PLEOCHROISM IN POTASSIUM COBALT SULFATE HEXAHYDRATE CRYSTALS

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A new method of growing potassium cobalt sulfate hexahydrate crystals from an aqueous solution of K_2SO_4 and $CoCl_2$ salts has been proposed. On the basis of X-ray diffraction researches, the chemical composition of crystals grown was confirmed. The corresponding transmission spectra in the range 200–800 nm were obtained for the crystallographic orientations (001) and (011). The pleochroism phenomenon associated with Co^{2+} absorption bands has been revealed. A relationship between the structural and optical spectral properties of the crystals obtained has been found.

1. Introduction

Studies of crystal optical spectra draw attention of researchers because of necessity in effective optical filters. In this connection, Tutton salts [1–12] are intensively studied. Data concerning their structure have been obtained [1–5]. In particular, the authors of work [5] studied low-frequency vibration spectra of crystalline Tutton salts with Co, Ni, and Zn ions. Potassium cobalt sulfate hexahydrate, $K_2Co(SO_4)_2{\cdot}6H_2O$ (KCSH), is an example of Tutton salts. This salt belongs to the compounds isomorphic to $M^I_2[M^{II}(H_2O)_6](SO_4)_2$, where M^I is an alkaline metal or NH_4, and M^{II} is a bivalent metal.

The features of the sulfate crystal growing and the solubility diagrams of those sulfates which are usually used to grow KCSH crystals were studied in work [6].

Crystals of $(NH_4)_2Co(SO_4)_2{\cdot}6H_2O$ salt can be used in experiments on the adiabatic demagnetization which is applied to obtain ultralow temperatures [7]. The theory of magnetic properties of cobalt Tutton salts was developed in work [8], the theory of paramagnetic resonance in hydrated cobalt salts in work [9], and experiments on proton nuclear magnetic resonance in a number of paramagnetic salts were carried out in work [10].

Nevertheless, the optical properties of KCSH practically were not analyzed. Earlier, we studied the spectra of mixed crystals $K_2Co_xNi_{1-x}(SO_4)_2{\cdot}6H_2O$ for the orientation (001) [11]. The low symmetry of crystals allowed us to expect that the position of absorption bands depends on the direction of light propagation. Therefore, in this work, we have studied KCSH crystals with various orientations.

2. Experimental Technique

Specimens to research were grown up by the method of slow evaporation at room temperature from the aqueous solution of potassium sulfate K_2SO_4 and cobalt chloride $CoCl_2$ taken in the stoichiometric ratio. A similar technique has already been applied by us for growing $K_2Zn(SO_4)_2{\cdot}6H_2O$ crystals [12]. To filter out the aqueous solution, we used filtering paper with an average pore diameter of 1-2.2 μm. Optically transparent homogeneous crystals were grown up for 40-60 days.

The fabricated crystals are exhibited in Fig. 1. The figure testifies that they are characterized by a well developed facet. The most pronounced are (001) and (011) facets. In addition, visually, the crystals have different colorings in different directions. In particular, they are light red in the direction (001) and saturated dark red in the (011) one. This testifies to their pleochroism.

X-ray diffraction studies were carried on a HZG-4A powder diffractometer. A tube with a Cu anode served as a source of X-rays (radiation emission with the wavelength $\lambda(\mathrm{Cu}\ K_\alpha) = 1.54185$ Å). Structural researches

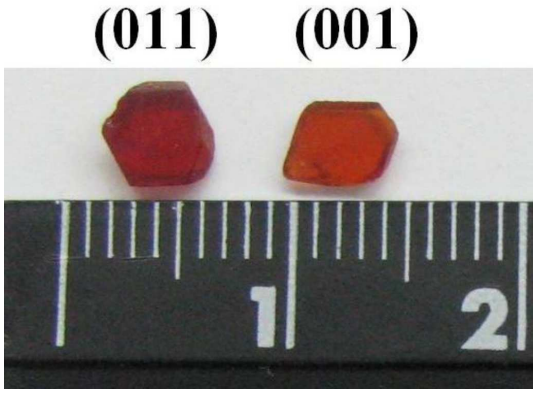

Fig. 1. Photograph of grown KCSH crystals

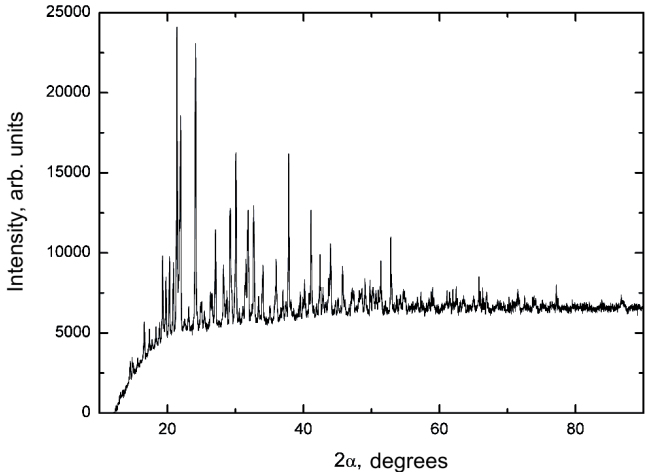

Fig. 2. Diffraction pattern of K_2SO_4+$CoCl_2$ powder

were carried using powder specimens obtained from the grown single crystals. The structural parameters were calculated with the help of a CSD universal software package (version 4.10) developed for the analysis of structural data of single crystals and powders [13].

The spectra of optical absorption were measured in non-polarized light at room temperature. We used a Shimadzu UV–3600 spectrometer in the range 200 − 800 nm with a step of 0.2 nm. Specimens for research were about 1 mm in thickness, and they were cut out perpendicularly to the directions (011) and (001). The spectral analysis was carried out by the derivative spectroscopy method with the use of the Microcal Origin software package.

3. Research Results

The diffraction pattern of a KCSH powder is shown in Fig. 2. The total variation range of the angle θ, in which the measurements were carried out, extended from 7 to 73° (with a step of 0.05°).

According to the results of X-ray diffraction studies, we may assert that KCSH crystals belong to the monoclinic spatial group $P2_1/a$ (C_{2h} in Schönflies notation) with the lattice parameters a = 9.0514(6) Å, b = 12.204(1) Å, c = 6.1528(4) Å, β = 104.825(3)°, v = 657.1(2) Å^3, Z = 2, and D_c = 2.2104(5) g/cm^3. These results agree well with the data of work [2].

Additionally, we made a computer-assisted analysis of the results of X-ray diffraction researches which allowed us to obtain atomic parameters of KCSH crystals. They are listed in Table 1.

On the basis of the results obtained and the data of work [12], it became possible to specify the elementary cell of a $K_2Co(SO_4)_2{\cdot}6H_2O$ crystal which is shown in Fig. 3. From the figure, one can see that the cobalt ion is surrounded by an octahedral environment. Figure 3 illustrates the spatial geometry of a CoO_6 octahedron. Every octahedral position of the Co^{2+} ion environment is occupied by an oxygen ion (2×O5, 2×O6, 2×O7). In addition, the structure clearly demonstrates tetrahedral groups SO_4 which are located between potassium ions. It is also worth noting that the octahedron CoO_6 is a little bit squeezed in the direction O7–Co1–aO7. It can

T a b l e 1. Atomic parameters for $K_2Co(SO_4)_26H_2O$ crystal

Atom	Coordinates, Å			Equivalent isotropic temperature parameter B(is/eq), Å^2
	x	y	z	
Co	0	0	0	1.531
S	0.411(2)	0.1340(12)	0.725(2)	1.212
O1	0.403(3)	0.232(2)	0.573(4)	0.623
O2	0.559(3)	0.068(2)	0.768(4)	0.623
O3	0.283(3)	0.066(2)	0.628(4)	0.623
O4	0.395(3)	0.171(2)	0.934(5)	0.623
O5	0.177(3)	0.115(2)	0.179(4)	0.623
O6	–0.174(3)	0.119(2)	0.041(4)	0.623
O7	–0.007(3)	–0.067(2)	0.293(4)	0.623
K	0.1311(13)	0.3493(9)	0.349(2)	1.595
H1	0.207(3)	0.093(2)	0.282(5)	0.935
H2	0.244(3)	0.122(2)	0.106(4)	0.935
H3	–0.253(3)	0.105(2)	–0.046(4)	0.935
H4	–0.143(3)	0.176(2)	0.009(4)	0.935
H5	–0.071(4)	–0.065(2)	0.336(5)	0.935
H6	0.030(3)	–0.134(3)	0.338(5)	0.935

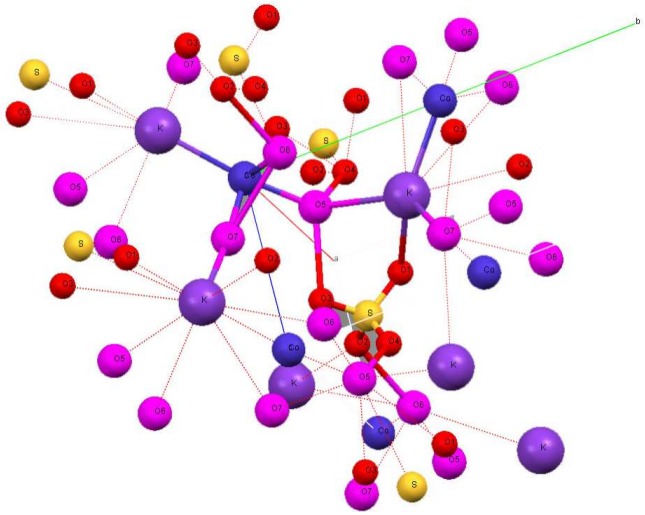

Fig. 3. Elementary cell of $K_2Co(SO_4)_2 \cdot 6H_2O$ crystal

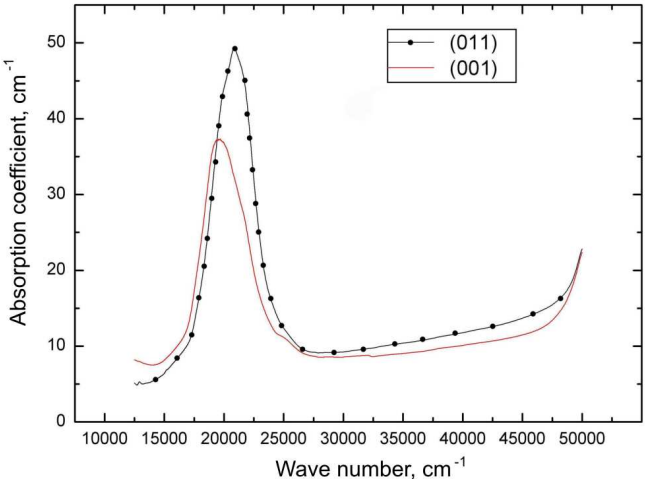

Fig. 4. Optical absorption spectra of a KCSH crystal for light propagating perpendicularly to the crystallographic planes (001) and (011)

be explained by the presence of hydrogen bonds which affect oxygen atoms.

The optical absorption spectra of KCSH crystals for light propagating along the directions perpendicular to the crystallographic planes (001) and (011) are depicted in Fig. 4. The figure demonstrates that the measured spectra, though being qualitatively different, have one maximum each. In particular, the absorption peak is more intense for the orientation (001), with that for the orientation (011) being shifted a little toward lower frequencies.

In accordance with the derivative spectroscopy method, the plots of optical spectra were used to find the second derivatives (Figs. 5,*a* and *b*), taking advantage of the computer software package. By analyzing the band maxima in the negative part of the plots, probable positions of the maxima of the simplest Gaussian functions were determined. These data were used to approximate the spectra concerned by sets of Gaussian functions (Figs. 5,*c* and *d*). The frequencies of elementary band maxima and the peak values of absorption coefficients obtained in such a way are listed in Table 2.

T a b l e 2. Frequencies of elementary vibrations in a KCSH crystal at the light propagation perpendicularly to the crystallographic planes (001) and (011)

	(011)		(001)	
	Peak position (cm^{-1})	Peak amplitude) (cm^{-1})	Peak position) (cm^{-1})	Peak amplitude) (cm^{-1})
A	–	–	19127 ± 38	25
B	19809 ± 40	33	–	–
C	–	–	20229 ± 40	18
D	21515 ± 41	31	21435 ± 43	19
E	23065 ± 46	14	–	–
F	–	–	24654 ± 49	11

As Figs. 5,*c* and *d* and Table 2 demonstrate, the absorption spectra of KCSH crystals contain six different bands (A–F). Band D manifests itself at both the studied directions of light propagation which are perpendicular to the planes (011) and (001). The figure also testifies that the intensity of this band is different for different directions of light propagation. Bands B (19778 cm^{-1}) and D (20815 cm^{-1}) emerge, when light propagates perpendicularly to the plane (011), and bands A, C, and F when perpendicularly to the plane (001).

4. Discussion

Figs. 4 and 5 (panels *c* and *d*), as well as the data quoted in Table 2, allow us to draw a conclusion that the pleochroism phenomenon in KCSH crystals is unambiguously associated with the anisotropy of optical absorption spectra for different directions of light propagation. For an explanation of the phenomenon observed, we can consider, as the first approximation, that the splitting of Co^{2+} ion energy levels occurs owing to the *O* symmetry, associated with the octahedral environment created by oxygen atoms (Fig. 3). However, according to the results of work [4], only two bands would be observed in absorption spectra in this case (Fig. 6). At the same time, as is seen from Fig. 5 and Table 3, six elementary absorption bands are observed in the spectra. Therefore, it is

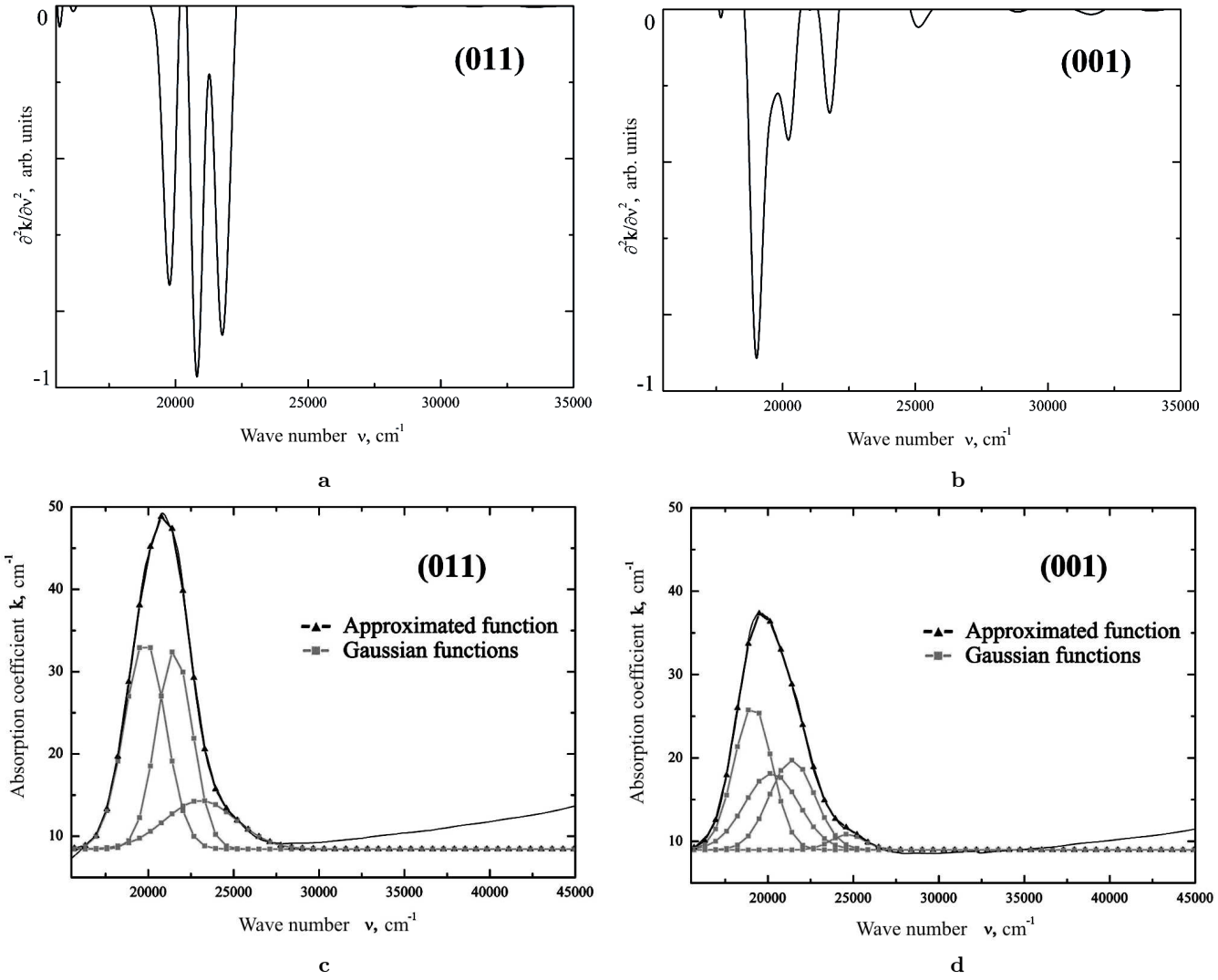

Fig. 5. (*a* and *b*) Second derivatives of the absorption spectra for different directions of light propagation and (*c* and *d*) the approximations of KCSH crystal spectra by Gaussian functions

evident that the symmetry of the Co ion environment in KCSH crystals is lower than the octahedral one. To find the energy level structure, let us take advantage of the symmetry-lowering method proposed by Bethe [15]. In our case, following this method, we adopt that the group O contains the subgroup D_4, i.e. the octahedron becomes deformed along the vertical axis of the fourth order. The irreducible representations of the groups O and D_4 are connected by the relation

$$P_\lambda = \frac{1}{g_{D_4}} \sum_R \chi^O(R)^* \chi^{D_4}(R), \tag{1}$$

where χ^O and χ^{D_4} are the traces of matrices that describe the representations of the groups O and D_4, respectively. The quantity P_λ defines how many times the representation of D_4 is contained in the irreducible representation of O. Using the notation of representations given in work [15], we write

$$A_{2g} \to B_1,$$

$$T_{1g} \to A_2 + E,$$

$$T_{2g} \to B_2 + E. \tag{2}$$

As is seen from expressions (2), the representation E is a unique degenerate representation of the group D_4.

This degeneration can be eliminated by selecting one of the second-order axes and lowering the symmetry of the complex shown in Fig. 3 to the monoclinic one (C_2). Using the table of characters of the group C_2, we obtain, by analogy with Eq. (1),

$$B_1 \to A,$$

$$E \to B_2 + B_3,$$

$$A_2 \to B_1,$$

$$B_2 \to B_1. \qquad (3)$$

The results of such an analysis concerning the splitting of energy levels are presented in Fig. 6.

The bases of the representations B_1, B_2, and B_3 are vectors directed along the axes z, y, and x, respectively. Hence, one may expect that the oscillations of the light-wave electric vector along each of three crystal-physics axes are accompanied by the appearance of two absorption bands. From the analysis of the results obtained, we may assert unequivocally that band A corresponds to the transition A–$B_3(T_1)$, and bands B and C to the transitions from the ground level to levels $B_1(T_1)$ and $B_2(T_1)$, respectively. Band D, which corresponds to the transition A–$B_3(T_2)$, is observed in the spectra of both specimens under investigation. The appearance of band D (Figs. 5,*c* and *d*) in the spectral decomposition for two directions of light propagation—perpendicularly to the planes (011) and (001)—is connected with the fact that, in both cases, the light-wave vector can oscillate along the x-axis direction.

Table 2 also demonstrates that all the bands (A to F) are responsible for the pleochroism phenomenon, because they either considerably change their intensity at different geometries of experiment (band D) or manifest themselves only at certain orientations (bands A, B, C, E, and F).

5. Conclusions

KCSH crystals of a good optical quality have been grown up from aqueous solutions K_2SO_4 and $CoCl_2$. The results of X-ray diffraction studies confirmed their structure. We have revealed the pleochroism phenomenon which manifested itself as a difference between the crystal colorings, when the specimen was observed at the orientations (001) and (011). By decomposing the optical transmission spectra of KCSH crystals into elementary bands, the corresponding absorption spectra were

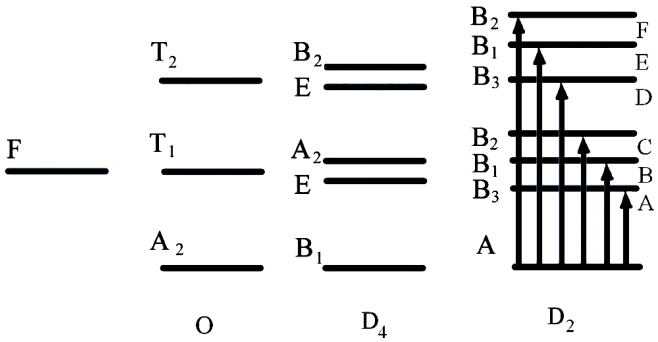

Fig. 6. Splitting of energy levels in a Co^{2+} ion

demonstrated to consist of six bands with the maxima observed at frequencies of 19127, 19809, 20229, 21435, 21515, 23065, and 24654 cm^{-1}. The analysis carried out in the framework of the group theory showed that, owing to a low symmetry of the environment around a cobalt ion, one should expect that the electric vector of a light wave propagating arbitrarily in a KCSH crystal would oscillate in three crystallographic directions, and two absorption bands should be expected to emerge for each of them. Therefore, various crystal colorings can be observed in any direction of light propagation. Such an effect of pleochroism is very promising for the creation of controlled optical polarization filters.

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ПЛЕОХРОЇЗМ У КРИСТАЛАХ КАЛІЮ КОБАЛЬТУ СУЛЬФАТУ ГЕКСАГІДРАТУ

І.І. Половинко, С.В. Рихлюк, В.Б. Коман, В.М. Давидов

Р е з ю м е

Запропоновано новий метод вирощування кристалів калію кобальту сульфату гексагідрату з водного розчину солей K_2SO_4 та $CoCl_2$. На основі рентгеноструктурних досліджень підтверджено хімічний склад вирощених кристалів. Отримано їх спектри пропускання в діапазоні 200–800 нм для кристалографічних орієнтацій (001) та (011). Виявлено явище плеохроїзму, яке пов'язане із смугами поглинання Co^{2+}. Встановлено зв'язок між структурою та оптичними спектральними властивостями отриманих кристалів.