

OSCILLATOR-OSCILLATOR INTERACTIONS AND THE PARAMETERS OF SPATIAL DISPERSION IN α -TeO₂ AND α -SiO₂

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In the framework of the coupled-oscillator model for a quasimolecular chain structure of the paratellurite lattice, the dependence of the parameter K in the Chandrasekhar formula on the spectral splitting $\Delta\lambda_0$ has been obtained. The value of 0.458×10^{-4} for the parameter of spatial dispersion in paratellurite has been determined. The gyrotropic parameters of paratellurite α -TeO₂ and quartz α -SiO₂ have been compared.

between them should be minimal. According to the newest data [3], $R_{\text{cryst}} = 1.878 \text{ \AA}$, and the angle between the Te–O bonds is equal to 103° .

The analysis of the atomic coordinates in a paratellurite elementary cell (Table 1) demonstrates that every Te atom is surrounded by an octahedron of six oxygens (Fig. 1). Such a structure is usually classified as a rutile-like one. But, in contrast to a typical rutile lattice (TiO₂), oxygen octahedra around Te atoms in TeO₂ are substantially deformed (Fig. 2). Of six bonds, there are two short ones (1.878 \AA), two longer axial ones (2.12 \AA), and two even more distant bonds which are conditioned by the so-called lone electron pairs [4]. In our opinion, it is this circumstance that governs the specific anisotropic properties of the material concerned.

1. Introduction

Paratellurite belongs to the tetragonal enantiomorphous class of symmetry (the spatial group is either $D_4^4 = P4_12_12$ or the enantiomorphous one $D_4^8 = P4_32_12$). According to the results of x-ray diffraction analysis [1], the corresponding lattice parameters are $a = 4.8082 \text{ \AA}$ and $c = 7.6120 \text{ \AA}$. The elementary cell contains four formula units.

TeO₂ compound is known to exist also in the molecular form [2], for which the length of the Te–O bond is equal to $R_{\text{mol}} = 1.83 \text{ \AA}$, and the angle between the bonds amounts to 110° . TeO₂ molecules (C_{2v} -symmetry) are not optically active.

While forming a paratellurite crystal, TeO₂ molecules almost preserve their configuration and become consistently reoriented in such a way that the energy of electrostatic (dipole-dipole) interaction

From the crystal-chemistry point of view, the lattice of paratellurite can be classified as a quasimolecular chain structure, where the deformed octahedra, which were mentioned above, make up chains that, in their turn, form helical curves with the axis directed along the axis of the fourth order in the crystal (the main optical axis c); the spiral torsion can be either right- or left-handed for the corresponding enantiomorphous shape of the crystal.

In this work, we made an attempt to determine the parameters of the TeO₂ crystal gyrotropy on the basis of the model of coupled oscillators. We have demonstrated that taking the oscillator-oscillator interaction into account gives rise to the splitting of the characteristic frequency of an electron oscillator, and that this splitting substantially influences the gyrotropic characteristics of the crystal.

Table 1. Coordinates of atoms in an elementary cell of paratellurite

Atom	$x, \text{ \AA}$	$y, \text{ \AA}$	$z, \text{ \AA}$
Te ₁	0.1289	0.1289	0.0000
Te ₂	2.2752	2.5330	1.9030
Te ₃	4.6793	4.6793	3.8060
Te ₄	2.5330	2.2752	5.7090
O ₁	0.6664	1.2386	1.4174
O ₂	1.1655	3.0705	3.3204
O ₃	4.1418	3.5696	5.2234
O ₄	3.6427	1.7377	7.1264
O ₅	3.0705	1.1655	4.2916
O ₆	1.7377	3.6427	0.4856
O ₇	1.2386	0.6664	6.1946
O ₈	3.5696	4.1418	2.3886

2. Physical Model

The essence of the model concerned consists in that every formula unit in an elementary cell is considered as a linear oscillator, the characteristic frequency of which is equal to ω_0 in the absence of intermolecular connections, with the oscillator strength being f . Making allowance

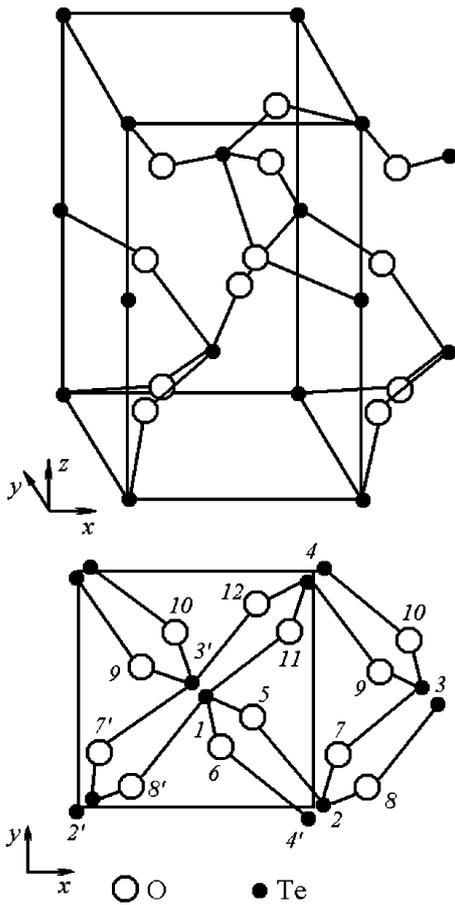


Fig. 1. Structure of the paratellurite lattice [3]

for a weak interaction between neighbor oscillators results in the splitting of ω_0 into components $\omega_1 = \omega_0 + \frac{\Delta\omega_0}{2}$ and $\omega_2 = \omega_0 - \frac{\Delta\omega_0}{2}$ (Fig. 3). Since $\Delta\omega_0 \ll \omega_0$, we can write

$$\omega_1^2 \approx \omega_0^2 + \omega_0 \Delta\omega_0$$

and

$$\omega_2^2 \approx \omega_0^2 - \omega_0 \Delta\omega_0$$

(the terms of the order of $\Delta\omega_0^2$ are neglected).

Coupled oscillators of the cluster type, which are located along the helical axis and are disoriented by an angle θ with respect to one another, will determine the specific rotatory power of paratellurite

$$\vartheta = \frac{\pi}{\lambda} (n_l - n_r), \tag{1}$$

¹In particular, if light propagates along the optical axis, i.e. $\vec{k} \parallel OZ$, we have $\gamma = 0$.

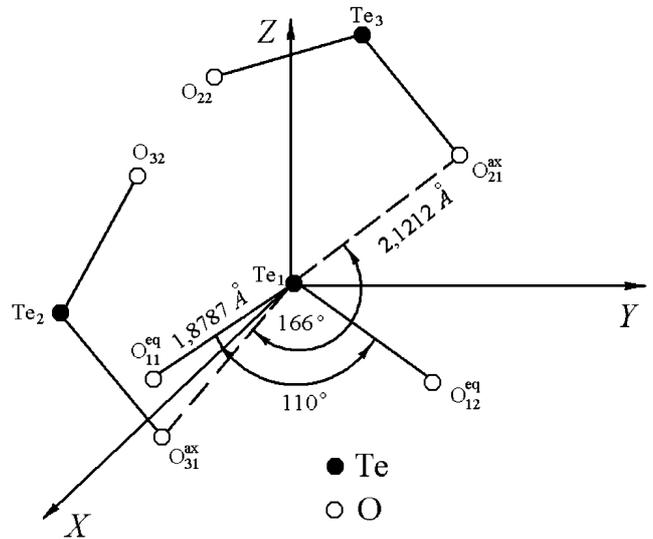


Fig. 2. Distorted octahedron around a Te atom

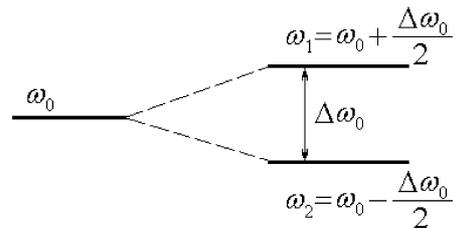


Fig. 3. Splitting of the characteristic frequency ω_0 in the model of two coupled oscillators

where n_l and n_r are the refractive indices for left- and right-handed, respectively, circularly polarized light.

3. Induced Dipole Moments and the Polarizability

Let a right-handed circularly polarized light wave with the amplitude E_0 and the frequency ω propagate along the OZ -axis (the optical axis of the crystal). It can be described by the oscillation equations

$$x = E_0 \cos \omega t$$

and

$$y = -E_0 \sin \omega t.$$

We denote the direction cosines of the coupled oscillator in the chosen coordinate system as α , β , and γ .¹ As

a result of the action of the light-wave field on such a cluster,² the dipole moment with the components

$$\mu_1 = \frac{Afe^2}{m} \frac{E_0}{\omega_1^2 - \omega^2} (1 + \cos \theta + \varphi \sin \theta) \quad (2)$$

and

$$\mu_2 = \frac{Afe^2}{m} \frac{E_0}{\omega_2^2 - \omega^2} (1 - \cos \theta - \varphi \sin \theta) \quad (3)$$

is induced [5]. In Eqs. (2) and (3), $A = \alpha^2 + \beta^2$,

$$\varphi = \frac{2\pi nd}{\lambda} \quad (4)$$

is the light-wave phase,

$$n = \frac{n_1 + n_r}{2}$$

is the ordinary (averaged) refractive index for light that propagates along the optical axis, and d is the distance between two neighbor oscillators reckoned along the optical axis.

Since the coupled oscillators are located successively around the fourth-order axis, one can readily show that the average polarizability of the right-handed circularly polarized oscillations per unit volume of the crystal amounts to

$$\alpha_r = \frac{N}{4E_0} (\mu_1 + \mu_2) = \frac{Afe^2 N}{4m} \times \left(\frac{1 + \cos \theta + \varphi \sin \theta}{\omega_1^2 - \omega^2} + \frac{1 - \cos \theta - \varphi \sin \theta}{\omega_2^2 - \omega^2} \right), \quad (5)$$

where N is the total number of oscillators in this volume.

For the left-handed circularly polarized light which is described by the oscillation equations

$$x = E_0 \cos \omega t$$

and

$$y = E_0 \sin \omega t,$$

we obtain analogously that

$$\mu_1 = \frac{Afe^2}{m} \frac{E_0}{\omega_1^2 - \omega^2} (1 + \cos \theta - \varphi \sin \theta), \quad (6)$$

$$\mu_2 = \frac{Afe^2}{m} \frac{E_0}{\omega_2^2 - \omega^2} (1 - \cos \theta + \varphi \sin \theta), \quad (7)$$

and

$$\alpha_l = \frac{Afe^2 N}{4m} \times \left(\frac{1 + \cos \theta - \varphi \sin \theta}{\omega_1^2 - \omega^2} + \frac{1 - \cos \theta + \varphi \sin \theta}{\omega_2^2 - \omega^2} \right). \quad (8)$$

²As was said, the coupled oscillator is characterized by two normal oscillation modes with frequencies ω_1 and ω_2 , one of which is symmetric and the other is antisymmetric with respect to the rotation operation.

4. Circular Birefringence and Specific Rotary Power

Knowing the macroscopic polarizabilities (5) and (8), one can easily calculate the dispersion of the refractive indices for circularly polarized light waves and, hence, the dispersion of the rotatory power of paratellurite:

$$n_l^2 - 1 \equiv 4\pi\alpha_l = \frac{\pi Afe^2 N}{m} \times \left(\frac{1 + \cos \theta - \varphi \sin \theta}{\omega_1^2 - \omega^2} + \frac{1 - \cos \theta + \varphi \sin \theta}{\omega_2^2 - \omega^2} \right), \quad (9)$$

$$n_r^2 - 1 \equiv 4\pi\alpha_r = \frac{\pi Afe^2 N}{m} \left(\frac{1 + \cos \theta + \varphi \sin \theta}{\omega_1^2 - \omega^2} + \frac{1 - \cos \theta - \varphi \sin \theta}{\omega_2^2 - \omega^2} \right). \quad (10)$$

Making use of these expressions and taking Eq. (4) into account, we obtain

$$n_l^2 - n_r^2 = \frac{4\pi^2 n Afe^2 N}{\lambda m} d \sin \theta \times \left(\frac{1}{\omega_2^2 - \omega^2} - \frac{1}{\omega_1^2 - \omega^2} \right). \quad (11)$$

Since $n_l^2 - n_r^2 = 2n(n_l - n_r)$ and

$$\frac{1}{\omega_2^2 - \omega^2} - \frac{1}{\omega_1^2 - \omega^2} \cong \frac{2\omega_0 \Delta\omega_0}{(\omega_0^2 - \omega^2)^2},$$

Eq. (9) gives rise to

$$n_l - n_r = \frac{4\pi^2 Afe^2 N}{\lambda m} \frac{\omega_0 \Delta\omega_0}{(\omega_0^2 - \omega^2)^2} d \sin \theta,$$

$$\vartheta(\lambda) = \frac{\pi}{\lambda} (n_l - n_r) = \frac{K\lambda^2}{(\lambda^2 - \lambda_0^2)^2}, \quad (12)$$

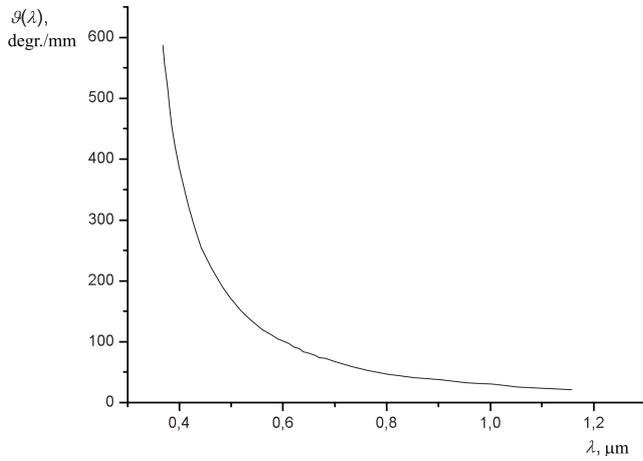


Fig. 4. Dispersion of the rotatory power of paratellurite

where

$$K = \frac{\pi A f e^2 N}{m c^2} \lambda_0 \Delta \lambda_0 d \sin \theta. \quad (13)$$

Thus, in the framework of the model of coupled oscillators, we succeeded in a consistent derivation of the approximation formula (12) which is known as the Chandrasekhar formula. One can see that the approximation parameter K depends explicitly on the strength of oscillator-oscillator interaction and is proportional to the amplitude of splitting

$$\Delta \lambda_0 = \frac{\lambda_0^2}{2\pi c} \Delta \omega_0.$$

While describing the ordinary dispersion of light, if it propagates along the optical axis of the crystal, the splitting factor is not essential ($\omega_1 = \omega_2 = \omega_0$), and the dependence $n^2(\lambda)$ can easily be determined on the basis of Eqs. (9) and (10):

$$n^2(\lambda) - 1 = \frac{(n_1^2 - 1) + (n_r^2 - 1)}{2} = \frac{K_1 \lambda^2}{\lambda^2 - \lambda_0^2}, \quad (14)$$

where

$$K_1 = \frac{A f e^2 N \lambda_0^2}{2\pi m c^2}. \quad (15)$$

It follows from Eqs. (12) and (13) that the quantity ϑ is proportional to $\sin \theta$, i.e. the direction of rotation of the polarization plane depends on the θ -sign: two enantiomorphous forms are characterized by the rotatory powers with opposite signs. Concerning the dispersion of the refractive indices, Eqs. (14) and (15) make it evident that its dependence on θ is absent.

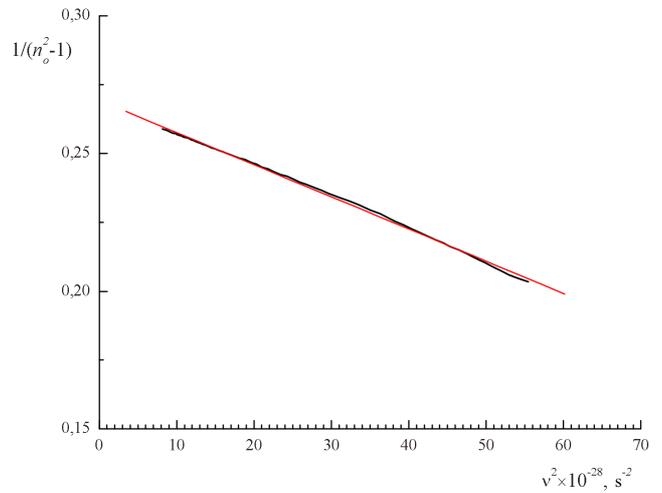


Fig. 5. Dependence of the quantity $n^2 - 1^{-1}$ on ν^2 for a TeO₂ crystal in the case of $\vec{E} \perp \vec{c}$ polarization

5. Experimental Part

The measurements of the dispersion of the rotatory power of paratellurite were carried out at room temperature and making use of paratellurite single crystals grown by the Czochralski method. Specimens in the form of plane-parallel plates with various thicknesses (from 0.2 to a few millimeters) were cut off perpendicularly to the optical axis of the crystal. The dependence $\vartheta(\lambda)$ was measured on an automated spectropolarimetric installation. The relative measurement accuracy for the specific rotatory power was $\pm 2\%$, and the accuracy of specimen orientation was not worse than $\pm 0.5^\circ$.

In the near-edge region ($\lambda > \lambda_g = hc/E_g$), the normal behavior of the rotatory power dispersion was observed (Fig. 4). The dependence $\vartheta(\lambda)$ is well approximated by formula (12) with the parameter values $K = 4.357 \text{ \AA}$ and $\lambda_0 = 2414.3 \text{ \AA}$.

In Fig. 5, the dependence of the quantity $(n^2 - 1)^{-1}$ on ν^2 is depicted for the light polarization $\vec{E} \perp \vec{c}$ and in the spectral range 400–1050 nm. The linear behavior of this dependence evidences for the validity of approximation (14) with the parameter values $K_1 = 3.7135 \text{ \AA}$ and $\lambda_0 = 1975.2 \text{ \AA}$.

6. Spectral Splitting and the Spatial Dispersion Parameter

According to the theory, where the gyrotropy of crystals is consistently considered as a spatial dispersion effect

of the first order [6], the approximation parameter in Eq. (12) is

$$K = 2\pi^2 K_1^2 \delta_{123}, \quad (16)$$

where the asymmetric tensor of the third rank δ_{123} is a quantitative characteristic of the spatial dispersion, which is responsible for the gyrotropy of a uniaxial crystal, provided that $\vec{k} \parallel OZ$. On the other hand, in the framework of the model of coupled oscillators, relations (13) and (15) bring about the following formula:

$$K = 2\pi^2 K_1 \frac{\Delta\lambda_0}{\lambda_0} d \sin \theta. \quad (17)$$

If one assume that the resonance frequencies and other characteristics of effective oscillators in the dependences $\vartheta(\lambda)$ and $n^2(\lambda)$ are identical, then, knowing the crystal-structure (d and θ) and dispersion (K , K_1 , and λ_0)³ parameters of a gyrotropic crystal, we can determine the magnitude of spectral splitting as

$$\Delta\lambda_0 = \frac{K\lambda_0}{K_1} \frac{1}{2\pi^2 d \sin \theta}.$$

For paratellurite, $K = 4.357 \text{ \AA}$, $K_1 = 3.7135$, $\bar{\lambda}_0 = 2194.73 \text{ \AA}$, $d = c/4 = 1.903 \text{ \AA}$, and $\sin \theta = \sin 90^\circ = 1$; whence, $\Delta\lambda_0 = 68.56 \text{ \AA}$.

Using Eqs. (16) and (17), we obtain the following relation between the magnitude of spectral splitting and the parameter of spatial dispersion:

$$\frac{\omega_0}{c} \delta_{123} \equiv \frac{2\pi}{\lambda_0} \delta_{123} = \frac{2\pi}{K_1} \frac{\Delta\lambda_0}{\lambda_0^2} d \sin \theta. \quad (18)$$

For paratellurite, $\frac{2\pi}{\lambda_0} \delta_{123} = 0.458 \times 10^{-4}$.

It is expedient to confront the gyration parameters of paratellurite and quartz, because the latter is considered as a specific standard in crystal optics [7]. Moreover, α -SiO₂ and α -TeO₂ have much in common with respect to the nature of chemical bonds in them. Table 2 presents

Table 2. Comparison of gyrotropic parameters for α -TeO₂ and α -SiO₂

Parameter	α -TeO ₂	α -SiO ₂
K , \AA	4.357	1.2541
$\lambda_0^{(\vartheta)}$, \AA	2414.3	926.283
K_1	3.7135	1.35
$\lambda_0^{(n)}$, \AA	1975.16	926.283
$\Delta\lambda_0$, \AA	68.56	28
$g_{33}(\lambda=6328 \text{ \AA})$	0.7005×10^{-3}	1.009×10^{-4}
$(2\pi/\lambda_0)\delta_{123}$	0.458×10^{-4}	0.236×10^{-3}

³The parameter K is dimensional. Since the specific rotatory power is usually expressed in grad/mm, and the value of λ in microns, we obtain $K = 24.968 \text{ grad} \times \mu\text{m}^2/\text{mm} = 4.357 \text{ \AA}$. The parameter K_1 is dimensionless. For λ_0 , we take the average value $\lambda_0 = \frac{1}{2}(2414.30 \text{ \AA} + 1975.16 \text{ \AA}) = 2194.73 \text{ \AA}$.

the principal gyration parameters of paratellurite and quartz. The differences between them stem, first of all, from the differences between the band structures and the electron spectra of relevant crystals. This problem deserves a separate research.

7. Conclusions

In the framework of the classical model of coupled oscillators, the dependences of the gyration parameters of paratellurite on the magnitude of spectral splitting of the characteristic frequency of a gyroactive electron oscillator have been obtained. The value of the parameter of spatial dispersion of the first order, which is responsible for the gyrotropic properties of α -TeO₂, has been determined. The corresponding parameters for α -TeO₂ and α -SiO₂ have been compared.

1. J. Leciejewicz, Z. Kristallogr. **116**, 3/6 (1961).
2. *Molecular Constants of Inorganic Compounds*, Ed. by K.S. Krasnov (Khimiya, Leningrad, 1979) (in Russian).
3. D.S. Yakovlev, A.P. Mirgorodskii, A.V. Tulub, and B.F. Shchegolev, Opt. Spektrosk. **92**, 3 (2002).
4. T. Uchino and T.J. Yoko, Non-Cryst. Sol. **204**, 3 (1996).
5. S. Chandrasekhar, Proc. Ind. Acad. Sci. A **37**, 5 (1953).
6. V.M. Agranovich and V.L. Ginzburg, *Crystal Optics with Spatial Dispersion and Excitons*, 2nd ed. (Springer, Berlin, 1984).
7. V.A. Kizel and V.I. Burkov, *Gyrotropy of Crystals* (Nauka, Moscow, 1980) (in Russian).

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ПАРАМЕТРИ ПРОСТОРОВОЇ ДИСПЕРСІЇ В α -TeO₂
ТА α -SiO₂ В МОДЕЛІ ВЗАЄМОДІЮЧИХ ОСЦИЛЯТОРІВ

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Резюме

У рамках моделі зв'язаних осциляторів ланцюжкової квазі-молекулярної структури ґратки парателуриту отримано залежність параметра K формули Чандрасекара від величини спектрального розщеплення $\Delta\lambda_0$: $K = \pi^2 K_1 c \Delta\lambda_0 / (2\lambda_0)$, де K_1 – параметр Зельмейера, c – стала ґратки. Визначено значення параметра просторової дисперсії $(2\pi/\lambda_0)\delta_{123} = \pi c \Delta\lambda_0 / (2K_1 \lambda_0^2) = 0,458 \cdot 10^{-4}$. Зіставлено гіраційні параметри парателуриту α -TeO₂ та кварцу α -SiO₂.