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THE INFLUENCE OF IMPURITY IONS OF TRANSITION METALS ON RADIATION INDUCED PROCESSES

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In work results of research of monocrystals of potassium sulphate are resulted. Pure of potassium sulphate, and also of potassium sulphate doped have been investigated by ions of cobalt, manganese and nickel. Optical measurements were carried out by a photo-electric method, by a standard technique with the help SPh-16. Researches have shown, that accumulation lightsum in pique TL at 280-300K goes in the doped crystal faster, than in a pique recombination luminescence with a maximum at 190K. We know, that as a result of an irradiation in x-ray quanta there is a change of a charging condition impurity ion of copper. It is shown, that influence to radiation leads to reduction of optical density in impurity strips of absorption. Authors of work give this a unique explanation: there is a change of a charging condition at initial ions of bivalent transitive metals, that is there is a formation of ions Me^+ or Me^{3+} .

Keywords: monocrystals, photo-electric method, accumulation lightsum, recombination luminescence, doped crystal faster.

The purpose of the given work is the establishment of the general laws of influence on recombination processes in crystals by impurities ions of transitive metals.

The objects of research are pure and doped by ions of cobalt, manganese or nickel monocrystals of potassium sulphate. The crystals for research have been grown up from water solutions at temperature 40 °C by a method of isothermal evaporation solvent. The doped monocrystals are received at addition in an initial solution of corresponding sulphates salts metals.

For measurement of thermoluminescence curves (TL) the object of research was cooled to temperature of liquid nitrogen and irradiated with x-rays by device URS-55a. For definition of the absorbed doses of x-ray radiation by us it was used the dosimeter of Frike. The luminescence was registered by photoelectronic multiplier (PhEU-79) which signal arrived on an input of the direct current amplifier, then one was registered and processed by the computer.

On TL curve at pure monocrystals of potassium sulphate peaks of recombination luminescence in area 190K and 280-300K (figure 1a) are observed [1, 2]. The high-temperature peak obviously nonelementary also represents two strongly blocked peaks of recombination luminescence. Spectral structure of all TL peaks at K_2SO_4 is the identical. It contains two bands of emission with maxima at 2.6 eV and 3.1 eV. In doped crystals by ions of bivalent copper does not lead to qualitative changes of recombination processes.

The recombinations processes in crystals $K_2SO_4-Cu^{2+}$ were investigated in work [2]. It was established that copper ions increase speed of accumulation the radiation defects in K_2SO_4 . Researches have shown that accumulation lightsum in TL peak at 280-300K goes in the activated crystal faster, than in TL peak with a maximum at 190K. As a result of an irradiation by x-ray there is a change of a charge of impurity copper ions. The ions Cu^{2+} at a irradiation are traps for electrons. On initial electronic structure of bivalent copper ions are similar to bivalent ions of cobalt, nickel and manganese.

In figure 1b TL curve for crystal $K_2SO_4-Co^{2+}$ is resulted. Comparison of the presented figures shows that presence impurity cobalt ions lead to occurrence of new TL peak with a maximum at 240K. Besides, in area 280-300K to dominating peaks of a luminescence TL peak is at 280K.

Redistribution of lightsum in TL peaks in area 280-300K at crystals $K_2SO_4-Co^{2+}$ and $K_2SO_4-Cu^{2+}$ the similar.

The spectral structure of TL peaks of potassium sulphate (at 190K and 280-300K) does not change by ions of cobalt and copper. It same as at pure potassium sulphate. Spectral structure of new recombination peak with a maximum at 240K it was not possible to measure a luminescence because of small intensity of emission. As a whole influence of ions of copper and cobalt on рекомбинационные processes in potassium sulphate are similar.

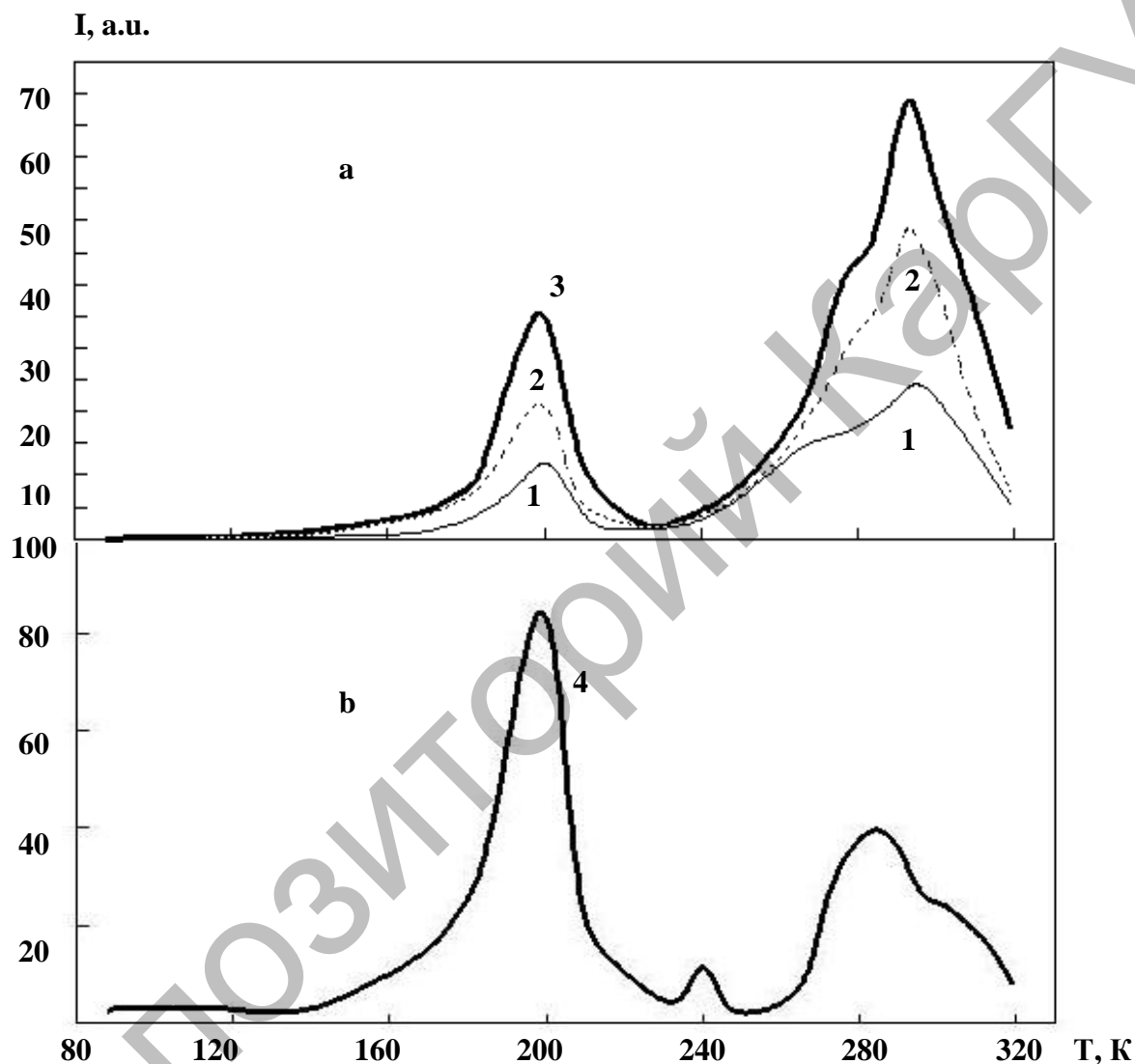


Fig.1. Curves TL for crystals K_2SO_4 (a) [1] and $K_2SO_4-Co^{2+}$ (b). Doses of an irradiation 100 kGy (1), 200 kGy (2), 400 кГр (3) and 400 kGy (4)

Similarity of a TL curves at crystals $K_2SO_4-Co^{2+}$ and $K_2SO_4-Cu^{2+}$ allows to expect that the role of these impurity ions in radiation induced processes is identical. In figure 2 the absorption spectrum measured at 80K for crystal $K_2SO_4-Co^{2+}$ before and after an irradiation by x-rays is shown. From figure it is visible that influence of irradiation leads to reduction of optical density in impurity absorption bands. For it there is a unique explanation: there is a change of a charge at initial ions of bivalent cobalt, i.e. there is a formation of ions Co^+ or Co^{3+} . Besides, there is a new band of absorption with a maximum at 5.30 eV. The given radiation induced band of absorption was

observed earlier in work [3]. In this work by EPR method it has been established that occurrence of this band of absorption is connected with the hole centres SO_3^- . Monocrystals of the pure potassium sulphate under the influence of irradiation are not coloured. Therefore authors of work [3] have connected it with the hole centre of the matrix, revolved bivalent impurity ion. The similar phenomenon was observed in crystals of potassium sulphate doped by bivalent copper ions. The radiation induced band of absorption in this sample is observed in the field of 5.61 eV [2]. In crystals of potassium sulphate doped by ions Cu^{2+} a new TL peaks are not present.

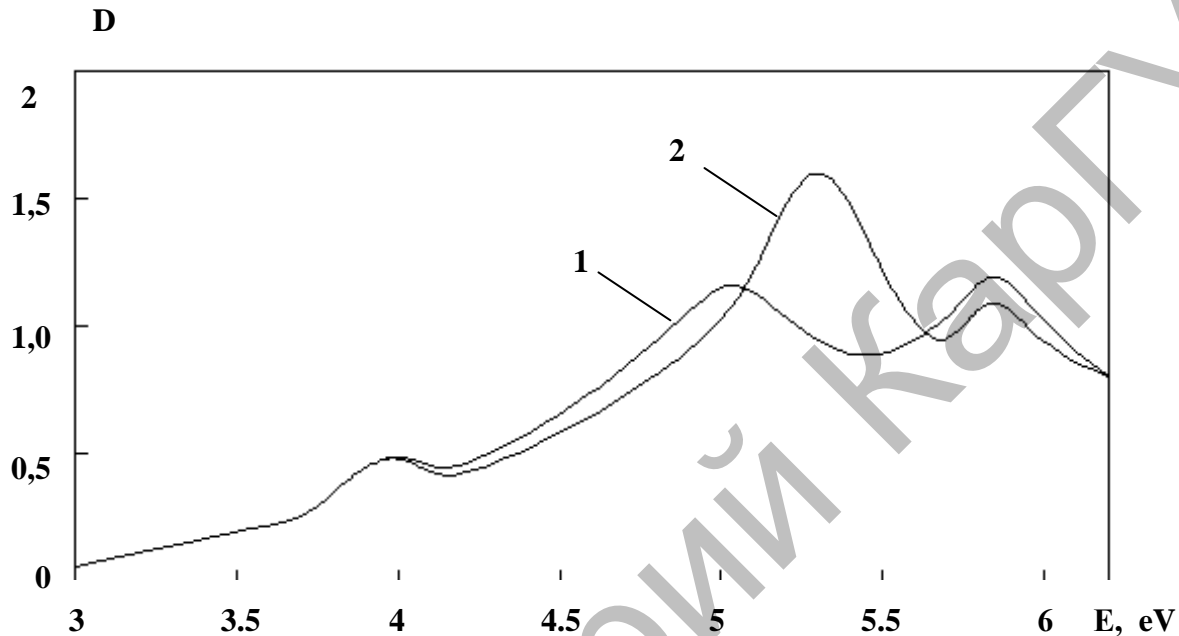


Fig. 2. Absorption spectrum at 80K for crystal $\text{K}_2\text{SO}_4\text{-Co}^{2+}$. 1 – before an irradiation. 2 - after an irradiation in x-ray quanta a dose 500 kGy.

Therefore, it is necessary to deal with a question on the nature of new recombination luminescence peak in crystal $\text{K}_2\text{SO}_4\text{-Co}^{2+}$ in area 240K. This peak a luminescence can be connected with disintegration revolved impurity ions of the hole centres of matrix, or with disintegration radiation induced impurity the centres which formation are proved by measurements in impurity band of absorption after an irradiation of samples.

Measurements of optical density in a band impurity absorption with a maximum 5.85 eV and in the radiation induced absorption band with a maximum at 5.30 eV from temperature has shown that decolouration of the radiation induced band of absorption occurs in two stages: in area 190K and in area 280-300K. Changes of optical density in the absorption band with a maximum at 5.30 eV in area 240K it is not fixed. On the other hand restoration of optical density in impurity absorption band at 5.85 eV occurs only in area 240K. Hence, TL peak with a maximum at 240K is connected with disintegration of the radiation induced impurity centres. They do not bring the contribution in recombination luminescence connected with disintegration of radiation defects of a matrix which give TL peaks at 190K and 280-300K. Thermal decolouration of the induced absorption band with a maximum 5.30 eV in crystal $\text{K}_2\text{SO}_4\text{-Co}^{2+}$ completely coincides with thermal decolouration the radiation induced absorption band with a maximum 5.61eV in crystal $\text{K}_2\text{SO}_4\text{-Cu}^{2+}$.

In work [1] it is shown that the mechanism of recombination processes in potassium sulphate crystals in about 190K and 280-300K is electronic. Measurements of thermodecolouration the radiation induced absorption band show that at these temperatures take place disintegration of the hole centres SO_3^- . It is unique known electron-superfluous defect in sulphates of alkaline metals. It is the ion O^- [4]. The given ion is stabilised in a crystal lattice near the ion SO_3^{2-} . The activation same

recombination process in various temperature areas is connected with features of a structure of a crystal lattice of potassium sulphate. In works [1, 5] by quantum-chemical calculations it is shown that energy of activation for ions migration O^- is defined by cationic environment. In a crystal lattice of potassium sulphate is available two nonequivalent cationic sites, differing with coordination of oxygen atoms. Distances O-K in lattice of potassium sulphate vary. They form three groups with differing O-K length. These variations of O-K lengths lead to formation of the electron-superfluous centres with differing levels of thermal stability. As a result same recombination process can be activated at various temperatures. The electronic nature recombination processes in matrix allows to establish, whether are impurity ions of cobalt acceptors or donors of electrons.

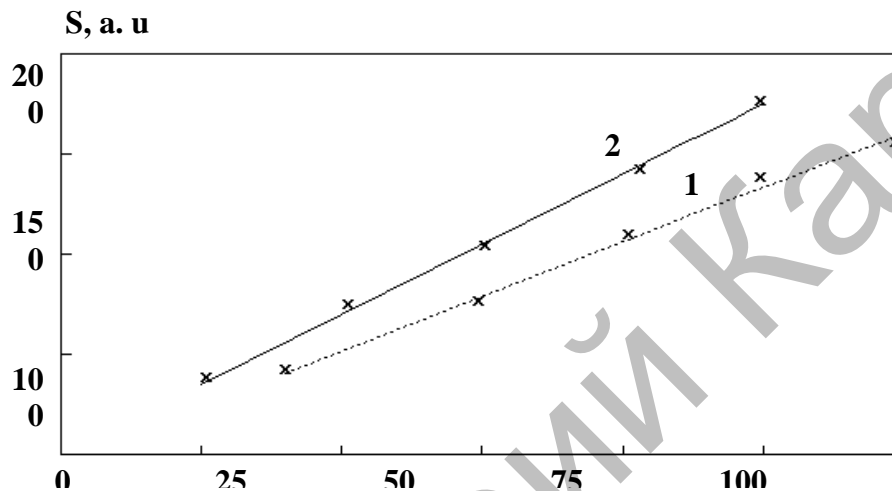


Fig. 3. Curve of lightsum accumulation in TL peak with a maximum are resulted at 190K from an irradiation dose in x-rays. 1 - for pure K_2SO_4 , 2 - for $K_2SO_4-Co^{2+}$.

In figure 3 curve of lightsum accumulation in TL peak with a maximum are resulted at 190K from an irradiation dose in x-rays. The curve 1 corresponds to the result received at measurements recombination luminescence for pure crystals of potassium sulphate and a curve 2 - for the crystal doped by cobalt ions. For comparison of quantitative results from different samples all measurements have been spent at invariable geometry of experimental installation, conditions and a regime of irradiation and signal registration. The samples, representing plates of almost identical thickness, were closed by a metal mask with apertures of the identical size. From figure it is visible that speed of lightsum accumulation in peak with a maximum at 190K is more than luminescence in the doped crystal than in pure. It was above said that given TL peak results from the electronic mechanism of recombination, i.e. mobile electron or electron-superfluous ion recombine with the motionless hole centre. At irradiation by x-ray of crystals the electronic subsystem is raised. As a result of ionisation are formed the free electrons and the hole centres SO_4^- . The last are characteristic paramagnetic radiating defects in sulphates of alkaline metals [6]. It is obvious that on radiating stages takes place two alternative processes: as a result capture by sulphate anions of free electrons stable radiating defects are formed; the second - return recombination of electron and holes. Introduction in a crystal lattice of traps for electrons leads to increase in probability of a survival for the hole centres. As cobalt ions in a crystal lattice of potassium sulphate replace cations. Their consideration as traps for electrons allows to explain increases in speed of lightsum accumulation in TL peak of a matrix.

Thus, it is experimentally established that in crystals $K_2SO_4-Co^{2+}$ impurity ions are traps for free electrons. Occurrence of new TL peak with a maximum at 240K is connected with thermal disintegration of electronic centres Co^+ .

Similar researches have been spent for sulphate crystals калия, the nickel activated by ions and manganese. In figure 4 typical TL curves for crystals $K_2SO_4-Mn^{2+}$ (a) and $K_2SO_4-Ni^{2+}$ (b) are shown. From figure it is visible that presence impurity ions of these transitive metals leads to occurrence of new peaks with maxima at 160K and 260K, accordingly. It is experimentally established that at an irradiation reduction of optical density in bands impurity absorption occurs. Restoration of manganese or nickel concentration in preliminary irradiated crystals occurs at temperatures of supervision of new TL peaks.

In the crystals doped by manganese or nickel ions the radiation induced absorption bands are observed. In table 1 positions of maxima and temperature decolouration these induced absorption bands are resulted.

Table 1. Positions of a maximum of the radiation induced absorption band and its temperature of decolouration.

Crystals	Positions of induced absorption bands , eV	Literature	Temperature decolouration
$K_2SO_4-Cu^{2+}$	5.61	[1]	190 K 280-300K
$K_2SO_4-Co^{2+}$	5.3	[3]	190 K 280-300K
$K_2SO_4-Ni^{2+}$	5.39		-
$K_2SO_4-Mn^{2+}$	5.49		190 K 280-300K

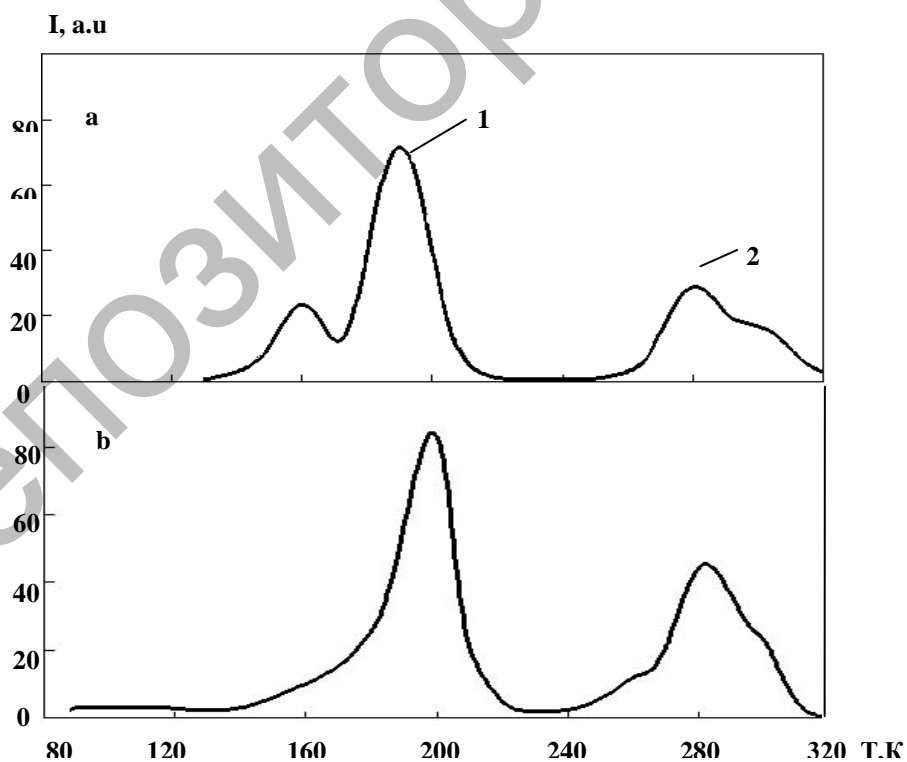


Fig. 4. Curves TL for crystal $K_2SO_4-Mn^{2+}$ (a) and $K_2SO_4Ni^{2+}$ (b)

As a whole influence of ions of cobalt, manganese and nickel on radiation induced processes in potassium sulphate crystals are similarly. Curve accumulation of lightsum in peak of a matrix with a maximum at 190K resulted on figure 7 testify to similarity of a role in these processes for all ions of transitive metals. From figure it is visible that impurity manganese and nickel ions increase speed of accumulation lightsum in this TL peak. Hence, these impurity ions are the capture centres of electrons. Besides, it is possible to assert that impurity manganese ions in potassium sulphate crystals are more effective traps for electrons.

From results it is possible to reveal following basic laws of a role and influence impurity bivalent ions of transitive metals on radiation induced processes in crystals of potassium sulphate:

1. In the activated crystals after an irradiation in x-rays there is a redistribution of lightsum in TL peaks;

2. In comparison with pure crystals of potassium sulphate the intensity of recombination luminescence in TL peak with a maximum at 190K in crystals doped by ions of transitive metals is dominate;

3. There are radiation induced absorption bands after irradiation in all considered objects. Curves of thermo decolouration of the given absorption bands in the crystals doped by cobalt, nickel or the manganese ions identical. Maxima positions of the radiation induced absorption bands depends from nature of impurity ions;

4. At an irradiation part impurity ions of transitive metals changes of its charge. In all studied crystals restoration of initial valency of the impurity ions occurs at temperature of supervision of new TL peak. Temperature positions of its maximum on TL curve varies depending on the nature impurity ions;

5. The ions of transitive metals in potassium sulphate are traps for free electrons which arise at an irradiation. It is shown in speed of lightsum accumulation in peaks of recombination luminescence from matrix.

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