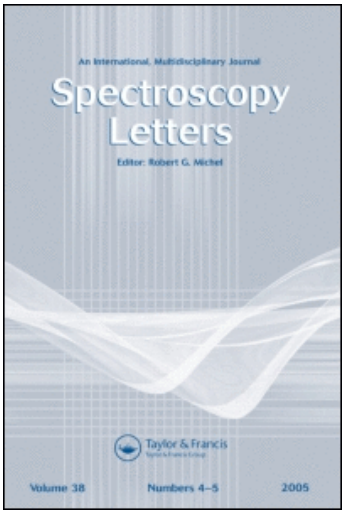

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ESR of Gamma Irradiated $C_2H_20_4.2H_2O$ Single Crystal

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ESR OF GAMMA IRRADIATED $C_2H_20_4.2H_2O$ SINGLE CRYSTAL

Key words: ESR, $C_2H_2O_4.2H_2O$, gamma-irradiated samples.

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ABSTRACT

The gamma-irradiated samples of vacuumed powder and single crystal of $C_2H_2O_4.2H_2O$ have been investigated by ESR method. The spectra of these single crystal and unvacuumed powder are attributed to $R\dot{C}HOH$ radical, but the peaks belonging to this radical in the gamma irradiated powder sample are not observed in the spectrum after having been vacuumed. After A and g tensor values of this radical have been calculated, it was observed to be anisotropic. At low temperature, a considerable change in the spectrum has not been observed.

INTRODUCTION

The effect of irradiation on structural and electrical properties and chemical reactivity of $C_2H_2O_4.2H_2O$ crystal has been investigated. It is known that bond strength and free volume are available within lattice, which is determined by crystal structure of compounds and influences the effects of radiation on simple and complex compounds [1,2]. Investigations on the anisotropic g tensor and anisotropic proton hyperfine splittings give valuable information on the electronic structure of paramagnetic centers.

Rao and Gordy [3] and Tezel *et al.* [4] investigated urea oxalate single crystal, and the $(NH_4)_2C_2O_4.H_2O$ and $K_2C_2O_4.H_2O$ crystals, respectively. Koksal and Yuksel [5,6] have also studied an ESR investigation of the gamma irradiated magnesium oxalate powder and crystal of $CdC_2O_4.3H_2O$. Horvath *et al.* [7] first reported an oxalate radical ($R\dot{C}HOH$) with $\bar{g} = 2.0036$ in the gamma-irradiated oxalate and oxalate salts. The oxalate radical with $\bar{g} = 2.0040$ and line width of 1mT were observed in the irradiated samples at room temperature. Furthermore, Horvath *et al.* [8] obtained the oxalate radical with $\bar{g} = 2.0036$ and line width of 0.1G at 77°C.

The $C_2H_2O_4.2H_2O$ crystal has monoclinic symmetry, and the space group is $P2_{1/n}$. The cell dimension of the $C_2H_2O_4.2H_2O$ is: a=6.119 Å, b=3.640 Å, c=12.051 Å, and β=106°16'. This crystal is a quaternary ring that consists of hydrogen bonds between water and oxalic molecules, and it is a helical structure with one axis being parallel to the b axis [9]. The center of each molecule is a symmetric planar molecule. The $C_2H_2O_4.2H_2O$ crystal structure is shown in Fig 1.

The current investigation describes the study of a single crystal of $C_2H_2O_4.2H_2O$. We have undertaken this investigation with the expectation of finding the chemical form and structure of the paramagnetic centers produced by gamma irradiation. In this study, ESR spectra were taken for vacuumed and unvacuumed gamma irradiated powder samples. Furthermore, ESR spectrum was also taken of the single crystal of the $C_2H_2O_4.2H_2O$.

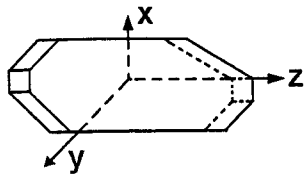

Fig. 1-The crystal form of $C_2H_2O_4.2H_2O$ and the rotation axes x, y, z.

The values of g and A were calculated. In this paper, we applied the ESR technique to clarify the local structure of the $C_2H_2O_4.2H_2O$ crystal and powder.

EXPERIMENTAL DETAILS

The single crystal of $C_2H_2O_4.2H_2O$ was grown in the laboratory by using their powders obtained from commercial sources. The crystal that is suitable for measurement was exposed to cobalt-60 gamma rays with activity of 0.4 Mrad/h for 24 hours. Powders were also irradiated using the same method. The powder of $C_2H_2O_4.2H_2O$ was dehydrated by a diffuse vacuum system with a power of 5.2 x 10^{-6} Torr for 12 hours.

The ESR spectra have been recorded with a Varian X-band E109C model ESR spectrometer. The g factors were found by comparing them with a DPPH sample ($\bar{g} = 2.0036$). The crystal was rotated about each of three orthogonal axes with 10° intervals. The rotation axes x, y, and z are shown in Fig 1.

The ESR spectra consist of four lines at x and z axes orientations of the magnetic field as shown in Fig 2.

The values $A^{(1)}$, $A^{(2)}$, and g for crystal are determined at every direction of the magnetic field for their rotation about the x, y, and z axes. Then the squares of these quantities have been plotted against the rotation angle θ. The best fitting values corresponding to experimental curves were determined by the least square

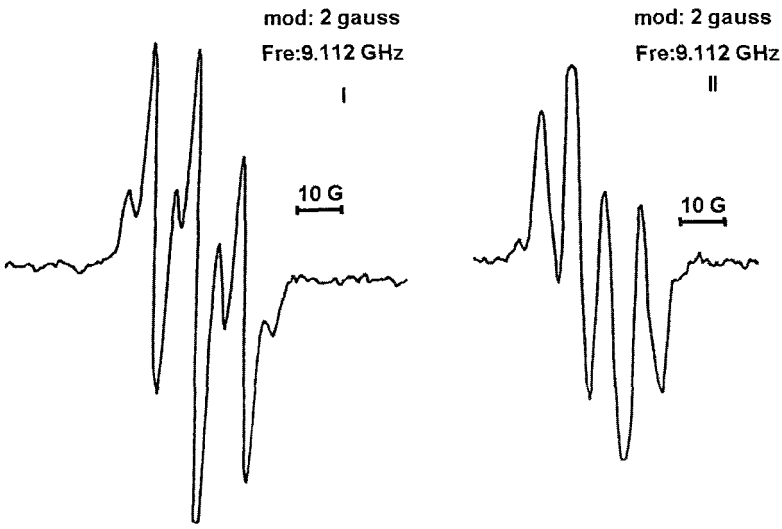

Fig. 2 Electron spin resonance spectrum of gamma irradiated single crystal of $C_2H_2O_4.2H_2O$ with static magnetic field to I) x axis and II) z axis.

computations using a computer programme. Then the obtained matrices were diagonalised and their principal values and direction cosines were found.

RESULTS AND DISCUSSION

The ESR spectra of gamma irradiated single crystal of $C_2H_2O_4.2H_2O$ are shown in Fig 2. They give two proton hyperfine splittings. The peak intensities are usually ca. 1:2:1 but have been found to be ca. 1:1:1:1 for some directions of the magnetic field. For some directions, more than four peaks were observed. In Figs. 3(a) and 3(b), the experimental and fitting curves for $A^{(1)}$, $A^{(2)}$ respectively of gamma irradiated single crystal of $C_2H_2O_4.2H_2O$ are given. They respectively, represent the rotation about the x, y, and z axes corresponding to z//H, x//H and y//H.

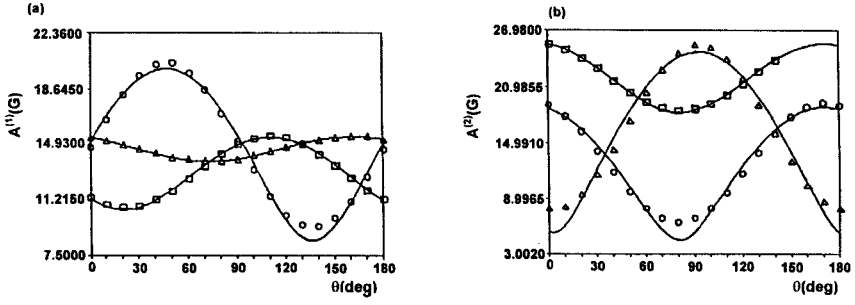

Fig. 3 The experimental and fitting curves for $A^{(1)}$ and $A^{(2)}$ of the gamma irradiated single crystal of $C_2H_2O_4.2H_2O$. They represent the rotation about x, y, and z axes which correspond to z//H, x//H and y//H, respectively. [O, Δ and □ symbols designate the changes in the xy, xz,and yz planes, respectively.]

The variation of A and g values are shown in Table 1. The principal values of g are 2.00151, 2.00828, and 2.00536, and the average value of g is 2.00505. The calculated average value of g is consistent with previous investigations [3,7]. Horvath *et al.* [7] suggested that this g value is quite similar to those where the free electron and unpaired electron are placed on the carbon atoms. Therefore, these peaks on the spectrum are attributed to the $R\dot{C}HOH$ radical because of hyperfine splitting of protons, so these lines are anisotropic since hyperfine splittings are anisotropic. The peak intensity and A value change depending on the direction of the crystal. At low temperature, the spectra no longer change. The small lines at the right and left sides of the spectrum in Fig 2(a) result from the forbidden transitions. The constant hyperfine splittings and anisotropic g tensor of the peaks in Fig 2 are consistent with the parameters of the $R\dot{C}HOH$ radical due to interaction between the two protons [3,4,6]. It seems that the lines are apparently radical pairs which existed in the other orientation.

TABLE 1.

The tensor $A^{(1)}$, $A^{(2)}$, g in laboratory system, their principal values and direction cosines from the laboratory to the principal axes systems of gamma irradiated single crystal of $C_2H_2O_4.2H_2O$.

	Tensor			Principal Values (gauss)	Direction Cosines		
	226.69	163.43	-41.85	A_x=8.14	(0.7237	-0.6555	0.2159)
$A^{(1)}$	163.43	241.89	-14.44	A_y=20.11	(0.6885	0.7070	-0.1615)
	-41.85	-14.44	162.66	A_z=12.68	(-0.0468	0.2655	0.9630)
				a=13.64			
	343.37	-55.97	-48.93	A_x=18.61	(-0.9712	0.1855	-0.1496)
$A^{(2)}$	-55.97	29.90	-29.15	A_y=4.23	(0.1781	0.9821	0.0612)
	-48.98	-29.15	628.30	A_z=25.24	(0.1583	0.0328	-0.9868)
				a=16.03			
	4.01917	0.0131	-0.00118	g_x=2.00151	(0.7185	-0.6927	0.0631)
=	0.01351	4.02007	0.00018`	g_y=2.00828	(0.6955	0.7161	-0.0590)
g							
	-0.00118	0.00018	4.02145	g_z=2.00536	(-0.0043	0.0863	0.9963)
				$\bar{g}$=2.00505			

After gamma irradiated powder samples were vacuumed, the peaks were not observed in the ESR spectrum. Therefore, it can be said that oxalate radical ($R\dot{C}HOH$) disappears after having been vacuumed.

The experimental and fitting curves for $A^{(1)}$ and $A^{(2)}$ respectively, of the gamma irradiated single crystal of $C_2H_2O_4.2H_2O$ are given in Figs 3(a) and 3(b). They represent the rotation about the x, y, and z axes corresponding to z//H, x//H and y//H, respectively. A and g values of $C_2H_2O_4.2H_2O$ single crystal are given in Table 1. The changes of g values in the three perpendicular planes are given in the Fig 4. After having been vacuumed, ESR spectra of gamma irradiated samples were taken, and the oxalate radical was not observed.

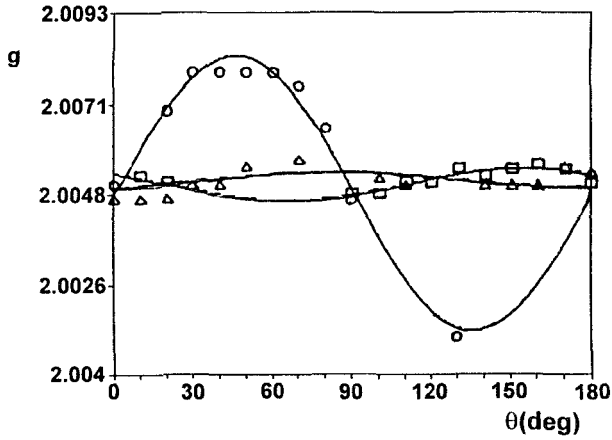

Fig.4 The changes of g values of the gamma irradiated $C_2H_2O_4.2H_2O$ single crystal in the three perpendicular planes. [O, Δ and □ symbols designate the changes in the xy, xz, and yz planes, respectively.]

Koksal and Yuksel [5,6] reported an ESR study of gamma irradiated magnesium oxalate powder and single crystal of $CdC_2O_4.3H_2O$. They found that the g value of the radical was anisotropic, and the average value of it was 2.0124. They suggested that this radical is attributed to the $R\dot{C}HOH$ radical. They also observed that the ESR spectra consists of 3 lines, sometimes of 4 lines. The obtained results in this study are found to be consistent with the previous investigation [6].

The analysis of experimental results leads to the conclusion that the species have the form whereby the unpaired electron is concentrated at the carbon atom and interacts with the two hydrogen atoms.

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