

## Evaluation of the fundamental absorption spectrum of a material by its refractive index dispersion in the transparency range

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A method has been elaborated to reconstruct the material absorption spectrum  $k(\omega')$  in the ranges of fundamental excitations ( $\omega'$ ) basing on the refractive index dispersion  $n(\omega)$  in the material transparency range ( $\omega$ ). The method has been applied to evaluate of the linear dichroism  $\Delta k(\omega')$  spectra of  $K_2Ca(SO_4)_2 \cdot H_2O$  crystals (syngenite) proceeding from its birefringence dispersion  $\Delta n(\omega)$ . The  $\Delta k(\omega')$  spectra of syngenite have been obtained and analyzed for several temperatures in the range of 293 to 450 K for mechanically free and uniaxially pressed ( $\sigma = 250$  bar) samples.

Предложен метод реконструкции спектра поглощения материала  $k(\omega')$  в областях фундаментальных возбуждений ( $\omega'$ ) на основании дисперсии показателя преломления  $n(\omega)$  в области прозрачности ( $\omega$ ). Метод применен для оценки спектра линейного дихроизма  $\Delta k(\omega')$  кристалла  $K_2Ca(SO_4)_2 \cdot H_2O$  (сингенит) на основании дисперсии двулучепреломления  $\Delta n(\omega)$ . Полученные спектры  $\Delta k(\omega')$  проанализированы для нескольких температур в области 293–450 К для механически ненапряженных и одноосно сжатых ( $\sigma = 250$  бар) образцов.

Investigations of the optical absorption spectra of solids in the vacuum ultraviolet photon energy range ( $h\omega > 6$  eV) by measuring its reflectance spectra are burdened by several technical difficulties. These are the lack of perfect polarizers, eventual contamination of the sample surface by residual molecules in the vacuum chamber, eventual destruction of the material surface in vacuum, especially at high temperatures, etc. Therefore, alternative methods for getting information on these spectra are desirable. One of such methods proposed in [1–3] is developed in this work.

In the work, we have studied the approximate spectra of linear fundamental dichroism,  $\Delta k(\omega')$ , for  $K_2Ca(SO_4)_2 \cdot H_2O$  crystals (syngenite) at different temperatures

and mechanical uniaxial pressures reconstructed on the basis of the corresponding birefringence dispersions  $\Delta n(\omega)$  in the transparency range [4]. The main peculiarity of syngenite is the characteristic temperature-induced transformation of the axes orientation of its optical indicatrix. At room temperature, optical axes of the crystal lie in its XY plane. The angle between these optical axes decreases as the temperature elevates, so that at 418 K, the crystal becomes uniaxial for the wavelength  $\lambda = 632.8$  nm with the optical axis being parallel to the principal  $n_p$  half-axis of optical indicatrix. This is the spectral inversion of birefringence sign (SIBS),  $\Delta n(\omega_i) = 0$ . The relations between the optical indicatrix axes,  $n_p$ ,  $n_m$ ,  $n_g$ , and crystallographic axes, X, Y, Z, of

syngenite are as follows:  $n_p \parallel X$ ,  $n_g \parallel Y$ ,  $n_m \parallel Z$ . At higher temperatures,  $T > 418$  K, the crystal becomes two-axial again with the optical axes arranged in  $XZ$  plane [4, 5].

The refractive index dispersion  $n(\omega)$  of a dielectric in the range of its optical transparency,  $\omega_1 \div \omega_2$ , is defined by the frequency dependences of absorption index  $k(\omega')$  in the frequency ranges of electron,  $\omega' > \omega_2$ , and phonon,  $\omega' < \omega_1$ , excitations according to the known Kramers-Kronig relation [1–3]:

$$\begin{aligned} n(\omega) - 1 &= \frac{2}{\pi} \int_0^{\infty} \frac{\omega' k(\omega') d\omega'}{\omega'^2 - \omega^2} = \\ &= \frac{2}{\pi} \int_0^{\omega_1} \frac{\omega' k(\omega') d\omega'}{\omega'^2 - \omega^2} + \frac{2}{\pi} \int_{\omega_2}^{\infty} \frac{\omega' k(\omega') d\omega'}{\omega'^2 - \omega^2}. \end{aligned} \quad (1)$$

The birefringence dispersion  $\Delta n_{jr}(\omega)$  of dielectric crystal, that is, the difference of refractive index dispersions for two spatially orthogonal directions  $j$  and  $r$  of light polarization,  $\Delta n_{jr}(\omega) = n_j(\omega) - n_r(\omega)$ , can be presented in the form (2) using the relation (1),

$$\Delta n_{jr}(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \Delta k_{jr}(\omega') d\omega'}{\omega'^2 - \omega^2}, \quad (2)$$

where  $\Delta k_{jr}(\omega')$  is the frequency dependence of linear fundamental dichroism,  $\Delta k_{jr}(\omega') = k_j(\omega') - k_r(\omega')$ .

The relation (2) can be considered as the integral equation when the frequency dependence of linear fundamental dichroism  $\Delta k_{jr}(\omega')$  has to be determined basing on birefringence dispersion  $\Delta n_{jr}(\omega)$  in the crystal transparency range. Solving of this problem is of interest, because the experimental measurement of the birefringence dispersion  $\Delta n_{jr}(\omega)$  of dielectric crystal in its transparency range is much easier than measurement of the frequency dependence of linear dichroism  $\Delta k_{jr}(\omega')$  in the ranges of phonon ( $\omega' < \omega_1 \approx 0.4$  eV) and electron ( $\omega' > \omega_2 \approx 5$  eV) excitations.

To obtain the  $\Delta k_{jr}(\omega')$  spectrum, the integral equation (2) has to be solved. In the case of syngenite, transparent in the range of 0.4 to 7.0 eV [4], the birefringence dispersion  $\Delta n(\omega)$  is formed by the electron ( $el$ ),  $\omega' > 7.2$  eV, and phonon ( $ph$ ),  $\omega' < 0.4$  eV, parts of the dichroism spectrum  $\Delta k(\omega')$ . Taking into account the frequency regions of phonon ( $0 \div \omega_1$ ) and electron ( $\omega' > \omega_2$ ) optical absorption and the crystal transpar-

ency region of ( $\omega_1 \div \omega_2$ ) and the relation (2), the condition for SIBS,  $\Delta n(\omega_i) = 0$ , can be written in the following form,

$$\begin{aligned} \Delta n_{jr}(\omega_i) &= \int_0^{\omega_1} \frac{\omega' \Delta k_{jr}^{(ph)}(\omega') d\omega'}{\omega'^2 - \omega^2} + \\ &+ \int_{\omega_2}^{\infty} \frac{\omega' \Delta k_{jr}^{(el)}(\omega') d\omega'}{\omega'^2 - \omega^2} = 0. \end{aligned} \quad (3)$$

Let us evaluate the relation between two integrals in the equation (3). First, one can estimate the magnitudes of two similar integrals (4) and (5) of the relation (1) for the refractivity  $[n(\omega) - 1]$ , originating from the phonon and electron light excitations, respectively:

$$I_{ph} = \frac{2}{\pi} \int_0^{\omega_1} \frac{\omega' k(\omega') d\omega'}{\omega'^2 - \omega^2}, \quad (4)$$

$$I_{el} = \frac{2}{\pi} \int_{\omega_2}^{\infty} \frac{\omega' k(\omega') d\omega'}{\omega'^2 - \omega^2} \approx \frac{2}{\pi} \int_{\omega_2}^{\omega_3} \frac{\omega' k(\omega') d\omega'}{\omega'^2 - \omega^2}. \quad (5)$$

In the case of syngenite, the following magnitudes of parameters in the equations (4) and (5) can be taken:  $\omega_1 = 0.4$  eV [6],  $\omega = 2.2$  eV ( $\lambda = 563.6$  nm),  $\omega_2 = 7$  eV,  $\omega_3 = 30$  eV [7]. It is known that the typical absorption index value for insulators in the phonon absorption range, 0 to 0.4 eV, is  $k^{(ph)} \approx 1$  [8], while the similar value in the range of electron absorption, 7 to 30 eV, is  $k^{(el)} \approx 0.5$  [9]. In this case, the calculations using relations (4) and (5) have shown that the contribution to the refractive index  $n$  in the crystal transparency range from the electron excitations exceeds one order of magnitude the corresponding contribution from the phonon ones:

$$I_{el} = \frac{2}{\pi} 0.5 \frac{1}{2} \ln \frac{\omega_3^2 - \omega^2}{\omega_2^2 - \omega^2} \approx 0.5,$$

$$I_{ph} = -\frac{2}{\pi} \frac{1}{2} \ln \frac{\omega^2}{\omega^2 - \omega_1^2} \approx -0.01.$$

Basing on the last estimation and suggesting the self-evident relationship  $\Delta k^{(ph)}/\Delta k^{(el)} \approx k^{(ph)}/k^{(el)}$ , one can obtain a similar result for estimation of the relation

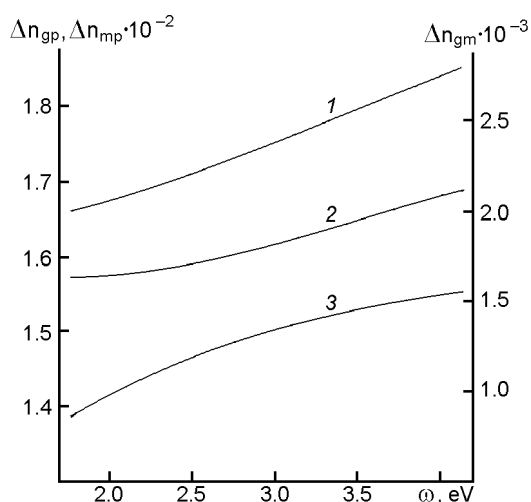


Fig. 1. Experimental linear birefringence dispersions  $\Delta n_{jr}(\omega)$  ( $j, r = p, m, g$ ) of syngenite in the transparency range at 294 K:

1—  $\Delta n_{gp}$ ; 2 —  $\Delta n_{mp}$ ; 3—  $\Delta n_{gm}$ .

between "phonon" and "electron" parts of the experimentally observed birefringence  $\Delta n$ ,

$$\Delta n^{(ph)} \ll \Delta n^{(el)}, \quad (6)$$

where  $\Delta n = \Delta n^{(ph)} + \Delta n^{(el)}$ .

The relation (6) confirms the suggestion that the principal peculiarities of the birefringence dispersion  $\Delta n(\omega)$  of a crystal, particularly the case of  $\Delta n(\omega)$  with SIBS, are defined by the peculiarities of the electron dichroism  $\Delta k^{(el)}(\omega')$  spectra.

As it seen in the introducing section, the phenomenon of birefringence sign inversion for syngenite is observed for the direction of light propagation along  $p$ -axes of optical indicatrix,  $\Delta n_{gm} = 0$  [4, 5]. (Hereafter, the indices  $p, m, g$  correspond to the appropriate directions of the optical indicatrix principal axes of syngenite at room temperature). The spectral dependence of birefringence  $\Delta n_{gm}(\omega)$  differs essentially from similar dependences  $\Delta n_{gp}(\omega)$  and  $\Delta n_{mp}(\omega)$  obtained for two others orthogonal  $m$ - and  $g$ -directions of light propagation (Fig. 1). This is displayed in relatively smaller magnitudes of  $\Delta n_{gm}$  and in negative magnitude of the value  $d^2(\Delta n_{gm})/d\omega^2$  instead of positive magnitudes of the values  $d^2(\Delta n_{gp})/d\omega^2$  and  $d^2(\Delta n_{mp})/d\omega^2$  in the high-frequency part of  $\Delta n_{jr}(\omega)$  dependences. The calculated approximate spectra of corresponding fundamental dichroism  $\Delta k_{jr}(\omega')$  for the mechanically free samples at 294 K are pre-

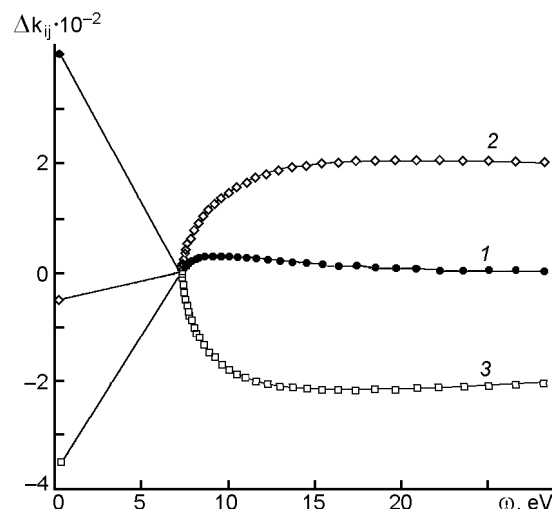


Fig. 2. Calculated approximate linear fundamental dichroism  $\Delta k_{jr}(\omega')$  ( $j, r = p, m, g$ ) spectra of syngenite for three principal directions of optical indicatrix at 294 K:

1—  $\Delta k_{gm}$ ; 2 —  $\Delta k_{mp}$ ; 3—  $\Delta k_{pg}$ .

sented in Fig. 2. Taking into account that  $\Delta n_{jr} = -\Delta n_{rj}$  and  $\Delta k_{jr} = -\Delta k_{rj}$ , one can notice that the dispersions of  $\Delta n_{jr}(\omega)$  in the transparency range, 1.8 to 4.2 eV (Fig. 1), and the corresponding spectra  $\Delta k_{jr}(\omega')$  in the fundamental absorption range, 7 to 30 eV (Fig. 2), are of the same sign for the temperature 294 K.

Experimental birefringence dispersions  $\Delta n_{gm}(\omega)$  for different temperatures and uniaxial mechanical stresses of syngenite are shown in Fig. 3. At higher temperatures, 400 and 470 K, the SIBS phenomenon in the transparency range (Fig. 3) arises together with the phenomenon of spectral inversion of dichroism sign (SIDS) in the fundamental absorption range  $\omega' > 7$  eV (Fig. 4). Taking into account this result and the equation (3), one can conclude that SIBS in the crystal transparency range,  $\Delta n_{jr}(\omega_i) = 0$ , is a special case of such spectral dependence of the fundamental dichroism  $\Delta k_{jr}(\omega')$ , for which the contributions to  $\Delta n_{jr}(\omega)$  from the of fundamental excitation spectral ranges with positive and negative  $\Delta k_{jr}(\omega')$  values according to Kramers-Kronig relation (2) become equal at the photon energy  $\omega_i$ .

Temperature dependences of the syngenite dichroism  $\Delta k_{gm}(T)$  shown in Fig. 5 correspond to the data presented in Fig. 4. The solution of the equation (3) shows that in spite of the relation  $\Delta k^{(ph)} > \Delta k^{(el)}$  (Fig. 5), the corresponding fraction of the

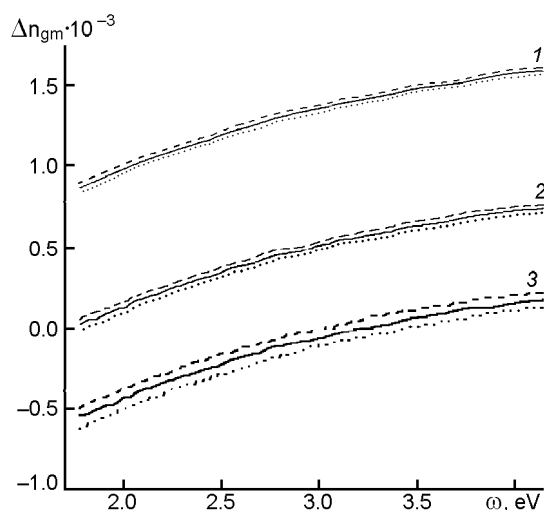


Fig. 3. Experimental linear birefringence dispersions  $\Delta n_{gm}(\omega)$  of syngenite in the transparency range for different directions of uniaxial stress at 294 (1), 400 (2), and 470 (3) K. Solid lines correspond to mechanically free sample,  $\sigma = 0$  — dotted curves; to  $\sigma_m = 200$  bar — dashed curves; to  $\sigma_g = 200$  bar — small points.

phonon part of the birefringence  $\Delta n^{(ph)}$  in the experimentally observed  $\Delta n$  value does not exceed 20 %:  $\Delta n^{(ph)} \approx 0.2 \Delta n$ . Therefore, it is reasonable that the SIBS in syngenite is due mainly to the peculiarities of optical spectra in the electron excitation range  $\omega' > 7$  eV.

Relative temperature change of the  $\Delta k_{gm}(T)$  dependence for the frequency of phonon excitation  $\omega' = 0.2$  eV is the smallest,  $\delta(\Delta k_{gm}^{(0.2)}) / \Delta k_{gm}^{(0.2)} \approx 0.07$ , as compared to similar values for the frequencies  $\omega' = 8.5$  eV and  $\omega' = 17$  eV of electron excitation:  $\delta(\Delta k_{gm}^{(8.5)}) / \Delta k_{gm}^{(8.5)} \approx 0.33$ ,  $\delta(\Delta k_{gm}^{(17)}) / \Delta k_{gm}^{(17)} \approx 1.75$ . The greatest temperature change of dichroism corresponding to the energy  $\omega' = 17$  eV is connected with the fact that this frequency is close to the range of SIDS localization region,  $\omega'_i > 14$  eV (Fig. 4). The results described show that temperature changes of the birefringence dispersions  $\Delta n_{gm}(\omega)$  are due mainly to temperature changes of the dichroism spectra  $\Delta k_{gm}(\omega')$  in the electron excitation range. These changes can be most probably caused by temperature changes of the frequency-dependent anisotropic polarizabilities of chemical bonds due to corresponding bond length changes in the crystal.

Proceeding from the spectral dependences of dichroism  $\Delta k_{gm}(\omega')$  obtained, the

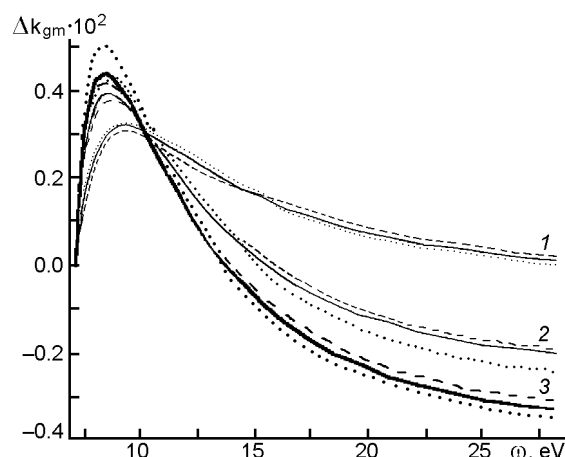


Fig. 4. Calculated approximate linear fundamental dichroism  $\Delta k_{gm}(\omega')$  spectra of syngenite for different temperatures 294 (1), 400 (2), and 470 (3) K and stresses ( $\sigma = 0$  — dotted curves; to  $\sigma_m = 200$  bar — dashed curves; to  $\sigma_g = 200$  bar — small points).

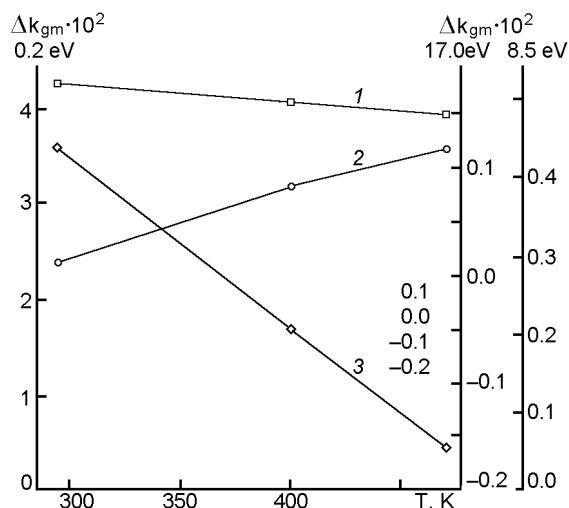


Fig. 5. Calculated temperature dependences of the linear fundamental dichroism  $\Delta k_{gm}(T)$  of syngenite at different photon energies, 0.2 (1), 8.5 (2), and 17.0 (3) eV, for mechanically free sample  $\sigma = 0$ .

birefringence dispersions  $\Delta n_{gm}(\omega)$  in the whole range of crystal transparency (0.5 to 7.0 eV) were calculated using the relation (2). These calculated birefringence dispersions  $\Delta n_{gm}(\omega)$  agree with corresponding experimental data to within 3 % of the  $\Delta n$  value.

An uniaxial mechanical stress  $\sigma$  causes the corresponding changes of the birefringence  $\delta(\Delta n)$  of the same sign within the spectral range 1.8 to 4.1 eV (Fig. 3). The corresponding changes of the dichroism spectra  $\delta(\Delta k)$  in the range of 7 to 28 eV are

seen in Fig. 4. A characteristic feature of the  $\Delta k(\omega')$  spectra for different stresses  $\sigma$  at the same temperature  $T$  is the presence of two separate spectral regions where the rates of mechanically induced dichroism change  $\delta(\Delta k)/\delta\sigma|_{\omega, T}$  are characterized by the opposite signs. Thus, the same sign of the mechanically induced birefringence changes  $\delta(\Delta n)$  in syngenite within the transparency region of 1.8 to 4.1 eV corresponds to spectrally different signs of similar dichroism changes  $\delta(\Delta k)$  in the fundamental absorption range of 7 to 28 eV. This may be due to some interaction between the mechanically induced changes in anisotropic electron polarizabilities of the chemical bonds corresponding to different photon energies.

To conclude, the phenomenon of spectral inversion of birefringence sign in the crystal transparency range,  $\Delta n_{jr}(\omega_i) = 0$ , is a particular case of such spectral dependence of the linear fundamental dichroism  $\Delta k_{jr}(\omega')$ , where the contributions to  $\Delta n_{jr}(\omega)$  from the fundamental excitation energy ranges of positive and negative values of  $\Delta k(\omega')$  according to Kramers-Kronig relation are equal to one another at the photon energy  $\omega_i$ . Temperature changes in the birefringence dispersions  $\Delta n(\omega)$  of syngenite are due mainly to temperature changes of the linear dichroism spectra  $\Delta k(\omega')$  in the electron excitation range of 7 to 28 eV. These temperature changes are most probably

caused by corresponding changes of chemical bond lengths of the crystal. The same sign of the mechanically induced changes in the birefringence  $\delta(\Delta n)$  of syngenite in the transparency region of 1.8 to 4.1 eV correspond to spectrally different signs of similar changes in the linear dichroism  $\Delta k(\omega')$  in the fundamental absorption range of 7 to 28 eV. This may be due to some interaction between the mechanically induced changes of anisotropic electron polarizabilities of chemical bonds corresponding to different photon energies.

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## Оцінка спектра фундаментального поглинання матеріалу за дисперсією його показника заломлення в області прозорості

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Запропоновано метод реконструкції спектра поглинання матеріалу  $k(\omega')$  в областях фундаментальних збуджень ( $\omega'$ ) на основі дисперсії показника заломлення  $n(\omega)$  в області прозорості ( $\omega$ ). Метод застосовано для оцінки спектра лінійного дихроїзму  $\Delta k(\omega')$  кристалу  $K_2Ca(SO_4)_2 \cdot H_2O$  (сингеніт) на основі дисперсії двоприменезаломлення  $\Delta n(\omega)$ . Отримані спектри  $\Delta k(\omega')$  проаналізовано для кількох температур в області 293–450 К для механічно ненапружених і одночасно стиснутих ( $\sigma = 250$  бар) зразків.