Peculiarities of temperature behaviour of the optical birefringence in α-ZnP_2 crystals

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Abstract

Using the Senarmont technique, the optical birefringence of tetragonal α-ZnP_2 single crystals is studied in the temperature range 20 -180 °C. Under certain conditions that depends on thermal prehistory of the sample, the birefringence exhibits a quasi-oscillatory temperature behaviour. The explanation of the effect related to the multiple light reflections is considered quantitatively, involving the data for the optical absorption. The hypothesis is shown to have serious difficulties. An alternative explanation of the effect related to the existence in α-ZnP_2 of incommensurate structure is critically analyzed.

Key words: crystal optics, birefringence, absorption, multiple reflections, incommensurate structure

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Introduction

Zinc diphosphide, ZnP_2, is a representative of a large family of semiconductor A^{II}-B^{V} materials [1]. Two crystal modifications exist for ZnP_2 which are very different in their physical properties: a tetragonal α-modification and a monoclinic β-modification. Single crystals of α-ZnP_2 belong to the point symmetry group *422*. They attract a permanent attention of researchers since 1960s and so their various characteristics are widely known, including the structural ones [1-4]. According to the review by Cummins [5], α-ZnP_2 crystals are probably incommensurate. The incommensurateness is of an "interface" type, i.e. the material has regions of simple crystalline structure separated by periodic or quasi-periodic defects such as stacking faults, antiphase boundaries or twin boundaries (see [3]).

Among the optical properties, at least the absorption, reflection and the luminescence parameters [1,6,7], the refractive indices [8,9], linear birefringence (LB) [10,11] and optical activity [10,12] are reported in literature. α-ZnP_2 manifests a remarkable Faraday effect and is also believed to be a promising nonlinear optical material [13]. Despite the extensive previous studies on the crystal optical properties of α-ZnP_2, we feel them still necessary. The reasons are that the mentioned above works and, in particular, the studies [10-12], have not been, in many respects, detailed enough and, moreover, the analysis of the corresponding experimental accuracy testifies a need in its further increasing.

The goal of the present work is to investigate in detail the temperature behaviour of LB in α-ZnP_2. We have also performed complementary measurements of optical absorption parameters in order to check a possibility for the influence of different optical properties on each other.

Experimental methods

We prepared a 1.41 mm thick (100) sample of α-ZnP_2 for the experiments, using standard methods for polishing. The sample surfaces were of a good optical quality. To avoid the effect of "smearing" the optical phase retardation Δ ($\Delta = (2\pi d / \lambda)\Delta n$, with d being the thickness of the sample, λ the light wavelength, and Δn the LB) through the cross section of the laser beam and the relevant "noises" in the Δ value measured in the course of a polarimetric experiment (see [14]), special care was paid to a plane parallelism of sample surfaces which was not worse than $2 \cdot 10^{-4}$ rad. A 50 mW He-Ne laser ($\lambda = 632.8$ nm) was chosen as a light source for the polarimetric experiment. The absorption spectra were measured in the range of 350 - 800 nm with the aid of standard equipment that included the halogen lamp as a light source and the ZMR-3 device as a monochromator.

We studied the LB of α-ZnP_2 in the range from room temperature up to 180 °C. The temperature was controlled with the accuracy of about 0.03 °C and measured with the copper-constantan thermocouple. The polarimetric measurements were performed in a regime of "quasistatic" temperature variations, i.e. the temperature of the sample was being changed continuously, at a constant scan rate dT/dt changing from 0.5 to 36 °C/h. All the data were obtained in the heating run.

The experimental method used for calculating the LB value was the well-known Senarmont technique. The standard PSCA polarimetric apparatus was the same as that utilized by the authors in the earlier studies [14,15]. The working formula for the phase retardation varying with temperature is as follows:

$$\Delta = 2\chi_C , \qquad (1)$$

where χ_C is the analyzer scale reading that corresponds to the emergent light polarization azimuth and is measured under the condition of the minimum light intensity in the PSCA system. Since the χ_C values are known up to a constant additive 360°m (with m being an integer), only relative Δ values are experimentally accessible. As we did not find the dilatation data for α-ZnP_2 and so were unable to make thermal expansion corrections to the phase retardation, the relative LB was calculated as $\delta(\Delta n) = \lambda\Delta/(2\pi d)$, assuming a constant sample thickness at all temperatures. It is known that the relevant corrections are about 1% or less for most of the crystals. The resulting inaccuracies for the LB caused mainly by the temperature instabilities and the "noises" in the phase retardation through the beam cross section were evaluated as being of the order of 5×10^{-7}–10^{-6}.

Temperature dependences of LB

Our first experiment was performed after keeping the sample at room temperature for about three months. The corresponding results for the temperature dependence of LB derived at relatively rapid temperature variations ($dT/dt = 36$ °C/h) are presented in Fig.1. It is seen that, in general, the LB increases monotonously with increasing temperature, the mean thermooptical coefficient being $d(\Delta n)/dT \approx 5.5\times10^{-5}$. A more careful study reveals a "fine structure" of the temperature curve consisting in ill-defined oscillatory (sometimes step-like) changes (see also Fig.1, inset). As far as we know, this type of behaviour has never been reported for α-ZnP_2, probably

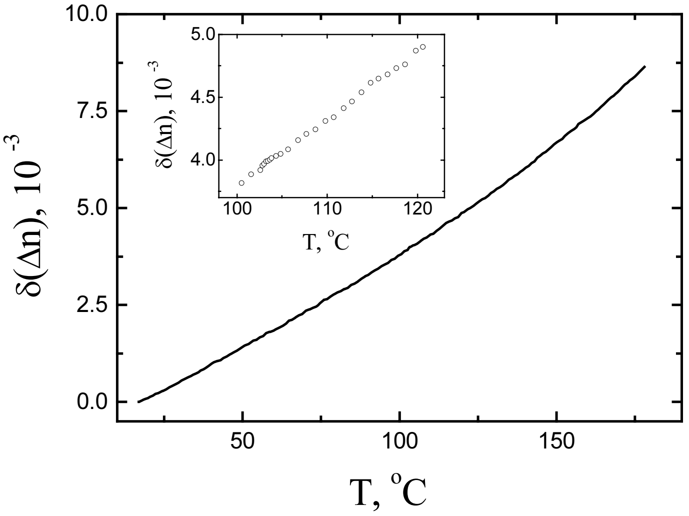

Fig.1. Temperature dependence of LB for the (100) α-ZnP_2 crystal with arbitrarily taken origin (temperature variation rate dT/dt = 36 °C/h). The inset shows greatly enlarged high-temperature part of the curve.

because of far lower experimental accuracies achieved [8,10]. The behaviour is peculiar for all the temperature range under test, while its main features remain almost the same.

Since a number of phase transitions have been earlier observed in the regions of 34–42 °C and 104–110 °C (see, e.g., [3,12,16]), we have paid special attention to those regions. However, no clear anomaly which can be attributed to the phase transformations in α-ZnP_2 (e.g., a notable discontinuity or a change in the temperature slope) is visible there, except for the weak peculiarity at 103–105 °C (see Fig.1, inset).

In order to elucidate better the phenomenon, we have undertaken numerous repeated experiments at different temperature scan rates and different thermal treatment conditions. It has appeared that the details of temperature behaviour of the LB depends strongly upon thermal prehistory of the sample. During a lasting thermal treating, those details have been changing from almost monotonous temperature dependence to almost regular "quasi-harmonic" oscillations, though the "intermediate regimes" have also occurred. We illustrate the analysis with only the two examples (Fig.2 and 3). Fig.2 shows almost perfect temperature oscillations with the period $\Delta T \sim 0.7$ °C recorded at essentially slower rate than that characteristic for the results of Fig.1 (dT/dt = 2.1 °C/h). Notice that the oscillatory behaviour has apparently proved to be a consequence of a long-term preliminary keeping of the sample in the temperature region under test. The same is also true of the other results not presented here. The curves 1 to 3 in Fig.3 which correspond to successive experiments carried out at different scanning rates manifest only slight irregularities but not a periodic behaviour.

Remembering the possibility for the existence of incommensurate superstructure in α-ZnP_2 and the so-called "temperature memory" effects (see [5]), we have attempted, to no avail, to find those effects. In particular, the sample temperature has been kept stable at 35.8 °C for 12 h and at 35.9 °C for 9 h, respectively, before recording the curves 2 and 3 in Fig.3. Nevertheless, the optical memory effect, typically specific for the incommensurate systems in the vicinity of the stabilized temperature points, is not observed in Fig.3.

Optical absorption

A natural explanation for the inmonotonous behaviour of LB that comes immediately to

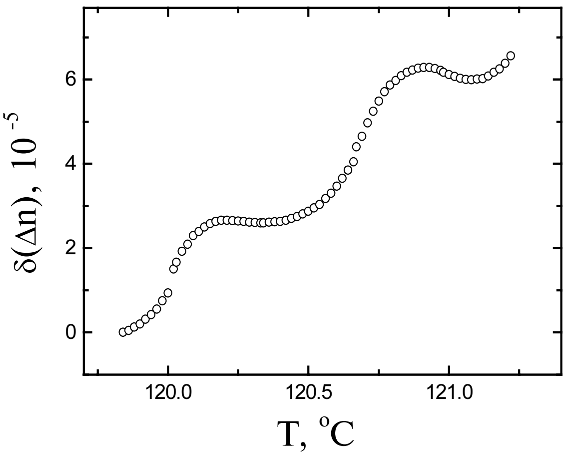

Fig.2. Temperature dependence of relative LB value for α-ZnP_2 crystal kept for three days in the region of 120 - 122 ^{0}C (dT/dt = 2.1 ^{O}C/h).

mind is the light interference in the sample owing to a multiple reflection (MR) effect (see, e.g., [17,18]). However, the assumption requires a detailed analysis, since it is known that the MR takes place for relatively thin crystal plates with high-quality, plane-parallel surfaces and, moreover, the effect is hindered by the absorption and scattering of light the crystal bulk and the boundary surfaces. It is not certain enough if α-ZnP_2 crystals, in general, and our sample, in particular, completely meet all these conditions.

According to [14,19], the MR effect manifests itself in such a way that the oscillations determined by the factor

$$R\cos 2\varphi = \left(\frac{\overline{n}-1}{\overline{n}+1}\right)^2 \cos\frac{4\pi d}{\lambda}\overline{n} \qquad (2)$$

are superimposed with a monotonous temperature behaviour of the phase retardation and the LB. In formula (2), R denotes the reflectivity defined approximately by the mean refractive index $\overline{n}$, and φ the absolute phase of electromagnetic wave. The oscillations arise mainly from the temperature variations of $\overline{n}$,

$$\overline{n}(T) = \frac{\partial\overline{n}}{\partial T}dT\ . \qquad (3)$$

Of course, formula (2) is valid for a perfect (non-scattering) and transparent crystal sample.

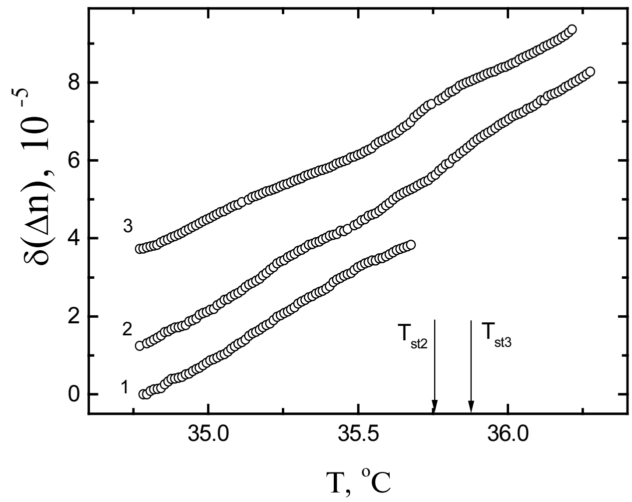

Fig.3. Temperature dependences of relative LB value for α-ZnP_2 crystal measured at different conditions: curve 1 - dT/dt = 0.5 ^{O}C/h, curve 2 - dT/dt = 0.7 ^{O}C/h, curve 3 - dT/dt = 1.3 ^{O}C/h. Before experiments 2 and 3 the temperature of sample was stabilized at T_{st1} = 35.8 ^{O}C and T_{st1} = 35.9 ^{O}C, respectively (see explanations in text).

In case of absorption available, the R coefficient should be replaced with bR, where b= $exp(-kd)$ and k is the absorption coefficient [19]. Furthermore, in order to take into account an inevitable light scattering effect on the MR, one is forced to introduce a purely phenomenological effective scattering parameter a, such that the final "reflectivity" becomes as abR .

Keeping in mind a possibility for deviations of the absorption coefficient from one sample to another, we measured the absorption of α-ZnP_2 in the visible region for the two alternative light wave polarizations. The k value was calculated from the measured transmittance J, using the relationship which, in its turn, accounts the MR [20],

$$J = \frac{(1-R)^2}{exp\,kd - R^2\,exp(-kd)}, \quad (4)$$

where the dispersion data for the R parameter may be easily found in literature.

The results are depicted in Fig.4, together with the parameter of dichroism Δk. As seen from Fig.4, our operating wavelength is located in the region of relative transparency, the residual absorption being approximately 3 cm^{-1}, while the dichroism ~ -0.06 cm^{-1}. On the other hand, our data are not in the best agreement with the results [6] (~ 7 cm^{-1}) and [7] (12 cm^{-1}) available in literature. In this respect, it is not clear if the authors [6,7] accounted for the MR effect when interpreting their initial data. Anyway, our attempt to calculate k with the limiting version of the formula (4) that neglects the MR effect, yielded in negative absorption coefficients (~ 0.5 cm^{-1}) in the 600 - 700 nm region.

Quantitative simulations of LB and discussion of results

Now that all the necessary optical parameters are known, we are in a position to analyze quantitatively the influence of the MR on our LB data. The working formula (1) of the Senarmont technique is then modified to [14]

$$tan\,2\chi_C = \frac{2(1+2R\cos 2\varphi)\tan(\Delta/2)}{1-(1+4R\cos 2\varphi)\tan^2(\Delta/2)}. \quad (5)$$

If one continues to interpret the Senarmont data using the approximate formula (1), then the temperature dependences of the measured phase retardation Δ_{meas} ($\Delta_{meas} = 2\chi_C$ where χ_C is determined according to (5)) look as in Fig.5 and 6. The theoretical curves of Fig.5 and 6 are plotted, assuming a monotonous temperature dependence of the "true" phase retardation Δ

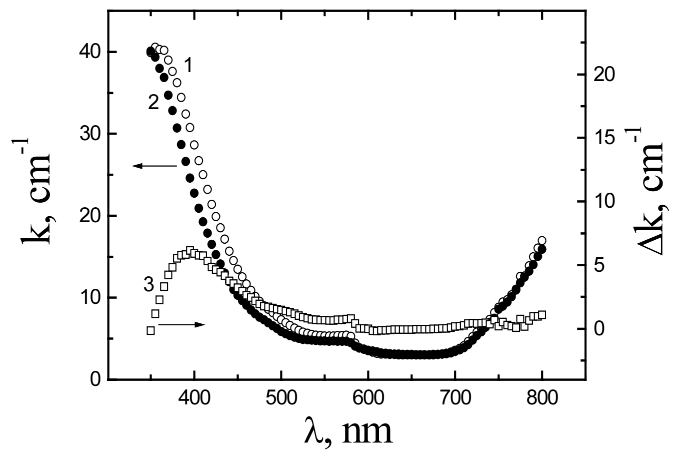

Fig.4. Dispersion of absorption coefficient for α-ZnP_2 crystal. Curve 1 - light polarization **E** $\|$ **c**, curve 2 - **E** $\perp$ **c**, curve 3 - dichroic difference $\Delta k = k_{\|} - k_{\perp}$.

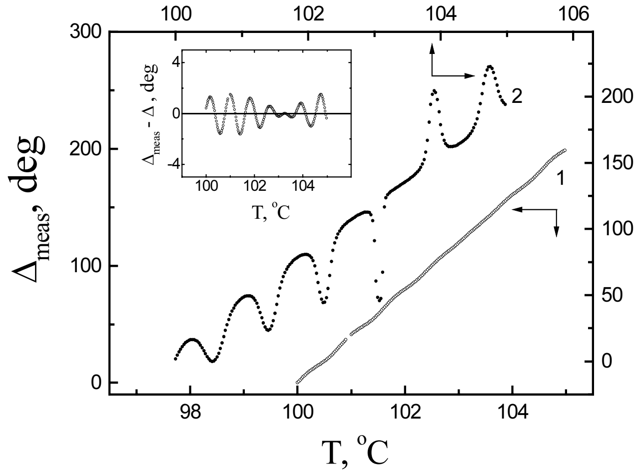

Fig.5. High-temperature dependences of relative phase retardation for α-ZnP_2 crystal calculated with the assumption of MR effect present ($d\bar{n}/dT$ = 2.7×10^{-4} $^oC^{-1}$, see text). Curve 1 - *ab* = 0.05, curve 2 - *ab* = 0.9. The inset shows the difference between the phase retardations measured in the presence (Δ_{meas}) and absence (Δ) of MR at *ab* = 0.05.

and using the thermooptical coefficients $d\bar{n}/dT = 1.4\times10^{-4}$ $^oC^{-1}$ and 2.7×10^{-4} $^oC^{-1}$ (see [8,9] and formula (3)) for the low- and high-temperature regions of the curve in Fig.1.

As seen from Fig.5, the value $ab = 0.9$ has nothing to do with our experimental data and so is completely unreliable. At the same time, the range of $ab = 0.05$ - 0.2 yields in the behaviour (see curve 1 in Fig.5 and curves 1-3 in Fig.6) which indeed resembles that observed in the experiments. Using the "unified" $k \sim 10\ cm^{-1}$ value ($b \approx 0.25$), one gets a=0.2–0.8. If the value $k \sim 3\ cm^{-1}$ is taken, then the appropriate a parameter should be about 2.7 times less. The oscillation amplitude for the retardation is of the order of 1 - 4 deg (see Fig.5, inset).

However, the MR hypothesis has too many weak points to explain exhaustively the inmonotonous temperature behaviour of the LB in α-ZnP_2. First, the oscillation amplitude should decrease with increasing temperature due to approaching the fundamental absorption edge and increasing absorption coefficient, whereas we observe the amplitudes almost independent of temperature. Second, we have preliminary results for the analogous temperature oscillations of the optical activity in α-ZnP_2, and the corresponding amplitudes can be explained only with the a parameter values less by an order of magnitude. Furthermore, the periods for the LB and the optical activity are different, although they must have been described by the same phase factor $\cos 2\varphi$ (see formula (2)). Third, the theory gives the periods for the oscillations approximately 1.5 - 2 times larger than the experimental values. It is hardly believable that the refractive index data in the works [8,9] are found with such a low accuracy that the accuracy in determining $d\bar{n}/dT$ coefficient may reach the values of 1.5 - 2. Moreover, we have observed that the periods do not notably depend on temperature, again in contrast to the theory which predicts twice less periods at high temperatures where $d\bar{n}/dT$ increases (see formula (3)). Finally, it is not understood why the reflectivity and the MR effect should depend on thermal prehistory of samples, the fact observed many times during our experiments.

Quite another explanation for the quasi-oscillatory behaviour of the LB arises from the availability of incommensurate modulation in α-ZnP_2. As said above, the materials with the interface type of the modulation often exhibit

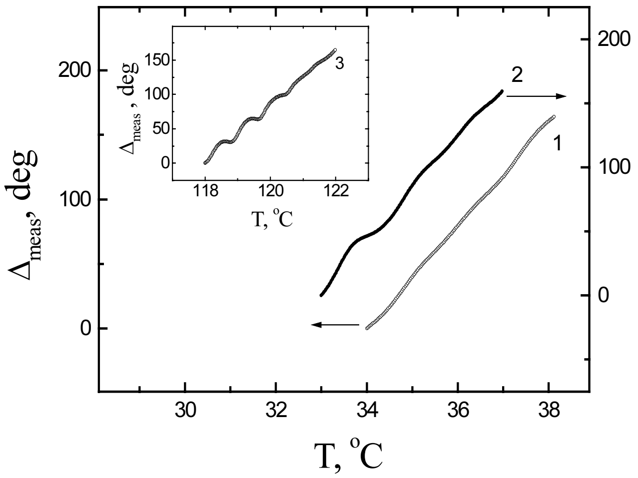

Fig.6. Low-temperature dependences of relative phase retardation for α-ZnP_2 crystal calculated with the assumption of MR effect present ($d\overline{n} / dT = 1.4\times10^{-4}$ °C^{-1}, see text). Curve 1 - *ab* = 0.1, curve 2 - *ab* = 0.2. The inset shows the corresponding high-temperature dependence with the same *ab* = 0.2 and $d\overline{n} / dT = 2.7\times10^{-4}$ °C^{-1}.

regions of a regular commensurate crystal structure separated by planar defect formations. The appropriate long-periodic superstructure may result from the antiphase boundaries observed in fact in α-ZnP_2 [3]. Such a system may exhibit a "devil's staircase" temperature behaviour of different physical parameters [5]. As a result, the optical properties may be influenced by the interaction of the incommensurate structure with available defects, resulting in an inmonotonous temperature behaviour. At least, this reasoning justifies a strong dependence of the observed effects on the thermal history, as is always the case with the "incommensurate structure-defects" system.

In this relation, the fact that the thermal memory has not been observed is not decisive, because it may be caused by a high mobility of defects which have enough time to "relax" during the term between the temperature stabilization and the successive experiment. Indeed, the results [21] show a very high mobility of the main structural defects (Zn^{2+} ions) along the direction **c** of incommensurate modulation. Summing up, the hypothesis of the oscillatory-like temperature behaviour of the LB in α-ZnP_2 arising from the incommensurate superstructure does not contradict the experimental data. However, it needs both further experimental evidence and still lacks quantitative considerations.

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