
EPR Study of Fe^{3+} Paramagnetic Centers in Doped Triglycine Sulphate Crystals

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This paper presents EPR study of Fe^{3+} in triglycine sulphate doped with Fe^{3+} crystal. Fe^{3+} ion is in a high spin state $S = 5/2$. EPR signal can be detected only below 200 K. At 4.2 K the EPR spectrum results from three non-equivalent sites of Fe^{3+} ions. The spin Hamiltonian: $H = \beta B \hat{g} S + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2)$ has been applied to describe the spectrum. The zero field splitting parameter in this case fulfills the condition: $D \gg h\nu$. An experimental spectrum reflects clearly only two resonance transitions: $|\pm 1/2\rangle$ (the lowest Kramers doublet) and $|\pm 3/2\rangle$ (the middle Kramers doublet). The iron complexes occupy interstitial positions in the crystal with distorted octahedral or tetrahedral co-ordination.

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1. Introduction

Triglycine sulphate (TGS) ($[\text{NH}_2\text{CH}_2\text{COOH}]_3\text{H}_2\text{SO}_4$) crystals doped with different paramagnetic ions have been extensively studied [1–4]. There has been only a few papers, however, on EPR of Fe^{3+} ion in TGS crystals [5, 6]. The EPR spectra of TGS: Fe^{3+} crystals have been studied only down to 77 K [5]. The aim of this paper is to extend the temperature range of EPR measurements of the iron-doped crystal paying particular attention to find a possibility of different iron co-ordinations and the dynamics of iron-glycine complexes. A detailed analysis of TGS: Fe^{3+} EPR spectra has become important to describe recently observed [7, 8] a UV irradiation effect on this crystal. Under UV irradiation the yellow crystal turns transparent, and the EPR signal disappears [8].

2. Experimental details

TGS: Fe^{3+} crystals were grown in ferroelectric phase ($T_c = 322$ K) by dynamic crystallization [9, 10] from aqueous solution containing 2% of $\text{Fe}_2(\text{SO}_4)_3$.

The solution in a cylindrical glass vessel was kept in a water bath at a constant temperature. The crystal nucleuses were rotated at 320 K. A large, 3-cm long, single monoclinic crystal with symmetry space group $P2_1/a$ [11, 12] was obtained. Samples of $2 \times 3 \times 4$ mm dimensions were cut along the pyramid of growth (001). The EPR co-ordinate system X, Y, Z was related to crystallographic axes as follows: a and b axes of the crystal are parallel to EPR X and Y axes, whereas crystallographic c -axis makes 15 deg with EPR Z axis. Measurements were carried out with an X -band EPR spectrometer equipped with ESR 900 Oxford helium cryostat.

3. Results

The samples do not exhibit an EPR signal at room temperature. At approximately 200 K, depending on the iron content manifested by the color of the crystal, a spectrum appeared. It consisted of two relatively broad lines of low amplitude at 210 mT and 130 mT for magnetic field parallel to the X -axis of the crystal. The angular dependence of the spectrum reflects the symmetry of the crystal. It shows two kinds of spectra associated to the effect of TGS iron-doping. These spectra are ascribed to defect I and defect I' . They are magnetically equivalent but have different orientation in the crystal. With decreasing temperature the integral intensity of the two lines increases according to the Curie law while the resonance field of the lines becomes slightly shifted. At 100 K both I and I' lines split giving a four-lines spectrum. The line I splits to A and B and I' line gives A' and B' . On further cooling, the intensity of the lines increased. As a result, new components of the spectrum appeared. Additionally, there is a further splitting of lines as a

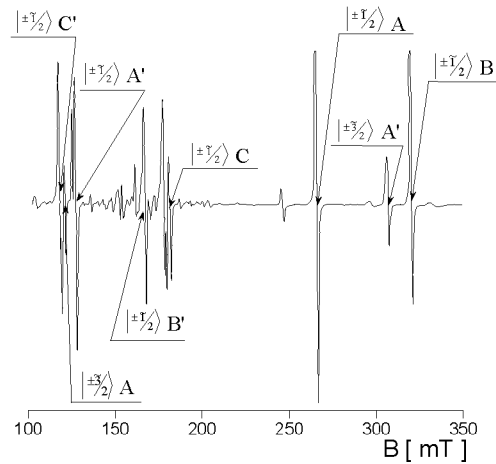


Fig. 1. Experimental spectrum of paramagnetic centers in monocystal TGS:Fe³⁺ at 4.2 K ($\nu = 9.1$ GHz) in XY plane for 28 deg from X axis.

result of the presence of another Fe^{3+} complex. The experimental spectrum at 4.2 K was a very complicated one (Fig. 1). In the figure, the lines of the spectrum analyzed in this paper are marked. It was assumed that there are almost 3 different paramagnetic complexes of iron Fe^{3+} in the crystal TGS: Fe^{3+} : A , B , and C . The complexes have a large (relative to microwave quantum $h\nu$) zero field splitting parameter D . The other lines of EPR spectrum in Fig. 1 are related to “inter-doublet” transitions. They are not observed in every crystal orientation, thus they have lower amplitudes.

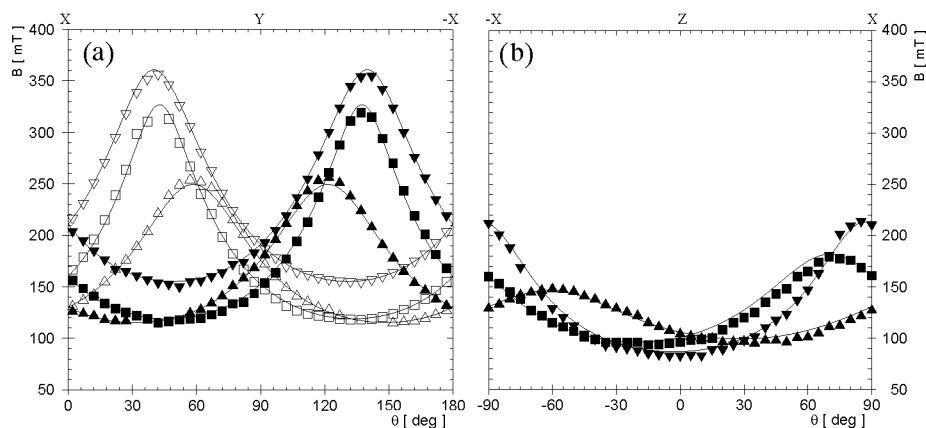


Fig. 2. Anisotropy of $|\pm 1/2\rangle$ transition for all Fe^{3+} complexes in TGS: Fe^{3+} at 4.2 K. Squares, triangles up and down denote magnetically non-equivalent complexes. Solid symbols mark mirror counterparts centers of the open ones. The lines present a fit of the Hamiltonian given by Eq. (1) to the experimental data; (a) in XY plane, (b) in ZX plane.

Figure 2 presents the anisotropy of $|\pm 1/2\rangle$ transition for all analyzed centers at 4.2 K. The anisotropy reflects the symmetry of the crystal. In XY plane six paramagnetic complexes are symmetrically located around Y -axis. The change of the rotational axis from Z to Y reduces the number of components in the spectrum from 6 to 3. The mirror plane in these orientations causes a coincidence of the lines from equivalent complexes. It shows that our spectrum really consists of three different paramagnetic complexes of iron and according to the symmetry of the crystal, the complexes have their mirror counterparts marked as A' , B' , and C' . The lines assigned to A and A' as well as B and B' emerged in the spectrum at 100 K as a result of the splitting of the line observed from 200 K.

We have checked our assignment by recording a powder spectrum of the sample (powdered TGS: Fe^{3+} crystal). It is presented in Fig. 3. The multi-component powder spectrum is characteristic of a high-spin state ($S = 5/2$) of Fe^{3+} ions with the large (relative to microwave quantum $h\nu$) zero field splitting parameter D [13].

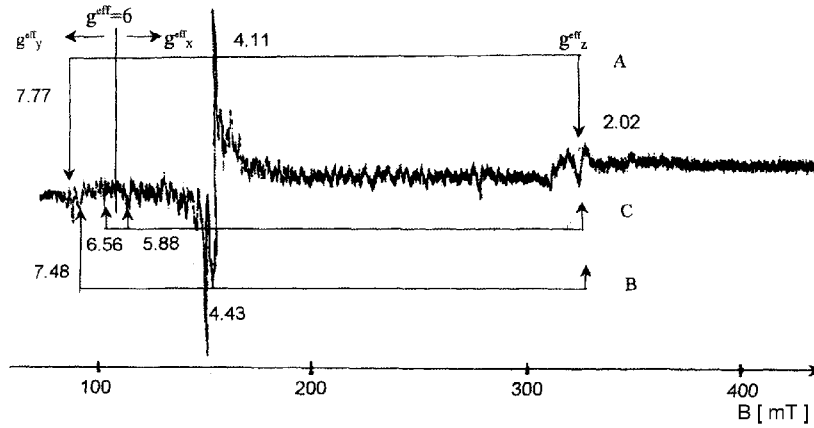


Fig. 3. Powder spectrum of Fe^{3+} glycine complexes in $\text{TGS}:\text{Fe}^{3+}$ crystal at 4.2 K ($\nu = 9.1$ GHz). No discernible signals were observed above 400 mT.

The EPR of $S = 5/2$ ion can consist of 3 lines due to the transitions between mixed $|\pm 1/2\rangle$; $|\pm 3/2\rangle$; $|\pm 5/2\rangle$ states [14, 15]. The transition from the lowest Kramers doublet $|\pm 1/2\rangle$ is of the highest intensity. In a powder spectrum we can find a trace of g tensor. The ground state for high spin paramagnetic iron complexes is 6S so the value of $g_z^{\text{eff}} \approx 2$, and it is the same for all complexes. Axial symmetry of the complex should give $g_y^{\text{eff}} = g_x^{\text{eff}} = 6$. In the powder spectrum in Fig. 2 we can see a strong two-component line at resonance fields corresponding to the following values of $g_x^{\text{eff}} = 4.11$; 4.43 and rather weak lines at $g_y^{\text{eff}} = 7.77$; 7.48 , and a line at $g_z^{\text{eff}} = 2.02$. Thus the values of g suggest a rhomboedric distortion for iron complexes marked as *A* and *B*. In Fig. 2 in the region of magnetic field which corresponds to a g value close to 6 we can find another two weak lines at $g_x^{\text{eff}} = 5.88$ and $g_y^{\text{eff}} = 6.56$. Thus two lines are connected to iron complexes marked as *C*. These kinds of complexes have a rhomboedric distortion too but the smaller values of g_x^{eff} and g_y^{eff} suggest a bigger parameter of zero field splitting compared to the microwave quantum. No signals are recorded above 400 mT in the spectrum.

The analysis of the spectra on a mono-crystal shows that complexes *A* and *A'* outnumber other complexes (*A* and *A'* constitute about 60% of Fe^{3+} complexes present in the crystal). The following assignment was made: the transitions $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ are visible for *A*, *A'*, *B*, and *B'* complexes whereas for *C* and *C'* only $|\pm 1/2\rangle$ transition appears in the experiment. In Fig. 4 the anisotropy of $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ transition is presented for *A* and *A'* complexes. It was recorded at 4.2 K in three perpendicular planes. The solid and dotted lines represent the fitting of Eq. (1)

$$H = \beta B \hat{g} S + D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2) \quad (1)$$

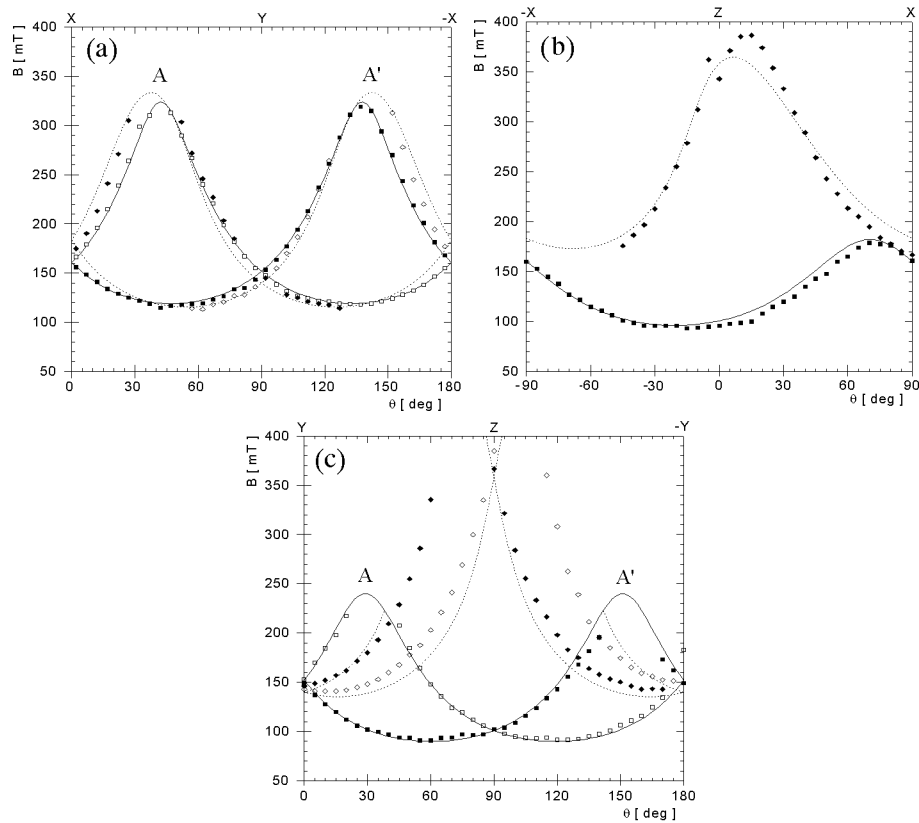


Fig. 4. Anisotropy of Fe^{3+} complexes marked as A (open) and A' (solid symbols) in TGS: Fe^{3+} at 4.2 K. For all centers: $|\pm 1/2\rangle$ transition (squares) and $|\pm 3/2\rangle$ transition (diamond) were observed. The lines present a fit to the Hamiltonian (Eq. (1)): solid line is the $|\pm 1/2\rangle$ transition, dotted line — $|\pm 3/2\rangle$ transition; (a) in XY plane, (b) in ZX plane, (c) in YZ plane.

to the experimental data. This Hamiltonian (Eq. (1)) does not include the parameter a and other terms, proportional to the fourth power of spin S , necessary to describe $S > 2$ complex in a cubic crystal field. These terms are assumed to be much smaller than the zero field splitting parameter D ($a \ll D$) in this crystal. On diagonalizing Eq. (1) in $S = 5/2$ manifold of the Fe^{3+} ($3d^5$; ${}^6S_{5/2}$) one obtains three Kramers' doublets which are a linear superposition of three pure spin states, $|\pm \psi\rangle = a_i|\pm 1/2\rangle + b_i|\pm 5/2\rangle + c_i|\mp 3/2\rangle$. The external magnetic field lifts degeneracy of the spin states, hence, for each complex, 3 lines can be observed. For a given D and E parameter, the coefficients a_i , b_i , and c_i depend only on the magnitude of magnetic field B . The most intense transition takes place between $|\pm 1/2\rangle$ states, lower intensity has $|\pm 3/2\rangle$ transition, and $|\pm 5/2\rangle$ transition is the less intense. Table I presents the spin Hamiltonian parameters of Eq. (1) for three

TABLE I

Spin Hamiltonian parameters for three non-equivalent high-spin $S = 5/2$ Fe^{3+} complexes in $\text{TGS}:\text{Fe}^{3+}$ crystal at 4.2 K. The estimated errors for D and E are $\pm 0.009 \text{ cm}^{-1}$.

	g	$D [\text{cm}^{-1}]$	$E [\text{cm}^{-1}]$	E/D
A	2.0023	0.407	0.033	0.081
B	2.0023	0.488	0.038	0.079
C	2.0023	1.163	0.04	0.024

TABLE II

Directional cosines for all Fe^{3+} complexes in $\text{TGS}:\text{Fe}^{3+}$ crystal marked as A , B , C and their magnetically equivalent mirror counterparts A' , B' , and C' . x , y , z denote principal directions of complexes in the EPR co-ordinate system X , Y , Z . The estimated errors are ± 0.001 .

Magnetically equivalent complexes						
	x	y	z	x	y	z
A	0.738	-0.377	0.559	0.738	0.377	0.559
	-0.356	0.486	0.798	0.356	0.486	-0.798
	-0.573	-0.788	0.225	-0.573	0.788	0.225
B	0.692	0.691	0.207	0.692	-0.691	0.207
	0.083	0.209	-0.974	-0.083	0.209	0.974
	-0.717	0.692	0.087	-0.717	-0.692	0.087
C	-0.674	0.618	0.405	-0.674	-0.618	0.405
	-0.493	0.033	-0.869	0.493	0.033	0.869
	-0.550	-0.786	0.282	-0.550	0.786	0.282

magnetically non-equivalent complexes. The directional cosines for all complexes of Fe^{3+} in $\text{TGS}:\text{Fe}^{3+}$ are given in Table II. Directional cosines show that the principal axis of the complex distortion makes a small angle with [111] direction of non-distorted octahedron surrounding the central ion. The crystal field at Fe^{3+} ion has a trigonal symmetry. The principal axes of distortion for complexes A and B make a 13-deg angle at 4.2 K.

4. Discussion

Paramagnetic complexes of Fe^{3+} ion are already formed in aqueous solution. In the crystal complexes occupy interstitial positions [16]. The Fe^{3+} ion in the complex is surrounded by two glycine molecules (GII and GIII) and two SO_4

groups, analogously to Cu^{2+} [1, 2] and Cr^{3+} [3] complexes in TGS crystal (Fig. 5). The anisotropy of the two-line EPR spectrum of paramagnetic complexes in TGS at 200 K exhibits two-fold symmetry relative to the b axis of the crystal. Previous EPR studies of Cu^{2+} and Cr^{3+} in TGS crystals [1, 2, 4], and TGS: Fe^{3+} crystal with a low concentration of iron dopant [5] revealed the same symmetry of paramagnetic complexes. The crystal with a very low Fe^{3+} concentration [5] showed the morphology of the undoped TGS. The Fe^{3+} EPR spectrum in this crystal was observed already at room temperature. The spectrum was ascribed to two Fe^{3+} complexes in a high spin state ($S = 5/2$). We have studied the crystal having a higher iron content. In a crystal with a higher iron concentration, the EPR spectrum is not observed at room temperature. It is a result of the broadening of the EPR line above 200 K, which is due to the thermal motion of ligands. The localized vibrations of the octahedrons result in a small difference in local symmetry at Fe^{3+} ion of each complex. Hence, the zero field-splitting parameter D of each complex has a slightly different value thus giving broadening of the EPR line. With decreasing temperature, the amplitude of the thermal motion of ligands decreases, so the EPR line narrows. At 100 K, the EPR spectrum splits. Two new orientations of paramagnetic complexes marked as A and B become visible in the spectrum.

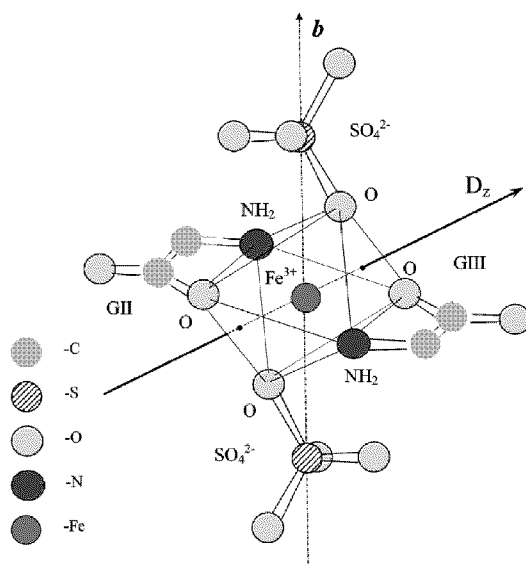


Fig. 5. The co-ordination of Fe^{3+} ion complex in TGS: Fe^{3+} . The orientation of principal axes is marked.

The EPR study of Fe^{3+} ion in TGS crystal [5] has shown that the zero field splitting parameter D increases with decreasing temperature. For a crys-

tal with a lower concentration of iron dopant, Ferrer-Anglada et al. [5] obtained $D = 0.216 \text{ cm}^{-1}$ at room temperature, whereas at 93 K the parameter D amounted to 0.336 cm^{-1} . The D parameters determined in this paper for Fe^{3+} in TGS: Fe^{3+} crystal (at a much higher iron concentration compared with [5]) at 4.2 K for non-equivalent complexes A and B (Table II) are of the same order. The values of the g tensor components obtained from the powder spectrum point to the small rhombic distortion. Hence, the complexes A and B have a symmetry of distorted octahedral co-ordination.

Besides A and B , there are also signals in the EPR spectrum marked as C (Fig. 2), ascribed to another non-equivalent complex in this crystal. The complex C is characterized by the D parameter much larger than that of the complexes A and B . EPR of the complex C can be observed only below 20 K. This implies that the relaxation time T_1 for this complex is probably much shorter than for A and B complexes. Hence, the co-ordination of the central ion is probably different. Mössbauer study of aqueous solution of TGS: Fe^{3+} crystal [16] has shown that besides complexes of octahedral co-ordination there are possibilities to find complexes of tetrahedral co-ordination. The paramagnetic complexes of iron ion are surrounded only by two glycine molecules. These imply a larger D value as resulted from a shortened metal–ligand distance. This type of complexes constitutes approximately 23% of all Fe^{3+} complexes in the studied TGS: Fe^{3+} crystal. This estimate is based on relative integral intensities of the EPR signals ascribed to A , B , and C complexes.

5. Summary

This paper presents the results of the EPR study of TGS crystal with a higher iron concentration than the one previously studied [5]. The statistical distribution of Fe^{3+} complex geometry yields the line broadening. Subsequently, the crystal at room temperature is EPR silent. The EPR study of iron paramagnetic centers in TGS: Fe^{3+} single crystals shows that Fe^{3+} complex has an axial symmetry with a small rhomboedric distortion. The complexes of Cu^{2+} and Cr^{3+} ions in TGS [1–3] occupy also interstitial positions in the crystal. The Fe^{3+} ion is in the high-spin state $S = 5/2$ in the studied temperature range (4.2–300 K). Thermal spin crossover processes changing the spin state of the center [17] have not been observed for Fe impurity in this crystal. The EPR spectrum of Fe^{3+} ion in TGS crystal was described by the spin Hamiltonian (Eq. (1)) for $D \gg h\nu$ and $D \gg a$. It is concluded that there are at least 3 types of complexes in TGS: Fe^{3+} crystal. The complexes A and B have symmetry of distorted octahedral co-ordination. It is also possible to find paramagnetic complexes with tetrahedral co-ordination in TGS: Fe^{3+} with a higher concentration of iron. The complexes denoted as A and A' constitute a majority (60%) of the iron centers in TGS.

Acknowledgments

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