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Temperature shift of the transmission edge in CdTe and Zn_3As_2, determined by the wavelength modulation method*

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A measuring setup has been made to determine spectral dependences for the coefficients of transmission and reflection and the derivatives of those dependences by the wavelength modulation method. The derivative of the transmission spectrum of CdTe and Zn_3As_2 with the 70–300 K temperature range has been measured and the magnitude of dE_g/dT for those compounds determined.

Introduction

The development of the studies on energy structure of semiconductors requires a continuous improvement of the measuring techniques. The relative measurements are more and more frequently replaced by the absolute measurements, while the modulation methods supplement the static methods. A common feature of all the modulating methods of spectroscopy is the fact that the subject of measurements is the derivative of the response (for instance, transmission or reflection) with respect to a chosen parameter. By applying the phase-sensitive detectors the high accuracy of such measurements may be achieved. According to the choice of the differentiating variable all the modulation methods may be divided into two groups:

1. The methods of wavelength (or frequency) modulation, in which the wavelength is the differentiating variable (see, for instance, [1,2]).

2. The methods of external condition modulation, in which the differentiating variable is an external perturbation applied to the sample, like deformation [3, 4], temperature [5], electric field [6,7] or magnetic field [8].

The measuring system described in the paper is based on the technique of the wavelength modulation. This method does not distroy the sample state and is pretty simple in technical realization, while the results obtained in this way allow to increase considerably the accuracy of the optical parameters determination in semiconductors.

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Measuring setup

The measuring setup has been built on the basis of a SMP-2 monochromator and consists of two independent parts (fig. 1):

— the system for absolute measurements of the reflection and transmission coefficients at the temperatures ranging from the liquid helium to the room temperature (described in detail in [9]);

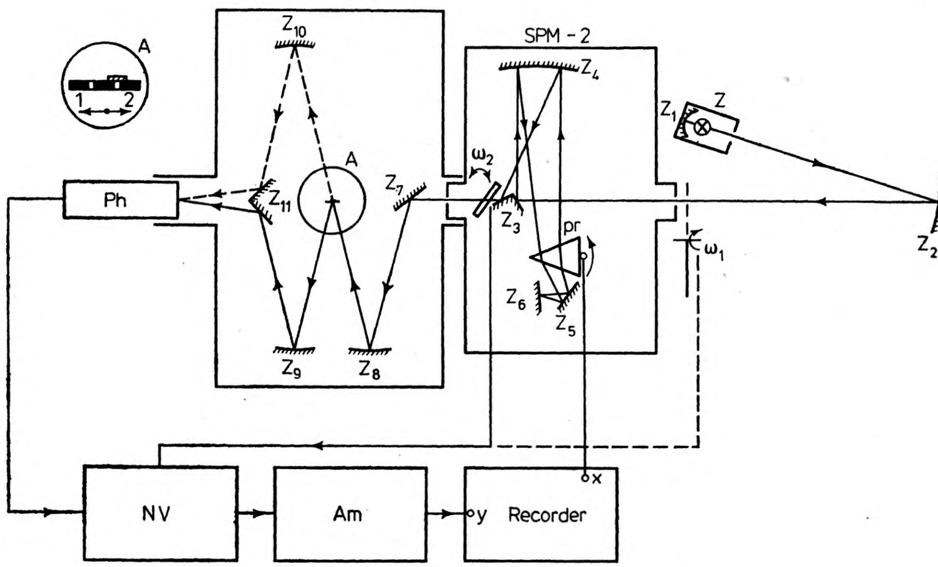

Fig. 1. Scheme of the measuring system

$Z_1, Z_2, Z_4, Z_8, - Z_{10}$ — spherical mirrors, $Z_3, Z_5, Z_6, Z_7, Z_{11}$ — plane mirrors, Z — source of radiation halogen or deuterium lamp or heated silite bar, ω_1 — amplitude modulation frequency, ω_2 — wavelength modulation frequency, *Ph* — photomultiplier (detector), *NY* — phase-sensitive device, homodyne nanovoltometer, *Am* — amplifier

— the modulation attachment with the equipment described in details in [10, 11].

Both the system and its modulating attachment have been designed at the Institute of Physics, Technical University of Wrocław. The system presented enables the measurement of the absolute coefficient of reflection for the incidence angle of the radiation falling on the sample less than 6°. The measurement of transmission is performed at normal incidence of the radiation.

A monochromatic light beam is focussed on the sample surface with the help of the mirror Z_8. The beam passing through the sample falls onto the mirror Z_{10} and being directed by the surface of the prism Z_{11} falls next on the surface of the detector. In this time the mirror Z_9 is diaphragmed. The radiation reflected from the sample during the reflection measurement falls onto the mirror Z_9 and after reflection from Z_{11} hits the detector surface.

The sample is fastened in a special holder, which may be put into two accurately defined positions; in the first one the radiation falls onto the sample (measurement of the passing or reflected beam intensity), in the second position it passes through the aperture of the area equal to that of illuminated sample and falls on the mirror Z_{10} (measurement of the beam incident on the sample). The mirrors Z_9 and Z_{10} are identical, so far as their parameters and their surface quality are concerned, the same being true also for the mirror surfaces of the prism. In this system the following devices are used: FQC-51 and FEU-62 photomultipliers for the 0.2–1.2 μm range and detectors of $Cd_xHg_{1-x}Te$ type produced at the Institute of Physics, Technical University of Wrocław for the longer (up to 16 μm) wavelength range. The cryostat specially adopted, and described in [12], enables the measurements within a broad temperature range — from the liquid helium to the room temperature. Within the applicability range of the photomultipliers it is possible to perform measurements for the monochromator slit width of about 0.02 mm which corresponds to a maximal error of beam energy determination equal to 0.0015eV [9]. With the $Cd_xHg_{x-1}Te$ detectors the slits applied allow to carry out the measurements with errors less than 0.005 eV [9].

To obtain a spectrum differentiated by the method of wavelength modulation a monochromatic light beam with the modulated wavelength should be used. The wavelength modulation may be realized in a number of ways, for instance, by using a plane parallel plate [13]. This method utilizes a parallel shift of the monochromatic light beam which occurs after passing through the plate positioned under a small angle with respect to the incident light wave direction. In order to obtain the light wavelength modulation the plate is put into vibrational motion arround the axis perpendicular to the light beam incidence direction. The plate is located within the monochromator close to its exit slit (fig. 1). A periodical displacement of the splitted spectrum across the exit slit realized by putting the plate into motion results in the respective wavelength modulation. The modulation depth of the light wavelength depends upon the maximal angle of the plate inclination, while the modulation frequency is consistent with the frequency of the plate vibration. The plates are made of a small dispersion material. In the system described both the quartz plate and NaCl plates are applied. The principle of operation and the details of the construction of light wavelengths modulator are exactly described in the paper [10].

Four measurements had to be performed in order to obtain the spectral distribution of the transmission coefficient derivative by the wavelength modulation method, since the spectral transmission distribution is overlapped by the sensitivity spectrum of the detector and the energy distribution spectrum of the wave incident on the sample. In the case when the light flux is not interrupted by the modulator and only the wavelength emerging from the monochromator is modulated the energy of the wave incident on the sample is proportional to

$$I(\lambda+\Delta\lambda\sin\omega_2), \tag{1}$$

where: I — beam intensity, λ — wavelength, $\Delta\lambda$ — modulation depth, and ω_2 — the wavelength modulation frequency.

After passing through the sample the light beam energy is proportional to

$$T(\lambda+\Delta\lambda\sin\omega_2)I(\lambda+\Delta\lambda\sin\omega_2), \tag{2}$$

where T — transmission coefficient.

The signal from the detector, on which the passing beam is falling, is proportional to the quantity

$$S(\lambda+\Delta\lambda\sin\omega_2)T(\lambda+\Delta\lambda\sin\omega_2)I(\lambda+\Delta\lambda\sin\omega_2), \tag{3}$$

where S — detector sensitivity.

The phase-sensitive measuring device (homodyne) tuned to the frequency ω_2 will measure the signal proportional to the expression

$$T\cdot I\frac{dS}{d\lambda}+S\cdot I\frac{dT}{d\lambda}+S\cdot T\frac{dI}{d\lambda}. \tag{4}$$

For the reference beam falling on the detector without passing through the sample the signal at the measuring device will be proportional to the sum

$$S\frac{dI}{d\lambda}+I\frac{dS}{d\lambda}. \tag{5}$$

By switching-on both the wavelength modulation and the wave amplitude modulator we may measure the signals proportional to $S(\lambda)\cdot I(\lambda)$ and $S(\lambda)\cdot T(\lambda)\cdot I(\lambda)$, respectively. If the amplitude modulation is switched-on the phase-sensitive device is adjusted to detect the signal of frequency ω_1, while the plane-parallel plate of the wavelength modulator is positioned perpendicularly to the direction of the monochromator optical axis. By dividing the expression (4) by the product $S(\lambda)\cdot T(\lambda)\cdot I(\lambda)$, and the expression (5) by the product $S(\lambda)\cdot I(\lambda)$, and the next substracting the quantities from each other we obtain $dT/T\cdot d\lambda$. This ratio represents correctly only the extreme positions in the spectrum. An increase of the accuracy may be achieved by determining the $dT/d\lambda$ and taking advantage of the measured dependence $T(\lambda)$.

The measurements and discussions

The measurements have been carried out in two stages. In the first stage the aim was to check the measuring system. The cadmium telluride (CdTe) was chosen as a testing material as its energy structure is well known. In the second stage a poorly known semiconductor Zn_3As_2 was examined.

The samples of the material were prepared in a standard way described in other papers, for instance in [14]. Only in the case of Zn_3As_2 the production of very thin samples appeared to be difficult and the respective solution has been reported in [15]. The CdTe samples of thickness about 100 μm and of Zn_3As_2 of thickness about 80 μm have been used to the measurements.

For achieving the proper signal-to-noise ratio the spectral width of the beam and the modulation depth have been minimized so that these values be close to each other. In this case the minimum error occurs which is determined by the resolving power of the system [16]. This error did not exceed 0.0004 eV when using the photodetectors and was equal to 0.01 eV for the $Cd_xHg_{1-x}Te$ detectors.

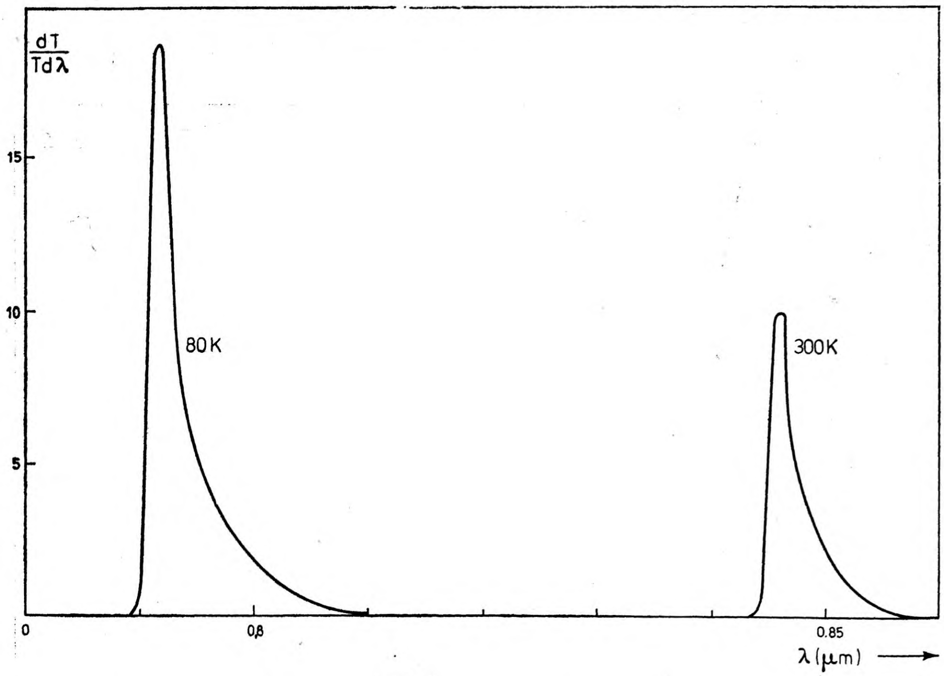

Fig. 2. Dependence $dT/Td\lambda$ upon the wavelength for CdTe at the temperatures 80 and 300 K

Fig. 2 presents the examplified dependences of the transmission derivative on the wavelength obtained for CdTe by the above technique. The maximum of the derivative corresponds to the maximal slope of the transmission curve. This occurred for the absorption coefficient equal to $a \approx 2 \cdot 10^2$ cm^{-1}. Energy corresponding to this maximum may be associated with the energy gap value. The following values have been obtained in this way: $E_g = 1.47 \pm 0.01$ eV at 300 K, and $E_g = 1.56 \pm 0.01$ eV at 80 K. The error of determining E_g is greater than that of determining the maximal transmission slope because absorption edge is not analysed directly. From the maximal values of the ratio $dT/Td\lambda$ it follows that with the increase of the temperature transmission edge slope diminishes. The values obtained are in good agreement with the values given in the paper [14], i.e. 1.45 eV for 295 K and 1.55 eV for 77 K.

The zinc arsenide (Zn_3As_2) is a relatively less known semiconductor from the $A^{II}B^{V}$ group. The up to now results of the examination of this compound show some deviations from each other. In particular, the published evaluations of the energy gap fluctuate within the limits 0.86–1.2 eV (if determined from the electric measurements [16–19]) and 0.93–1.1 eV (if determined from the optical measurements at the room temperature [19–26]).

In the present paper the temperature shift of the energy gap in Zn_3As_2 has been examined within the range of 80–300 K by using the method of wavelength modulation. Fig. 3 shows examplified spectral dependences

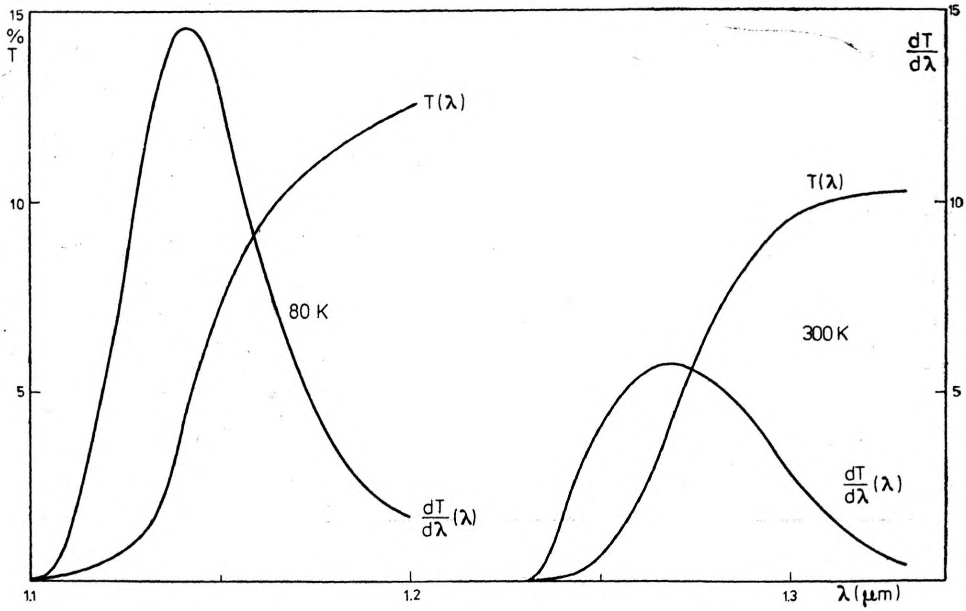

Fig. 3. Spectral dependences for transmission T and its derivative $dt/d\lambda$ for Zn_3As_2 at the temperatures 80 and 300 K

of transmission and its derivative with respect to λ at the temperatures of 80 and 300 K, respectively, while the energy gap in Zn_2As_3 determined from this measurement as the energy corresponding to the maximal slope of the transmission edge ($\alpha \approx 4 \cdot 10^2$ cm^{-1}) amounts to 1.09 ± 0.015 eV and 0.98 ± 0.015 eV at 80 and 300 K, respectively. These values are perfectly consistent with the results reported in [15]. From the results presented it may be seen, that similarly to the CdTe case, the transmission edge slope diminishes with the temperature. Analogical measurements carried out for ten intermediate temperatures (the results of which are shown in fig. 4) allow to present the linear dependence of the energy gap

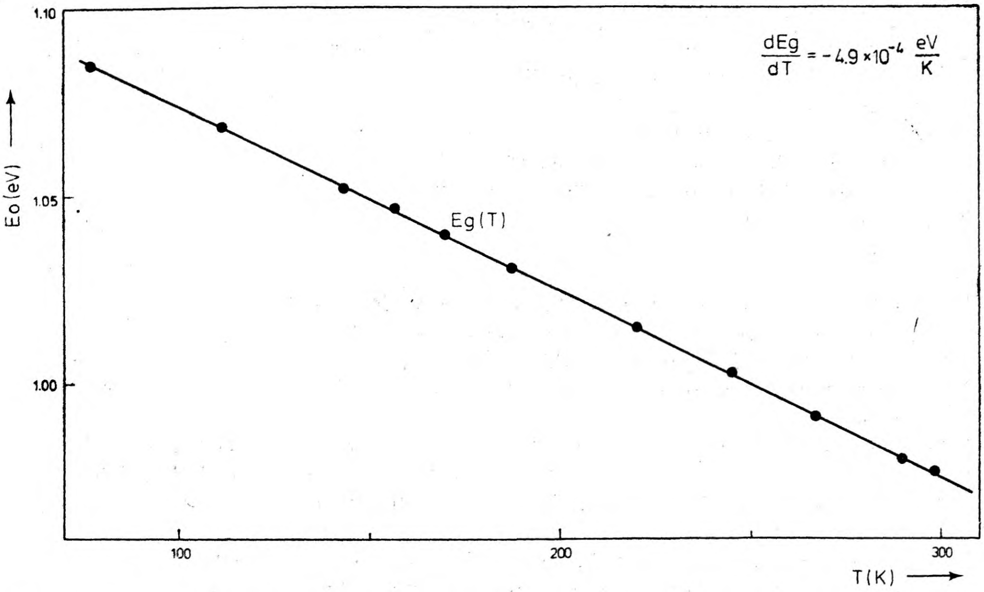

Fig. 4. Dependence of the energy gap in Zn_3As_2 upon the temperature within the 80–300 K range

in Zn_3As_2 within the temperature range 80–300 K. The value of so determined temperature coefficient of the energy gap in Zn_3As_2 amounts to $dE_g/dT = -4.9 \cdot 10^{-4}$eV/K.

The presented method for determination of the energy gap and its temperature dependence allows to increase the accuracy of the energy gap determination and simplifies the performance of the measurements of E_g at the intermediate temperatures between the boiling temperatures of the used gases.

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Температурное смещение ребра пропускания в CdTe и Zn_3As_2, определенное методом модуляции длины волны

Изготовлен стенд для спектральных измерений зависимости коэффициентов пропускания и отражения, а также производных этих зависимостей методом модуляции длины волны. Измерено производное спектра пропускания CdTe и Zn_3As_2 в температурном интервале 80–300 K и определены значения dE_g/dt для этих соединений.