THE SPECTRUMS OF INFRARED REFLECTION AND COMBINATIONAL DISPERSION OF LIGHT IN OXIDE-SULPHIDE OF LANTAN CRYSTALS

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The frequencies of normal fluctuations of a crystal La_2O_2S, active in spectra of combinational dispersion of light are determined. The dispersion method of the analysis of spectra of reflection determines frequencies and constants of attenuation longitudinal (TO) and cross (LO) phonons, is calculated the imaginary part complex of dielectric permeability (ε'').

For realization of a number of physical researches and creation of devices on a basis oxide-sulphide rare-earth of elements is necessary the knowledge of such characteristics as width of lines of optical transitions, speed non-radiative relacsation, structure electron - oscillatory spectra. A basis for understanding of processes electron - oscillatory interaction and first investigation phase of dynamics of a crystal lattice is that information about single-phonon processes, which follows from optical oscillatory spectra of crystals.

The basic information on dynamics of a crystal lattice can be received at research single-phonon's of spectra of infra-red reflection and combinational dispersion of light. In single-phonon's processes of infra-red reflection participate phonons with a wave vector $\kappa<10^3 sm^{-1}$, while at edge of a Brilljuen zone $\kappa \approx 10^8 sm^{-1}$. It gives the basis to carry out classification of fluctuations, active in the given processes, assuming $k=0$. Thus usually consider, that the equivalent atoms of a crystal distinguishing on a vector primitive compilations, change in phase in all primitive cells. Thus, the cell participates in fundamental fluctuations everyone primitive equally and at the analysis of types of fluctuations of a crystal it is possible to be limited only it to one consideration. The primitive cell lantan oxide-sulphide contains 5 atoms, that defines 15 fluctuations, from which three concern to acoustic (mixture of a cell as whole, the frequencies of these mixtures are close to zero), and stayed 12 fluctuations concern to optical.

The complete oscillatory representation of group D_{3d} will be, consist of the following not resulted representations:

$$\Gamma = 3A_{2u} + 2A_{1g} + 3E_u + 2E_g \qquad (1)$$

from which acoustic fluctuations: $\Gamma_{ak} = A_{2u} + E_u$

The information on the stayed types of fluctuations can be received from spectra of combinational dispersion. (In these spectra the fluctuations A_{1g} and E_u) are active. Tensor of combinational dispersion for various types of fluctuations looks like:

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}; \quad E_{g1} = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}; \quad E_{g2} = \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}, \qquad (2)$$

where: a, b, c, d - not zero tensor components of combinational dispersion. The spectra of combinational dispersion of light were raised by lines argon laser λ_B = 476,3 and 488,0 nm in 90° geometry and were registered at room temperature with the help double monochromator ДФС - 24, with the sanction it is not worse $1 sm^{-1}$. The radiation argon laser has sufficient intensity in a continuous mode for supervision active in spectra of combinational dispersion of light of fluctuations. In a fig. 1 the spectra of combinational dispersion of light for crystals $La_{1,95}Nd_{0,05}O_2S$ are given at various directions of polarization of falling and absent-minded light, and in tab.1 of frequency of normal fluctuations.

For crystals with spatial group D_{3d}^3 the circuit of dispersion XX and YY, agrees tensor of combinational dispersion, are identical, therefore was to lead researches in one of these geometry enough. In geometry YY by rules of selection all normal fluctuations of crystals Ln_2O_2S should be shown. For identification of normal fluctuations of a class E_g it is enough to investigate a spectrum of combinational dispersion in XZ of geometry, that unequivocally defines a low-frequency style of a class E_g (tab. 1). In geometry XY the high-frequency style of a class E_g is shown. The spectrum of combinational dispersion in ZZ of geometry unequivocally defines frequencies of normal fluctuations of a class A_{1g}.

Table 1

Frequencies of normal fluctuations in spectra of combinational dispersion of light.

Crystal	$\nu_1(A_{1g})$,sm^{-1}	$\nu_2(A_{1g})$,sm^{-1}	$\nu_3(E_g)$,sm^{-1}	$\nu_4(E_g)$,sm^{-1}
$La_{1,95}Nd_{0,05}O_2S$	193	402	110	352

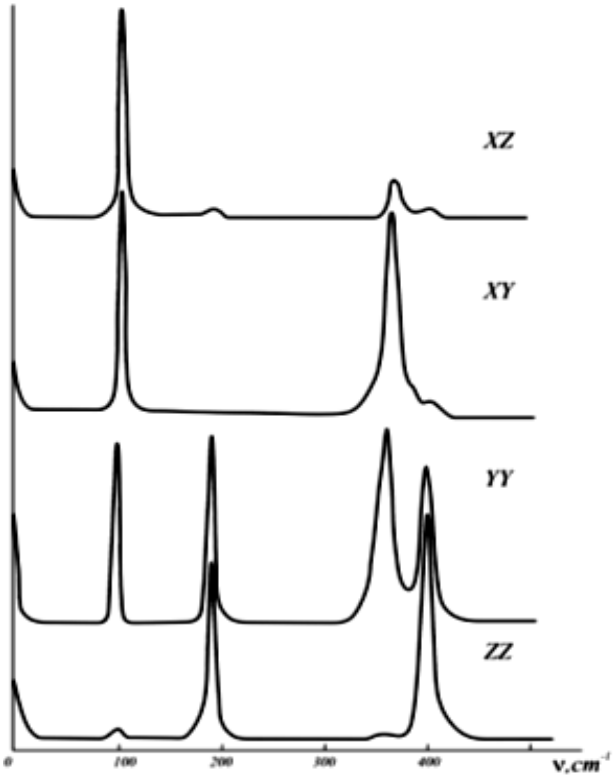

Fig. 1 Spectra of combinational dispersion of light of a crystal. $La_{1,95}$ $Nd_{0,05}O_2S$ at T=293K λ_B = 488,0 nm.

The collateral maxima in spectra of combinational dispersion specify an error of orientation of crystals, and also discrepancy of exhibiting of samples during measurement. The polarized spectra of infra-red reflection were received by us with the help longwave infra-red spectrometer ИС АН USSR - ДВИКС. The experimental installation for research of optical properties of materials in longwave area of a spectrum represents one-beam spectrometer with difraction lattice assembled on the circuit Cherny-Terper. The optical circuit spectrometer is submitted in a fig. 2.

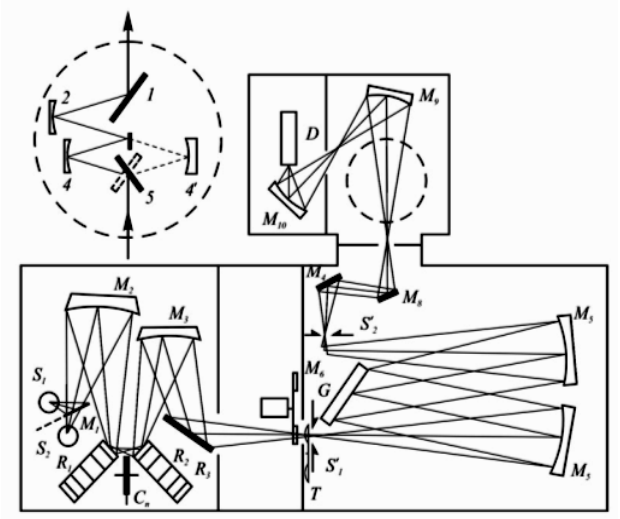

Fig. 2. Spectrometr's optical circuit. S_1, S_2– sources (globar and mercury lamp accordingly); M1,M6–flat mirrors; M2–M5, M7–M9–spherical mirrors; M10 – ellipsoid mirror; R1,R2 and R3–reflecting filters; T– passing filter; S1′, S2′- entrance and target crack; C_n - modulator; G - diffraction lattice tice; Д – ; detector (Goley's cell) 1,5–flat mirrors of a prefix ИПО–22;2, 4, 4′-toroidal mirrors; 3 - location of a sample.

Essential difference spectrometer ДВИКС from industrial (HITACHI) ФИС- 21 is the presence in last of intermediate focus (prefix ИПО- 22 ЛОМО in tray branch spectrometer). The quantity of substance necessary for experiment, has decreased approximately in 40 times, thus became to possible research of reflection and missing of samples of the small sizes 4 x 5 mm^2 at an irradiation them monochromatic light. In quality of polarizator were used aluminium polyethylene lattices.

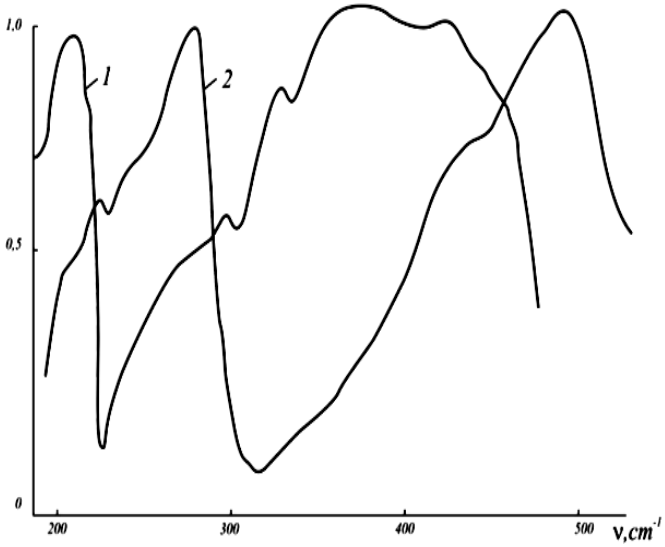

Fig. 3. The polarized spectra of infra-red reflection of monocrystals $La_{1,95}Nd_{0,05}O_2S$ at 293K for $E \perp C$ (1) and $E \,||\, C$ (2) polarization.

We carried out measurements with the sanction not worse 1,5 sm^{-1}, with an error of definition of reflective ability it is not worse 3 %. In a fig. 3 the spectra of reflection of monocrystals $La_{1,95}Nd_{0,05}O_2S$ in $E \perp C$ and $E \,||\, C$ geometry . One of the basic tasks of mathematical processing of spectra of reflection is the reception from them of function complex dielectric of permeability:

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \quad (3)$$

as it characterizes interaction of electromagnetic radiation with substance. The decision of the put task is searched or with the help dispersion of the attitudes Kramers-Kroning, or on the basis of model dispersion oscillator.

Elementary mathematical formula of a parity Kramers-Kroning allows to present factor of mirror reflection as:

$$\theta(\omega_i) = \frac{2\omega_i}{\pi} \int_0^\infty \frac{\ln R(\omega) - \ln R(\omega_i)}{\omega^2 - \omega_i^2} d\omega \quad (4)$$

Using the formulas

$$n^*(\omega) = n(\omega) + ik(\omega)$$
$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad (5)$$

$$n(\omega) = \left(1 - R^2(\omega)\right) / \left(1 - 2R(\omega)\cos\theta(\omega) + R^2(\omega)\right); \quad (6)$$

$$k(\omega) = 2R(\omega)\sin\theta(\omega) / \left(1 - 2R(\omega)\cos\theta(\omega) + R^2(\omega)\right); \quad (7)$$

$$\varepsilon'(\omega) = n^2(\omega) - k^2(\omega); \quad (8)$$

$$\varepsilon'' = 2n(\omega) \cdot k(\omega), \quad (9)$$

where $n^*(\omega)$ – complex parameter of refraction ; $R(\omega)$ – reflective ability of a crystal; $k(\omega)$ – the parameter of absorption, is possible to receive a spectrum $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ – from a spectrum $R(\omega)$.

Knowing dependence dielectric permeability from frequency, we receive cross frequencies of phonons ω_{TO} as a maximum of function $\varepsilon''(\omega)$, and frequency ω_{LO} longitudinal phonons, as maxima of function - $Im\left(1/\varepsilon(\omega)\right)$.

In a method Kramers-Kroning there is a mistake at calculation of integral (4), as the spectrum of reflection is measured only in the limited area, therefore integral is calculated not from 0 to ∞, and from $\omega_{нижн}$ to $\omega_{верх}$. The elementary approach for reception $\theta(\omega_i)$ is the acceptance $R=const$ outside area of integration [1].

The dispersion oscillator method allows to pick up parameters which are included in expression

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_{n=1}^{N} \frac{S_{tn}}{\omega_{tn}^2 - \omega^2 - ig_{tn}\omega}; \quad (10)$$

where S_{tn} –intensity; ω_{tn} and g_{tn} –frequency and constant of attenuation n's cross (TO) fluctuations; ε_∞ - the contribution of high-frequency electronic fluctuations, so that a deviation of a settlement spectrum of reflection from experimental was minimal [2].

For the analysis of complex spectra of the reflection consisting of close located strips of residual beams the expression for $\varepsilon(\omega)$, containing frequencies TO and LO phonons [3, 4] is used:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{n=1}^{N} \frac{\omega_{LOn}^2 - \omega^2 + i\omega\gamma_{LOn}}{\omega_{TOn}^2 - \omega^2 + i\omega\gamma_{TOn}}; \quad (11)$$

Using expression for $R(\omega)$:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2, \quad (12)$$

minimize criterion function $\delta\left(\omega_{TO_n}, \gamma_{TO_n}, \omega_{LO_n}, \gamma_{LO_n}, \varepsilon_\infty\right)$

$$\delta = \sum_{j=1}^{M} \left(R_{эксп}(\omega_j) - R_{расч}(\omega_j)\right)^2 \quad (13)$$

where M –number of experimental points; $R_{эксп.}(\omega_j)$ – experimental factor of reflection on frequency ω_j ; $R_{расч.}(\omega_j)$ –factor of reflections counted on the formulas (11) and (12).

The value ω_{TO}, ω_{LO}, at which the minimum of criterion function (13) is reached, corresponds to frequencies cross and longitudinal phonons.

The interaction phonons results to frequency dependences γ_{TO}, γ_{LO}, ω_{TO}, ω_{LO}. In a method dispersion oscillator these values are considered constant, that results in a mistake of account of frequencies of fluctuations and optical characteristics.

In our case (fig. 3) distance on a scale of frequencies between oscillators is more than attenuation of each of them, therefore application of a method dispersion oscillator does not result to essential errors in definition of parameters these oscillators [5].

The oscillators' parameters were defined with the help of the program ЕОДА [5]. The basis of the program ЕОДА is made by the subroutine FUMILI. Its algorithm represents a method of the short matrix second made $\frac{\partial^2\delta}{\partial x_m \partial x_k}$ [6]. The minimum is reached or on border of a range of definition, or in points of the decision of system of the equations

$$\frac{\partial\delta}{\partial x_i} = 0, X_{4n-3}=\omega_{TOn},\ X_{4n-2}=\gamma_{TOn},\ X_{4n-1}=\omega_{LOn},$$
$$X_{4n}=\gamma_{LOn},\ X_{4N+1}=\varepsilon_\infty,\ n=1,2,\ \ldots\ldots,N, \quad (14)$$

where N – number of oscillator.

By the form of spectrum of reflection it is possible to define parameters X_i with accuracy 10 % for and up to 50 % for γ and to take them as initial approach. The successful choice of initial approach excludes hit in a local minimum. At the large root-mean-square deviation it is necessary to use the designed oscillators' parameters and ε_∞ for the following approach. The process of calculation of oscillators' parameters ε_∞ also is considered completed, if values $k+1$ –s' approacsimates' coincides with settlement (k –s') to with some small positive size eps. The analysis of spectra of infra-red reflection by a method dispersion oscillator has allowed to define values of frequencies $\nu(\Gamma)$ for longitudinal TO and cross LO of fluctuations and parameters γ_{TO} and γ_{LO}, describing processes of attenuation oscillator (tab. 2), and also dispersion of dependence of an imaginary part complex dielectric permeability in various polarization of falling light (fig. 4).

Table 2

Frequencies of normal fluctuations and constants of attenuation oscillators in spectra of infra-red reflection of light in crystals $La_{1,95}Nd_{0,05}O_2S$

Crystal	Polarization	ν (г)	ν_{TO}, sm^{-1}	ν_{LO}, sm^{-1}	γ_{TO}	γ_{LO}	ε_∞
$La_{1,95}Nd_{0,05}O_2S$	$E \parallel C$	$\nu_5(A_{2u})$ $\nu_6(A_{2u})$	414 241	562 304	12 6,4	27 13	5,31
	$E \perp C$	$\nu_4(E_u)$ $\nu_8(E_u)$	325 198	488 221	11 3,1	15 3,6	7,17

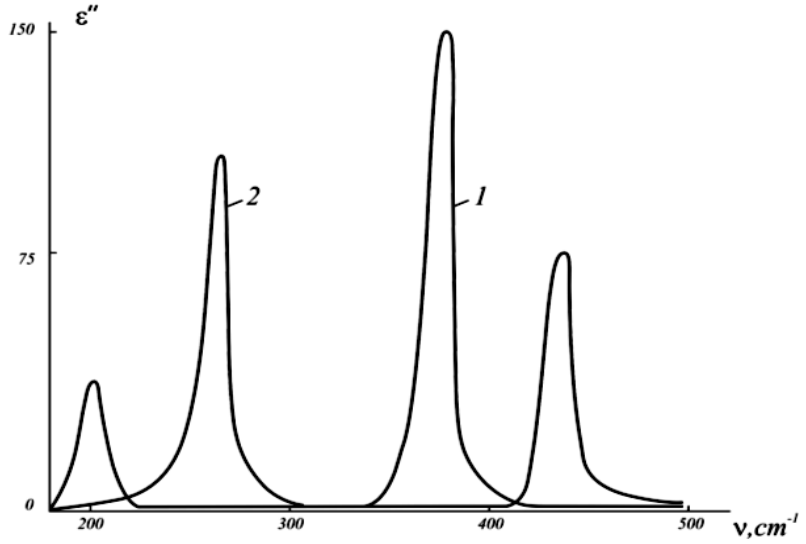

Fig. 4. Spectra of an imaginary part of complex permeability of a crystal $La_{1,95}Nd_{0,05}O_2S$ at 293K for E ⊥C (1) and E || C (2) polarization

We found vectors of mixtures of atoms at normal fluctuations.

In a fig. 5 they are given for active in spectra of infra-red absorption and combinational dispersion of optical styles. Really, the atoms *La* participate in all fluctuations. The reference of various fluctuations of the same symmetry on frequencies was carried out on the basis of the following reasons. In fluctuations ν_6 and ν_8 groups of atoms incorporated in parallelogram La_2O_2 go as whole (along an axis Z for ν_6 and in a plane XOY for ν_8), and thus connection S - La, weakest participates only in these fluctuations.

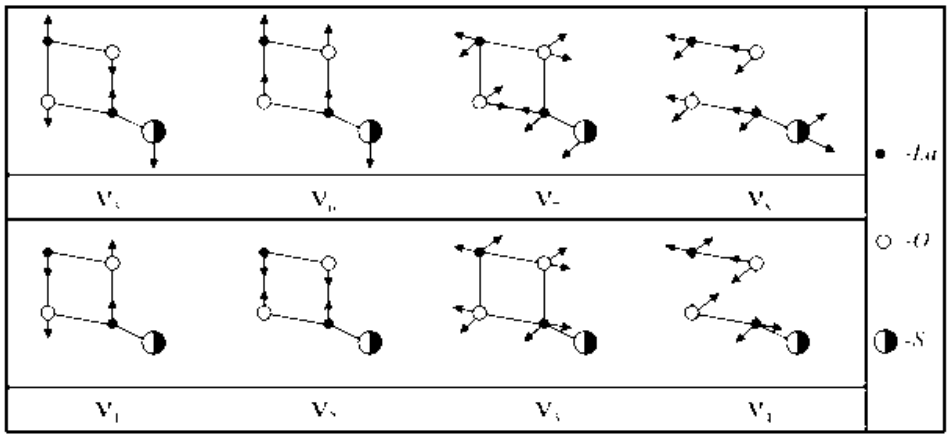

Fig. 5. Vectors of displacement of atoms at normal fluctuations of a crystal La_2O_2S

Therefore it is natural to assume, what exactly these fluctuations will be low-frequency. From a fig. 5 follows, that the fluctuations ν_7 result in prompting much greater dipolar moment, than ν_8. It will be coordinated with much more LO - TO splitting for ν_7 in comparison with ν_8.

Let's note, that in all these fluctuations does not participate is sulphur. It explains affinity of frequencies of fluctuations La_2O_2S and isostructure connection of La_2O_3.

[1] *M. Gottliev.* Optical properties of lithium floride in the infrared. – J. Opt. Soc. Am, 1960, V.50, №4 p. 343 – 349

[2] *W.G.Spitzer, R.C.Miller, D.A.Kleinman, L.E.Howarth.* Far infrared dielectric dispersion in Ba TiO_3, $ScTiO_3$ and TiO_3 – Phys. Rev, 1962, V 12^b, №5. P. 1710 – 1721

[3] *H.T. Bowlden, T.K. Wilmshesrst.* Evaluation of optical constants J. Opt. Soc. Amer. 1963. V.53. №9 p. 1073 – 1078.

[4] *M.V. Belousov.* Vosstanovlenie infrakrasnogo spektra dielektricheskoy pronitsaemosti iz spektrov kombinatsionnogo rasseyaniya. FEE, 1973, t. 15, № 10, s. 1206 – 1212.

[5] *V.M. Burlakov, D.A. Rzayev, V.M. Pirkov* Metodika raschota opticheskix xarakteristik iz spektrov IK otrajeniya monokristallov. Preprint № 6 Fronts, IS AN SSSR, 1985, s.28.

[6] *B.P. Demidovich, N.A. Maron.* Osnovi vichislitelnoy matematiki. M., Nauka,1980, s. 660.

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LANTAN OKSİSULFİDLI KRİSTALLARINDA İNFRAQIRMIZI QAYITMA VƏ İŞIĞIN KOMBİNASİON SƏPİLMƏSİ

Kombinasion səpilmə spektrlərində La_2O_2S kristalının aktiv olan normal rəqslərin tezliyi təyin edilmişdir. Qayıtma spektrlərindən dispersion analiz metodu ilə, uzununa (TO) və eninə (LO) fononların tezliyi və sönmə əmsalı təyin edilmiş, dielektrik nüfuzluğunun (ε'') xəyali hissəsi hesablanmışdır.

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СПЕКТРЫ ИНФРАКРАСНОГО ОТРАЖЕНИЯ И КОМБИНАЦИОННОГО РАССЕЯНИЯ СВЕТА В КРИСТАЛЛАХ ОКСИСУЛЬФИДОВ ЛАНТАНА

Определены частоты нормальных колебаний кристалла La_2O_2S, активные в спектрах комбинационного рассеяния света. Методом дисперсионного анализа спектров отражения определены частоты и константы затухания продольных (TO) и поперечных (LO) фононов, вычислена мнимая часть комплексной диэлектрической проницаемости (ε'').

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