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PECULIARITIES GYPSUM CRYSTALS STRUCTURE BASED ON ELECTRON PARAMAGNETIC RESONANCE RADIATION DEFECTS

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ABSTRACT

Electron paramagnetic resonance (EPR) at 77 K in the X-band are studied natural gypsum crystals ("Marino" glass, Russia), previously irradiated at room temperature by X-rays of different doses. Detected earlier observed spectra of paramagnetic centers $SO_3^-(B); SO_3^-(A_1); SO_3^-(A_2)$ [Crystallog. Rep., vol. 59(3), pp.399–406. 2014]. It was found two new spectrum with magnetic multiplicity $K_M = 2$ (C_i symmetry center) and super hyperfine splitting of the interaction of the electron spin S = 1/2 and the proton nuclear spin I = 1/2. These spectra are assigned to the centers $SO_4^- - {}^1H$, which differ from each other in the position of a proton H(1) gypsum structure. The mobility of water molecules in the channels of the structure activates the formation of two or more centers $SO_4^- - {}^1H$, $SO_3^- - {}^1H$. From the angular dependence of the spectra in the three orthogonal planes were found the parameters of the spin Hamiltonian (SH). It has been established that the differences in radiation sensitivity of the paramagnetic centers depends on charge redistribution processes in the crystal.

Keywords: Gypsum, EPR, crystal structure, water molecular, radiation defect

INTRODUCTION

The real crystals always contain a part of the point defects, which are sensitive to changes in external conditions. Subjecting various crystal exposed to radiation or heat treatment, can produce a redistribution of charges in a system of point defects. Systems of point defects can be changed if "heal" their own defects or create new ones. Research and identification of point defects successfully are carried out using the EPR method. However, an analysis of published data shows that sometimes the calculations of the EPR spectra of radical ions in the presence of an unpaired electron interaction with the nuclear spins are carried out with the "overstatement" symmetry spin Hamiltonian (SH), inaccurate identification of the "forbidden" transition because of the lack of computing transition intensities [1]. EPR method allows you to use your own crystal defects as paramagnetic markers to identify the characteristics of the structure.

Peculiarities gypsum crystals structure based on EPR studies radiation defects was to purpose of the present work. For this purpose the angular dependence of the EPR spectra at 77 K in three orthogonal planes of a single crystal of natural gypsum

("Marino" glass from Kamsko-Ust'insky Mine in the Republic Tatarstan, Russia) was studied. The parameters of the spin Hamiltonian (SH) were fitted and the topological characteristics of the tensor and SH were compared with crystalline gypsum structure.

Gypsum $CaSO_4 \cdot 2H_2O$ is one of the most common rock-forming minerals, so the specificity of its formation, which is manifested, in particular, in the crystal structure peculiarities, will contribute to the understanding of geological processes and allows to reconstruct the circumstances of its formation [2-5].

Actuality of the research is natural minerals and mineral associations by the fact that their formation processes are essential for geological processes; on the other hand a natural technology can be a continuity basis for creating composite building materials. Determination of the combination of minerals that enhance the strength characteristics of these associations, and the study of physical and chemical conditions of their formation are the main task of genetic mineralogy.

EXPERIMENTAL RESULTS

For EPR measurements of gypsum crystal was drunk by the crystallographic axes to setting C2/c [3]. Two crystals were irradiated with different doses of X-ray irradiation (300K, λCuKα, 40 kV) at the time of exposure 3 - 6 hours and a current value at 20 and 30 mA, respectively. Irradiation of the crystals was carried out at different times and the dose happened to be different.

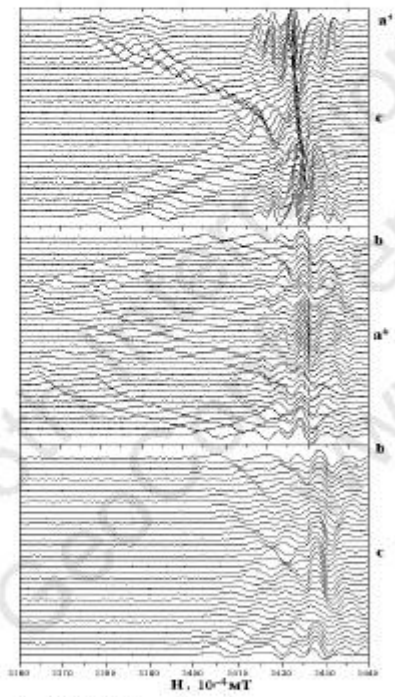

Fig.1. The EPR spectra of gypsum crystals in three orthogonal planes (**a*c**), (**ba***), (**bc**) to set **C2/c.**

EPR spectra in the gypsum crystal were studied at 77 K on X-band BRUKER Spectrometer Company. As a reference range used DPPH. Recording spectra was carried out every 5° crystal while rotating from 0 to 180° in three orthogonal planes (**a*c**), (**ba***), (**bc**) to set **C2/c**. Control of installation crystal in the cavity was carried out by the EPR spectral lines merge with K_M = 2 along and perpendicular to the **b** axis of the crystal.

In the first crystal two kinds of spectra with different anisotropy was observed (Fig. 1).

Group lines with weak anisotropy contains five lines which were previously identified [4] is composed of two types of centers. Central intense line is obliged SO_3^- center without splitting. Two pairs of lateral lines, the duty two centers $SO_3^- - {}^1H$ each of which undergoes splitting of a nuclear spin equal to I = 1/2 of the different protons.

The anisotropic paramagnetic spectrum is the simplest form in the plane **ba*** (Fig. 1) and consists of two pairs of lines. The center has multiplicity equal to two (K_M = 2) and corresponds to the symmetry C_i. Each line

cleaved by interaction of the unpaired electron and nuclear spin equal to I = 1/2.

According to the symmetry of the paramagnetic center in the space group in the plane (**a*c**) spectra of the conjugate centers should merge, however (Fig. 1) is visible to a more complex picture of the spectrum associated with the appearance of forbidden lines. The plane (**bc**) must observe splitting of conjugate centers.

To calculate the parameters of the SH is produced a numerical matrix diagonalization SH at each point of H (θ,φ) measured the resonance field values of EPR spectral lines in three orthogonal planes of the crystal, and then is minimized the sum of squared deviations between the calculated and the operating frequency of the spectrometer according to the program [6]. According to the calculated values of the parameters SH angular dependence of the resonance magnetic field values were calculated for all transitions, as well as transition probabilities (Fig.2). Theoretical and experimental lines of the spectrum are presented inset.

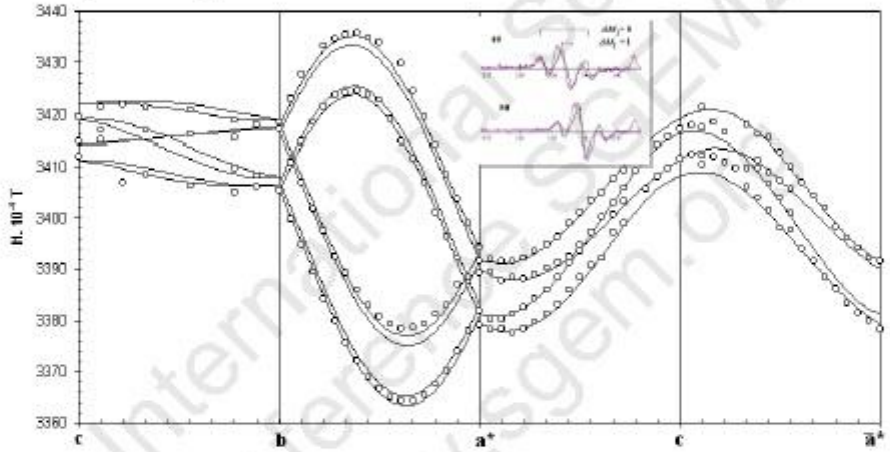

Fig.2. Angular dependence of experimental (circles) and calculated (lines) resonance magnetic field values center I - $SO_4^- - {}^1H$. Theoretical and experimental permitted (ΔM_I=0) and forbidden (ΔM_I=1) lines of the spectrum are presented the inset separately.

In the second crystal only one anisotropic spectrum was detected. The second crystal was found to have strong lines belong to the new center II (Fig.3), while the less intense the center line I correspond to the previously defined parameters in the first crystal (line spectrum along **b** - axis shown in the inset).

The study of the angular dependence of the lines of the EPR spectra of paramagnetic centers in these crystals demonstrated that they consist of two pairs of lines (K_M = 2) with super hyperfine (SHF) structure due to the interaction of the spin S = 1/2 of the unpaired electron with the nuclear spin J = 1/2. It is natural to assume that the nuclei have a spin in the studied crystal nuclei are hydrogen atoms.

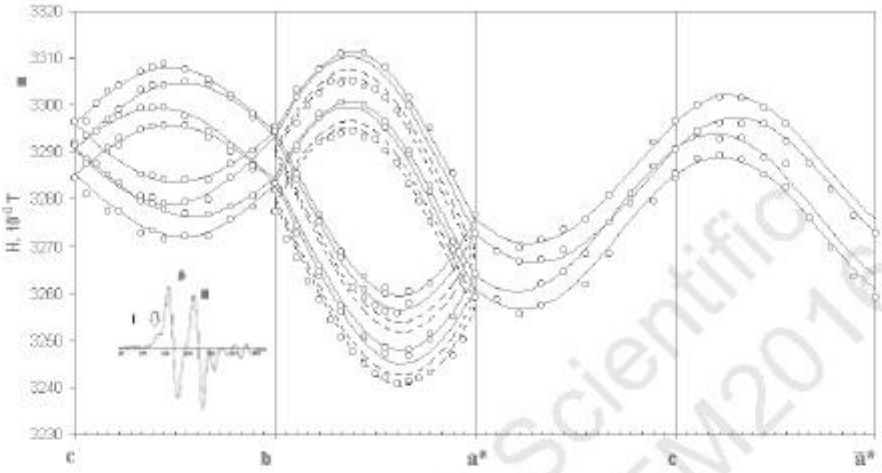

Fig.3. Angular dependence of experimental (circles) and calculated (lines) resonance magnetic field values center II - $SO_4^- - {}^1H$. Spectrum along **b**-axis was shown in the inset.

The principal values of g- and A- tensors and guide angles in XYZ coordinate system are determined by numerical diagonalization of tensors in representation of the Cartesian coordinates [7]. The following table lists the parameters SH center I - $SO_4^- - {}^1H$ and center II - $SO_4^- - {}^1H$ in the orthogonal coordinate system $X_0 \| c$, $Y_0 \| a^*$, $Z_0 \| b$, where value g_{ii} and A_{ii} of principal axes, its isotropic part ($A_{iso} = \sum A_i / 3$) and anisotropic part ($B_i = A_{ii} - A_{iso}$ in Gauss) and the orientation of the principal axes of the tensor relative orthogonal axes system.

Table.

The parameters SH center I - $SO_4^- - {}^1H$ and center II - $SO_4^- - {}^1H$ in gypsum structure

I center $SO_4^- - {}^1H$										
	g_{ii}	g_{ii}-g_{iso}	X_0	Y_0	Z_0	A_{ii}(G)	B_{ii}	X_0	Y_0	Z_0
X	2.0093	-0.0062	14.8°	81.8°	102.8°	11.9	5.0	83.2°	70.7°	20.6°
Y	2.0015	-0.0140	77.6°	36.6°	56.2°	13.5	6.7	79.5°	23.1°	110.4°
Z	2.0356	0.0201	96.4°	33.5°	122.7°	-4.9	-11.7	**12.5°**	**102.2°**	**92.8°**
iso	2.0155					6.8				
II center $SO_4^- - {}^1H$										
X	1.9986	-0.0146	72.1	63.0°	33.2°	11.5	3.2	82.8°	70.6°	20.8°
Y	2.0055	-0.0078	27.1	116.6°	94.8°	14.5	6.2	100.5°	21.0°	107.9°
Z	2.0356	0.0224	70.3	39.6°	122.8°	-1.2	-9.5	**12.79°**	**82.4°**	**100.2°**
iso	2.0133					8.3				

PECULIARITIES OF THE STRUCTURE GYPSUM CRYSTALS

The values of the principal values of g- and A- tensors give reason to identify the observed paramagnetic centers I and II as a radical ion, which is an unpaired electron interacts with the nuclear spin of the proton, as $SO_4^- - {}^1H$. The choice of a proton as the nucleus involved in the observed SHF interaction determined by the splitting and changes the intensity of the permitted and forbidden transitions. Such paramagnetic center was observed previously in the single crystal Zn-astrakhanite ($Na_2Zn(SO_4)_2 \cdot 4H_2O$) [8].

Furthermore B_{ss} directions in table with the highest absolute value components anisotropic interaction center I (12.53^0; 102.2^0; 92.8^0) and the center II (12.79^0; 82.4^0; 100.21^0) are closed to direction O(1) -H(1) in the crystal structure of gypsum (16.43^0; 81.69^0; 104.07^0) (Fig.4b), indicating a possible interaction of the unpaired electron spin localized mainly in the oxygen O(1) with a nuclear spin of H(1) proton.

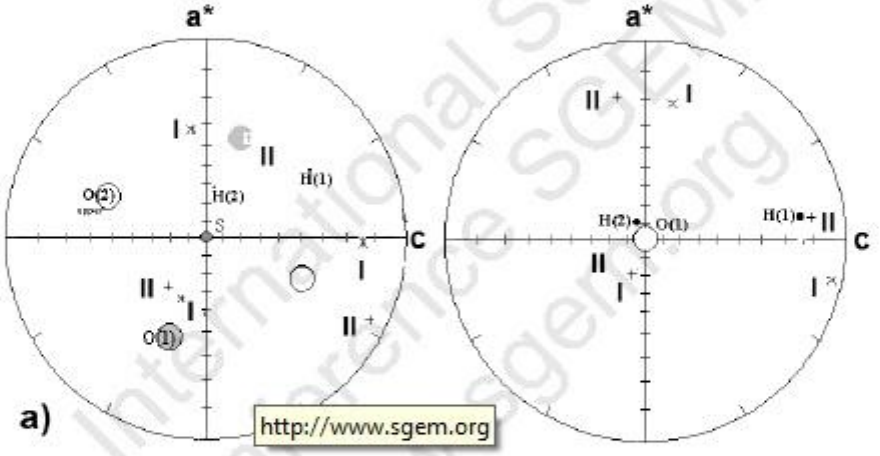

Fig.4. Stereographic projection directions: a) S-O in [SO_4] tetrahedron and the principal axes of the g- tensor I and II center; b) O(1) – H(1), H(2) protons of water molecules and the principal axes of the A- tensor.

Based on the experimental values (B_{ss} = -11.69 G to I center and B_{ss} = -9.46 G to center II), it follows that the proton is close to the oxygen ion at a distance r = 1.341 Å in the model I center and at a distance r = 1.440 Å in the model II center. This fact can be explained by the collapse of the water molecules in the gypsum structure of the channels under the scheme $H_2O \leftrightarrow OH + H$ [9] and their migration to the stabilization of the paramagnetic center. In the second case, the high probability is to formation of paramagnetic diatomic hydroxyl radical OH [10]. However, it was not detected in the test crystal, and therefore, the occurrence of $SO_4^- - {}^1H$ centers should be associated with the different positions of the proton in the crystal structure gypsum as a result of the capture of the hydrogen atom of oxygen ion O(1).

The formation of the center I, in contrast to the center II, accompanied by changes in position oxygen O(1) and, accordingly, the position of a proton H(1). Such a change is

possible, if we assume that there are a vacancies Ca ion and water molecules in the nearest neighborhood of the paramagnetic complex $SO_4^- - {}^1H$. Calcium vacancy will entail not only a change in the coordination number around the vacancy to 7, but also the displacement of oxygen O(1) in the direction of the calcium vacancies, as shown in the model paramagnetic center by arrow (Fig. 5).

The proof of this hypothesis is the simultaneous deviation of g_{ss} axis orientation on the stereographic projection (Fig.4a) and the axis A_{ss} (on Fig.4b) paramagnetic center I at the same ~ 23° angle from the direction S-O(1) and O(1) - H(1), respectively. Another argument in favor of this hypothesis are used data on leaving water of crystallization in the [100] direction perpendicular to the plane (010) at rebuilding gypsum structure in the bassanite.

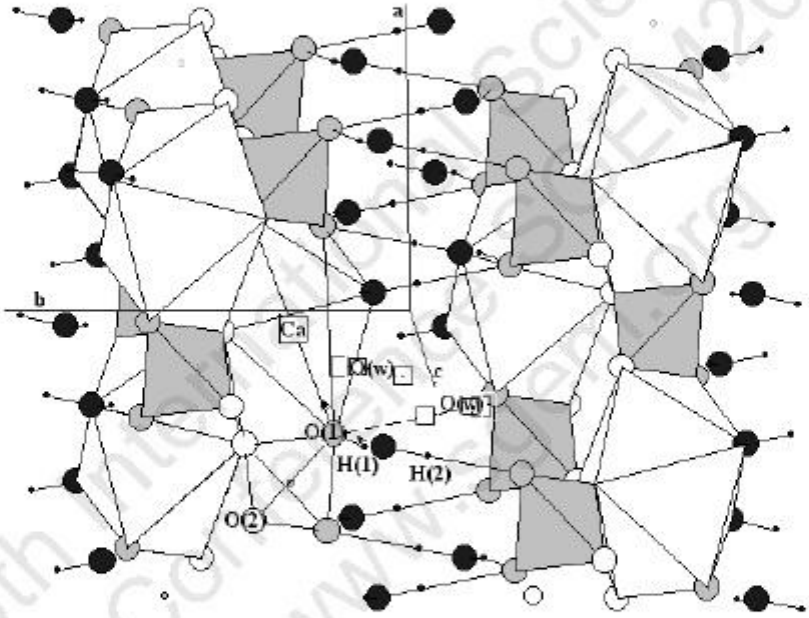

Fig. 5. Model paramagnetic center I $SO_4^- - {}^1H$. Oxygen O_w water molecule denoted by the dark circle. Square is designated atom vacancy. The arrow shows the direction of displacement oxygen O(1) and hydrogen H(1).

Direction S-O(1) in the [SO4] tetrahedron and the direction of one of the axes g_{ss} = 2.0356 are almost identical to the paramagnetic center II, and at the same time forming an angle ~ 23° Center I (Fig.4.a).

The direction of the oxygen O(1) -H(1) and the direction of one of the axes of the dipole-dipole part B_{ss} = -9.46 G differ by 3° to the paramagnetic center II, and at the same time the same direction B_{ss} = -11.7 G forms an angle of about 23° to center I (Fig.4b).

Vacancy of water molecules surrounding the paramagnetic center II lowers the local symmetry of the tetrahedron to C_1 without changing the position of the tetrahedron ions

[SO_4]. For local compensation in the paramagnetic center II, probably, the proton H(1) is shifted to the oxygen side of the O(1), as follows from the value splitting A_{iso}.

In crystals of gypsum Ceara (Brazil) irradiated with X-rays (Cu, 40 KeV and 20mA) by 3 hours at room temperature was observed four paramagnetic centers [2]. Studies EPR centers were performed to set **I2/a** gypsum crystal ($\mathbf{X_0 \parallel a, Y_0 \parallel c^*, Z_0 \parallel b}$). However, when writing the SH were not taken into account the nuclear Zeeman interaction of the proton. The directions of the principal axes of the tensor g- and A- may can be different, when the C_i symmetry of the paramagnetic center. Preliminary settings SH of D center were calculated and amounted to [2]: g_{xx} = 2.000, g_{yy} = 2.002, g_{zz} = 2.037 and A_{xx} = ± 14 G, A_{yy} = ± 12 G, A_{zz} = ± 4 G. The values equal g_{iso} = 2.013 and A_{iso} = 10 G may be compare with data in table. It's closer to the values g_{iso} = 2.0133 and A_{iso} = 8.3 G of center II. It is possible that the center D is more likely to present as a third type of two possible $SO_4^- - {}^1H$ centers I and II, studied in this paper, while the authors of [2] D center was identified as the OH^-.

CONCLUSION

The study of the EPR spectra of radiation centers gypsum crystal ("Marino" glass from Kamsko-Ust'insky Mine in the Republic Tatarstan, Russia) following the structural peculiarities are found:

-the two new spectrum with magnetic multiplicity K_M = 2 (C_i symmetry center) and super hyperfine splitting of the interaction of the electron spin S = 1/2 and the proton nuclear spin I = 1/2;

- the two centers $SO_4^- - {}^1H$, which differ from each other in the position of a proton H(1) gypsum structure;

- the mobility of water molecules in the channels of the structure activates the formation of two or more centers $SO_4^- - {}^1H$, $SO_3^- - {}^1H$;

- the differences in radiation sensitivity of the paramagnetic centers $SO_4^- - {}^1H$, $SO_3^- - {}^1H$ depends on charge redistribution processes in the crystal

- although the probability of the formation of a paramagnetic radical OH in the gypsum structure, but it was not detected in these crystals.

The studies found that both host paramagnetic centers SO_n^-, and impurity paramagnetic centers AsO_n^{2-} [5] can be serve as indicators the process of structural transformation of gypsum associations, and it possible to reconstruct of physical and chemical processes of formation of hydrogenic minerals [11].

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