
Optical Properties of Langbeinites

1. Electrooptical effect and optical activity

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Abstract

The review paper is devoted to the collection and analysis of experimental results obtained by different researches investigating the optical properties of langbeinites. This investigation in general consists of the electrooptical effect, optical activity, Raman scattering, crystalloptics of domains and temperature studying of the birefringence. Langbeinites with their simple structure and cubic symmetry could be model crystals for the development of the microscopic theory of electrooptical effect and optical activity. Most of the number of investigations concerning the domains configuration, temperature behavior of birefringence and Raman scattering were conducted in langbeinites because of quite an interesting and unusual sequence of structural phase transitions in these crystals. It is shown in the present paper that optical methods of investigations of phase transitions, particularly in langbeinites, lead to obtaining important information on the change of symmetry at phase transition, the temperature dependence of the order parameter and lattice dynamics.

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Introduction

Langbeinites - is a wide crystal family (more than 30 compounds) that possess the structure of mineral $K_2Mg_2(SO_4)_3$. It is interesting to remember that an other langbeinite - $K_2Mn_2(SO_4)_3$ was founded in Vesuvium lava in 1923 [1]. Langbeinites belong to the group of crystals with the general chemical formula $M_2^+M_2^{++}(SO_4)_3$, where M_2^+ [K, Rb, Tl, (NH_4) ,

Cs] and M_2^{++} [Co, Cd, Ca, Zn, Mg, Mn, Fe, Ni] are univalent and divalent ions, respectively [2]. Most of them are cubic at room temperature and belong to the space group of symmetry $P2_13$ [3]. Investigation of the optical properties of langbeinites started from the study of the electrooptical effect [4]. It was assumed that cubic langbeinites could be used as elements of wide aperture electrooptical devices. On the

other hand cubic noncentrosymmetrical langbeinites are good model crystals for the investigations of optical activity [5]. But the most important role of optical investigations in the langbeinite family belong to optical methods of investigations of phase transitions. These investigations in general consist of the Raman scattering, crystalloptics of domains and temperature studying of the birefringence. The change of the domains configuration can lead to the conclusion about the change of symmetry at phase transition. Moreover, as it will be shown below, the problem of the domains has a separate meaning in the ferroelastics langbeinites. Temperature dependence of the order parameter and respective critical exponents can be derived from the temperature dependence of birefringence. And finely, conclusions about the lattice dynamic and microscopic nature of phase transitions can be made from the results of Raman spectrum investigations.

The aim of the present review is to collect and analyze experimental results obtained by different research on optical properties of langbeinites.

1. Electrooptical effect

The study of the electrooptical effect was began in 1964 from the measurements by C.F.Buhrer and L.Ho [6] of the electrooptical coefficients $n_0^3 r_{41}$ in $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{Mn}_2(\text{SO}_4)_3$ crystals. It was found that these coefficients equal $3.0 \times 10^{-12} \text{m/V}$ and $2.5 \times 10^{-12} \text{m/V}$, respectively. The following experiments here conducted by Emmenegger F., Nitsche R. and Miller A. J. in 1968 [4]. The authors measured the electrooptical power of five langbeinite compounds - $(\text{NH}_4)_2\text{Mn}_2(\text{SO}_4)_3$, $\text{K}_2\text{Mn}_2(\text{SO}_4)_3$, $\text{Rb}_2\text{Mn}_2(\text{SO}_4)_3$, $\text{Tl}_2\text{Mn}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Ni}_2(\text{SO}_4)_3$. The results of the experiment are given in Table 1. On the base of the analysis of the polarizability of cations and anions F.Emmeneger et al come to the conclusion that the principal contribution to the electrooptical effect comes from the sulfate ions. For manganese compounds, with the exception of $(\text{NH}_4)_2\text{Mn}_2(\text{SO}_4)_3$ crystals, electrooptical power is found to be approximately constant. Its value appears to increase as the polarizability of the univalent ion increases, which implies that univalent ions makes a small contribution to the electrooptical similar with the same sign as that

Table 1. Electrooptical data of langbeinites .

Compound	n_o	$n_0^3 r_{41}, 10^{-12} \text{m/V}$	$r_{41}, 10^{-12} \text{m/V}$
$(\text{NH}_4)_2\text{Mn}_2(\text{SO}_4)_3$ [6]	1.63	0.70 ± 0.07	0.16 ± 0.01
$\text{K}_2\text{Mn}_2(\text{SO}_4)_3$ [4]	1.62	8.6 ± 0.9	2.0 ± 0.2
$\text{Rb}_2\text{Mn}_2(\text{SO}_4)_3$ [4]	1.60	7.7 ± 0.8	1.9 ± 0.2
$\text{Tl}_2\text{Mn}_2(\text{SO}_4)_3$ [4]	1.80	12.4 ± 1.2	2.1 ± 0.2
$\text{K}_2\text{Ni}_2(\text{SO}_4)_3$ [4]	1.70	4.9 ± 0.5	1.0 ± 0.1
$\text{K}_2\text{Co}_2(\text{SO}_4)_3$ [4]	1.60	too strained [4]	
$(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ [6]	1.606	3.0	0.21 [9], 0.67[10]
$\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ [7]	1.730	0.57	0.11
$\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ [8]	1.535	0.43	0.12
$\text{K}_2\text{Cd}_2(\text{SO}_4)_3$ [11,12]	$n_1=1.5882,$ $n_2=1.5902,$ $n_3=1.5912$		$r_{41}=0.24,$ $r_{52}=0.18,$ $r_{63}=0.35$ $r_{41}=0.6$ (in cubic phase)

of the sulfate contribution. For the ammonium compound the electrooptical effect is nearly zero. It means that unlike the other univalent cations, the highly acentrosymmetric ammonium ion makes a large contribution nearly equal in magnitude to that of the sulfate ion and opposite in sign. The difference in electrooptical power for the $K_2Mn_2(SO_4)_3$ and $K_2Ni_2(SO_4)_3$ suggest that the divalent ions also contribute significantly to the electrooptical effect.

The electrooptical effect in langbeinites was studied also by A.S.Vasilevskaya et al [7] and I.P.Kaminov et al [8]. The authors of [7,8] measured the electrooptical coefficients in the $Tl_2Cd_2(SO_4)_3$ and $K_2Mg_2(SO_4)_3$ crystals that equal $r_{41}=0.11 \times 10^{-12} \text{ m/V}$ and $r_{41}=0.12 \times 10^{-12} \text{ m/V}$ (for $\lambda=0.546 \mu\text{m}$), respectively.

The electrooptical effect in $(NH_4)_2Cd_2(SO_4)_3$ crystals was studied by N.Ivanov, J.Fousek and Ch.Konak [9,10]. At room temperature $r_{63}=(0.67 \pm 0.05) \times 10^{-12} \text{ m/V}$ for $\lambda=0.633 \mu\text{m}$ and fully agreeing with data presented in Table 1 obtained by Buhner C.F. and Ho L. [6]. It means that the conclusion about the opposite sign of the contributions to the electrooptical effect from ammonium and sulfate groups is not correct and the microscopic theory of electrooptical properties of this family of crystals has not yet been developed. The

behavior of the electrooptical effect and birefringence of $(NH_4)_2Cd_2(SO_4)_3$ will be described below.

Dicadmium-dipotassium sulfate ($K_2Cd_2(SO_4)_3$) is a unique langbeinite crystal that at room temperature belongs to the space group of symmetry $P2_12_12_1$ [11]. The dispersion of the refractive indices and electrooptical coefficients of $K_2Cd_2(SO_4)_3$ crystals are presented on Fig. 1 and Fig. 2, respectively [12,13]. Refractive indexes of $K_2Cd_2(SO_4)_3$ equal $n_1=1.5882$, $n_2=1.5902$, $n_3=1.5912$ and electrooptical coefficients of these crystals are quite small $r_{41}=0.24 \times 10^{-12} \text{ m/V}$, $r_{52}=0.18 \times 10^{-12} \text{ m/V}$, $r_{63}=0.35 \times 10^{-12} \text{ m/V}$ for $\lambda=0.633 \mu\text{m}$. Temperature dependence of refractive indices of $K_2Cd_2(SO_4)_3$ crystals at the ferroelastical phase transition are presented on Fig. 3. At the heating and cooling transition through T_c the transposition of refractive indices n_z and n_y was observed. Such behavior is connected with the peculiarities of the domains in these crystals.

In order to summarize the results of the study of the electrooptical effect in langbeinite crystals one can come to the conclusion that these crystals are not applicable for use in electrooptical devices but they could be used as a good model for the analysis of the electrooptical effect on a microscopic level.

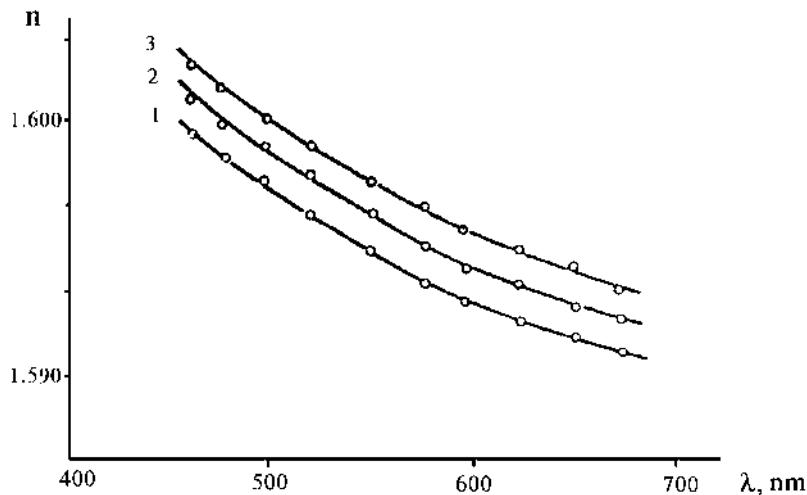


Fig. 1. Dispersion of the refractive indices of $K_2Cd_2(SO_4)_3$ crystals at $T=295\text{K}$: 1- n_x , 2- n_y , 3- n_z .

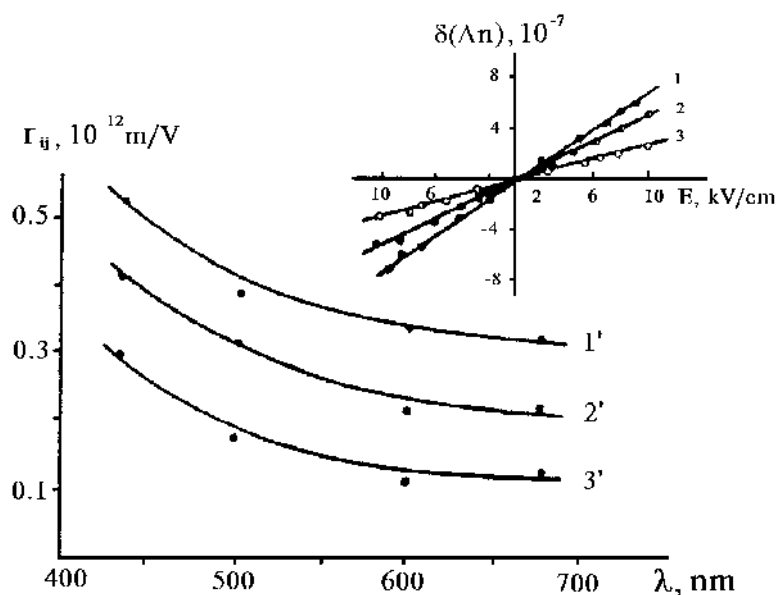


Fig. 2. Dispersion of the electrooptical coefficients of $K_2Cd_2(SO_4)_3$ crystals at $T=295K$: 1'- r_{63} , 2'- r_{52} , 3'- r_{41} ; Insert: dependencies 1- $\delta(\Delta n)_{xy}=f(E_z)$; 2- $\delta(\Delta n)_{xz}=f(E_y)$; 3- $\delta(\Delta n)_{zy}=f(E_x)$.

2. Optical activity and circular dichroism spectrums

Despite the noncentrosymmetrical point groups of langbeinites prolong a long time there a point of view that these crystals do not possess the optical activity [6]. First data on measuring the optical activity in langbeinites appeared only in 1974 [10]. N.Ivanov and C.Konak measured the optical activity in $(NH_4)_2Cd_2(SO_4)_3$ crystals in the cubic phase. It was found that $g_{11}=10^{-6}$ for $\lambda=0.633\mu m$. A few years later this result was confirmed by J.Kobayashi, Y.Uesu et al who studied the temperature dependence of the gyration constant g_{11} in the paraelectric phase (Fig. 4) [14].

The temperature dependence of gyration constants of $K_2Cd_2(SO_4)_3$ crystals at ferroelastic phase transition, the shape of the gyration surface and the temperature dependence of the piezogyration effect were studied by R.Vlokh et al [12, 15-18]. The $K_2Cd_2(SO_4)_3$ crystals possess a proper ferroelastical phase transition at $T_c=432K$ with a change of space group of symmetry $P2_13 \rightarrow P2_12_12_1$ [19,20]. On Fig. 5 and Fig.6 the dispersion and temperature dependencies of optical rotary power and

gyration tensor components of the $K_2Cd_2(SO_4)_3$ crystals are presented. Rotation of the polarization plane was measured at the propagation of the optical beam along one of the optical axes while the gyration constants - at the optical beam propagation along the principal crystallophysical axes Z and X by the oscillation method of the azimuth of ellipse of polarization. It was found that at $T=423K$ the optical rotary power changes the sign to an opposite one, which is connected with a temperature transfer of the optical axis from the positive part of the gyration surface to the negative one (Fig. 7). The cross sections of the gyration surfaces were calculated on the basis of the relation

$$G=\rho\lambda n_2/\pi=g_{33}\cos^2V-g_{11}\sin^2V, \quad (1)$$

where G - scalar gyration parameter, ρ - optical rotary power, λ - optical wavelength, n_2 - refractive index along optical axis, g_{33} and g_{11} - components of gyration tensor and V - half of the angle between optical axes.

It is interesting to note that reinvestigation of the optical rotary power in $K_2Cd_2(SO_4)_3$ crystals conducted by W.Kaminsky [21] show that the temperature change in the sign of the rotation of polarization plane takes place not at

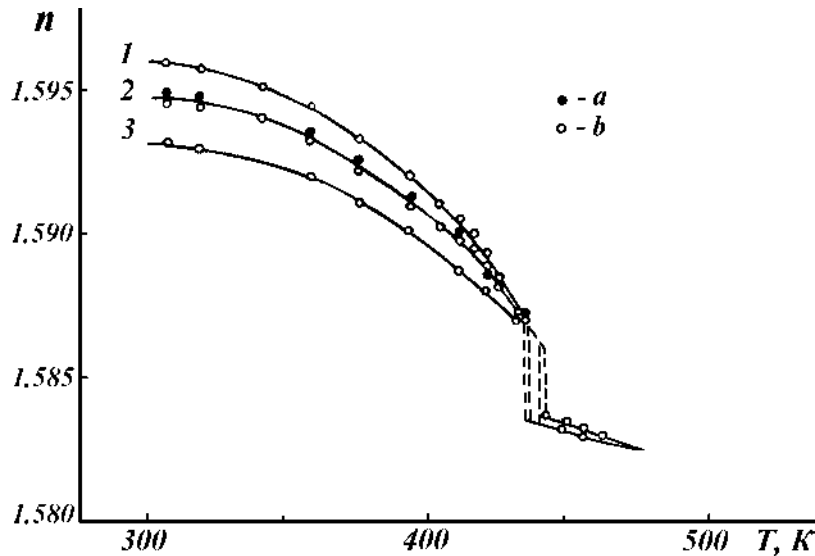


Fig. 3. Temperature dependence of refractive indices of the $K_2Cd_2(SO_4)_3$ crystals: 1- n_z , 2- n_y , 3- n_x ; a and b dependencies correspond to the transposition of the refractive indices n_z and n_y at heating and cooling crossing of T_c . [12]

temperature T_c -9K but at T_c . Such a disagreement between our results and the results presented in [21] can be explained by the peculiarities of the domain structure of the $K_2Cd_2(SO_4)_3$ crystals that will be described in paragraph 3. For example as it was shown in [22] the paraelastic phase of langbeinites usually consists of enantiomorphic domains the existence of which can lead to the difference of the signs of optical activity as in phase $P2_13$ as well as in phase $P2_12_12_1$. The topography of the optical activity in the cubic phase of the $K_2Cd_{0.4}Mn_{1.6}(SO_4)_3$ is shown on Fig. 8.

Similar temperature dependence of optical activity to $K_2Cd_2(SO_4)_3$ crystals was observed by us [23] in $K_2Cd_{1.8}Mn_{0.2}(SO_4)_3$ solid solutions (Fig. 9). The optical rotary power possesses a different sign in paraelastic and ferroelastic phase of these solid solutions. It was impossible to measure the optical activity already at 30K below T_c because of the sufficient change of the angle between optical axis with temperature.

The induced piezogyration effect in potassium-cadmium langbeinite was studied by R.Vlokh et al [18] in conditions of light propagation along one of the optical axes and application of the compressive strain along

Y-axis. The change of the scalar gyration parameter can be written as

$$\Delta G = (\beta_{3322} \cos^2 V + \beta_{1122} \sin^2 V) \sigma_{22}, \quad (2)$$

where β_{3322} and β_{1122} are the components of piezogyration tensor and σ_{22} - mechanical strain.

The temperature dependence of combined components of the piezogyration tensor is presented in Fig. 10. At room temperature the value of the combined component of the piezogyration effect tensor is equal

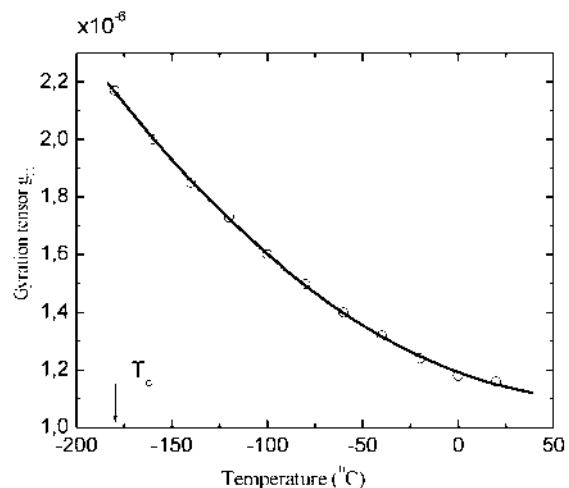


Fig. 4. Temperature dependence of the gyration coefficient g_{11} of $(NH_4)_2Cd_2(SO_4)_3$ crystals in the cubic phase [14].

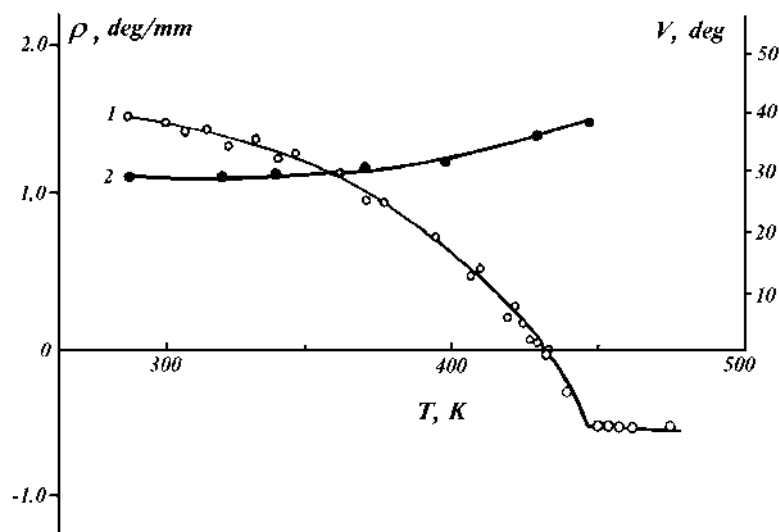


Fig. 5. Temperature dependencies of optical rotary power and angle between optical axis of the $K_2Cd_2(SO_4)_3$ ($\lambda=632.8nm$)[12].

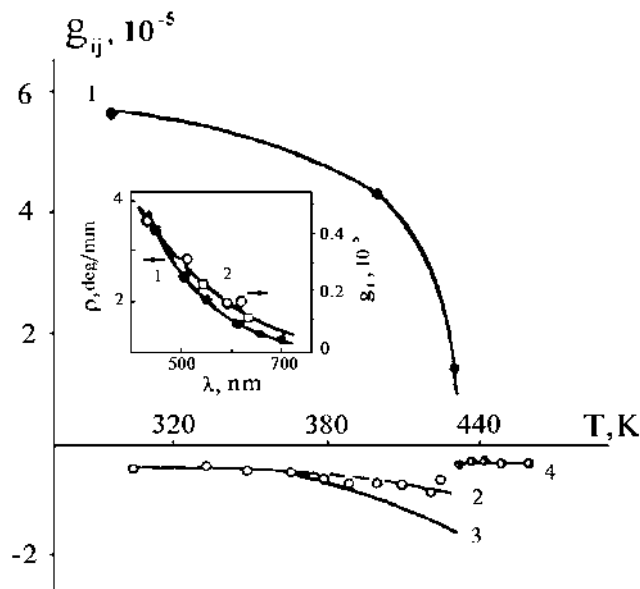


Fig. 6. Temperature dependence of the gyration tensor components in $K_2Cd_2(SO_4)_3$ crystals ($\lambda=632.8nm$): 1- g_{33} , 2- g_{11} (experimental results), 3- g_{11} (calculated on the base of the equation (1)), 4- g_{11} in the paraelastic phase; Insert: dispersion of the gyration tensor component and optical rotary power.

$$0.396\beta_{3322}+0.604\beta_{1122}= \\ =\Delta\rho\lambda n_2/\pi\sigma_{22}=(5.6\pm 1.2)\times 10^{-13}m^2/N, \quad (3)$$

The systematic investigations on the nature of optical activity in langbeinites was conducted by Z.Perekalina, O.Baturina et al [5, 24-26]. The authors studied the absorption spectrums, spectrums of the circular dichroism and dispersion of the optical rotary power of

$K_2Co_2(SO_4)_3$, $K_2Mg_2(SO_4)_3$, $Tl_2Cd_2(SO_4)_3$, $Rb_2Cd_2(SO_4)_3$ and $(NH_4)_2Cd_2(SO_4)_3$ crystals. Optical rotary dispersion and circular dichroism in $K_2Co_2(SO_4)_3$ crystals was studied also by B.Brezina et al [27]. It was shown that in the spectrum range 130nm-400nm there are two kinds of absorption lines: lines which are connected with the intermolecular electronic transitions inside SO_4 -groups (A) and lines of

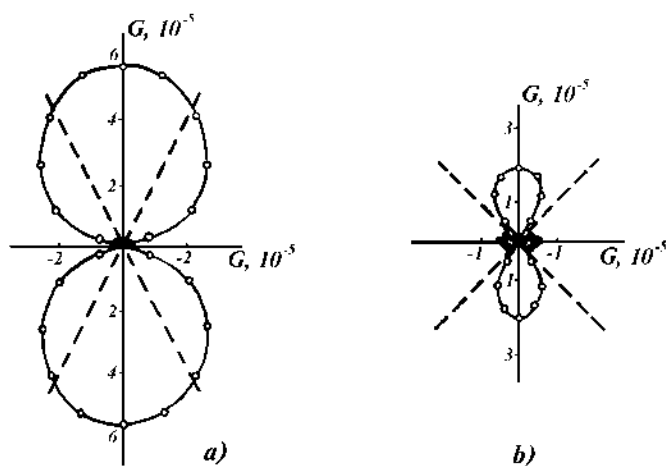


Fig. 7. Crosssections of the gyration surfaces of $K_2Cd_2(SO_4)_3$ crystals by $\langle 010 \rangle$ plane at a) $T=293K$, b) $T=423K$, $\lambda=632.8nm$.

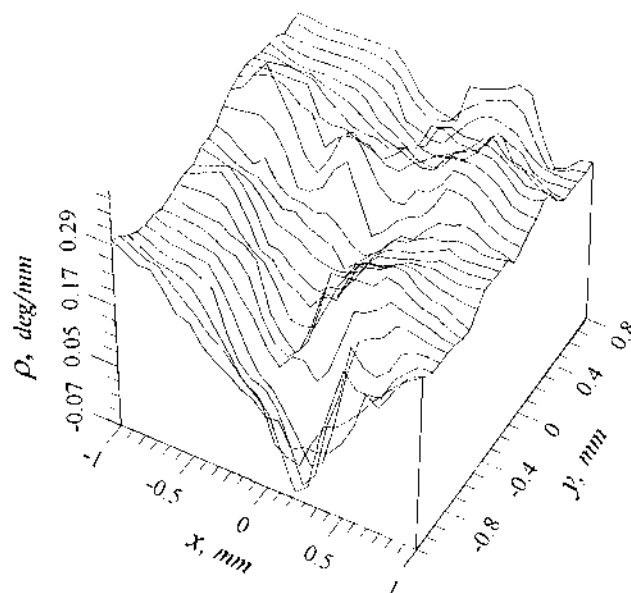


Fig. 8. Topography of the optical activity in cubic phase of the $K_2Cd_{0.4}Mn_{1.6}(SO_4)_3$ [23]

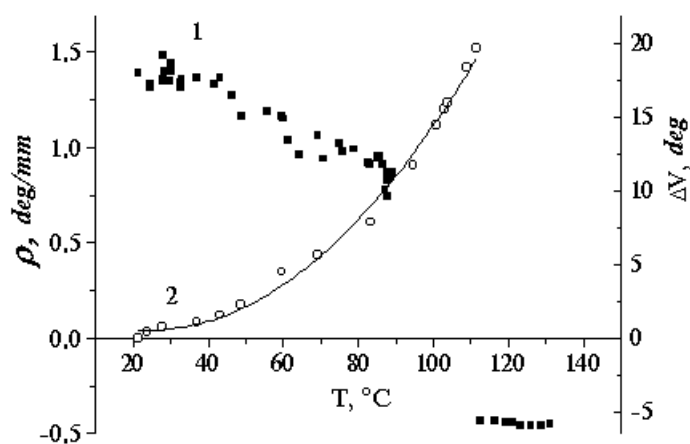


Fig. 9. Temperature dependence of optical activity in $K_2Cd_{1.8}Mn_{0.2}(SO_4)_3$ solid solutions [22].

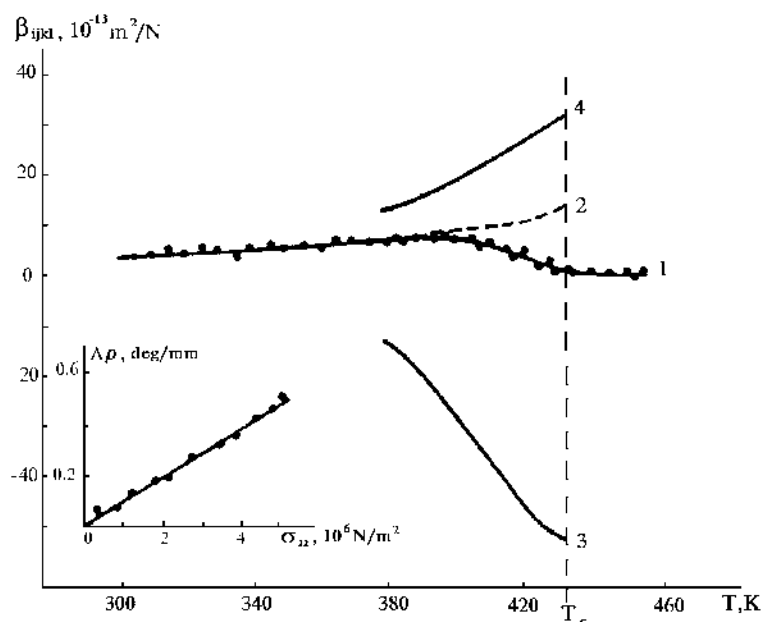


Fig. 10. Temperature dependence of combined components of the piezogyration tensor of $K_2Cd_2(SO_4)_3$ crystals [18] ($\lambda=632.8\text{nm}$): experimental dependence of $\Delta G/\sigma_{22}$, 2-approximation of $\Delta G/\sigma_{22}$ accounting the change of the angle between optical axis, 3,4-calculated dependence of β_{1122} and β_{3322} , respectively; Insert: dependence of the optical rotation power on mechanical strain σ_{22} .

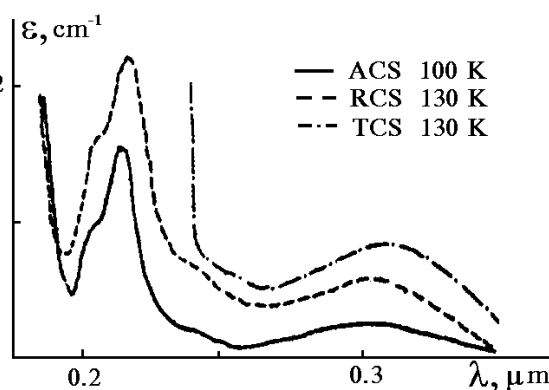


Fig. 11. The absorption spectrums of the $Tl_2Cd_2(SO_4)_3$, $Rb_2Cd_2(SO_4)_3$ and $(NH_4)_2Cd_2(SO_4)_3$ crystals [5,24-26].

charges transferred from the orbitals SO_4 -groups to the cations orbitals (B).

In Fig. 11 the absorption spectrums of the $Tl_2Cd_2(SO_4)_3$, $Rb_2Cd_2(SO_4)_3$ and $(NH_4)_2Cd_2(SO_4)_3$ crystals are presented. Both lines exist in these spectrums – a low intensity A-line and a high intensity B-line. It was found that a circular dichroism (Fig. 12) also exists at the wavelength of these lines while the dispersion of the optical rotary power in this spectrum range possesses normal behavior (Fig. 13).

The contribution of the divalent ion to the

optical activity was studied on the example of $K_2Co_2(SO_4)_3$ crystals. It was found that absorption lines of the correspond to the absorption of Co^{2+} (Fig. 14) and all of them possess a circular dichroism (Fig. 15).

But the results of the measurement of optical activity dispersion show that only most intensive lines lead to the abnormal dispersion of optical activity (Fig. 15). Temperature dependencies of optical activity of different langbeinites in the cubic phase are shown on Fig. 16.

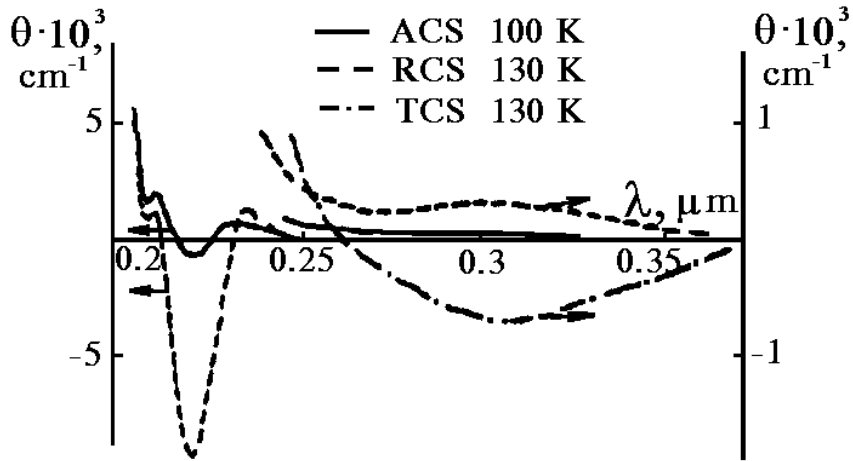


Fig. 12. Spectrums of the circular dichroism of the $\text{Ti}_2\text{Cd}_2(\text{SO}_4)_3$, $\text{Rb}_2\text{Cd}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ crystals [5,24-26].

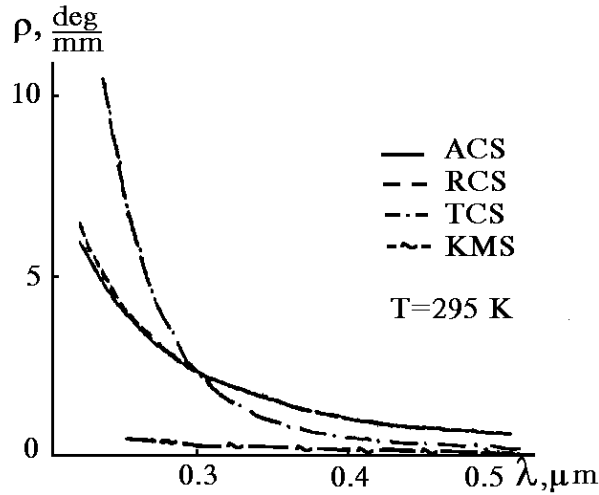


Fig. 13. Dispersion of optical activity of ACS, RCS, TCS and KMS crystals[5,24-26].

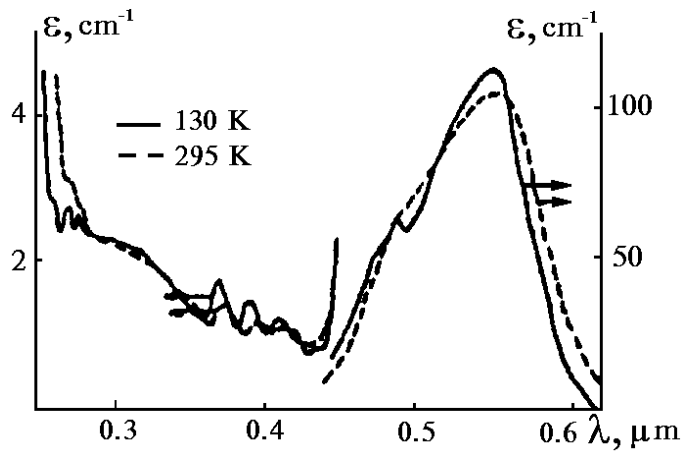


Fig. 14. Absorption spectrums of the $\text{K}_2\text{Co}_2(\text{SO}_4)_3$ crystals [5,24-26].

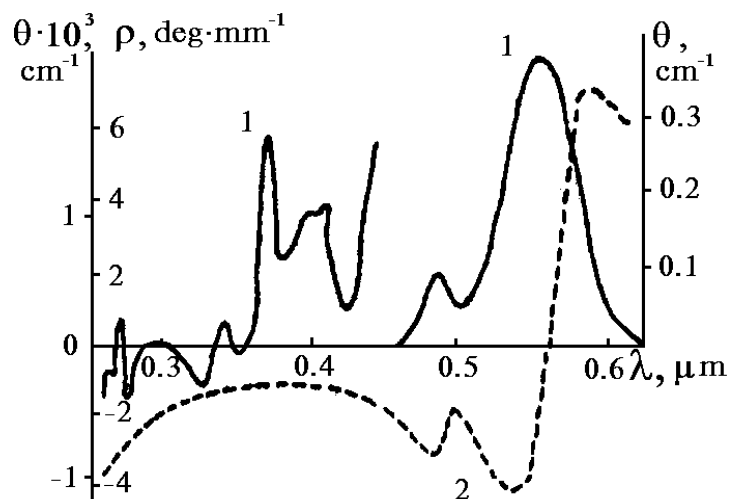


Fig.15. Spectrums of the circular dichroism and optical activity of the $K_2Co_2(SO_4)_3$ crystals [5,24-26].

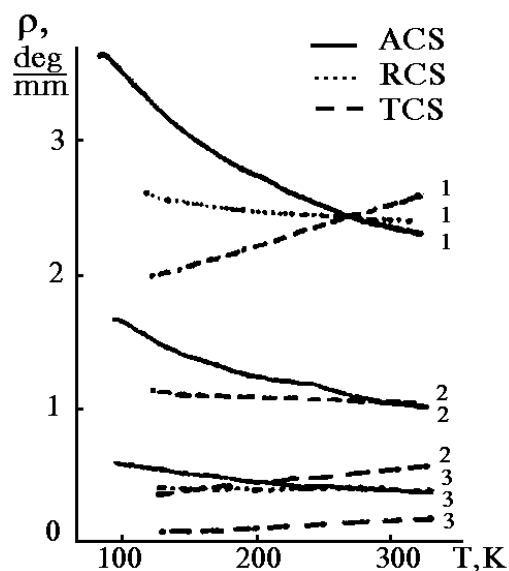


Fig. 16. Temperature dependencies of the optical rotary power of the $Tl_2Cd_2(SO_4)_3$, $Rb_2Cd_2(SO_4)_3$ and $(NH_4)_2Cd_2(SO_4)_3$ crystals at different wavelength: 1-300nm; 2-400nm; 3-650nm [5,24-26].

On the base of fitting the dispersion of optical activity $\rho(\lambda)$ of the studied langbeinite crystals by the formula

$$\rho(\lambda) = \sum_i \frac{k_i^{(1)} \lambda^2}{(\lambda^2 - \lambda_{oi}^2)^2} + \sum_i \frac{k_i^{(2)}}{\lambda^2 - \lambda_{oi}^2}, \quad (4)$$

where k_i - are the constants that are proportional to the rotation power of the electronic transition and λ_{oi} - the wavelength of the optical active absorption lines it was concluded that optical activity in langbeinites possess a “molecular”

nature and appear as the result of interactions in the SO_4^{2-} - tetrahedrons with the symmetry C_1 .

(To be continued)

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