

Electron paramagnetic resonance study of the paramagnetic centers in gamma-irradiated oxalic acid dihydrate single crystal

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ABSTRACT

The Electron Paramagnetic Resonance (EPR) spectra of the radicals produced by γ -irradiation of a single crystal of oxalic acid dihydrate (C₂H₂O₆) have been reported. The EPR spectra of gamma-irradiated single crystals of oxalic acid dihydrate have been studied for different orientations of crystals in a magnetic field. As a result of studies carried out along three axes, it has been determined that there are two biradicals. The EPR spectra have been investigated at temperatures between 125 and 450 K. The spectra have been found to be temperature independent. The g values of the radiation damage centers observed in oxalic acid dihydrate acid single crystal and the hyperfine structure constants of the free electron with nearby protons have been obtained from the single crystal EPR analysis.

1. Introduction

Electron paramagnetic resonance is an important spectroscopic technique using to provide information on the electronic structure, radiation chemistry, and kinetic information of organic, inorganic, biological and solid state. EPR is being used for the study of paramagnetic species (unpaired electrons) such as free radicals, biradicals, transition metal complexes, rare earth species and triplet excited states of diamagnetic molecules effect (Symons, 1978; Perkins, 1994; Bešić, 2009; Sagstuen et al., 1992).

The paramagnetic property can either be acquired later through external influence, or the matter itself is paramagnetic (Caliskan and Caliskan, 2017a, 2017b; Caliskan et al., 2017). One of these external effects is to use the ionizing radiation effect. Free radicals and radical ions can be produced in solid samples through high energy radiation such as gamma rays (Caliskan, 2014; Caliskan et al., 2006, 2007, 2014). One of the best examples of solid samples are single crystals (Caliskan and Tokgoz, 2014; Caliskan et al., 2016; Aras et al., 2004). Single crystal studies cover a very wide and important area among EPR Spectroscopy studies (Caliskan and Caliskan, 2018, 2019a, 2019b).

Oxalic acid is produced naturally from plants. Oxalic acid has been shown to play an important role in the prevention of chronic diseases (osteoporosis, obesity) (Errakhi et al., 2008) and in production of antibiotics like oxytetracycline and chloramphenicol. Its acidity causes it to

form salt with an ion present in the environment. Oxalic acid that enters the body or biological living system forms salt with these ions. Calcium oxalate is the most common salt, it can play a leading role in the formation of kidney stones by causing accumulation in the kidney. Oxalic acid dihydrate is used as titration standard in alkalimetry and manometry, quantitative analysis of calcium and separation of rare earth metals. Oxalic acid dihydrate is used to treatment of varroosis (Varroa destructor) in honey bee colonies (Oxalic acid dihydrate, 2020).

In this study, it is aimed to determine the structural defects caused by gamma irradiation in oxalic acid dihydrate single crystal using Electron Paramagnetic Resonance Spectroscopy.

2. Experimental design

The oxalic acid dihydrate single crystals were grown in the laboratory by slow evaporation of concentrated ethanol solution. The oxalic acid dihydrate crystals belong to the monoclinic, C_{2h}² - P2₁/n space group and the unit cell dimensions are a = 6.119 Å, b = 3.607 Å, c = 12.057 Å, $\alpha = 90^\circ$, $\beta = 106^\circ 19'$, $\gamma = 90^\circ$. The unit cell contains two molecules (Z = 2) (Sabine et al., 1969; Delaplane and Ibers, 1969; Zachariassen, 1934; Leiserowitz, 1976; Coppens et al., 1981; Ahmed and Cruickshank, 1953).

Oxalic acid dihydrate single crystals were irradiated with a ⁶⁰Co γ -ray source at 0.854 kGy h⁻¹ for 162 h at room temperature. The samples

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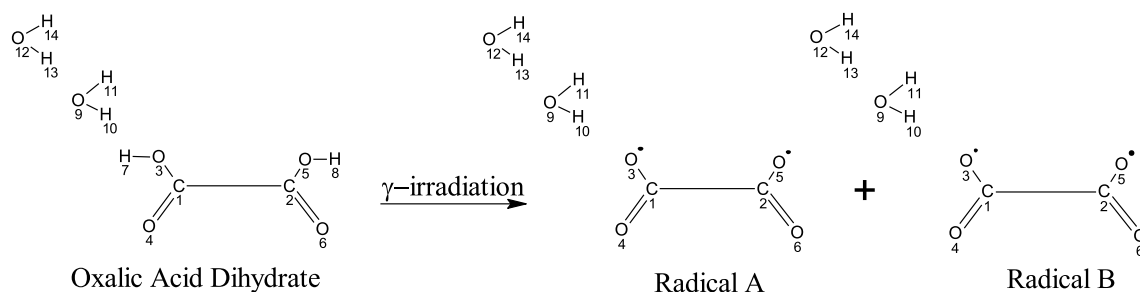


Fig. 1. Structure of two biradicals observed in oxalic acid dihydrate single crystal.

were exposed to a total absorbed dose of about 138.3 kGy. Gamma irradiation was carried out with SVST Co-60-1 type tote-box gamma radiation source capable of continuous and intermittent irradiation at the Turkish Atomic Energy Authority (TAEK) Sarayköy Nuclear Research and Training Center. The EPR spectra were recorded with a

Bruker EMX 081 EPR Spectrometer. EPR work was done for different microwave power values. Step-by-step examination was performed between 0.01 and 20 mW. At higher power values, however, the result was not very good. It was seen that the best EPR signal was received at a power of 3.970 mW. In the EPR spectrometer, TE₁₀₂ standard

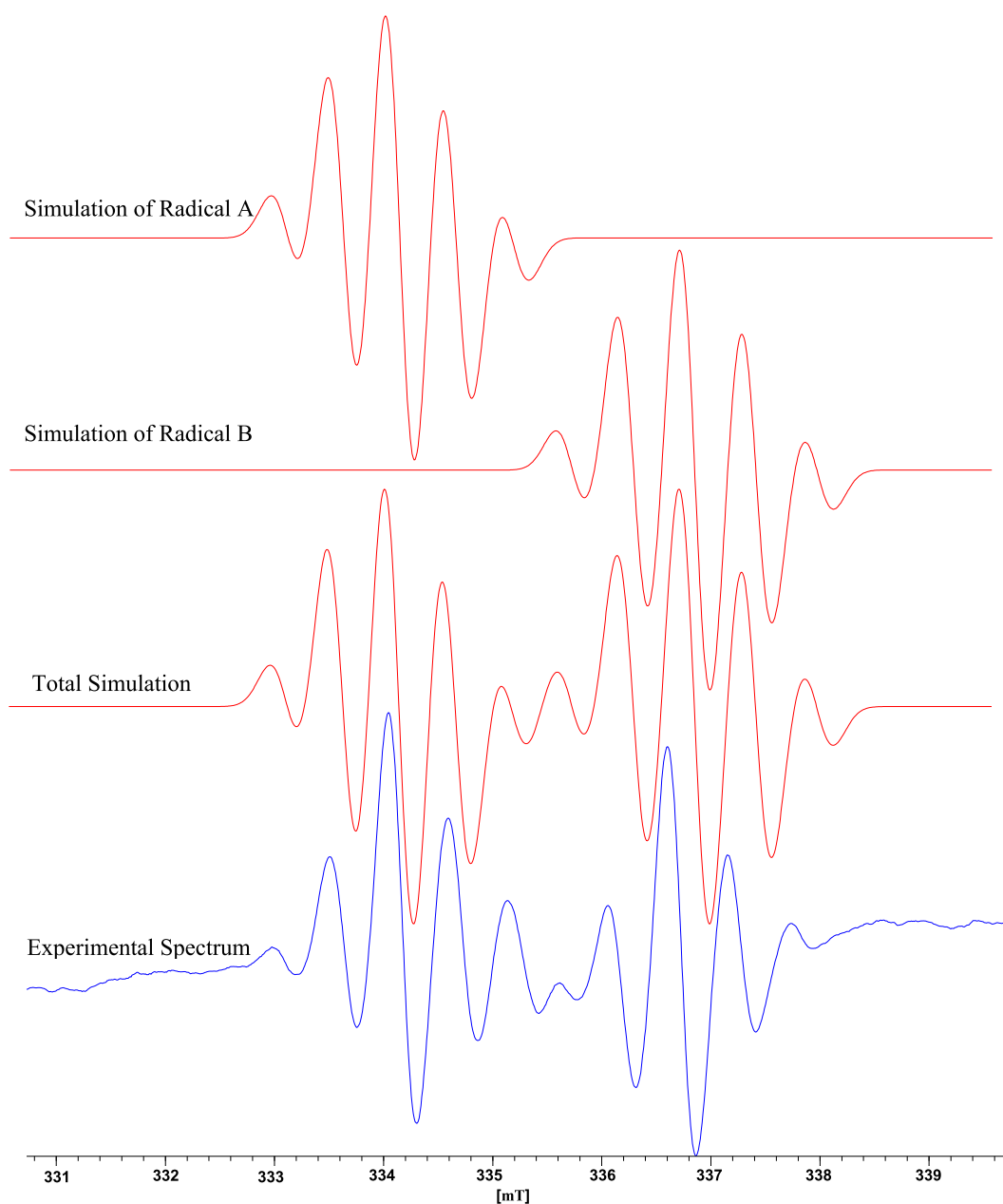


Fig. 2. Experimental and simulated EPR spectra of oxalic acid dihydrate single crystal when the magnetic field is in the a^*b plane at an angle 30° towards the axis.

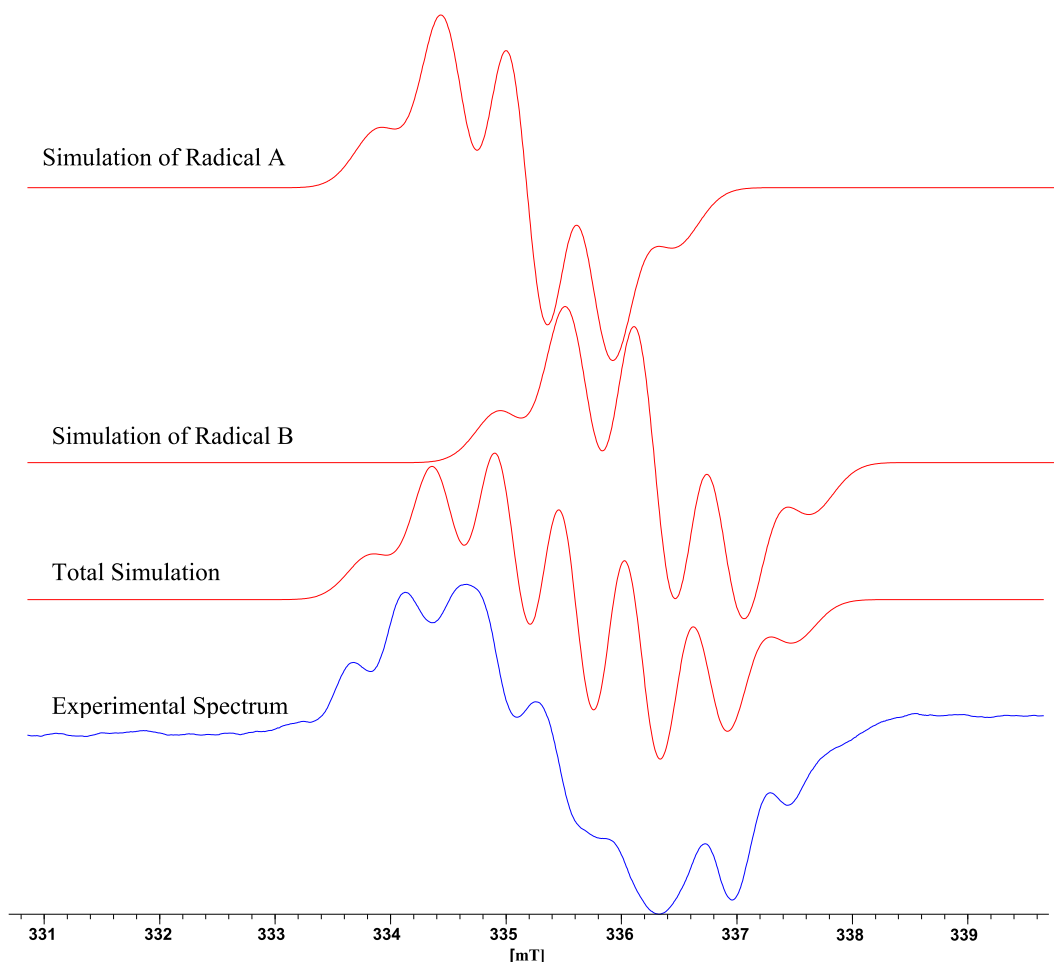


Fig. 3. Experimental and simulated EPR spectra of oxalic acid dihydrate single crystal when the magnetic field is in the bc plane at an angle 50° towards the axis.

rectangular resonator was used. The microwave frequency of the EPR spectrometer is 9.409 GHz for the a^* -axis, 9.419 GHz for the b -axis, and 9.419 GHz for the c -axis. Here, a^* , b and c indicate the axes in the monoclinic system. The modulation frequency of the magnetic field was 100 kHz and the modulation amplitude was 0.25 mT. The single crystals were mounted on a goniometer and the spectra were recorded in three mutually perpendicular planes by rotating the crystals around a^* , b and c axes at 10° intervals from 0° to 180° .

The low temperature measurements were made using the Bruker temperature control unit for different temperature values in the range of 125 K–450 K. Frequency shift occurred frequently at low temperatures. This made it difficult to get EPR spectra. The lowest temperature we could descend without a frequency shift was 125 K. No difference was observed in EPR spectra at different temperature values. Since the peaks of the EPR spectra at 125 K are more pronounced than the EPR spectra at other temperatures and the amount of noise is less at 125 K, all EPR spectra for the three axes of the oxalic acid dihydrate single crystal were obtained at 125 K.

Since two radicals were formed in our study, the cleavages caused by each radical were taken into consideration and the central magnetic field value of each radical was found. These values are resonance magnetic field values (H_r). Resonance magnetic field values were used in the resonance condition formula given with

$$h\nu = g \beta H_r \quad (1)$$

and g -values were calculated. Here, h is the Planck constant; ν is the frequency and β is the Bohr magneton.

The simulations of the EPR spectra were carried out using the Win-

EPR software.

3. Results

EPR spectra of oxalic acid dihydrate single crystal were obtained in three separate axis systems. These spectra have been studied in detail. With the effect of gamma radiation, hydrogen atoms in $-OH$ groups bound to carbon atoms break away from the environment. Two unpaired electrons are formed that settle on the oxygen atoms. In other words, a biradical occurs. As a result of the EPR analysis of the oxalic acid dihydrate single crystal, the presence of two biradicals was detected. Fig. 1 shows the structure of two biradicals observed in oxalic acid dihydrate single crystal.

The simulation values of the hyperfine coupling constants of the simulated spectra in Fig. 2, Fig. 3 and Fig. 4 are given in Table 1. These parameters were slightly modified until a reasonable agreement between simulated and experimental spectra were reached.

The EPR parameters belonging to the radical A and radical B observed in oxalic acid dihydrate are included in Table 2. The angular variations of A -value and the g -value of the radical A and radical B in oxalic acid dihydrate single crystal are shown in Fig. 5 and Fig. 6, respectively.

4. Discussion

As a result of the EPR analysis of the gamma irradiated oxalic acid dihydrate single crystal, two biradicals were detected. It was understood that biradicals have the same structure. Each proton in the two $-OH$

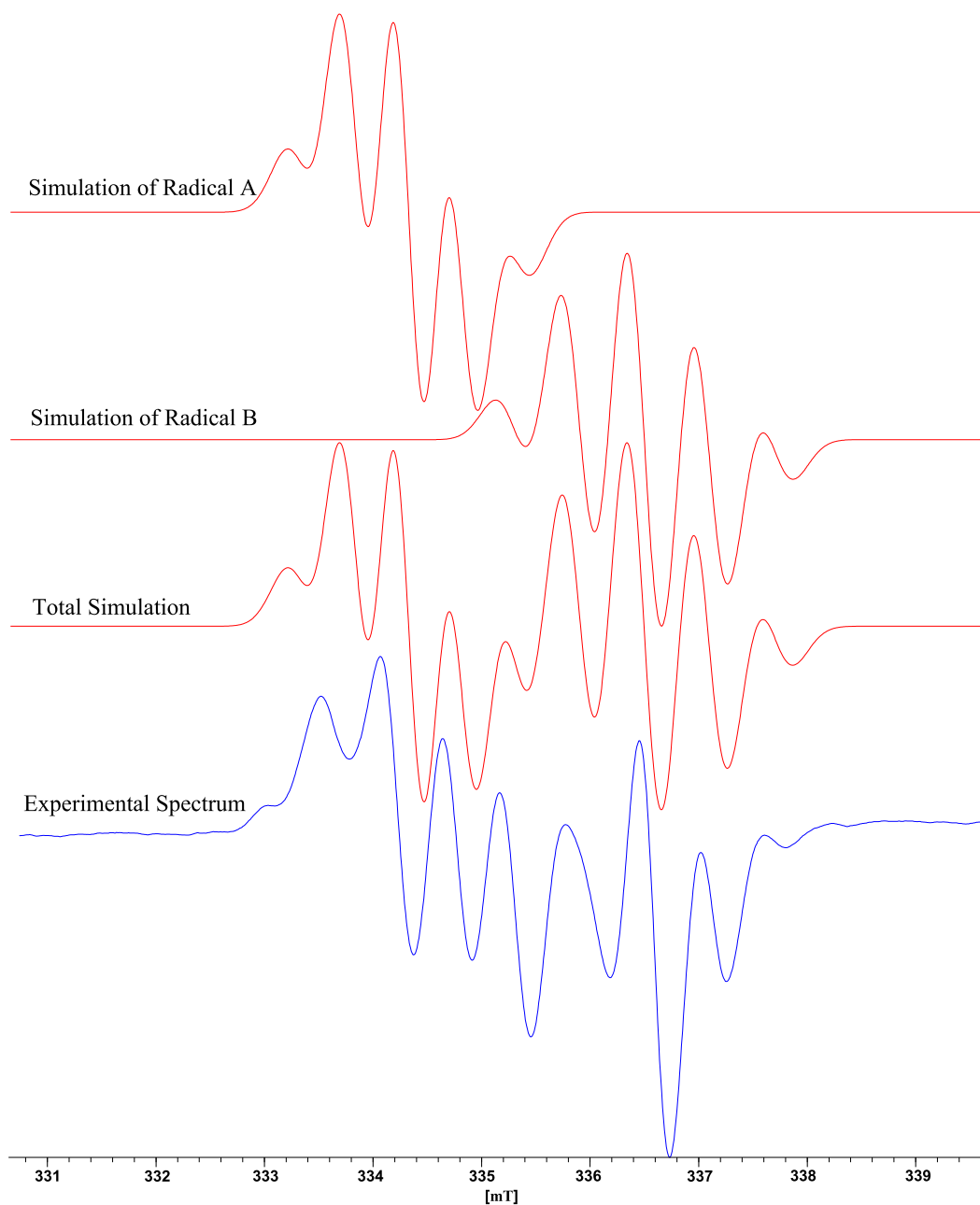


Fig. 4. Experimental and simulated EPR spectra of oxalic acid dihydrate single crystal when the magnetic field is in the bc plane at an angle 150° towards the axis.

Table 1
EPR parameters of simulated spectra.

Figure	Radical A	Radical B
Fig. 2	$[(A_{2H_2O})_\alpha]_A = 0.515$ mT Center Field = 335.2 mT $\nu = 9.368$ GHz Line Width = 0.3 mT	$[(A_{2H_2O})_\alpha]_B = 0.561$ mT Center Field = 335.2 mT $\nu = 9.4438$ GHz Line Width = 0.3 mT
Fig. 3	$[(A_{2H_2O})_\alpha]_A = 0.541$ mT Center Field = 335.2 mT $\nu = 9.389$ GHz Line Width = 0.48 mT	$[(A_{2H_2O})_\alpha]_B = 0.568$ mT Center Field = 335.2 mT $\nu = 9.420$ GHz Line Width = 0.48 mT
Fig. 4	$[(A_{2H_2O})_\alpha]_A = 0.473$ mT Center Field = 335.2 mT $\nu = 9.371$ GHz Line Width = 0.38 mT	$[(A_{2H_2O})_\alpha]_B = 0.593$ mT Center Field = 335.2 mT $\nu = 9.432$ GHz Line Width = 0.38 mT

groups in the parent molecule moves away from the structure. That is, the H(7) and H(8) protons attached to the O(3) and O(5) atoms left the environment. As a result of the separation of protons in the $-OH$ group, unpaired electrons settle on the oxygen atoms of the $-OH$ group.

When the EPR spectra of the oxalic acid dihydrate single crystal were examined in detail, it was understood that only the H(10), H(11), H(13) and H(14) protons in the water molecule interacted with the unpaired electron as magnetic equivalents. As a result of this interaction, it was understood that hyperfine structure splittings occurred. It is seen that the same situation is valid for radical A and radical B.

In the study of Moulton et al., they made a comment that the protons in water molecules can interact with the unpaired electron, resulting in hyperfine structure splittings. However, they could not explain this interpretation in detail. They have not been able to present any concrete material to support this explanation and have not been able to base it on a solid foundation (Moulton et al. (1967)). Our work is consistent with the comments made by Moulton et al. Our experimental work is

Table 2

The EPR parameters of the radical A and radical B observed in oxalic acid dihydrate. (Note: The errors are estimated to be ± 0.00005 and ± 0.005 mT for all the calculated g- and A-values, respectively.)

Radical Parameters (Radical A and Radical B)	Principal values	Direction cosines	
$(A_{2H_2O})_A$ (mT) (For radical A)	$A_{xx} = 0.537$	0.480114-0.875490 0.054836	
	$A_{yy} = 0.492$	0.871314 0.483190 0.085674	
	$A_{zz} = 0.460$ $a_{av} = 0.496$	-0.101503 0.006646 0.994813	
	g_A (For radical A)	$g_{xx} = 2.01473$	0.304559 0.620251-0.722864
		$g_{yy} = 2.01131$	-0.774901-0.279961 -0.566702
		$g_{zz} = 2.01019$	-0.553871 0.732742 0.395368
	$(A_{2H_2O})_B$ (mT) (For radical B)	$A_{xx} = 0.572$	0.230948 0.825327 0.515266
		$A_{yy} = 0.521$	-0.890398 0.392776-0.230041
		$A_{zz} = 0.489$ $a_{av} = 0.527$	-0.392243-0.405664 0.825580
		g_B (For radical B)	$g_{xx} = 2.00037$
$g_{yy} = 1.99940$			0.011015 0.153850 0.988033
$g_{zz} = 1.99898$			0.101357-0.983175 0.151964

theoretically supported by simulation studies. The compatibility and consistency of EPR spectra obtained from simulation studies with the experimentally obtained EPR spectra are concrete evidence supporting the accuracy of the radical we identified.

Looking at the intensity ratios of these spectra, it is seen that four hydrogen atoms interact as magnetic equivalents. It is generally seen that the intensity ratios are trying to protect the structure of 1: 4: 6: 4: 1: 1: 4: 6: 4: 1. However, as a result of the overlapping of the spectra, the intensity ratios change. The intensity ratios of the EPR spectrum in Fig. 3 are 1: 4: 6: 4: 1: 1: 4: 6: 4: 1. The intensity ratios of the EPR spectrum in Fig. 4 are 1: 4: 7: 8 : 7: 4: 1. The intensity ratios of the EPR spectrum in Fig. 5 are 1: 4: 6: 4: 2: 4: 6: 4: 1.

The angular dependences of EPR spectra were obtained for different orientations of the static magnetic field with respect to the crystalline axes. For the radical A and radical B, the spectroscopic splitting factors and the hyperfine coupling constants are slightly anisotropic. For the radical A, the average values of the g-factor and the hyperfine coupling constant were obtained as $g_A = 2.01208$ and $(a_{2H_2O})_A = 0.496$ mT, respectively. For the radical B, the average values of the g-factor and the hyperfine coupling constant were obtained as $g_B = 1.99958$ and $(a_{2H_2O})_B = 0.527$ mT, respectively. The values found in our study are consistent with the value found by Moulton et al. (1967).

It is seen that there are a few previous studies on the investigation of the oxalic acid dihydrate compound by the EPR spectroscopy method. However, when these studies were reviewed, it was understood that they did not contain sufficient and precise information (Moulton et al., 1967; Medvedev et al., 1975; Tezel et al., 2000).

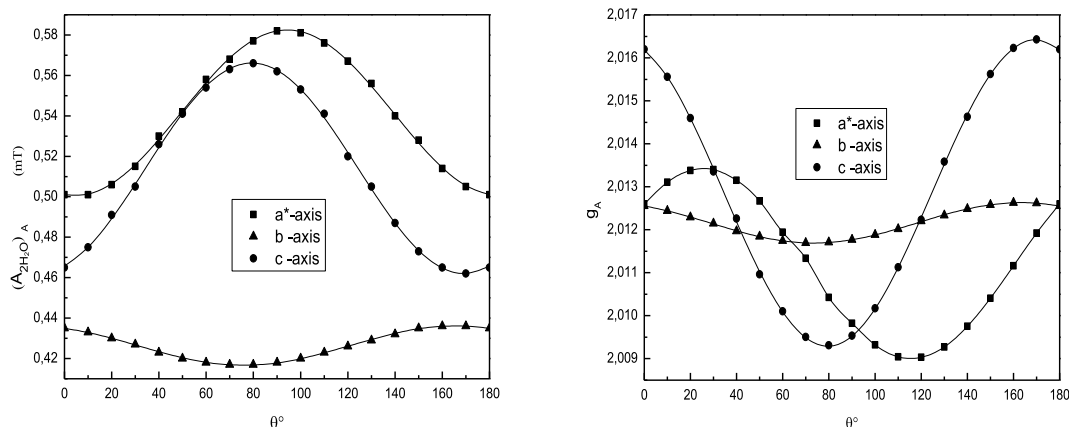


Fig. 5. a) Angular variation of the $(A_{2H_2O})_A$ -tensor of the radical A, b) Angular variation of the g-tensor of the radical A.

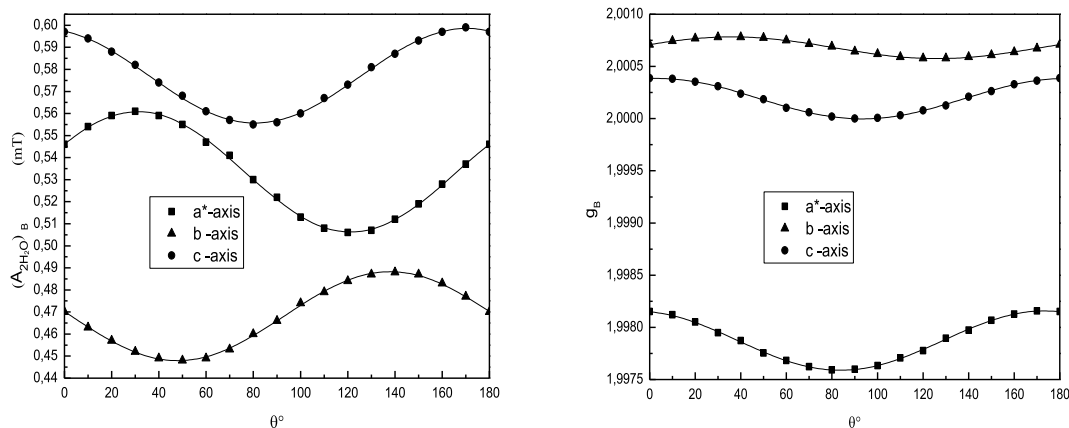


Fig. 6. a) Angular variation of the $(A_{2H_2O})_B$ -tensor of the radical B, b) Angular variation of the g-tensor of the radical B.

5. Conclusions

The EPR study of oxalic acid dihydrate single crystal, showed that after γ -irradiation two biradicals (Radicals A and B) with the same radical feature were formed. It has been found that the protons in water molecules produce hyperfine structure splittings. As a result of the EPR study of oxalic acid dihydrate single crystal, it was understood that spectroscopic splitting factors and hyperfine structure splittings showed an anisotropic change. Simulations of the experimentally obtained EPR spectra were also obtained, and these simulations were found to be extremely consistent.

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CRediT authorship contribution statement

Betul Caliskan: Investigation, Calculation, Writing. **Ali Cengiz Caliskan:** Investigation, Calculation, Writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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