Optica Applicata, Vol. XII, No. 1, 1982

Measuring setup with a GDM-1000 monochromator to measure the anisotropy of optical properties of Zn_3P_2*

ZBIGNIEW GUMIENNY, JAN MISIEWICZ

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

An automatized setup for spectral measurements of the reflection and transmission of the polarized electromagnetic wave within the wavelength range 0.28–1.33 μm was designed and constructed. A grating monochromator of GDM-1000 type was employed, which enabled to achieve the resolving power better than 0.1 meV. This system may be also applied to other spectral measurements, in particular, to examine photoelectric effects as well as the pleochroism and birefringence of anisotropic crystals. In order to check the system suitable measurements of birefringence and dichroism in Zn_3P_2 were made and the anisotropy of photovoltaic effect in the In-Zn_3P_2 contact was examined.

1. Introduction

The optical measurements are one of the most important sources of information about the band structure of semiconductors. The parameters determined by these measurements are applied in all the empirical methods of band structure calculations. Therefore, the design of more and more perfect measurement systems is of great importance.

The design of the experimental setup for examining the optical properties of semiconductors may be based on various principles and depends on the wavelength of the electromagnetic wave, temperature at which the measurements are carried out, the sizes of the samples to be tested and the like. The systems applied most frequently to measure the reflection make use of a convergent beam focussed on the sample surface and incident on it under a small incidence angle to realize an almost normal incidence (5–10°). The measurements may be carried out either in nonmonochromatic or monochromatic light. In particular, the second solution is preferred for measurements at low temperatures. The system described in this paper is adapted to the measurements in monochromatic light. The secondary light source is a GDM-1000 monochromator with a halogen or xenon illuminator. The setup enables an automatical determination of spectral characteristics of both reflection and transmission as well as photoconductance and the photovoltaic effect. These examinations may be carried out in the plane-polarized light and, in particular, the pleochroism and birefringence of anisotropic crystals may be measured.

* This work has been sponsored by Research Project PR-3.8.

2. Measuring setup

The setup is composed of three parts: illuminator, monochromator and measuring chamber (Fig. 1). Due to the fact that the entrance and exit slits of monochromator are positioned side by side the measuring part and the illuminators are located in a common housing.

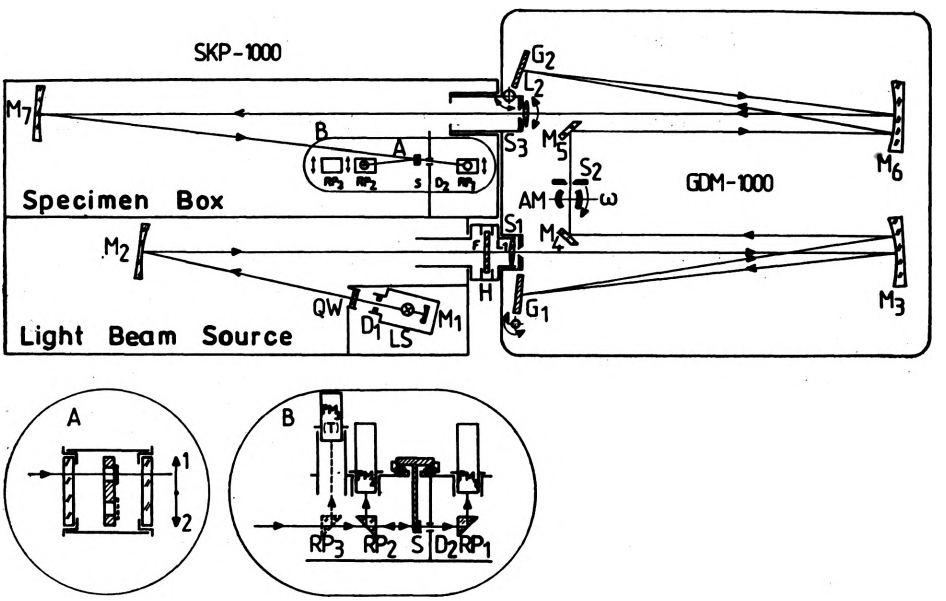

Fig. 1. The configuration of the optical elements in the measuring setup

2.1. Illuminator

As a light source in the visual and near infrared regions a halogen lamp of 150 W was used. The lamp was mounted in a modernized housing of the halogen illuminator. A high pressure xenon lamp installed in an antiexplosive housing was the light source in the visual region. Both the lamps are fed by stabilized d.c. suppliers.

The configuration of the optical elements in the illuminator is shown in Fig. 1. The schematic field (FR) and aperture ray (AR) tracing in the illuminating system are presented in Fig. 2a. In the lamp housing a reflector mirror (M_1) is mounted as well as a circular diaphragm (D_1) restricting the convergence of the light beam entering the system. The lamp housing is cooled by a free air stream. The chamber is separated from the remaining part of the system by a quartz window (QW) to protect the other elements of the illuminator against the dust. A spherical mirror (M_2) images the light source (LS) onto the entrance slit of the monochromator (S_1). In front of the entrance slit a spherical lens (L_1) is placed. This lens avoids the vignetting of the beam by the diffraction grating of the monochromator. The lens is fastened close in front of the monochromator entrance slit in a set (H) of exchangeable glass edge filters. This set of filters couples mechanically the illuminator with the monochromator assuring a light-tight connection.

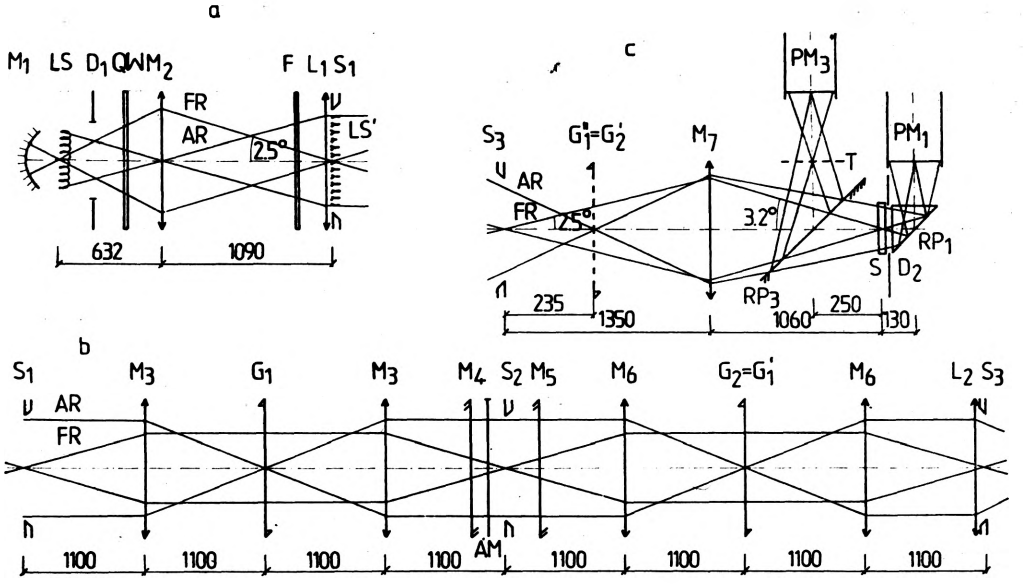

Fig. 2. Ray-trace for the field and aperture rays, respectively: a — for illuminating system, b — for monochromator, c — for measuring chamber

2.2. Monochromator

The configuration of optical elements is shown in Fig. 1 while Fig. 2b presents the trace of the field and aperture rays.

Modulator (AM) assures the chopping of the light stream with the frequency ω = 6–60 Hz. The lens (L_2) located in front of the exit slit (S_3) corrects the curvature of the curved spectral lines caused by the dispersive elements. Because of this the exit slit need not be profiled.

2.3. Measuring chamber

The optical system is closed in a light-tight housing (Fig. 1). Such a solution enables a considerable lowering of the noise level. The optical scheme is shown in Fig. 2c.

A spherical mirror (M_7) images the exit slit of monochromator (S_3) onto the surface of the examined sample (S). Simultaneously, the images of the diffraction gratings are projected onto the photocathodes of the photomultipliers (PM). Reflecting prisms (RP_1, RP_2, RP_3) are mounted on movable stages in front of the photomultipliers. In the beam region only those prisms are introduced which are suitable for a given measurement.

The prism RP_1 directs the beam to the photomultiplier, which measures the intensity of light passing through the sample. After the removal of the sample the same photomultiplier may measure the intensity of the reference light beam. The prism RP_2 is used to measure the reflection. The prism RP_3 directs a part of the beam to another photomultiplier which generates the reference signal in the automatic measurement. By applying the prisms of total internal reflection ($R = 100\%$ — independently on the polarization state) to achieve the change of ray direction, the errors due to change of polarization

state occurring usually for flat mirror deflections are avoided. This is of special importance for the examination of anisotropic materials in polarized light, since the possible changes in the type of light polarization after passing through the sample or reflection from its surface do not result in intensity attenuation of the light beam reaching the detector.

During the measurements the examined sample is fastened in a suitable holder or on a cold finger of the cryostat enabling to perform the measurements at the temperature down to 5 K. The cryostat or sample holder is fastened in a nest which may be shifted across the beam cross-section in both the perpendicular directions as well as rotated and inclined. Thanks to such a solution the sample region to be illuminated may be selected arbitrarily without perturbing the run of the rays, and the beam incidence angle may be suitably adjusted.

For automatic measurements a part of the beam is directed toward the photomultiplier PM_3 or the thermocouple (T) (photoelectric measurements) using the prism RP_3. The travel of the stage, to which this prism is fastened, enables the option of the measuring-to-reference-beam-ratio most advantageous for the definite examinations. Due to the fact that the surface of thermocouple is small the latter is located at the possition where the exit slit of the monochromator is imaged. There, the light spot sizes are the same as on the sample surface ($h = 0$–8 mm, $d = 0$–2.3 mm).

3. Methods of measurements

The block scheme of the measuring system is presented in Fig. 3. In addition to the monochromator and the spectral measuring chamber the measuring system includes: two homodyne (or selective) nanovoltmeters, a beam splitter described in [1], a compensating plotter and stabilized supplier of the illuminator and a photomultiplier.

The signals from the detectors A and B are introduced to the input of the nanovoltmeters. Only the separated signals of frequency ω are amplified. In the splitting device

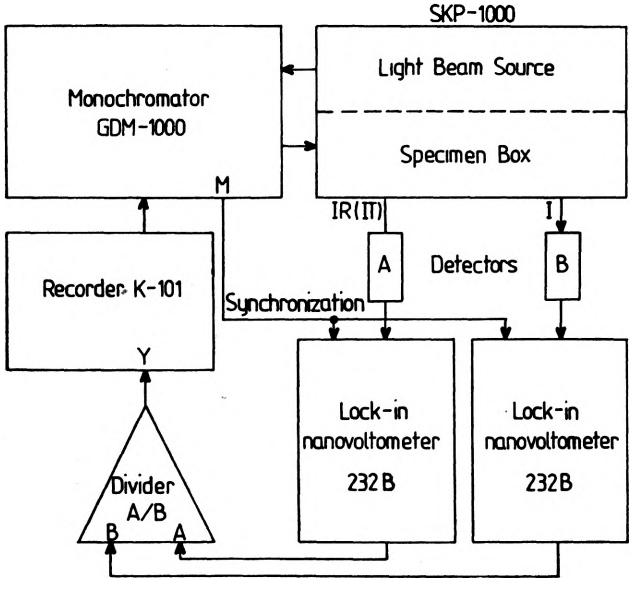

Fig. 3. Block scheme of the setup

the signal A is divided by the reference signal B and the result is recorded by the plotter. If the dividing system is not used, the measurement signal (after having been amplified) is transferred directly to the plotter.

During the measurement of the total light transmitted through the sample S a PM_1 photomultiplier fastened in the holder above the prism RP_1 is used as a detector A. In the case of the reflection coefficient measurement the same photomultiplier (PM_2) is used as the detector but this time it is fastened under the prism RP_2. In both the measurements the reference signal detector B is the photomultipliers PM_3 which is located in the holder above the prism RP_3. This prism divides the front of the beam illuminating the sample (S) and directs a part of the beam toward the detector B.

In the case of photoelectric measurements a thermocouple T is used as a detector, while the measurement signal A comes directly from the sample.

The construction of optical system assures the possibility of performing the measurements of transmission, photoelectric effects, pleochroism and birefringence, for the perpendicular beam incidence onto the samples. In the case of reflection coefficient measurement the angle contained between the optical axis of the beam and the normal to the surface position amounts to 3.2°.

The measurements in the polarized light require some additional conditions. All the windows must be made of the isotropic and strainless material. The plane polarization of light is realized by using the UV polaroids (of Carl Zeiss production) either of UV type working in the 0.28–0.7 μm range or of IR-1.3 type working in the range 0.67–1.33 μm. The polarizer in the rotating holder is placed in front of the prism RP_3 and the analyzer is installed just behind the sample. In order to measure the birefringence the polarizer and analyzer are positioned so that their polarization vectors be perpendicular to each other and directed under the angle 45° to the optical axis of the crystal.

In order to determine the optical sign of the single axis crystal an oriented muster crystal (quartz, for instance) is used. In the setup configuration, like that to measure the birefringence, the muster crystal, oriented so that its optical axis is parallel to the sample, is placed in front of the sample. The analysis of the changes of the runs obtained with and without the standard sample allows also to determine the sign of the crystal examined.

Table

Wavelength range [μm]	Photomultiplier type	Filter type
0.28–0.50	M12 FQS 52 A	BG-24
0.33–0.475	M12 FQS 52 A	BG-12
0.45–0.625	M12 FC 51	VG-9
0.47–0.76	M12 FC 51	GG-5
0.50–0.76	M12 FC 51	GG-14
0.55–0.76	M12 FC 51	OG-5
0.57–0.76	M12 FC 51	RG-1
0.57–1.00	FEU-62	RG-5
0.62–1.11	FEU-62	RG-6
0.69–1.31	FEU-62	RG-7
1.20–1.35	FEU-62	RG-5 + BG-12

The correct exploitation of GDM-1000 monochromator requires the application of a suitable set composed of photomultiplier and filters to eliminate simultaneous illumination of the sample with two wavelengths coming from different interference orders. In the table the available sets of filters and photomultipliers are given which cover the whole spectral range of the used monochromator fulfilling the above condition. What should be taken care of is that

both the photomultipliers used for automatic measurements have the same spectral sensitivity characteristics.

4. Measurements and results

The zinc phosphite belongs to relatively little known materials, which, however, are being intensively examined these days [2]. A particular interest is devoted to the photoelectric properties of this compound [3]. The examinations of the basic optical properties carried out in the nonpolarized light are reported in [4]. From these examinations it follows that the fundamental energy gap is oblique and amounts to 1.315 eV in 300 K and to 1.335 eV in 80 K and 5 K.

Since the elementary cell of Zn_3P_2 has the tetragonal symmetry described by the group D_{4h}^{15}, for a precise determination of the bandstructure it is necessary to perform the meas-

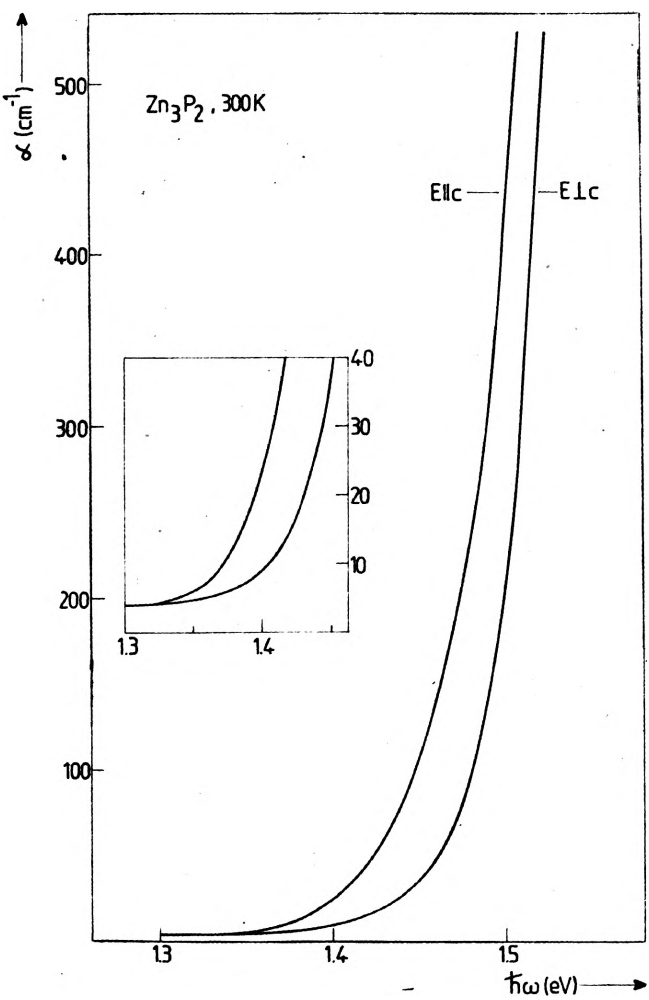

Fig. 4. Illustration of the dichroism in Zn_3P_2 at 300 K

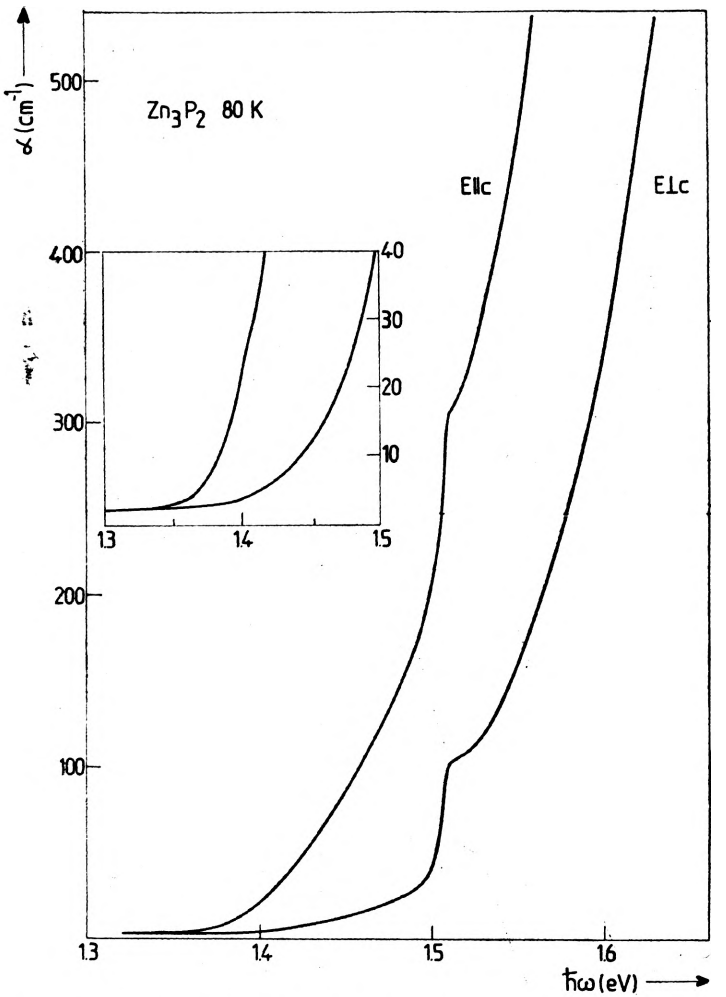

Fig. 5. Illustration of the dichroism in Zn_3P_2 at 80 K

urement in the polarized light on the oriented samples. The basic difficulties making impossible the performance of such examinations for a long time were:

— lack of the measurement setup enabling these measurements to be made with sufficient accuracy,

— lack of sufficiently great uniform oriented crystals of Zn_3P_2.

Recently, however, these difficulties have been overcome. The crystals of Zn_3P_2 were produced from the gaseous phase by Królicki from the Institute of Inorganic Chemistry and Metallurgy of Rare Earths, Technical University of Wrocław (Poland), where they were also preliminary oriented. The oriented cuts of the samples were done at the Institute of Physics, Polish Academy of Sciences in Warszawa. After a standard processing, i.e., polishing and etching in the bromium-in-methanol solution described in [4] the samples of the thickness 100–2200 μm and of the surface area of 3–6 mm^2 with the axis c parallel to the sample surface have been obtained. The absorption coefficient was calculated ac-

cording to the known formula

$$T = \frac{I_t}{I_0} = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)}, \tag{1}$$

where t is the sample thickness, while R denotes the reflection coefficient.

Figure 4 illustrates the dichroism of Zn_3P_2 at the temperature of 300 K and for the absorption coefficient α ranging from 4 to 530 cm^{-1}. Below the energy of 1.315 eV no dichroism is observed. This energy seems to indicate the fundamental optical transition for $E \parallel c$ polarization. The energy distance between the edges for both the light polarization reaches the maximal value of about 39 meV for the absorption coefficient α equal to about 50 cm^{-1}. For the greater value of α both the edges approach slightly to one another.

The behaviour of both the edges at 80 K, shown in Fig. 5, is quite different. The maximal distance between them amounts to about 80 meV and occurs for α at the level of

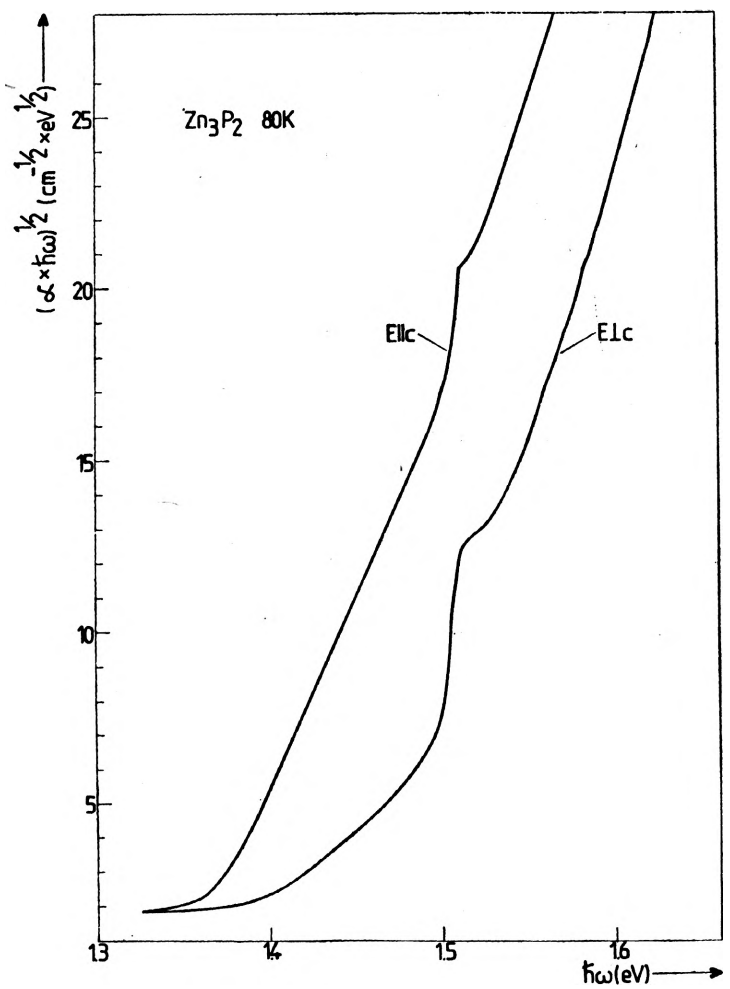

Fig. 6. Dependence of $(\alpha\hbar\omega)^{1/2}$ upon $\hbar\omega$ at 80 K

40 cm^{-1}. For the energy of 1.51 eV in both the polarizations we observe a distinct threshold. Its presence has been stated earlier in the examinations in the nonpolarized light [4]. Below the energy of 1.335 eV a decay of dichroism is observed, therefore, it seems that this indicates the beginning of the fundamental transitions for $E \parallel c$ at 80 K. A distinct temperature-induced shift of the edge for $E \parallel c$ at the presence of a much weaker dependence of the edge for $E \parallel c$ upon the temperature speaks for the fact that these edges correspond to the interband transitions occurring at different points of the Brillouin zone. The lower-energy edge at the temperature 80 K fulfils the following relation (see Fig. 6):

$$(\alpha\hbar\omega)^{1/2} \sim \hbar(\omega - \omega_0). \tag{2}$$

This relation is characteristic of the oblique optical transitions. This seems to confirm the results given in [4, 5], where the optical transitions of the oblique type are stated.

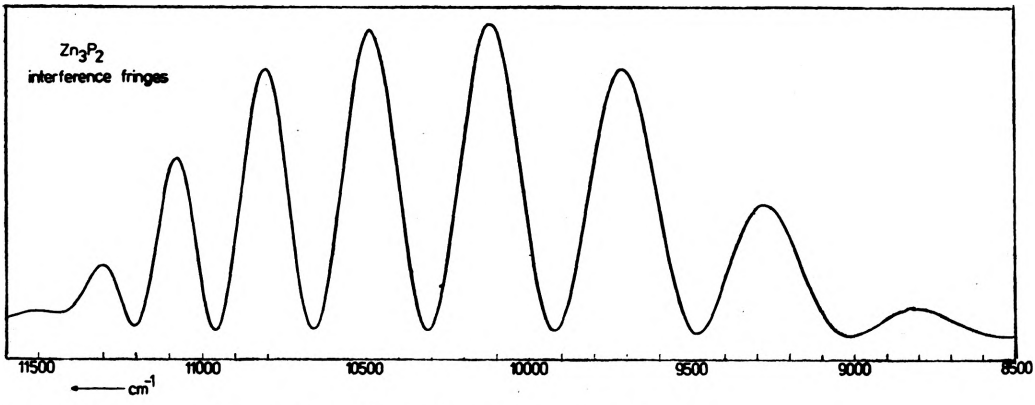

Fig. 7. Interference fringes illustrating the birefringence in Zn_3P_2

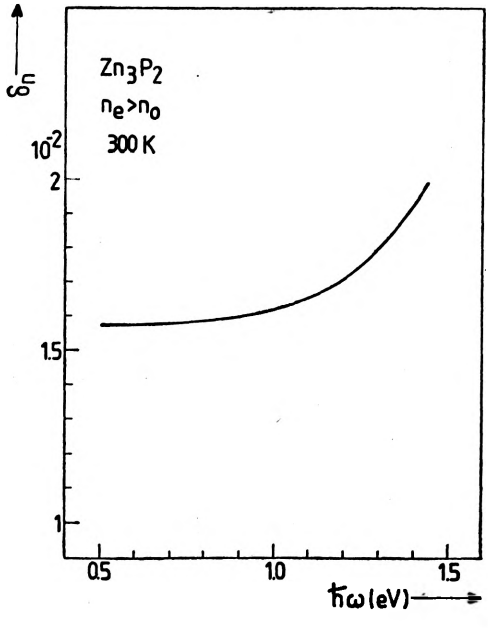

Fig. 8. Birefringence in Zn_3P_2

The examinations of birefringence and the determination of its sign are based on the interference method. An exemplified picture of the interference fringes is shown in Fig. 7. Complementary measurements of birefringence in the range of 1.2–2.5 μm were carried out in the system with SPM-2 monochromator [6]. The spectral characteristic of birefringence was determined in the way described in [7]. The obtained dependence is presented in Fig. 8. For small energies the birefringence tends to a constant, while a strong dispersion is obtained when approaching the absorption edge. The sign of birefringence is determined to be positive by using the standard quartz crystal.

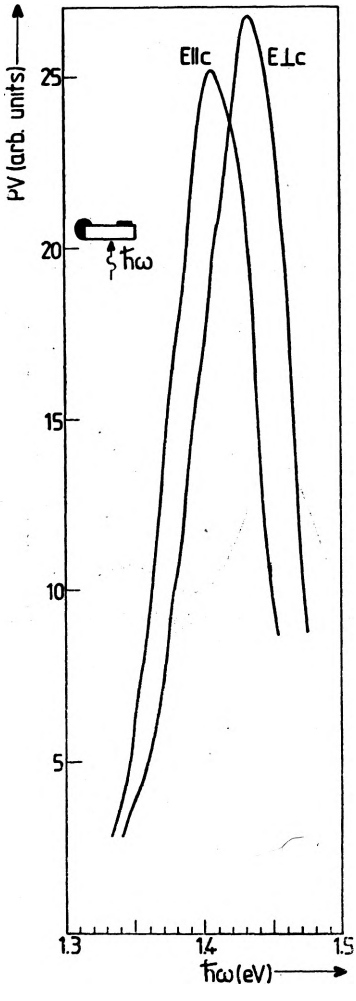

Fig. 9. Anisotropy of the photovoltaic affect at the junction In-Zn_3P_2. Configuration illuminating the sample

The anizotropy of Zn_3P_2 crystals manifests itself also in photoelectrical properties of this material. The measurements of the spectral dependences of the photovoltaic effect in the In-Zn_3P_2 junctions were carried out in [3]. In Fig. 9 the results of these measurements for both the light polarizations are shown. An exact analysis of both optical and photochemical examination will be possible after calculating the band structure of this compound taking account of the real symmetry of its cell.

The results presented are partly a repetition of the examinations performed earlier by the Solid State Group at the Institute of Experimental Physics, University of Warsaw [8]. A very good agreement has been stated.

Acknowledgements – The authors thank heartily Doc. Dr. J. M. Pawlikowski for helpful discussions. Warm words of gratitude are addressed to Doc. Dr. A. Kubica for valuable remarks and help during construction and mounting of the setup. We feel indebted to Dr. F. Królicki for supplying the single crystals of Zn_3P_2 and to Mrs. N. Mirowska, Mr. K. Nauka and Mr. M. Kiwus for the assistance during measurements.

References

[1] BECLA P., Report No. 297/78, Institute of Physics, Technical University of Wrocław, Wrocław 1978 (unpublished), in Polish.

[2] PAWLIKOWSKI J. M., Infrared Physics **21** (1981), 181.

[3] PAWLIKOWSKI J. M., MIROWSKA N., BECLA P., KRÓLICKI F., Solid State Electron. **23** (1980), 755.

[4] PAWLIKOWSKI J. M., MISIEWICZ J., MIROWSKA N., J. Phys. Chem. Solids **40** (1979), 1027.
[5] ŻDANOWICZ L., ŻDANOWICZ W., PETELENZ D., KŁOC K., Acta Phys. Polon., **A57** (1980), 159.
[6] BECLA P., GUMIENNY Z., MISIEWICZ J., Opt. Appl. **11** (1979), 143.
[7] WARDZYŃSKI W., Proc. Roy. Soc. **A260** (1961), 370.
[8] MISIEWICZ J., GAJ J. A., Phys. Stat. Solidi **B105** (1981), K23.

Received March 24, 1981

Применение измерительной системы с монохроматором GDM-1000 для исследования анизотропии оптических свойств Zn_3P_2

Описан запроектированный и созданный автоматизированный стенд для спектрального измерения отражения и пропускания поляризованной электромагнитной волны в диапазоне длин волн 0,28–1,33 мкм. Был использован решётчатый монохроматор типа GDM-1000 при достижении разрешающей способности, лучшей чем 0,1 мэВ. Система может использоваться для других спектральных измерений, в частности фотоэлектрических эффектов, а также исследований плеохроизма и двупреломления анизотропных кристаллов. Для проверки системы проведены измерения двупреломления и дихроизма Zn_3P_2, а также исследована анизотропия фотовольтаического эффекта на контакте In-Zn_3P_2.