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## Application of modulation spectroscopy for defining band gap of Cd<sub>1-x</sub>Mn<sub>x</sub>Te solid solution

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The modulation spectroscopy was used for defining band gap of monocrystalline Cd<sub>1-x</sub>Mn<sub>x</sub>Te solid solutions, the properties of which vary with molar composition  $x$  and the surface preparation quality. It was found that for such samples it is useful to measure differential transmission spectrum  $T'_w$ , the main peak of which is governed by the composition  $x$  and the substrate thickness  $d$ . Therefore, it is important to measure  $E_g(d)$  for at least three samples of the same composition and different thickness. Using these data, the band gap can be obtained by extrapolating  $E_g(d)$  dependence in a logarithmic scale up to intersection with the energy axis at  $\lg d = 0$ , which corresponds to the sample thickness of 1  $\mu\text{m}$ .

**Keywords:** semiconductor, band gap, modulation spectroscopy.

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### Introduction

Band gap ( $E_g$ ) is one of the most important parameters of a semiconductor material that determines its physical properties, establishing the possible application ranges. Among the many methods used to determine  $E_g$ , optical measurement remain the most popular [1] by being non-destructive and allowing to study the response of the material under different external influences such as temperature, pressure, electric and magnetic fields, presence of ionizing radiation, etc. Many of optical methods consist in analysis of reflection spectrum  $R_\omega$ , either alone or compounded with the absorption spectrum  $K_\omega$  for the energies approaching the expected value of material's band gap. The obtained experimental curves are then fitted with a set of theoretical models seeking to determine band gap value with major precision, yet each such fitting may have its subtle drawbacks. As absorption spectrum is usually calculated from the transmission spectral data  $T_\omega$  measured close to the edge of intrinsic absorption [2], it is important to ensure the reliability of  $T_\omega$  measurement using very thin samples ( $d \leq 100 \mu\text{m}$ ), growing of which may be quite complicated from technological point of view.

For thicker samples it is more appropriate to measure reflection spectra, which are independent on sample

thickness. At the same time, the precision and reliability of reflection spectra are defined by the structural perfection of material and the quality of the sample surface. To obtain material with high structural perfection it is necessary to fine-tune many parameters of growing process in order to ensure good control over chemical composition and crystallographic orientation, to reduce the concentration of point defects, etc., all of which add quality constraints to both material growth technology and sample preparation technology. Therefore, it is important and timely to develop a simple and reliable method for determination of semiconductor band gap. For this purpose, we propose to use modulation spectroscopy [3, 4], illustrating its potential with an example study of Cd<sub>1-x</sub>Mn<sub>x</sub>Te solid solutions.

### I. Samples and research methodology

We have chosen Cd<sub>1-x</sub>Mn<sub>x</sub>Te as an object of study because addition of manganese to the solid solution produces a diluted magnetic semiconductor with a number of important physical properties – the Giant Faraday effect and spin splitting, inter-center optical transitions, and non-linear transmission [5, 6]. These remarkable properties open promising application perspectives for Cd<sub>1-x</sub>Mn<sub>x</sub>Te in the fields of magneto-

optics, spintronics, lasers, and power optics. It is important to mention that increase of manganese molar content  $x$  leads to larger values of  $E_g$ , enhancing temperature and radiation stability of the crystals and devices based on them. Unfortunately, the same high molar content  $x$  deteriorates structural perfection of the material, though solid solution is considered to be homogeneous for  $x \leq 0.77$  [6]. Reference [7] reports that  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  may contain cubic-phase clusters of  $\beta\text{-MnTe}$  as structural imperfections due to the presence of a UV band in photoluminescence spectrum of the samples with  $x = 0.05\text{-}0.5$  with its peak centered at 3.24 eV that corresponds to the band gap of  $\beta\text{-MnTe}$  at 300 K [8].

The present research was carried out for a set of flat samples  $4 \times 4 \text{ mm}^2$  in size, cut from a Bridgman-grown bulk  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ . The melt used for crystal growth contained different concentrations of Mn ( $x = 0.04$ ;  $x = 0.1$ ;  $x = 0.25$  and  $x = 0.4$ ). The samples obtained featured p-type conductivity defined by intrinsic defects at room temperature. Series of samples of the same composition were produced; these were further polished to achieve the required variation of thickness  $d$ . First, the thickness of the samples was adjusted by polishing them with diamond paste AM5. The obtained plates were further mechanically polished and chemically etched in bromine methanol, completing the process with careful rinsing in distilled water. The resulting samples featured mirror-reflecting surface. Three samples with different thickness in the range 150-750  $\mu\text{m}$  were produced for every composition  $x$  mentioned above.

The differential spectra of reflection  $R'_W$  and transmission  $T'_W$  were measured using the universal measuring setup including the diffraction monochromator MDR-23 and a standard synchro-detector. We used a halogen lamp with a smooth radiation spectrum as a light source. The spectra were

recorded with the photomultiplier FEU-112. The  $\lambda$ -modulation was achieved by oscillation of a flat mirror of MDR-23 monochromator with a frequency of 33 Hz. All measurements were performed at room temperature.

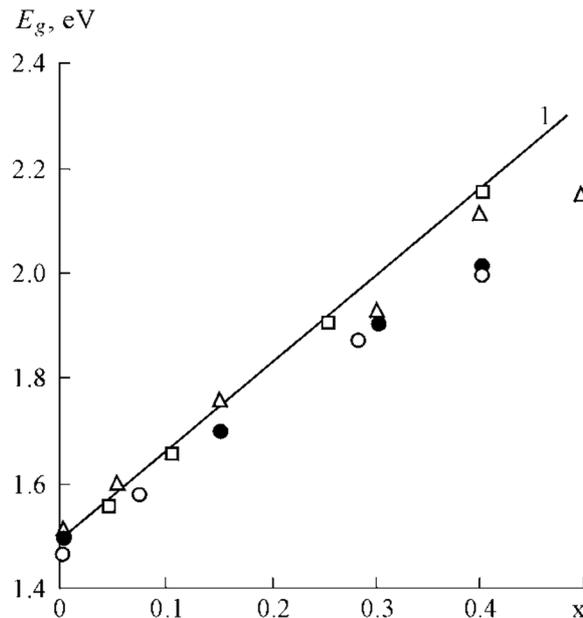
## II. Results and discussion

The solid solution  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  features zinc blend structure in the entire composition range, decreasing its lattice constant linearly with increase of  $x$  [6]. Under these circumstances, it is natural to expect that dependence of  $E_g(x)$  should be linear as well, which is confirmed experimentally by the empirical relation [9-11]

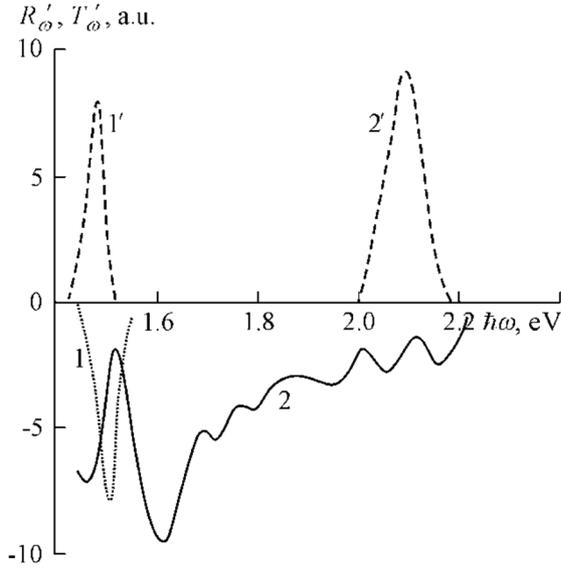
$$E_g(x) = E_{g0} + ax. \quad (1)$$

At the same time, experiment measures deviate from the values  $E_{g0} = 1.5 \text{ eV}$  and  $a = 1.74 \text{ eV}$  expected from a straightforward application of linear band gap regression carried out for the limit cases of  $x = 0$  ( $\text{CdTe}$ ,  $E_g = 1.5 \text{ eV}$  at 300K) and  $x = 1$  ( $\text{MnTe}$ ,  $E_g = 3.24 \text{ eV}$  at 300 K). This idealized linear dependence is plotted in Figure 1, curve 1. Several experimental band gap values are displayed in the same figure for comparison. The experimental points after Refs. [9-11] are marked with triangles and circles; our data are shown with squares, featuring very good agreement with the theoretical curve.

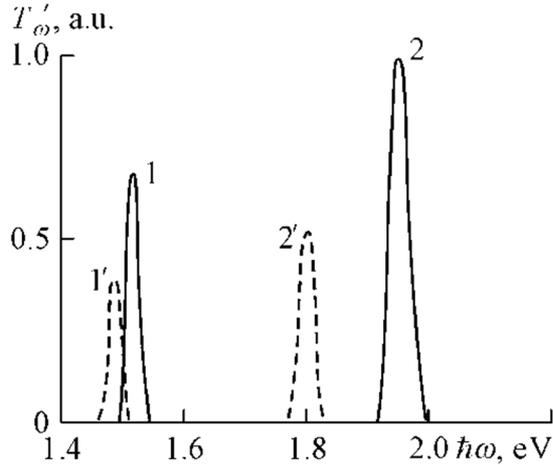
As one can see, for low manganese content  $0 \leq x \leq 0.15$ , the band gap values matching the theoretical prediction were reported in Ref. [11]. These values were obtained from reflection measurements performed over freshly-cleaved surfaces. At the same time, the use of absorption spectra provides considerably underestimated band gap value for a wide range of  $x$  [9, 11]. This problem is predicted by the Bouguer law, in accordance to which the edge of fundamental absorption for a direct-



**Fig. 1.** Band gap variation  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  solid solutions with molar content  $x$ . Theoretical curve 1 was calculated using Eq. (1) with  $E_{g0} = 1.5 \text{ eV}$  and  $a = 1.74 \text{ eV}$ . The experimental points were adapted from the following sources: empty circles, Ref. [9]; filled circles, Ref. [10]; triangles, Ref. [11]. Squares plot our measurements at  $T = 300 \text{ K}$ .

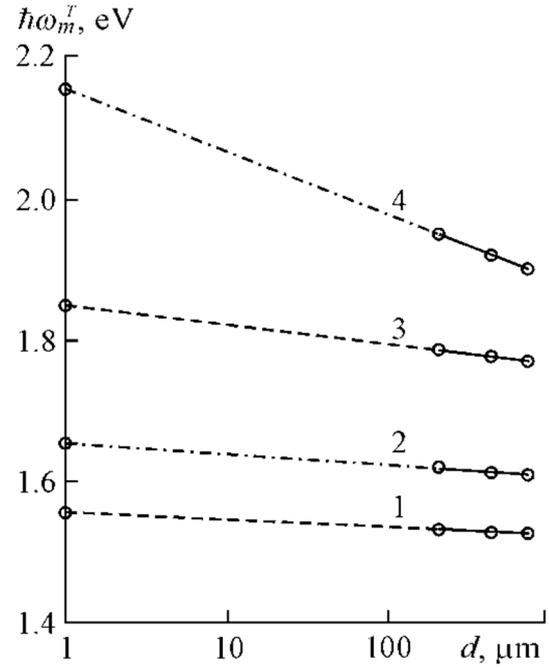


**Fig. 2.** Differential optical reflection  $R'_W$  (curves 1, 2) and transmission  $T'_W$  (curves 1', 2') for CdTe (curves 1, 1') and  $\text{Cd}_{0.6}\text{Mn}_{0.4}\text{Te}$  (curves 2, 2') measured at  $T = 300$  K.



**Fig. 3.** Differential optical transmission  $T'_W$  for the samples of  $\text{Cd}_{0.96}\text{Mn}_{0.04}\text{Te}$  (curves 1, 1') and  $\text{Cd}_{0.6}\text{Mn}_{0.4}\text{Te}$  (curves 2, 2') with thickness of  $750 \mu\text{m}$  (curves 1, 2) and  $170 \mu\text{m}$  (curves 1', 2'), measured at  $T = 300$  K.

band semiconductor suffers red-shift upon increase of sample thickness. The band gap values for  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  reported in Ref. [10] are also underestimated, though they were obtained from reflection measurements. This problem, to our opinion, appears because the  $R'_W$  curves feature considerable sensitivity on sample structural perfection and the quality of surface preparation. We illustrate this point with Figure 2, showing that the curve of  $R'_W$  for  $\text{Cd}_{0.6}\text{Mn}_{0.4}\text{Te}$ , in contrast to that of CdTe, has numerous peaks that considerably complicate definition of the band gap. It is important to mention that the samples used to measure the data for Fig. 2 were prepared using the same technological procedure and



**Fig. 4.** Shifting of differential transmission peaks for different thickness of  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  samples, measured for the following Mn contents: 1)  $x = 0.04$ , 2)  $x = 0.10$ , 3)  $x = 0.25$  (3) and 4)  $x = 0.40$ . All measurements were carried out at  $T = 300$  K.

their surfaces were mirror-reflective upon visual inspection.

In contrast to  $R'_W$  curves, the differential spectra of optical absorption  $T'_W$  featured a single band centered at  $\hbar\omega_m^T \approx E_g$  for all samples produced in this study (Fig. 3). As one can see from the figure, the position of  $\hbar\omega_m^T$  shifts as sample thickness varies, in full accordance with predictions provided by Bouguer law.

The empirical formula describing the experimental dependence of band gap on the sample thickness  $d$  is reported in Ref. [12]:

$$E_g(d) = E_g - b \lg d \text{ [eV]}. \quad (2)$$

Here parameter  $\beta$  determines the slope of a segment plotted in coordinates  $E_g(d) - \lg d$ , and the value of  $E_g$  is obtained as an intersection of the aforementioned segment with the energy axis for  $\lg d = 0$ . The latter corresponds to  $d = 1 \mu\text{m}$ , which is important value of thickness as for semiconductor samples with  $d \leq 1 \mu\text{m}$  optical transmission for energies lower than band gap value becomes almost independent on  $\hbar\omega$ . As one can see from Figure 4, Eq. (2) holds well for all  $\hbar\omega_m^T(d)$  data produced for the samples of solid solutions studied in this paper. Linear extrapolation of the corresponding segments up to intersection with the ordinate axis provides the band gap value for solid solutions, which fits well the theoretical prediction for the entire range of chemical composition studied (Fig. 1, curve 1 for theoretical data and squares for the experimental data), proving high potential of modulation spectroscopy for

defining the band gap of semiconductor compounds.

thickness. The linear extrapolation of  $E_g(d)$  plots is then used to define the band gap of semiconductor material.

## Conclusions

We illustrate a successful application of modulation spectroscopy to define band gap of semiconductors. The suggested methodology has considerable benefits in comparison with other optical methods. The precision of obtained band gap values depends on the type of spectra being measured, which in the first place is defined by the quality of the sample surface. For the freshly-cleaved surfaces, it is more convenient to use the differential reflection spectra. For less-perfect surfaces, the most viable approach will be to measure differential transmission spectra for a set of samples with different

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## Застосування модуляційної спектроскопії для визначення ширини забороненої зони твердого розчину Cd<sub>1-x</sub>Mn<sub>x</sub>Te

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Для визначення ширини забороненої зони монокристалічних твердих розчинів Cd<sub>1-x</sub>Mn<sub>x</sub>Te, властивості яких змінюються з молярним складом  $x$  та якістю підготовки поверхні, використано модуляційну спектроскопію. Виявлено, що для таких зразків доцільно вимірювати диференційний спектр пропускання, основний пік якого регулюється складом  $x$  та товщиною підкладки  $d$ . Відповідно, потрібно виміряти  $E_g(d)$  принаймні для трьох зразків однакового складу та різної товщини. Використовуючи такі дані, екстраполяцією залежності  $E_g(d)$  в логарифмічній шкалі у точці перетину з віссю енергії  $\lg d = 0$  отримано значення ширини забороненої зони, що відповідає товщині зразка 1 мкм.

**Ключові слова:** напівпровідник, ширина забороненої зони, модуляційна спектроскопія.