Optica Applicata, Vol. XII, No. 3-4, 1982

Birefringence and dichroism in Zn_3P_2

ZBIGNIEW GUMIENNY, MANFRED KIWUS, JAN MISIEWICZ

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

Birefringence and dichroism measurements in Zn_3P_2 at 10, 80 and 300 K are described. A simple theoretical model is used to explain the obtained results.

1. Introduction

Zn_3P_2 has lately received growing attention due to its interesting photoelectric properties [1]. Its fundamental band structure parameters are not exactly known yet. Zn_3P_2 crystallizes in the tetragonal systems with D_{4h}^{15} space symmetry. The ratio of lattice parameters approximately equals to $\sqrt{2}$. The existence of a noticeable optical anisotropy of this compound is obvious and was first observed in paper [2].

In this work the birefringence and dichroism investigations are presented more precisely

2. Birefringence and dichroism

In tetragonal crystals we observe the difference between refractive indices for the light polarized parallel and perpendicular to the optic axis c. This is a natural birefringence:

$$\delta n = n_{\parallel} - n_{\perp}. \tag{1}$$

The birefringence is connected with the dichroism, i.e., the difference between absorption coefficients for the light polarized parallel and perpendicular to the axis c:

$$\delta \alpha = \alpha_{\parallel} - \alpha_{\perp}. \tag{2}$$

The measurement of birefringence is equivalent to determining the difference between real part of dielectric constants which are connected with the difference of imaginary parts and further with dichroism. The connection is made by Kronig-Kramers relations [3]. We can write

$$\delta n(E) = \frac{\hbar c}{\pi} \int_0^\infty \frac{\delta \alpha(\xi)}{\xi^2 - E^2} d\xi , \tag{3}$$

where E - photon energy.

By measuring the birefringence we can obtain information about the dichroism plot in the photon energy range not attainable in transmission measurement. It makes possible the analysis of optical transitions which occur in this energy range.

Two simple models are used to describe dichroism plot [3]:

- Delta function type model

$$\alpha_{\parallel} - \alpha_{\perp} = A\,\delta(E - E_0), \tag{4}$$

where A - constant, E_0 - characteristic energy.

- Step model

$$\alpha_{\parallel} - \alpha_{\perp} = \begin{cases} \Delta\alpha; & E \geq E_p, \\ 0; & E < E_p. \end{cases} \tag{5}$$

Using formula (3) we can fit experimental results of birefringence to the above models and interpret the types of the dominant optical transitions.

3. Measurements

The most useful and exact method of determining the birefringence as a function of wavelength is based on the measurements of interference fringes in polarized light. This method was applied by WARDZYŃSKI [4]. It is the following idea: The plane parallel plate of crystal with the axis c lying in the plane of the sample is placed between the crossed polarizers so that the angle between the axis c and direction of the electric vector be 45° (Fig. 1). Both polarized, parallel and perpendicular to the axis c parts of the light entering into the crystal are at identical phase and of the same amplitude. If the refractive

indices for these polarizations were different, the change of phase would be equal to

$$\varphi = \frac{2\pi d}{\lambda} \delta n, \tag{6}$$

where λ - wavelength of light, d - thickness of crystal, and δn - birefringence.

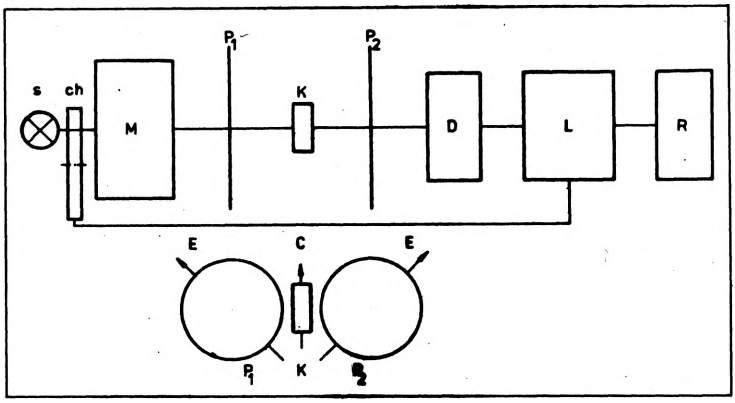


Fig. 1. Scheme of optical equipment used for birefringence measurements:
s - source of light, ch - chopper, M - monochromator, P_1, P_2 - polarizers,
K - crystal, D - detector, L - lock-in nanovoltmeter, R - recorder

Polarization of the light coming out from the crystal depends on the value. For

$$\varphi = 2k\pi \tag{7}$$

transmission of the light passing by polarizer P_2 is theoretically equal to zero.

When the value $d \cdot \delta n$ is appropriately large in comparison with λ we will obtain measurable interference fringes with the following condition for minimum transmission

$$2k\pi = \frac{2\pi d}{\lambda_m} \delta n, \tag{8}$$

where k - integral number.

Figure 2 presents an example of these fringes for the Zn_3P_2 sample.

When δn does not depend on λ (this is fulfilled for a sufficiently great wavelength) we get the linear relation

$$\frac{1}{\lambda_m} = \frac{1}{d\,\delta n}\,k. \qquad (9)$$

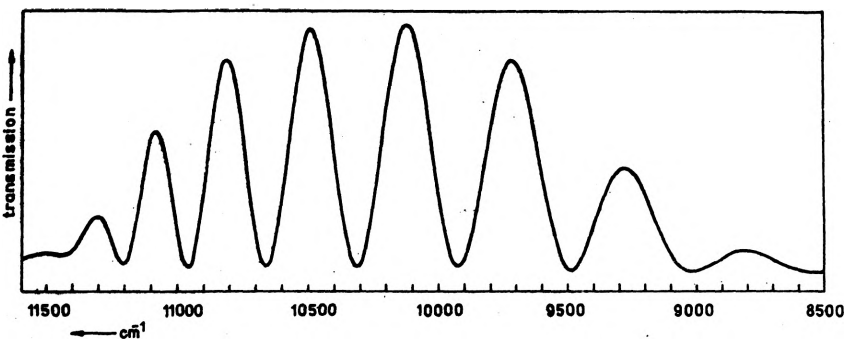


Fig. 2. Example of interference fringes for Zn_3P_2

Figure 3 presents these relations for one sample. The long-wave part of this plot marks the beginning of the k-number. From this we obtain the value of birefringence n for successive λ_m, using the formula (9). Analogical procedure may be performed for the maxima of spectrogram (it has been made to verify the correctness of determining k-values).

The sign of the birefringence may be determined by using for example an oriented quartz crystal. Both crystals with parallel optics axes are placed in the system presented in Fig. 1. Interference fringes are condensed, which means that the signs of both crystals are positive.

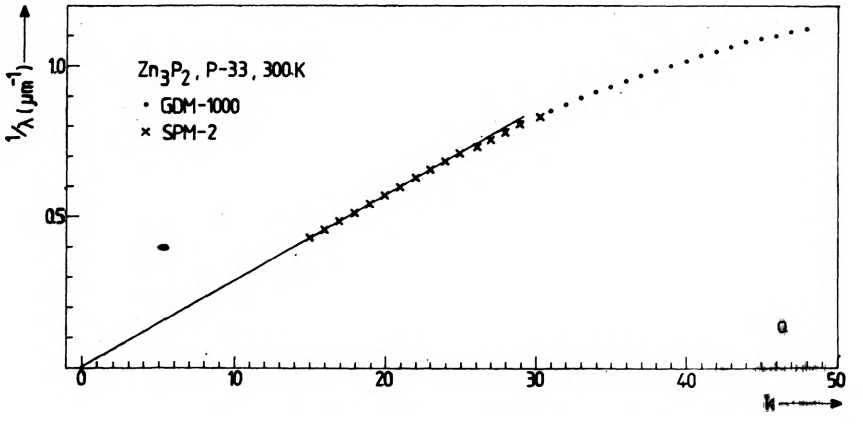


Fig. 3a

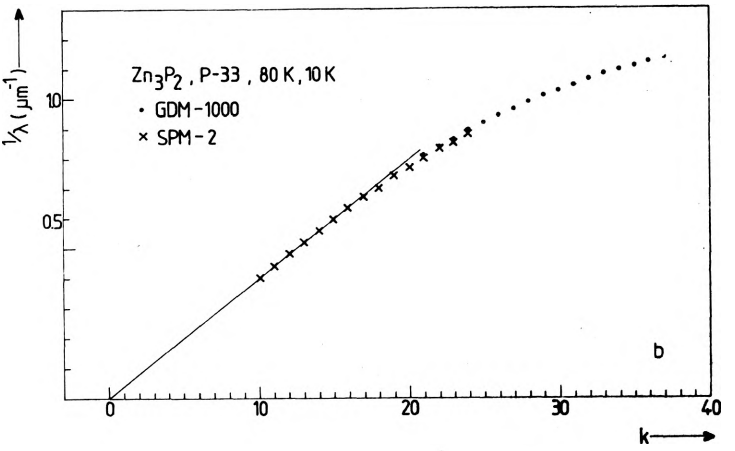


Fig. 3 a,b. Dependence $1/\lambda$ on the number of minimum transmission

Our measurements were carried out on several well oriented Zn_3P_2 samples prepared by a gas transport method [5]. We present results obtained on P-21 (thickness 1150 μm) and P-33 (thickness 2220 μm).

Spectral investigations are performed using special equipment with a GDM-1000 monochromator, described in detail in [6] on the 0.85-1.3 μm waverange and typical set-up with SPM-2 monochromator [7] on the 1.2-2.5 μm waverange.

4. Results and discussion

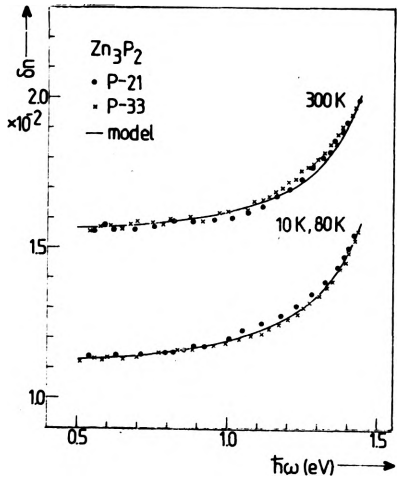
Spectral plots of birefringence obtained by the method described above are presented in Fig. 4. Not measurable difference between results obtained at 80 and 10 K is observed. Both plots have the same character. They tend to a constant value for decreasing energy and show a strong dispersion when approaching the absorption edge. A noticeable decrease of δn when the temperature decreases from 300 to 80 K is an interesting phenomenon.

We made some attempts to fit numerical experimental results to both theoretical models. Using relation (3) into (4) and (5) we obtain

$$\delta n(E) = \frac{\hbar c}{\pi} \frac{A}{E_0^2 - E^2}, \tag{10}$$

for delta function type model of dichroism, and

$$\delta n(E) = \frac{\hbar c}{2\pi} \frac{\Delta \alpha}{E} \ln \frac{E_p + E}{E_p - E}, \quad \text{for step dichroism model.} \tag{11}$$



We obtained a satisfactory fit for the delta function type model with the assumed constant level of birefringence δn_0, connected probably with transitions at energy greater than E_0 (Table).

Characteristic energy gap E_0 agreed sufficiently with the value of the direct energy gap: 1.51 eV at 300 K, 1.645 eV at 80 K, and 1.685 eV at 5 K

Fig. 4. Birefringence of Zn_3P_2 samples, $n_{\parallel} > n_{\perp}$. Curves describe delta function type theoretical models

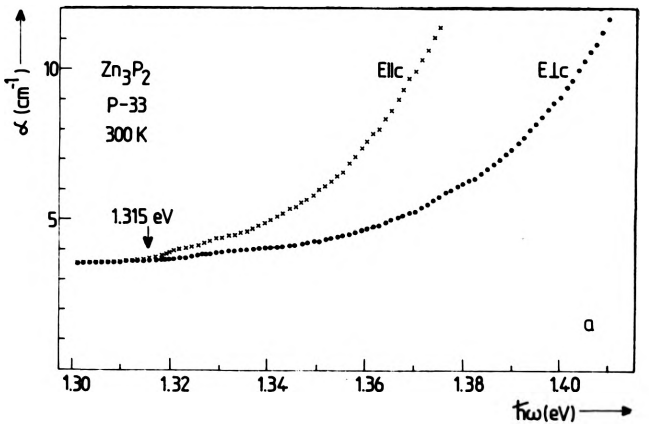
[8]. Investigations of the absorption edge in unpolarized light and wide temperature and absorption coefficient ranges have been performed in [8].

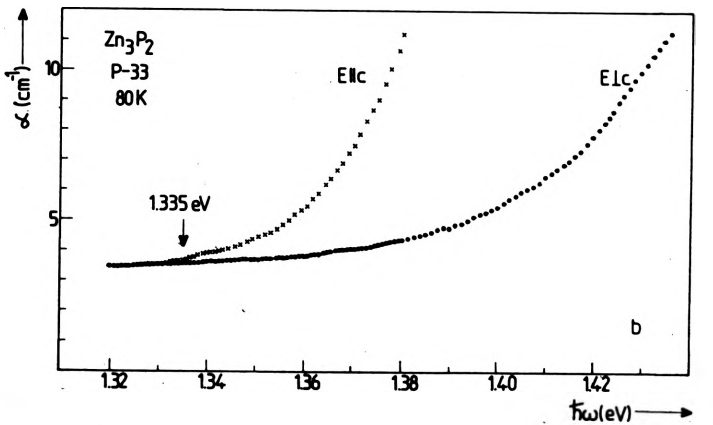
Table

Temperature [K]	300	80 and 10
E_0 [eV]	1.60	1.64
A [$cm^{-1} \times eV$]	445	573
δn_0	0.0144	0.0098
σ	1×10^{-4}	3×10^{-5}

σ - square standard deviation experimental points from theoretical curve.

A dichroism in the range of $3\text{-}5 \times 10^2$ om^{-1} was presented in [2]. In this work we concentrate only on small values of absorption coefficients, performing transmission measurements with high spectral resolution. Two edges: for $E \parallel o$ (at lower energy) and for $E \perp o$ (at higher energy) are observed. At 300 K for photon energy lower than 1.315 eV curves for both polarizations coincidence (within the range of error). A similar situation occurs at 80 K and 10 K for photon energy lower than 1.335 eV. These energy marks remain in very good agreement with energies interpreted as indirect optical transitions in [8].





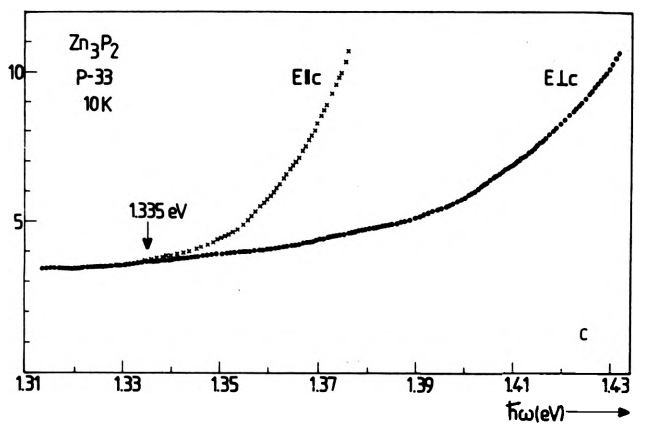


Fig. 5 a,b,c. Pictures of dichroism for thick (2220 μm) sample of Zn_3P_2

References

[1] PAWLIKOWSKI J.M., Infrared Phys. 21 (1981), 181.

[2] MISIEWICZ J., GAJ J.A., Phys. Stat. Sol.(b) 105 (1981), K 23.

[3] GAJ J.A., Proc. 3-rd Nat. Symp. II-VI Semicond.

[4] WARDZYŃSKI W., Proc. Roy. Soc. A260 (1961), 370.

[5] KRÓLICKI F., private communication.

[6] GUMIENNY Z., MISIEWICZ J., Optica Applicata 12 (1982), 35.

[7] MISIEWICZ J., Doctor's Thesis. Technical University of Wrocław, 1979 (unpublished).

[8] PAWLIKOWSKI J.M., MISIEWICZ J., MIROWSKA N., J. Phys. Chem. Solids 40 (1979), 1027.

Received April 14, 1982

ДВУПРЕЛОМЛЕНИЕ И ДИХРОИЗМ В Zn_3P_2

Представлены результаты исследований двупреломления и дихроизма в Zn_3P_2. Для интерпретации полученных результатов применена соответствующая теоретическая модель.