall allow one to obtain the difference between refractive indexes along different directions in the solids considered, which can then be analyzed in the context of an excitonic model.

1. What should you know before attempting the experiment?

I- Basic knowledge of the physics of semiconductors [1, 2, 3, 5]:
  a. Band structure, electrons, holes, excitons,
  b. Mechanisms for light absorption above the absorption edge. Spectral response (shape) of different optical transitions,
  c. Selection rules for absorption.
II- Optical properties of semiconductors [1, 2, 3, 5]:
  a. Refractive index,
  b. Crystal birefringence [4],
  c. Relationship between optical constants (α, n) – The Kramers-Kronig relation [7],
III- Parameters of CdS and CdSe [6]:
  a. Crystal structure,
  b. Band structure around k = 0, energy gap,
IV- Experimental techniques for the measurement of optical birefringence [6],
V- Basic techniques for optical measurements
  a. Inner workings of a monochromator,
  b. Lockin-based (modulation-based) measurement techniques.

To prepare for the experiment, you should be familiar with the text below. Special attention should be paid to terms and words in **bold** letters.

In a crystalline solid, electrons are subjected to a periodic potential. Their wavefunction, in this situation, can be described in terms of **Bloch functions**. Free carriers in this material, thus, do not behave as non-interacting electrons in vacuum. Instead, they have different values of **mass** and can possess positive charge. The latter are conventionally termed as **holes**, and usually inhabit the **valence band** of a material. Meanwhile, carriers with negative mass, called electrons, exist in the **conduction band**. In insulators or semiconductors, the conduction and valence bands are separated by an **energy gap**.

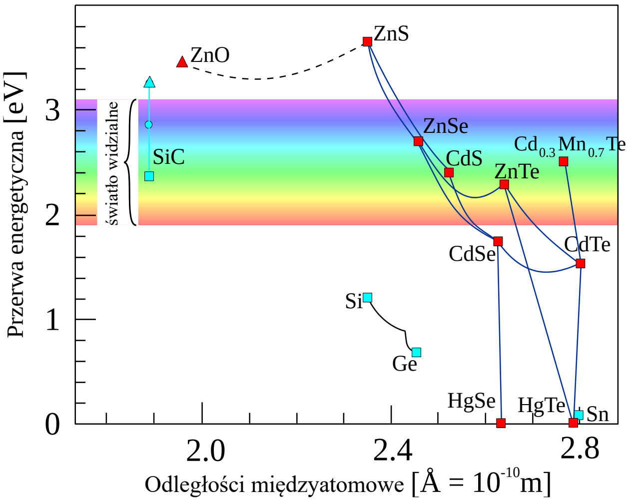


Figure 1 – Gap vs. lattice parameter of alloys pertaining to the II-IV family.

Besides the well-known monoatomic semiconductors of the group IV of the periodic table, there exist a family of semiconductors composed by alloying elements of the family III and V of the periodic table, as well as alloying those of the family II and VI. These are named, rather dully, as II-V and II-VI semiconductors. A diagram representing different materials of these groups are presented in Fig. 1, together with their respective energy gaps.

Semiconductors of the II-VI family are compounds in which cations are metals of the group II of the periodic table (Zn, Mg, Cd, Hg,Mg), whereas anions are elements of group VI of the periodic table (O, S, Se, Te). The width of the Energy gap in this family ranges from values close to 0 eV (CdHgTe) to those above 3.5 eV(ZnS). The possibility to achieve mixtures of alloys with fractional stoichiometries (e.g. Cd0.3Mn0.7Te as an alloy composed by 30% CdTe and 70% MnTe) allows the precise engineering of the energy gap of the semiconductors of this family.

Conventional semiconducting alloys usually crystallize in two similar structures: **Zinc-blend** (cubic symmetry) and **wurtzite** (hexagonal symmetry). In the latter, one of the crystalline axis is differentiated, which enables the occurrence of a phenomenon known as **birefringence.**

Light is an electromagnetic wave. In an isotropic medium, it can be described according to

$$\vec{E} = \overrightarrow{E_0} \exp\left[i\left(\vec{k} \cdot \vec{r} - \omega t\right)\right], \\ \vec{B} = \overrightarrow{B_0} \exp\left[i\left(\vec{k} \cdot \vec{r} - \omega t\right)\right] \qquad (1.1)$$

where the electric field $\vec{E}$ and magnetic field $\vec{B}$ are orthogonal to the direction of propagation of the wave, denoted by $\vec{k}$. Such a description means that light is a **transversal wave**, from which we may define its **polarization**. As a convention, the direction of the vector $\vec{E}$ is chosen as the polarization axis of the light. In a material medium, the speed of light is reduced, with its wavevector amplitude being given by

$$k = n\frac{\omega}{c} \qquad (1.2)$$

where n is defined as the refractive index of the medium in question.

In medium with an **anisotropic refractive index**, the speed of propagation of the light depends on its polarization. In a birefringent crystal, the component of light with polarization parallel to the material's **optical axis** will have a different propagation velocity, than light polarized perpendicular to it. Therefore, the **refractive index** of each polarization will be different ($n_{\parallel} \neq n_{\perp}$).

The spectra response of $n(\hbar\omega)$ below the absorption edge due to **excitonic** phenomena (crossed-resonances) is well-described through

$$n(\hbar\omega) = n_0 + \frac{Ne^2}{2\varepsilon m}\frac{(E_X - \hbar\omega)}{((\hbar\omega)^2 - E_X^2)^2 + (\hbar\omega)^2\Gamma^2}, \qquad (1.3)$$

Where N, E_X and Γ are the density of states, Energy, and resonance widening due to excitons, respectively. The parameter n_0 is the refractive index without any excitonic contribution. The widening of the excitonic resonance line Γ is caused mainly by oscillations of the atomic lattice (also called **phonons**), and possess a value of the order of few meV at room temperature. At lower temperatures, Γ tends to drop towards very small values. It is easy to see that if $\Gamma \to 0$, equation (1.3) becomes simply a peak function of the type $\delta(E_G - \hbar\omega)$.

Note that birefringence is affected by different selection rules for excitons, whose degeneracies of the energy spectra are lifted by crystalline fields in the solid. The spectral response of the refractive index of a birefringent material can be approximated by the function (see fig. 2a)

$$\Delta n(\hbar\omega) = \Delta n_0 + \frac{\beta}{((\hbar\omega)^2 - E_G^2)^2 + (\hbar\omega)^2\Gamma^2}, \qquad (1.4)$$

Where E_G is the gap energy and Γ is a broadening factor with different origins.

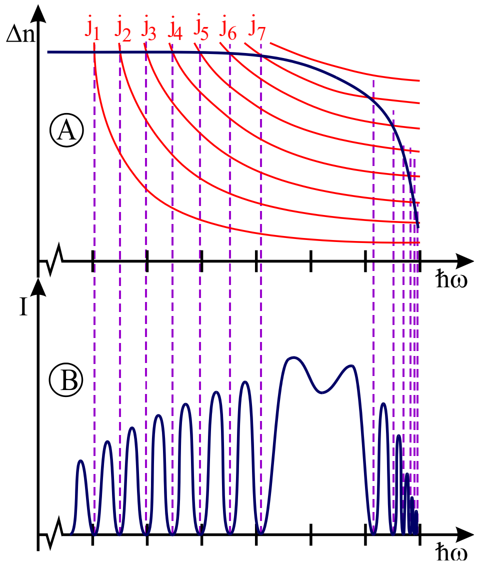


Figure 2 – A) Dispersion spectrum and B) interference spectrum in a birefringent material

Because the refractive index n and the absorption coefficient α are both functions of the dielectric constant ε, it is possible to obtain one of these parameters by knowing the other. This is done through the **Kramers-Kronig** relation, which enables the calculation of the spectral response of $n(\hbar\omega)$ from the absorption spectra $\alpha(\hbar\omega)$, and vice-versa,

In the experiment treated here, the light will be led through a birefringent material (a crystal with Wurtzite structure), propagating perpendicular to the crystal's optical axis. The polarization of the electric vector, therefore, will lie in the same plane of the optical axis, and shall be set at 45 deg. relative to it. This allows the description of the light propagation in the material as the superposition of two waves with orthogonal polarizations: one polarized perpendicular to the optical axis, and one polarized along it. Because the polarization is set at 45 deg, both components will have the same amplitude, but will propagate in media with different refractive indexes and – therefore – at different (phase) velocities. When exiting the material, the phase difference between both light components will be given by

$$\phi = \Delta n \times d \times k_0 \tag{1.5}$$

with d the crystal thickness and k_0 the light wave vector in the air. By measuring the light emerging from the material at a polarization angle perpendicular to the incident beam, an interference pattern should be observed (work out why this happens and why for this polarization). For each $\phi = 2\pi j$ (j integer), a minimum of intensity will be observed (see fig. 2B). Through equation 1.2, it is possible to relate such intensity minima with the photon energy $\hbar\omega$ according to

$$\hbar\omega = \frac{hc}{d \cdot \Delta n} j, or$$

$$\Delta n(\omega) = \frac{2\pi c}{d \cdot \omega} j, \qquad j = 1,2,3\ldots \tag{1.6}$$

Therefore, the interference pattern of the transmitted light shall allow the extraction of the spectral response $\Delta n(\hbar\omega)$.

2. Experimental procedure

A. Prepare the optical setup for measurements:
   a. Measure the sensitivity of the experimental setup with two different detectors
   b. Define the figure of merit of the polarizers available $D(\hbar\omega)$:

$$D(\hbar\omega) = \frac{I_{\parallel}(\hbar\omega) - I_{\perp}(\hbar\omega)}{I_{\parallel}(\hbar\omega) + I_{\perp}(\hbar\omega)}, \tag{2.1}$$

   where $I_{\parallel}$ and $I_{\perp}$ are the transmitted light intensities through two polarizers in the co- and cross-polarized configurations, respectively,

B. Measure the transmission spectra for CdS and CdSe (use the appropriate polarizer and detector),
C. Measure the spectral response of the birefringence for CdS and CdSe through the interference method,
D. Analyze the results using a model accounting for the light-matter interaction.

3. How to prepare the report

The report should contain the following sections:

1. Abstract,

2. Theoretical introduction,
3. Description of the samples and experimental setup,
4. Results and their analysis,
5. Summary and conclusions, based on the measured data.

Please note that:

1. The abstract should consist of a few sentences containing the description of the experiment and its main results,
2. All equations should be justified, and their origins explained,
3. In the description of the experimental setup, the characterization of the polarizers ($D(\hbar\omega)$) and the calibration curves of the monochromator (using different detectors) should be presented.
4. The results of the experiment are the transmission and interference spectra. Considering the transmission spectra (and the optical response of the detectors), one should calculate the spectral response of the absorption coefficient $\alpha(\hbar\omega)$. At the same time, the interference spectra should be analyzed in order to determine the number j of interference fringes and to obtain $\Delta n(\hbar\omega)$ through equation 1.6. We define the number j by assuming that $j(\hbar\omega = 0) = 0$, and $\Delta n = constant$ for small values of j (define *small*).
   The spectral response $\Delta n(\hbar\omega)$ should be discussed and adjusted through the theoretical equation (1.4). The fitting parameters are Γ, Δn_0 and β. Take E_g as known from the literature and assume that β is a negative number.
5. Provide a physical explanation for the observed results.
6. When preparing the presentation, please remember that figures must be correctly labelled (e.g. Fig. 1, 2, 3, etc...), and should be referred by their labels (NOT by "see the figure below"). Figures should be accompanied by a description below the figure. Tables (if any) should also be numbered. However, differently from figures, tables are titled (i.e. the description is atop the table, not below it). Whenever a reference is used, or results from other authors are cited, they should follow with the appropriate reference between brackets (e.g. [1]). The referencing style is up to the author of the report, but should be consistent.

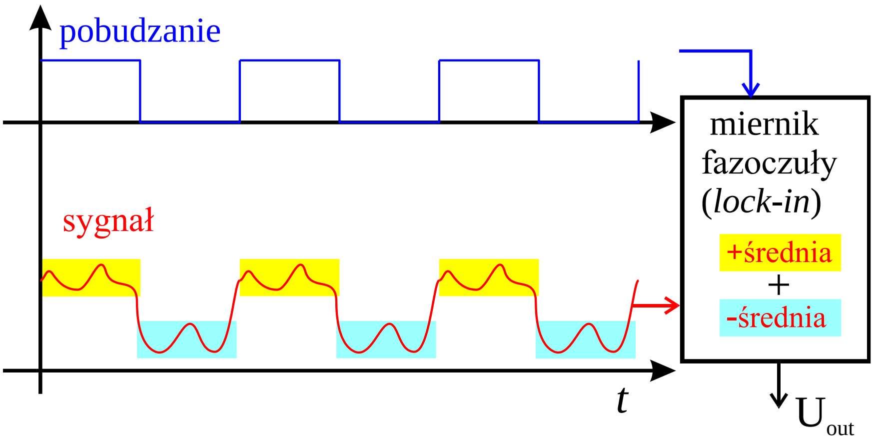
4. **Further reading**

1. J. Ginter - „Wstęp do fizyki atomu, cząsteczki i ciała stałego"
2. K. W. Szalimowa - „Fizyka półprzewodników"
3. T. S. Moss - „Optical properties of semiconductors"
4. S. Pieńkowski - „Fizyka doświadczalna", tom III - Optyka
5. J. Pankove - „Zjawiska optyczne w półprzewodnikach"
6. M Nawrocki, JA Gaj, J Żuk , 'Birefringence of CdSe and CdS in the vicinity of the fundamental absorption edge', physica status solidi (b) **68**, K181 (1975) https://doi.org/10.1002/pssb.2220680264
   W. Wardzyński 'Dichroism and birefringence of single crystals of cadmium selenide', Proc. Roy. Soc. A **260**, 370 (1961) https://doi.org/10.1098/rspa.1961.0039
7. http://en.wikipedia.org/wiki/Kramers-Kronig_relations
8. Encyklopedia fizyki lub Wikipedia w wersji angielskiej - hasło: monochromator,

K.K., R.S., BC 08. IV

Appendix A: phase-locked voltmeter (Lockin)

A phase-locked voltmeter is a device that measures the component of voltage that is modulated to a certain frequency. All other components of the signal (with different frequencies) are disregarded. This allows a very precise noise rejection, by exciting the system with a known frequency and measuring only the system response at the same frequency of the excitation. A visual explanation of the procedure is shown in fig. A1



Rys. A1. Principle of working of a phase-locked voltmeter. The signal (lower curve) is compared with the excitation (upper curve). The excitation is known. The output of the measurement is calculated as the difference between the measured signal during the “0n” cycle (taken as the average of the signal during that period) minus the signal during the “off” cycle. By using this method, all frequencies much larger or much lower than the excitation signal are rejected.

For more information, look at „lockin amplifiers” on Wikipedia, or the encyclopedia of your choice

https://en.wikipedia.org/wiki/Lock-in_amplifier
(last accessed on 08.04.2023)