

## Fundamental absorption edge of pure and doped magnesium sulfite hexahydrate ( $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ) single crystals

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Absorption spectra of magnesium sulfite hexahydrate ( $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ), pure and doped with Co and Ni have been studied in the spectral range of the fundamental absorption edge. The investigations have been carried out from 208 nm to 230 nm with linear polarized light  $\vec{E} \parallel \vec{c}$ ,  $\vec{E} \perp \vec{c}$  ( $\vec{c}$  is the optical axis of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ) which propagates in the direction  $(1\bar{2}10)$ . The influence of the Co and Ni ions on the spectral position of the absorption edge has been proved. The structure of the absorption edge manifests good expressed linear dichroism in the mentioned direction. The peculiarities of the linear dichroism in dependence of the impurity ions in the crystal lattice of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  are analyzed and discussed.

**Key words:** magnesium sulfite hexahydrate, fundamental absorption edge, linear dichroism.

### INTRODUCTION

The magnesium sulfite hexahydrate ( $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ) crystals are of the crystallographic class  $C_3$  (without a center of symmetry). The crystal symmetry suggests presence of nonlinearity, piezo- and pyro-electric properties and gyrotropy as well [1], [2]. The unit cell of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  contains an octahedron  $\text{Mg}(\text{H}_2\text{O})_6^{2+}$  and a pyramidal ion  $\text{SO}_3^{2-}$  [3], [4], [5]. The density measurements of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  are presented in [5].

Single crystals of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  (pure and doped with Ni, Co and Zn) for the time being are grown only by the original method developed in the Laboratory for Crystal growth at the Faculty of Physics of Sofia University.

The impurities provoke changes of electrical, optical and magnetic properties of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  [6], [7], [8]. The influence of Ni and Co impurities on the absorption spectra has been investigated in direction  $(1\bar{2}10)$  with linear polarized light  $\vec{E} \parallel \vec{c}$ ,  $\vec{E} \perp \vec{c}$  ( $\vec{c}$  is the optical axis of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ).

Absorption spectra of magnesium sulfite hexahydrate ( $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ), pure and doped with Co and Ni have been studied in the spectral range of the fundamental absorption edge in the present paper. The ions  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  are in the same isomorphous order with  $\text{Mg}^{2+}$ . Therefore the ions

$\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  can replace  $\text{Mg}^{2+}$  ions in the crystal lattice of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ . The concentration of Ni and Co has been found by the analytical chemistry methods and it amounts to 0.17 weight %.

The optical spectra give an opportunity to obtain information about the fine spectral structures, the transition selection rules and the impurity states in the forbidden band [9].

The anisotropy of the crystal is conditioned by the particles in the crystal lattice, by their mutual dispositions and by the character of the chemical connection. The linear dichroism in the optical spectra is a result of the crystal anisotropy and can be determined by measurements of the absorption coefficient with linear polarized light  $\vec{E} \parallel \vec{c}$  and  $\vec{E} \perp \vec{c}$ . The linear dichroism appears in all spectral regions in the optical spectra of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ .

The  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ -ions influence considerably on the optical spectra at the fundamental absorption edge of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ .

### EXPERIMENTAL RESULTS

The structure around 210–220 nm in the optical spectra of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  is the fundamental absorption edge. The forbidden band width can be determined from the position of edge.

The optical spectra are measured with linear polarized light from 208 nm to 230 nm for pure and

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Ni doped  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  and from 200 nm to 280 nm for Co doped  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ . The spectra are presented at Fig. 1, Fig. 2, Fig. 3. The wave vector of the incident light is  $k \parallel (\bar{1}\bar{2}10)$ ,  $\vec{k} \perp \vec{c}$ .

The absorption coefficient spectra at the fundamental edge have a typical unusual form – a rapid value decreasing to the short length wave (Fig.1, 2, 3). The part of the spectrum to the longer waves belongs structurally to the fundamental absorption edge.

The spectral positions of the fundamental edges of pure and doped  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  for light polarization  $\vec{E} \parallel \vec{c}$ ,  $\vec{E} \perp \vec{c}$  are presented in Table 1.

The absorption coefficient spectra are most strongly influenced by the presence of Ni and Co in the spectral region of the fundamental edge. The impurities cause a displacement of edge spectral positions for  $\vec{E} \parallel \vec{c}$ ,  $\vec{E} \perp \vec{c}$  to the longer light wave.

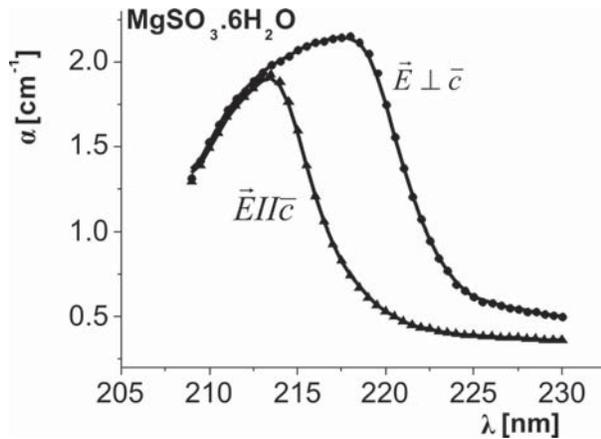


Fig. 1. Absorption spectrum of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  for light polarization  $\vec{E} \perp \vec{c}$  and  $\vec{E} \parallel \vec{c}$

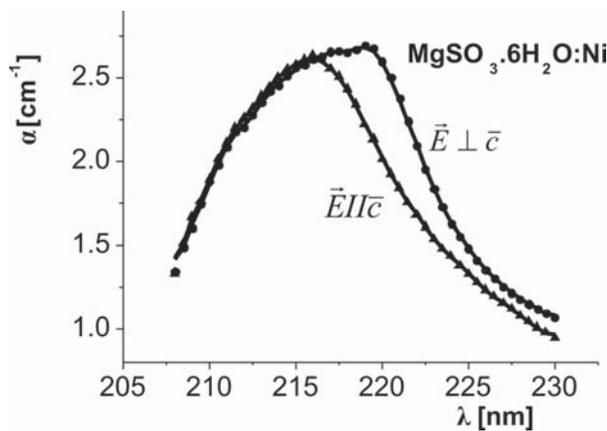


Fig. 2. Absorption spectrum of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}$  for light polarization  $\vec{E} \perp \vec{c}$  and  $\vec{E} \parallel \vec{c}$

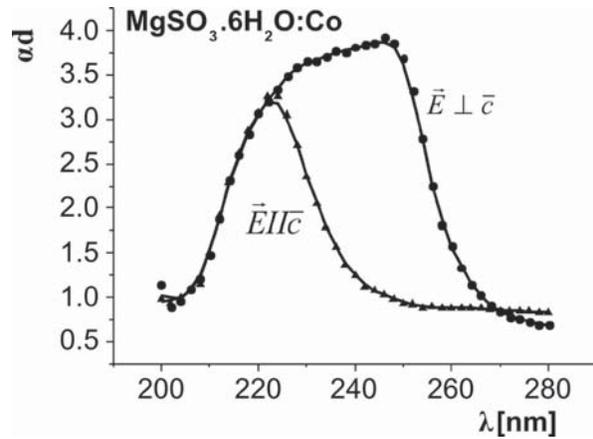


Fig. 3. Absorption spectra of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Co}$  for light polarizations  $\vec{E} \perp \vec{c}$  and  $\vec{E} \parallel \vec{c}$

The value change of the absorption coefficient in the vicinity of the fundamental edge is proportional to the impurity atoms concentration.

The optical structure at the edge for  $\vec{E} \perp \vec{c}$  has a doublet character (Fig. 1, 2, 3).

The presence of linear dichroism ( $\Delta\alpha$ ) shows that the crystal anisotropy influences essentially the absorption of pure and doped  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ . The linear dichroism in the region of the fundamental edge is characterized with a maximum at: 218.6 nm for  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ; 220.0 nm for  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}$  and 247.2 nm for  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Co}$ , (Fig.4, 5, 6).

The linear dichroism changes its sign in the short wave range for  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}$  and in the long wave range for  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Co}$ .

## DISCUSSION

The analysis of the spectra in Fig. 2, 3 shows that the Ni and Co-ions influence on the position of the absorption edge and change the value of the absorption coefficient.

The linear dichroism in the optical spectra of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  is well expressed. It is a result of the selection rules for the transitions from the valence subbands to the conduction band.

The difference in the magnitude of the maximum in the linear dichroism at the edge for pure and doped  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  can be explained by the different coefficients of the edge impurity displacement for both polarizations.

The position change of the maximum in the linear dichroism explains the disturbances in  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  conditioned by Co and Ni presence.  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions create additional vacancies in the crystal lattice. These vacancies cause the arising of

**Table 1.** Spectral positions of the fundamental edges of pure and doped  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  for light polarization  $\vec{E} \parallel \vec{c}$ ,  $\vec{E} \perp \vec{c}$  at room temperature

$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$	216.7 nm for $\vec{E} \parallel \vec{c}$	221.7 nm for $\vec{E} \perp \vec{c}$
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}$	221.5 nm for $\vec{E} \parallel \vec{c}$	223.4 nm for $\vec{E} \perp \vec{c}$
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Co}$	233.6 nm for $\vec{E} \parallel \vec{c}$	256.9 nm for $\vec{E} \perp \vec{c}$

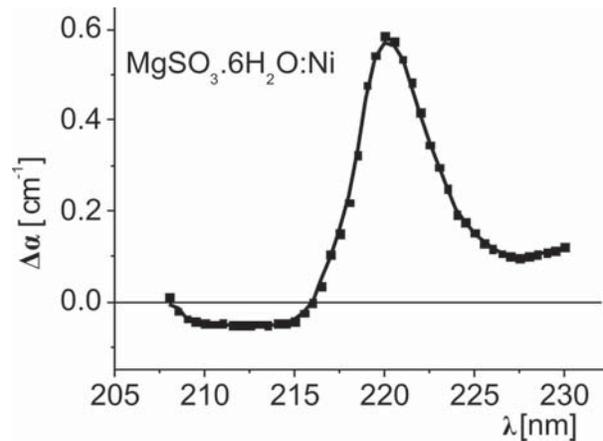
random strains and Coulomb interaction [10] which contribute to the change of the local electric fields [11] and smear the low energy periphery structure of the absorption edge [12].

The appearance of Ni and Co impurity states in the forbidden band is one of the basic mechanisms for the explanation of the spectral position change of the absorption edge. It can be concluded on the basis of the absorption spectra around the fundamental edge of pure crystal, that the edge displacement is caused by impurity levels which are localized at the minimum of the conduction band. The additional impurity states influence the character of electron transitions as a result of a deformation of the band structure at the bottom of the conduction band. The influence manifests itself as a change of the spectral positions of the edge structure to the longer waves.

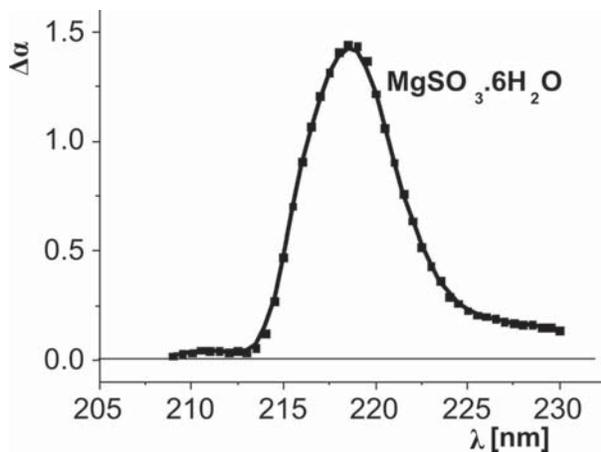
The experimental absorption spectrum in the vicinity of the fundamental edge of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}$  is described with Urbach's rule [14].

The theory shows that the linear dichroism contains information about the electron transitions [13]. The changes of the value and the sign of the linear dichroism in the spectral range of fundamental edge in accordance with the theory is an indication that the band-band electron transitions are influenced by the presence of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ -ions. Therefore the

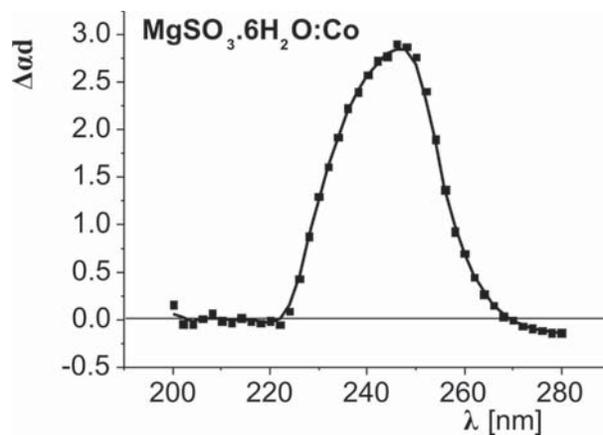
sign-changed shape of the linear dichroism spectrum (Fig. 5, 6) is a consequence of the unparallelism of the moments of the interband transitions. This unparallelism can be considered as a result of the asymmetry of the spin-orbit interaction in the Ni and Co-ions. The asymmetry can be caused by the internal crystal field [15].



**Fig. 5.** Linear dichroism spectrum at the absorption edge of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Ni}$



**Fig. 4.** Linear dichroism spectrum at the absorption edge of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$



**Fig. 6.** Linear dichroism spectrum at the absorption edge of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}:\text{Co}$

The established difference of the maximum positions in the linear dichroism spectra  $\Delta\alpha(\lambda)$  (Fig. 5, 6) is a result of the additional spin-orbit splitting of the valence band due to the ions of the transition metals Co and Ni located in the crystal lattice of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  [16].

The energy band scheme of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  is not developed. It can be concluded on the basis of the experimental spectra that the energy gap of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  is direct. We assume that the valence band is split in two subbands (A and B) due to the spin-orbit interaction. The transitions from subband A are allowed only for polarization  $\vec{E} \perp \vec{c}$ . The transitions from subband B are allowed for both polarizations ( $\vec{E} \perp \vec{c}$ ,  $\vec{E} \parallel \vec{c}$ ).

The change of the edge spectral positions of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  for  $\vec{E} \parallel \vec{c}$ ,  $\vec{E} \perp \vec{c}$  in presence of Ni and Co is caused by the impurity states arising in the forbidden band near to the bottom of the conduction band. The transitions from these levels determine the edge displacing but the selection rules are the same as by the pure  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ .

## CONCLUSIONS

1. Absorption spectra of pure and Ni and Co doped  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  have been measured in the spectral range of the fundamental absorption edge with linear polarized light  $\vec{E} \parallel \vec{c}$  and  $\vec{E} \perp \vec{c}$  in direction  $(1\bar{2}10)$ .

2. It has been established that the forbidden band of  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  is direct. It has been also experimental proved that the Ni and Co cause a displacement of edge spectral positions to the longer light wave and a value change of the absorption coefficient in the vicinity of the fundamental edge.

3. The linear dichroism due to the crystal anisotropy is established and analyzed in the vicinity of the fundamental absorption edge. It is proved

that the impurities influence the linear dichroism spectrum.

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АБСОРБЦИОННИ ЕФЕКТИ ОКОЛО РЪБА НА ПОГЛЪЩАНЕ  
НА НЕЛЕГИРАНИ И ЛЕГИРАНИ МОНОКРИСТАЛИ ОТ МАГНЕЗИЕВ  
СУЛФИТ ХЕКСАХИДРАТ ( $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ )

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(Резюме)

Изследвани са спектрите на поглъщане на магнезиев сулфит хексахидрат ( $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ), нелегиран и легиран с кобалт и никел, в спектралния диапазон около ръба на поглъщане. Изследванията са проведени от 208 nm до 230 nm с линейно поляризирана светлина  $\vec{E} \parallel \vec{c}$ ,  $\vec{E} \perp \vec{c}$  ( $\vec{c}$  е оптичната ос на кристала  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ). Светлината се разпространява по направление  $(1\bar{2}10)$ . Доказано е влиянието на Co и Ni йони върху спектралното положение на ръба на поглъщане. Структурата при ръба на поглъщане проявява добре изразен линеен дихроизъм, когато светлината се разпространява в направление  $(1\bar{2}10)$ . Анализирани и дискутирани са особеностите в линейния дихроизъм, дължащи се на примесните йони в кристалната решетка на  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ .