

ON THE NATURE OF GYROTROPY IN PARATELLURITE

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An excitonic band (A -band), which is responsible for the dispersion of optical rotatory power in the transparent region and in the region of absorption edge ($h\nu < E_g$), has been revealed in the fundamental spectrum of paratellurite. The parameters of an optically active oscillator – the dissociation energy $G_{\text{ex}} = 115$ meV and the exciton radius $r_{\text{ex}} = 8.0$ Å – have been determined. The proximity of r_{ex} to the lattice parameter c of the TeO_2 chain structure indicates that excitons of intermediate radius can be actual in paratellurite.

1. Introduction

Paratellurite (TeO_2) single crystals demonstrate the strong optical activity along their optical axis. The gyrotropy of those crystals is known to be connected with their crystalline structure; however, the mechanism of the phenomenon has not been elucidated till now. For the solution of this problem to be obtained, detailed optical spectral researches and the decoding of the energy structure of a crystal are needed. Clarifying the nature of a basic optically active oscillator in TeO_2 and determining its parameters constitute the main purpose of this work.

2. Methods of researches

Specimens with various thicknesses, which were cut off normally to their optical axis, were studied. The spectra of rotatory power and edge absorption were measured on an automated spectrophotometric installation (Fig. 1). Single crystals were grown up by the Czochralski method. All specimens concerned were left-handed. The measurement accuracy for the specific rotatory power was $\pm 2\%$; and the accuracy of the orientation of specimens was not lower than $\pm 0.5^\circ$.

The absorption spectrum $K(E)$ in the depth of the fundamental band was calculated by applying the Kramers–Kronig relations (KKRs) to the measured reflection spectrum [1]. In the range of long-wave absorption edge, the calculated spectrum was in good agreement with experimentally measured one (Fig. 2).

While measuring the dispersion of rotatory power, the transmission spectrum of the system “polarizer – optically active crystal – analyzer” (PCA, Fig. 3) was registered.

The transmission function of the PCA system looks like

$$I = I_0 \left[\cos \varphi \cos \psi + \frac{\alpha_0}{l} \sin \varphi \left(\sin \psi - \frac{a}{p^2} \sin(2\theta + \psi) \right) \right]^2 + \left[\frac{a}{pl} \sin \varphi \cos(2\theta - \psi) \right]^2, \quad (1)$$

where

$$\varphi = \frac{\omega}{2c} (n_+ - n_-) d = kd \frac{n_+ - n_-}{2},$$

$$p = \frac{1}{n_+} + \frac{1}{n_-}; \quad l = \left| \frac{1}{n_+} - \frac{1}{n_-} \right|,$$

I_0 and I are the light intensities at the input and the output of the system, respectively; d is the thickness of a specimen; ψ is the angle between the directions of oscillations in a polarizer and an analyzer; θ is the angle between the main directions of a polarizer and the crystal; α_0 is a scalar characterizing the optical activity of the crystal; a is a parameter characterizing the linear anisotropy of the crystal; and n_+ and n_- are the refractive indices for left-hand and right-hand circularly polarized light waves, respectively.

The transmission spectra of the PCA system were registered in the geometry $\gamma = 0$ ($\vec{k} \parallel \vec{c}$), when $a = 0$ and $\alpha_0 = l$, and provided $\psi_{\pm} = \frac{\pi}{2} \pm |\beta|$:

$$T_{\pm\beta}(\lambda) = \cos^2 \left[\varphi(\lambda) - \frac{\pi}{2} \mp |\beta| \right] = \sin^2 [\varphi(\lambda) \mp |\beta|]. \quad (2)$$

The difference spectrum is

$$\Delta T(\lambda) = T_{-\beta}(\lambda) - T_{+\beta}(\lambda) = \sin [2\varphi(\lambda)] \sin |2\beta|, \quad (3)$$

whence the specific rotatory power is

$$\vartheta(\lambda) = \frac{1}{2d} \arcsin \left[\frac{\Delta T(\lambda)}{\sin |2\beta|} \right]. \quad (4)$$

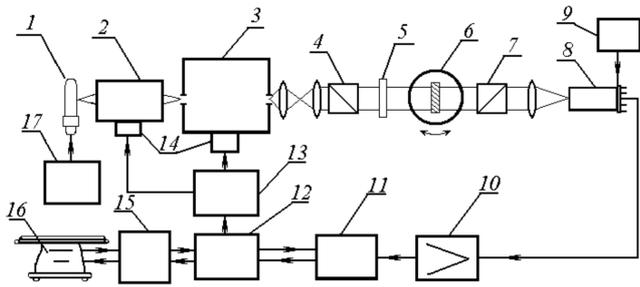


Fig. 1. Scheme of the automated spectropolarimetric installation: 1 – light emission source (a deuterium lamp or an incandescent lamp); 2 – illuminator; 3 – MDP-12 monochromator; 4 – polarizer; 5 – $\lambda/4$ -plate; 6 – turn table for the fixation of a specimen; 7 – analyzer; 8 – photomultiplier (FEU-100 or FEU-62); 9 – power unit for photomultiplier; 10 – dc amplifier; 11 – digital voltmeter; 12 – input-output device; 13 – control block; 14 – step motors; 15 – computer; 16 – printer; 17 – power unit for light emission source

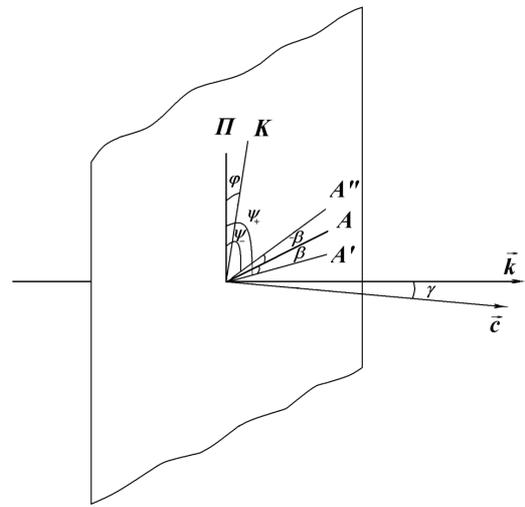


Fig. 3. Basic vectors of the PCA system

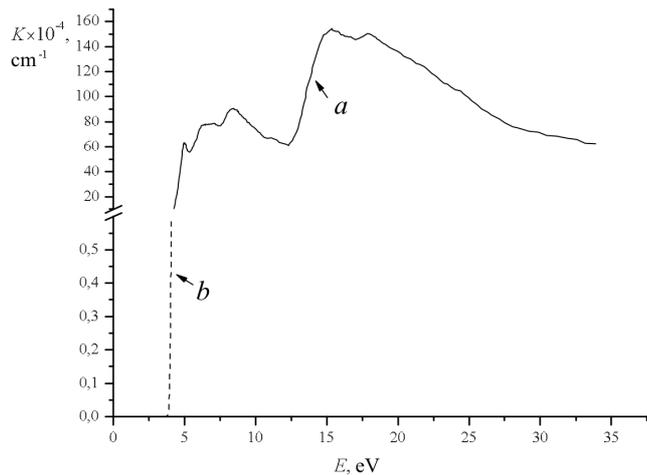


Fig. 2. Spectrum of fundamental absorption of paratellurite: a – calculations by the Kramers–Kronig relations; b – measured edge absorption

3. Structure of Absorption Spectrum

Narrow band A located deeply in the fundamental absorption band of the paratellurite spectrum (Fig. 4) is associated with excitonic absorption, while bands B, C, D, and F with interband transitions.

In works [2, 3], it was shown that, for gyrotropy of the crystal origin, the dispersion of rotatory power is described by the following formula:

$$\vartheta(\lambda) = \frac{S\lambda^2}{(\lambda^2 - \lambda_0^2)^2}.$$

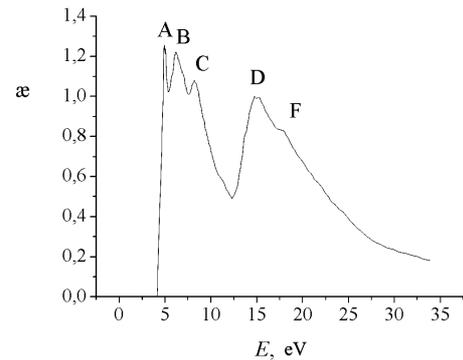


Fig. 4. Spectrum of the absorption index $\varkappa(E) = \frac{chK(E)}{2E}$ for a TeO_2 crystal

Therefore, we carried out the corresponding approximation and found the parameters $S = 24.97$ and $\lambda_0 = 241.43 \text{ nm}$ ($E_0 = 5.13 \text{ eV}$). The resonance energy E_0 almost coincides with the position of A-peak ($E_A = 5.01 \text{ eV}$). At the same time, the dependence $\varepsilon(\lambda) = n^2(\lambda)$, which is determined by the strength of an effective linear oscillator, is described well by the Drude–Sellmeier formula with parameters $S_1 = Ne^2f\lambda_0^2/(\pi mc^2) = 3.71$ and $\lambda_0 = 197.52 \text{ nm}$ ($E_0 = 6.27 \text{ eV}$) in the spectral range $0.40 - 1.05 \mu\text{m}$. It is clear that, in this case, λ_0 is close to the peak position of the interband absorption band ($E_B = 6.23 \text{ eV}$).

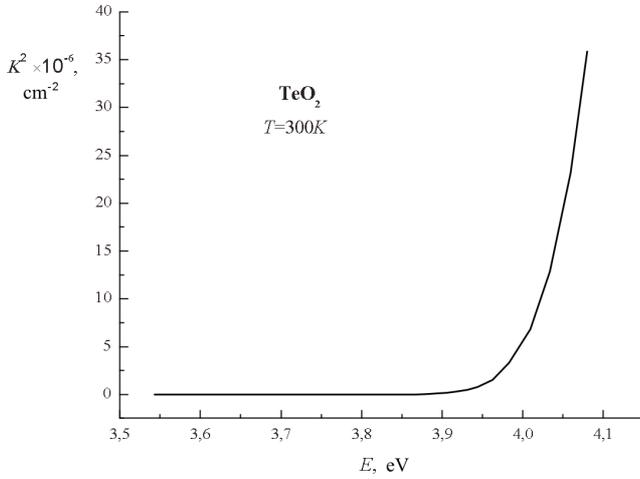


Fig. 5. Dependence $K^2(E)$ in the near-edge region

4. Parameters of a Gyroactive Oscillator

We have determined the key parameters of the excitonic A -peak we identify as that associated with the main gyroactive oscillator of paratellurite. For this purpose, it was necessary to find first the reduced effective mass of carriers μ , since TeO_2 is a gyrotropic semiconductor. The edge of absorption is described by the function

$$K(E) = \frac{2e^2(2\mu)^{3/2}}{m^2c\hbar^2n} |P_d|^2 \frac{(E - E_g)^{1/2}}{E}, \quad (5)$$

where $\mu = \frac{m_e m_h}{m_e + m_h}$, $|P_d|^2 = mEf/2$ is the square of the matrix element of dipole transition, n is the refractive index of the crystal at $E = E_A$, E_g is the interband gap value, and f is the oscillator strength. From Eq. (5), we obtain

$$K^2(E) = \frac{8\mu^3 e^4 f^2}{m^2 c^2 \hbar^4 n^2} (E - E_g), \quad (6)$$

so that the edge slope equals

$$\frac{\Delta[K^2(E)]}{\Delta E} = b = \frac{8\mu^3 e^4 f^2}{m^2 c^2 \hbar^4 n^2}, \quad (7)$$

and the expression for the reduced effective mass reads

$$\frac{\mu}{m} = \frac{1}{2} \left(\frac{r_B^2 m c^2 n^2 b}{f^2} \right)^{1/3} = 1.42 \times 10^{-8} \left(\frac{n^2 b}{f^2} \right)^{1/3}. \quad (8)$$

In Fig. 5, the dependence $K^2(E)$ is plotted, the linear behavior of which in a wide interval of variation in K evidences for the validity of approximation (6).

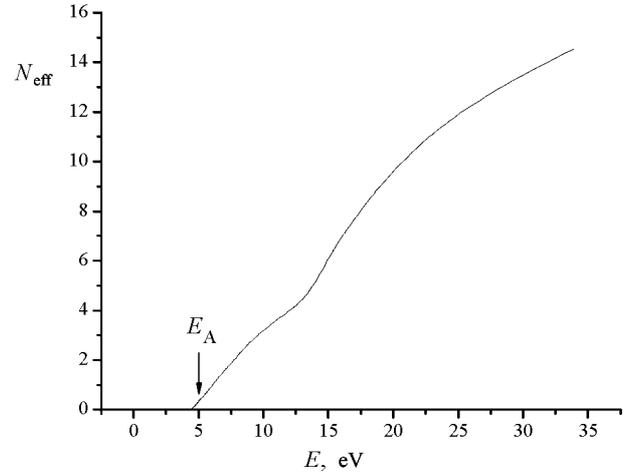


Fig. 6. Function $N_{\text{eff}}(E)$ for a TeO_2 crystal

The experimentally determined value for the absorption edge slope in TeO_2 was

$$b = 6.1858 \times 10^8 \text{ cm}^{-2} \text{ V}^{-1}.$$

The oscillator strength f was determined by the Smakula formula [4]

$$f = 1.29 \times 10^{17} \frac{1}{N} \frac{n}{(n^2 + 2)^2} K_{\text{max}} H, \quad (9)$$

where K_{max} is the value of absorption coefficient in the maximum of the gyroactive oscillator band, H is the halfwidth of this band, N is the number of oscillators in unit volume, i.e.

$$1/N = V/(zN_{\text{eff}}).$$

Here, V is the volume of an elementary cell in paratellurite, z is the number of formula units in a unit cell of the crystal, and N_{eff} is the effective number of valence electrons which participate in interband transitions at $E = E_A$. The function $N_{\text{eff}}(E)$ (normalized to a formula unit) was calculated by the KKR's and is exhibited in Fig. 6.

Substituting the parameter values $K_{\text{max}} = 56.86 \times 10^4 \text{ cm}^{-1}$, $H = 0.8045 \text{ eV}$, $V = ac^2 = 176.36 \times 10^{-24} \text{ cm}^{-3}$, $z = 4$, and $N_{\text{eff}} = 0.3$ to formula (9), we obtain $f = 0.249$. Formula (8) gives $\mu/m = 0.518$, and we can calculate the key parameters of a gyroactive exciton in TeO_2 : the energy of exciton dissociation

$$G_A = R \frac{(\mu/m)}{\varepsilon^2} = 115 \text{ meV}, \quad (10)$$

and the exciton radius

$$r_A = \frac{r_B \varepsilon}{(\mu/m)} = 8.0 \text{ \AA}. \quad (11)$$

5. Conclusions

An attempt to distinguish and identify linear and gyroactive oscillators, which are responsible for the dispersion of refractive indices and the rotatory power, respectively, in a wide spectral range (the transparency and near-edge regions), has been made for the first time, using a gyrotropic semiconducting crystal of paratellurite as an example. It has been shown that the function $\vartheta(E)$ in TeO_2 is determined by a gyroactive effective oscillator of the excitonic nature (a circular exciton). The fact that the exciton radius turned out close to the value of the lattice parameter c of the TeO_2 chain structure ($c = 7.6 \text{ \AA}$) testifies that, in paratellurite, we probably deal with excitons of intermediate radius.

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ПРО ПРИРОДУ ГІРОТРОПІЇ ПАРАТЕЛУРИТУ

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Резюме

У структурі фундаментального спектра парателуриту виявлено екситонну смугу (А-смугу), відповідальну за дисперсію поворотної здатності в області прозорості та у прикорайовій області спектра $h\nu < E_g$. Визначено параметри гіроактивного осцилятора: енергію дисоціації $G_{\text{ex}} = 115 \text{ меВ}$ та екситонний радіус $r_{\text{ex}} = 8,0 \text{ \AA}$. Той факт, що r_{ex} виявився близьким до параметра ґратки c ланцюжкової структури TeO_2 , вказує на те, що у парателуриті, імовірно, маємо справу з екситонами проміжного радіуса.