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# Dispersion of Refractive Index of Dielectrics as a Basis for Reconstruction of Fundamental Absorption Spectrum

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The method for reconstruction of the material's absorption spectrum $k(\omega')$ in the range of fundamental excitations ($\omega'$) on the basis of the refractive index dispersion $n(\omega)$ in the range of its transparency has been elaborated and applied to the investigation of ferroelectric crystal TGS. The deviation of the refractive index dispersion of TGS crystal from the expected behavior can be explained by the change of dispersion relation caused by the interaction of optically active valence electrons. Temperature dependence of the parameters of this interaction in the region of phase transition of TGS crystal ($T_c = 49°C$) is discussed.

**Keywords:** absorption spectrum, refractive index, phase transition.

## I. Introduction

Investigations of the optical absorption spectra of solid materials in the vacuum ultraviolet photon energy range $h\omega > 6$ eV by means of measuring its reflectance spectra are burdened by several technical difficulties. These are the lack of perfect polarizers, eventual pollution of the sample's surface by the residual molecules in the vacuum chamber, eventual destruction of the material studied in vacuum, especially at high temperature. Therefore, the alternative methods for obtaining information about these spectra are desirable. One of such methods proposed in [1] is developed in the present paper.

## II. Method of calculations

The spectral dependence (dispersion) of refractive index $n(\omega)$ of material in the range of its optical transparency, $\omega_1 \div \omega_2$, is formed by the spectrum of absorption index $k(\omega')$ in the ranges of phonon, $\omega' < \omega_1$, and electron, $\omega' > \omega_2$, excitations according to the known Kramers-Kronig's relation [2]:

$$n(\omega) - 1 = \frac{2}{\pi}\int_{0}^{\infty}\frac{\omega' k(\omega')d\omega'}{\omega'^2 - \omega^2} = \frac{2}{\pi}\int_{0}^{\omega_1}\frac{\omega' k(\omega')d\omega'}{\omega'^2 - \omega^2} +$$
$$+ \frac{2}{\pi}\int_{\omega_2}^{\infty}\frac{\omega' k(\omega')d\omega'}{\omega'^2 - \omega^2} = I_{01} + I_{2\infty}. \qquad (1)$$

The relation (1) is a partial case of the Fredholm integral equation of the first kind:

$$\int_{a}^{b} R(x,s)k(s)ds = f(x), \qquad c \le x \le d . \qquad (2)$$

Here $R(x,s)$ is the kernel and $f(x)$ is the known right-hand part of the equation determined in the range [c, d], $k(s)$ is unknown function determined in the range [a, b]. The range [a, b] is not superimposed with the range [c, d] in our case. Therefore the integral equation (1) is the ill-posed one [3].

Second, "electron" part of the integral (1) can be presented in the following form:

$$I_{2\infty} = \frac{2}{\pi}\int_{\omega_2}^{\infty}\frac{\omega' k(\omega')d\omega'}{\omega'^2 - \omega^2} =$$
$$= \frac{2}{\pi}\int_{\omega_2}^{\omega_3}\frac{\omega' k(\omega')d\omega'}{\omega'^2 - \omega^2} + \frac{2}{\pi}\int_{\omega_3}^{\infty}\frac{\omega' k(\omega')d\omega'}{\omega'^2 - \omega^2} = I_{23} + I_{3\infty} \qquad (3)$$

When the photon energy $\omega'$ is sufficiently large ($\omega' > 30$ eV) then the plasma-like excitations take place for the majority of valence electrons and the absorption spectrum can be approximated satisfactorily by the power relation [4]:

$$k(\omega') = k(\omega_3)\left(\frac{\omega_3 - \omega_p}{\omega' - \omega_p}\right)^p . \qquad (4)$$

Typical magnitudes of the plasma frequency $\omega_p$ and the power p for dielectrics are equal to $\omega_p \approx 20$ eV and $p = 1.5 \div 2.5$. In the case of the dependence (4) the integral $I_{3\infty}$ can be calculated analytically for the magnitude p = 1.5, 2.0 or 2.5 and known magnitude of $k(\omega_3)$. The proper magnitude of p can be selected on the basis of known data on absorption indices $k(\omega')$ for two frequencies, for instance $\omega'_1 \approx 30$ eV and $\omega'_2 \approx 1000$ eV.
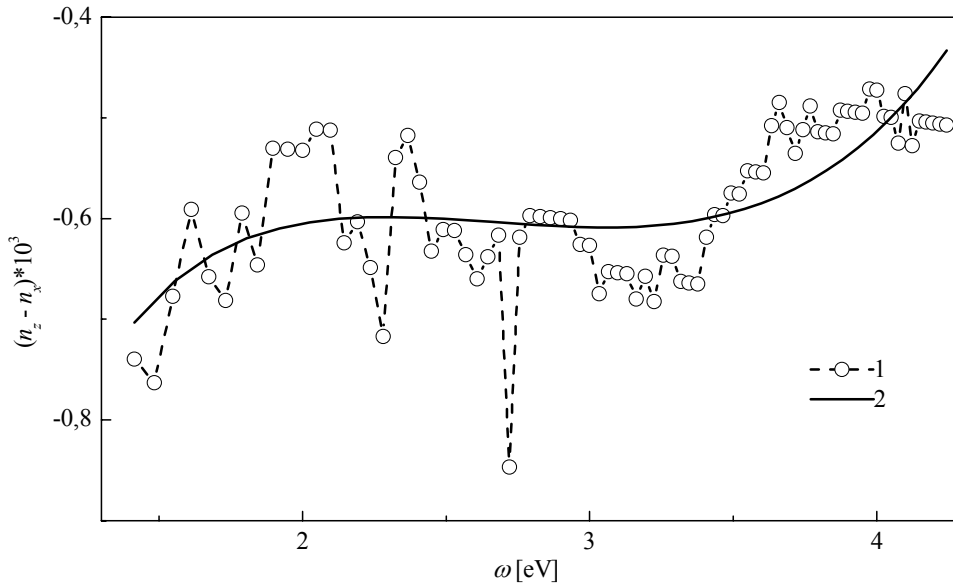
**Fig. 1.** Dispersion of the refractive index difference ($n_z$ - $n_x$) of LiKSO$_4$ crystal in the range of transparency:
1 – experimental; 2 - calculated using the formula (6).

The last magnitude of $\omega'_2$ corresponds to the frequency region of X-ray radiation, in which the typical absorption index k is sufficiently small to be measured experimentally. After that the problem is reduced to solving of the following integral equation:

$$\frac{2}{\pi}\int_0^{\omega_1}\frac{\omega' k(\omega')d\omega'}{\omega'^2-\omega^2}+\frac{2}{\pi}\int_{\omega_2}^{\omega_3}\frac{\omega' k(\omega')d\omega'}{\omega'^2-\omega^2}=n(\omega)-1-I_{3\infty}=n'(\omega)-1. \qquad (5)$$

The energies $\omega_1$ and $\omega_2$ are the upper edge of the phonon and the lowest edge of the electron absorption spectra, respectively. A contribution into the refractivity dispersion, $\eta(\omega) = n(\omega) - 1$, from the electron excitations ($I_{2\infty}$) is much greater than the analogous input from the phonon excitations ($I_{01}$). This is caused by much greater width of the electron spectrum ($20 \div 40$ eV) than of the

phonon one ($0.2 \div 0.4$ eV) and by the same order of magnitude of the absorption index k in these spectral ranges. Therefore, the whole range of phonon excitation $[0, \omega_1]$ was represented by only one effective oscillator at $\omega'_1 = 0.5\omega_1 = 0.2$ eV with absorption index $k(\omega'_1)$. The range of electron excitation $[\omega_2, \omega_3]$ was separated into $N_e$ subranges (in our case $N_e = 37$) with corresponding absorption indices $k(\omega'_j)$, $j = 2, 3, ..., N_e + 1$. The magnitude $N_e = 37$ corresponds to the width of subranges $\Delta\omega'_j \approx 0.5$ eV in the characteristic range $5 \div 25$ eV of valence electron excitation of most dielectrics and semiconductors.

This subdivision of the range $[\omega_2, \omega_3]$ permits to present the integral equation (5) in the form of system of $N = N_e + 1 = 38$ linear equations with N unknowns
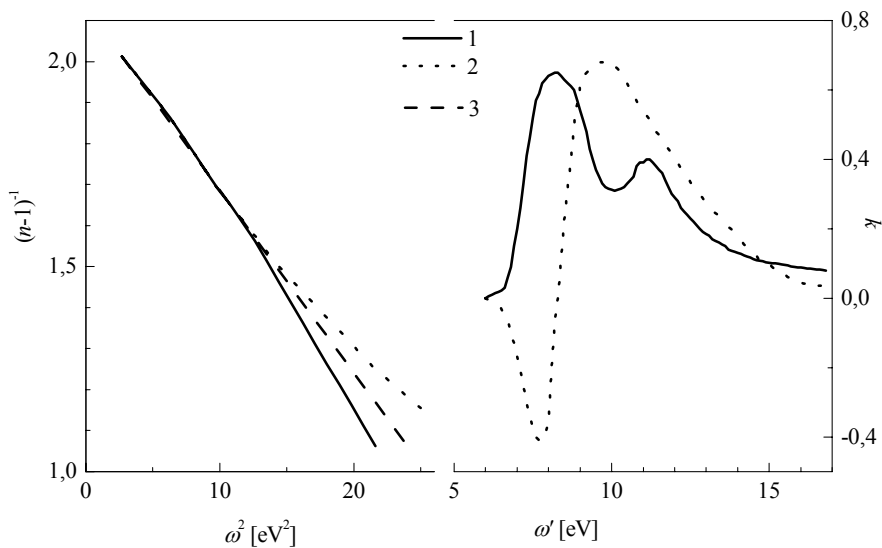


**Fig. 2.** Dispersions of refractive indices $(n - 1)^{-1} = f(\omega^2)$ and absorption spectra $k(\omega')$ for: 1 – for correct experimental data $n(\omega)$; 2 – for incorrect experimental data $n(\omega)$; 3 – for hypothetical material with only one oscillator.

$k(\omega'_j)$, $j = 1, 2, ..., N$,

$$\sum_{j=1}^{N} R(\omega'_j, \omega_i) k(\omega'_j) r(\omega'_j) = n'(\omega_i) - 1, \qquad (6)$$

$(i, j = 1, 2, ..., N)$

where $r(\omega'_j)$ are normalizing coefficients depending only on the grid of frequencies $\omega'_j$. The system (6) was solved by the least square method [3]. Because the right-hand part of the equations (5) and (6) includes the unknown value $k(\omega_3)$, the equation (6) was solving using the method of serial approximations.

The experimental dispersion of refractive index $n(\omega_i)$ of the material studied was used for calculation of the spectrum of absorption index $k(\omega'_j)$ by means of solving the system of equations (6). This spectrum $k(\omega'_j)$ was used to obtain the calculated dispersion $n_c(\omega_i)$ and divergence of experimental and calculated dispersions, $n(\omega_i) - n_c(\omega_i)$, using the same relation (6). This divergence is caused especially by the experimental error of refractive index measurement $(2 \cdot 10^{-4})$. Illustration of the last remark is seen in Fig. 1, where the example of such dependence is shown. The calculated spectral dependence of $(n_z - n_x)_c$ approximates very well the corresponding experimental one $(n_z - n_x)$.

Before calculation, the experimental dispersion $n(\omega_i)$ was presented in the form $(n - 1)^{-1} = f(\omega^2)$ characterizing by the minimal curvature, that gave possibility to eliminate the greatest experimental inaccuracies. Really, if the fundamental absorption band is formed by only one oscillator at $\omega_j$, then the sum (6) will have only one member and the dependence $(n - 1)^{-1} = f(\omega^2)$ will be exactly linear with zero curvature (Fig. 2).

The proposed presentation of the refractive index dispersion $(n - 1)^{-1} = f(\omega^2)$ gives also possibility to evaluate the correctness of corresponding experimental measurements. Our study showed that the correct dispersions of refractive index is characterized by the typical form for which the module of first derivative $d(n - 1)^{-1}/d\omega^2$ is not decreasing at approaching the band of fundamental absorption (Fig. 2). If the latter condition does not take place in the whole range of $\omega^2$, then the spectral sections of negative, not real absorption indices, will appear in the calculated spectrum $k(\omega'_j)$. Presentation of the refractive index dispersion in the ordinary form $n(\omega)$ does not give possibility to estimate its correctness.

The proposed method of reconstruction of absorption spectrum was verified by using the following test. At the beginning, the dispersion $n(\omega_i)$ in the range of $0,4 \div 5$ eV was calculated on the basis of the known spectrum $k(\omega'_j)$ of the hypothetical material in the range of $5 \div 25$ eV using directly the relation (6) with maximal computer accuracy $10^{-15}$. Then the spectrum $k_c(\omega'_j)$ was calculated by means of solving the integral equation (6) on the basis of the former calculated dispersion $n(\omega_i)$. Comparison of the spectra $k(\omega'_j)$ and $k_c(\omega'_j)$ has shown that even relatively narrow spectral band $(\Delta\omega' = 2 \div 3$ eV) can be reconstructed satisfactorily if it is placed close to the low-energy edge $\omega_2$ of the fundamental absorption band.

## III. Results and discussion

Two absorption spectra $k(\omega')$ for TGS crystal are shown in Fig. 2. The spectra have been obtained by two different methods: from the calculation by the experimental reflection spectra $R(\omega')$ in the 5-22 eV range (1) [5] and from the calculation by the refractive index dispersion $n(\omega)$ in the range of 1.5-5.2 eV (2). The spectrum 2 looks like the averaged spectrum 1. Small energy region $\Delta\omega' \sim 1$ eV with negative $k(\omega')$ values is observed in the low-energy range of the spectrum 2. Our analysis have shown that these negative values of $k(\omega')$ can be caused by some change of the dispersion relation
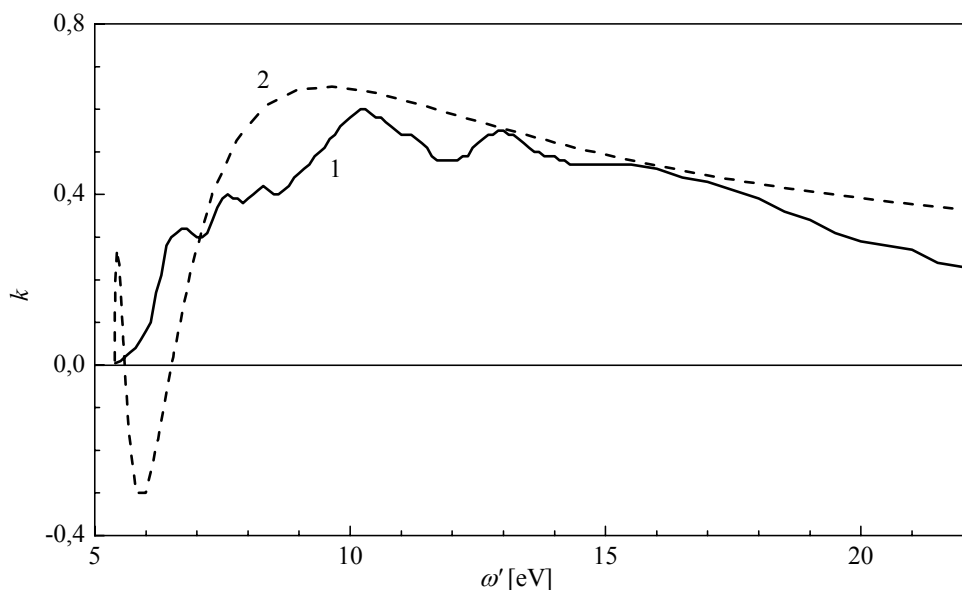


**Fig. 3.** Absorption spectra $k(\omega')$ of TGS crystal at 25°C: 1 – obtained from experimental reflection spectra; 2 – calculated from the system (6).
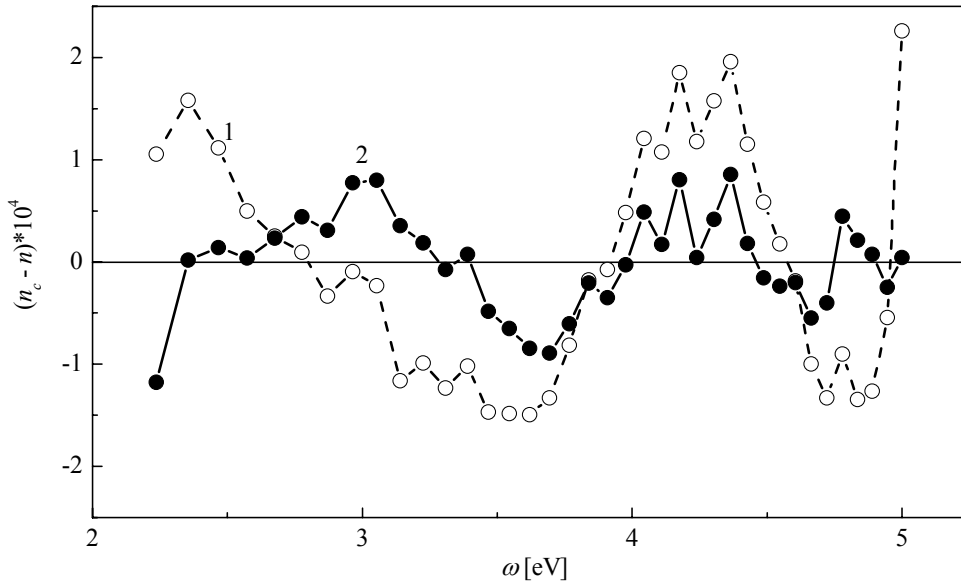
**Fig. 4.** Spectral dependences of the discrepancy $\delta n(\omega) = n_c(\omega) - n(\omega)$: 1 – $n_c(\omega)$ is calculated from the system (6) without regarding spatial dispersion; 2 – $n_c(\omega)$ is calculated from (6) with the kernel (8).

(1) and the kernel $R(\omega'_j, \omega_i)$ in (6) due to two reasons.

First, the damping of electron excitations can be included into kernel R:

$$R(\omega', \omega) = \frac{2 \cdot \omega'}{\pi(\omega'^2 - \omega^2 + \dfrac{\gamma^2 \omega^2}{\omega'^2 - \omega^2})} . \qquad (7)$$

The characteristic damping parameter $\gamma$ can be interpreted as some effective half-width of spectral fundamental band, which is inverse proportional to the damping time $\tau$ of the electron excitations ($\tau \sim 1/\gamma$).

Second, the effect of spatial dispersion, which can be displayed at high energies $\omega$ of refractive index dispersion, is also not accounted in the relations (1), (3) and (5). Spatial dispersion is the dependence of polarization of dielectric on the wavelength vector q [7,8], which can change the refractive index dispersion $n(\omega)$. It is known that spatial dispersion effects can be essential near the exciton resonances, and its value can be characterized by the effective mass $M_{eff}$ [7]. This effect can be taken into consideration in the second form of the kernel R [8],

$$R(\omega', \omega) = \frac{2 \cdot \omega'}{\pi(\omega'^2 - \omega^2 + \dfrac{\omega' \cdot \omega^2}{M_{eff} c^2})} , \qquad (8)$$

where c is light velocity in vacuum. Both corrections in the kernels (7) and (8) decrease the refractive indices n.
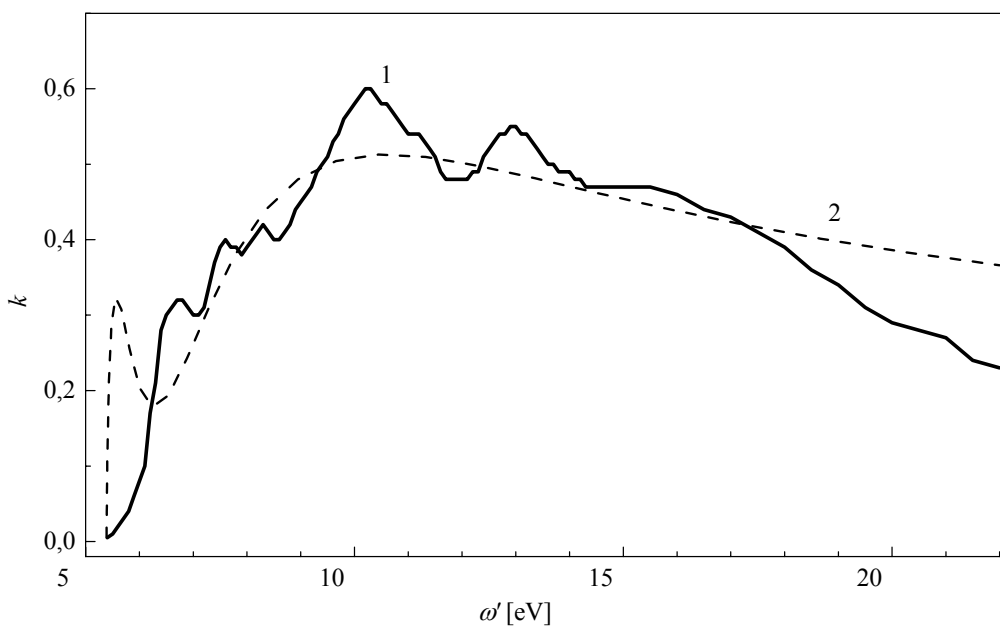


**Fig. 5.** Absorption spectra $k(\omega')$ of TGS crystal at 25°C: 1 – obtained from the reflection spectrum; 2 – calculated using the kernel (8).
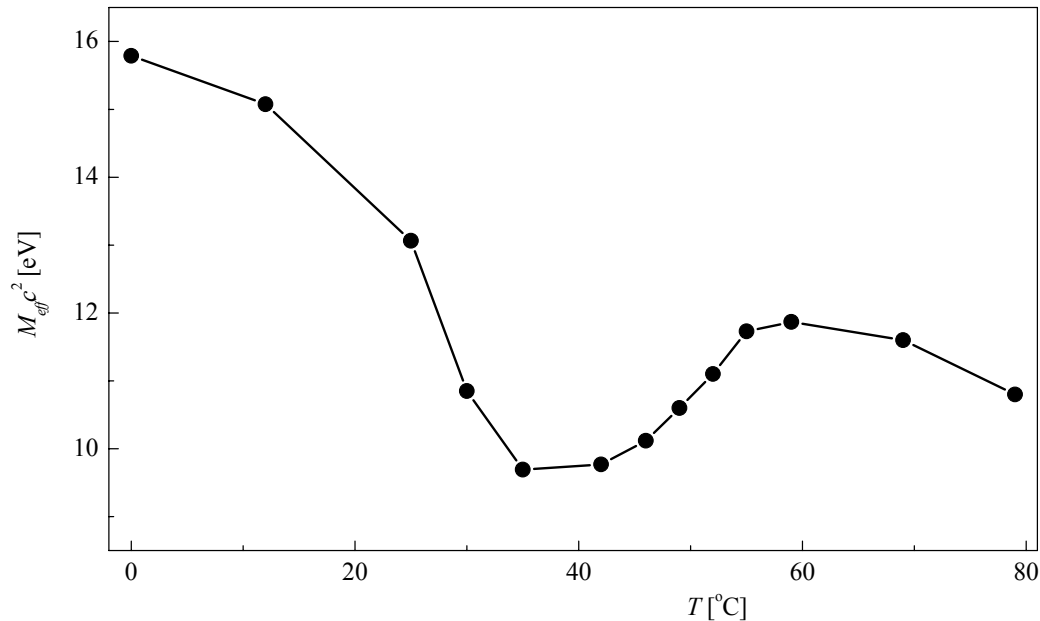
**Fig. 6.** Temperature dependence of the parameter $M_{eff}(T)$ for TGS crystal.

The ignoring of this peculiarity can lead to the negative absorption index values observed at the low-energy region of fundamental absorption spectrum $k(\omega')$ (Fig. 3).

Application of the kernels (7) and (8) to the absorption index calculations of TGS crystal has shown a necessity of the relatively considerable corrections for the kernel R to avoid negative values in the spectrum $k(\omega')$. These are the relatively large effective half-width, $\gamma \sim 5$ eV, or the relatively small mass $M_{eff} = 5 \cdot 10^{-4} m_e$. The mentioned above corrections of the kernel R lead to the essential decrease of the discrepancy $\delta n(\omega) = n_c(\omega) - n(\omega)$ of the calculated and experimental refractive index dispersions. The decrease of this discrepancy is 200-300% of the value corresponding to the not changed kernel R (Fig. 4).

The curves 2 in Fig. 4 and Fig. 5 correspond to the dependence of the effective mass, $M_{eff} \sim \omega'/\omega$, for which the only positive values of $k(\omega')$ are observed (Fig. 5). Existence of excitons in this region of TGS fundamental absorption was shown earlier [9]. Spatial dispersion can be interpreted as the presence of elastic bonds between spatially separated electron oscillators [8]. From the other side, the damping of electron excitations in crystal is also realized due to some bonds of the active oscillator with the surrounding particles. Thus, both mentioned above mechanisms can reflect common physical feature. It is the bonding between elementary oscillators (optically active valence electrons) in the characteristic range of optical radiation (wavelength $\lambda \sim 10^2$ nm). As the phase transitions in crystal is a cooperative effect, therefore investigations of the temperature dependencies of effective mass $M_{eff}(T)$ or damping parameter $\gamma(T)$ can be useful for study of these critical phenomena.

On the basis of the refractive index dispersion $n(\omega)$ of TGS crystal measured at 13 temperatures in the range of $0 \div 79°C$ [6], the temperature dependence of the effective exciton mass $M_{eff}(T)$ has been calculated (Fig. 6). If one will perform calculation of the absorption

spectra $k(\omega')$ for different temperature of crystal using the kernel (7) and the appropriate form of the spectral dependence $\gamma(\omega') = h/\tau(\omega')$, then the obtained temperature dependence of the characteristic time $\tau(T)$ will have similar characters to the observed dependence $M_{eff}(T)$. Taking into account this proportionality, $M_{eff} \sim \tau$, one can conclude the anomalous increase of the electron excitation damping time $\tau$ in the region of 40 - 60°C of TGS crystal on the background of temperature decrease of this parameter in the whole temperature range studied $0 \div 79°C$ (Fig. 6). The latter can be interpreted like the anomalous decrease of original electron-phonon interaction in the temperature range 40-60°C centered by the phase transition point $T_c = 49°C$ of TGS crystal.

## IV. Conclusions

**1.** The method for reconstruction of the absorption spectrum $k(\omega')$ of material in the range of fundamental excitations ($\omega'$) on the basis of the refractive index dispersion $n(\omega)$ in the range of its transparency has been elaborated and applied to the investigation of ferroelectric crystal triglycine sulphate (TGS).

**2.** Negative values of absorption indices $k(\omega')$ in the narrow photon energy range $\Delta\omega' \sim 1$ eV on the low-energy side of absorption band 5-22 eV of TGS crystal can be explained by the not accounted damping of electron excitation and/or by the spatial dispersion effects. The last factors, if taken into consideration, lead to the only positive, real values of $k(\omega')$ and to the decrease of discrepancy between calculated and experimental refractive index dispersions.

**3.** The increase of the effective mass $M_{eff}$ and damping time $\tau$ of electron excitations in the temperature range of 40-60°C can be interpreted as the anomalous decrease of the electron-phonon interaction in the region

close to the phase transition point $T_c = 49°C$ of TGS crystal.

[1]   B.V. Andriyevsky. Reconstruction of fundamental absorption spectrum of material by the refractive index spectrum in the range of its transparency // *Proceedings of SPIE*, (2648), pp. 112-117 (1995).

[2]   T.S. Moss. *Optical Properties of Semiconductors*. Butterworths Scientific Publ., (1959).

[3]   A.N. Malyshev. *Vvedenie v vychislitelnuju linejnuju algebru*. Izd. Nauka, Novosibirsk, (in Russian) (1991).

[4]   L.C. Feldman, J.W. Mayer. *Fundamentals of Surface and Thin Film Analysis*. North-Holland Publ., New-York - Amsterdam - London, (1986).

[5]   N.A. Romanyuk, B.V. Andriyevsky and I.S. Zheludev. Optical properties of triglycine sulphate crystals in the 5 to 22 eV region // *Ferroelectrics,* **1-4**(21), pp. 333-335 (1978).

[6]   M.O. Romanyuk, O.M. Kostetsky and V.F. Vibly. Dispersion and temperature dependence of refractive indices of triglycine sulphate // *Ukrainskyi Fizychnyi Zhurnal,* (in Ukrainian), **2**(21), pp. 207-209 (1976).

[7]   S.I. Pekar. Theory of electromagnetic waves in crystals in which excitons appear // *Zhurnal Eksperimentalnoj i Teoreticheskoj Fiziki,* (in Russian), **4**(33), pp. 1022-1036 (1957).

[8]   J.J. Hopfield and D.G. Thomas. Theoretical and experimental effects of spatial dispersion on the optical properties of crystals // *Phys. Rev.*, **2(**132**)**, pp. 563-572 (1963).

[9]   N.A. Romanyuk, B.V. Andriyevsky and V.M. Gaba. About the nature of absorption spectra of triglycine sulphate and Rochelle salt crystals at the long-wavelength edge of fundamental band // *Optika i Spektroskopiya*, (in Russian), **1**(50), pp. 126-129 (1981).

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# Дисперсія показника заломлення діелектриків як основа для відновлення фундаментального спектра поглинання

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Метод для відновлення спектра поглинання матеріалу k(ω') в області фундаментальних збуджень (ω') на основі дисперсії показника заломлення n (w) в області пропускання був розроблений і використовувався в дослідженні сегнетоелектричного кристала. Девіацію дисперсії показника заломлення кристала від очікуваної поведінки можна пояснити змыною дисперсыйного співвідношення, викликаного взаємодією оптично активних валентних електронів. Обговорено температурну залежність параметрів цієї взаємодії в області фазового переходу кристала ($T_c = 49°C$).