ESR of Paramagnetic Species Produced by Gamma Irradiation in Cadmium Oxalate Three Hydrate Single Crystal

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Paramagnetic species produced in a single crystal of cadmium oxalate three hydrate ($CdC_2O_4 \cdot 3H_2O$) by gamma irradiation have been investigated with the method of electron spin resonance. Only one radical species was observed at room temperature. Analysis of the experimental results leads to the conclusion that the species has the form $R\dot{C}HOH$ in which the unpaired electron is concentrated at the carbon atom and interacts with the two hydrogen atoms. The ESR pattern was observed nearly undiminished for more than three months after the irradiation. The g factor was found to be only very slightly anisotropic with an average value of 2.0124. The hyperfine interaction tensors of the unpaired electron with the two H nuclei have been determined.

1. Introduction

Electron spin resonance spectroscopy is now a well established method of identifying the damage centers produced by high energy radiation. Investigations on the anisotropic g tensor and anisotropic proton hyperfine splittings yield valuable information on the electronic structure of the paramagnetic centers. Although a large number of organic and inorganic materials has been investigated with this method, little work has been done on oxalates. Rao and Gordy [1] investigated urea oxalate single crystal, and another work was our recent paper on magnesium oxalate powder [2].

The present work describes the study of a single crystal of cadmium oxalate. We undertook this investigation in the hope of finding the chemical form and structure of the paramagnetic centers produced by gamma irradiation.

2. Experimental Considerations and Results

a) Experimental Procedure

The cadmium oxalate crystals were found to be triclinic with two molecules per unit cell. The unit cell dimensions were $a = 5.953$, $b = 7.541$, $c = 8.960$ Å and $\alpha = 118.40°$, $\beta = 113.19°$, $\gamma = 68.89°$. The crystals were exposed to a Cobalt-60 gamma-ray source (250 c) for 24 hours. The ESR spectra have been recorded at the Hacettepe University of Ankara with an X-band Varian-E-line commercial spectrometer with a 15″ magnet using 2 mW microwave power. The crystal was rotated about each of three orthogonal axes with 10° intervals. The crystal axes a, b, c and the rotation axes x, y, z are shown in Figure 1.

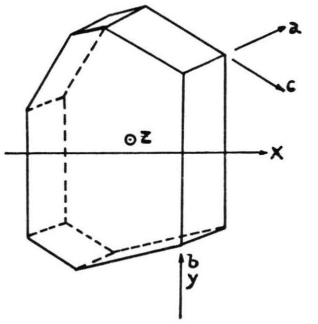

Fig. 1. The crystal axes a, b, c and the rotation axes in cadmium oxalate.

The ESR spectrum consists of four lines at most orientations of the magnetic field as shown in Figure 2. When the magnetic field explores the xy-

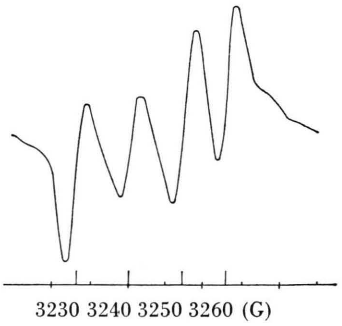

Fig. 2. The Spectrum obtained from cadmium oxalate. The magnetic field is parallel to the z-axis.

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plane at the orientation of 170° with the y-axis it takes nearly the 121 pattern.

b) Nature of the Paramagnetic Species

A qualitative analysis of the recorded spectra makes evident that the paramagnetic species responsible for the ESR spectra should be a kind of free radical which has two proton spin moments interacting with the electron spin. The coupling of both protons is anisotropic, and with different orientations of the crystal in the magnetic field the splitting of one proton varies from $3-7$ and the other from $6-14$ gauss. We think the present crystal is hydrogen bonded according to Figure 3. From this formula one possible free radical which could give unequal anisotropic two proton-couplings is the OH free radical. But both the g value and the range of variation in the proton coupling are significantly smaller than those found for OH free radicals by McMillan, Matheson, and Smaller[3]. Therefore we propose that the radical shown in Figure 4 forms by removal of a hydrogen atom on gamma irradiation. This radical is entirely consistent with the observed results. On the other hand the disappearance of the observed signal after dehydration of the crystal shows that the radical should be related with the crystal water. This is in agreement with the proposed radical.

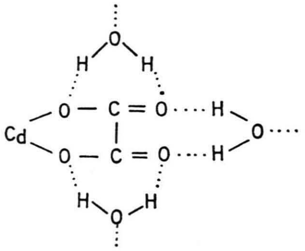


Fig. 3. The chemical structure of cadmium oxalate three hydrate single crystal.

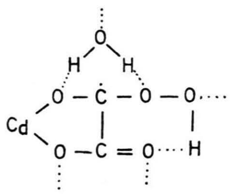


Fig. 4. The radical formed during gamma irradiation of cadmium oxalate three hydrate single crystal.

c) Determination of the **g** *and the Hyperfine Tensors*

When both the g and the hyperfine tensors are anisotropic then the spin Hamiltonian is written as

$$\mathcal{H}=\beta\,\mathbf{H}\,\mathbf{g}\,\mathbf{S}+\mathbf{S}\,\mathbf{A}\,\mathbf{I} \qquad (1)$$

where β is the Bohr magneton, **S** and **I** are electron and nuclear spinoperators, resp., **H** the applied magnetic field, **g** and **A** spectroscopic splitting (**g** tensor) and hyperfine coupling tensors. For the evaluation of **g** and **A** the matrix representation of the Hamiltonian is written in the basis of $|++\rangle$, $|+-\rangle$, $|-+\rangle$, $|--\rangle$. The matrix elements which connect different M_s states are neglected. Then only two 2×2 matrices are diagonalized. The energy eigenvalues obtained from these matrices are,

$$E_{1,2}=\tfrac{1}{2}\,g\,\beta\,H\pm\tfrac{1}{4}A_{\text{exp.}}\,,\qquad E_{3,4}=-\tfrac{1}{2}\,g\,\beta\,H\pm\tfrac{1}{4}A_{\text{exp.}} \qquad (2)$$

where

$$A_{\text{exp.}}=(U^2+V^2+W^2)^{1/2} \qquad (3)$$

and

$$U^2=\frac{1}{g^2}\,(X\,A_{xz}+Y\,A_{yz}+Z\,A_{zz})^2$$

$$V^2=\frac{1}{g^2}\,(X\,A_{xx}+Y\,A_{xy}+Z\,A_{xz})^2 \qquad (4)$$

$$W^2=\frac{1}{g^2}\,(X\,A_{xy}+Y\,A_{yy}+Z\,A_{yz})^2\,.$$

According to our notation A_{ij} are components of the hyperfine tensor which appear in the Hamiltonian. The quantity $A_{\text{exp.}}$ is the experimentally measured hyperfine splitting and can be expressed

$$A^2_{\text{exp}}=\frac{1}{g^2}\,\mathbf{l}\,\mathbf{g}\,\mathbf{A}^2\,\mathbf{g}\,\mathbf{l}\,. \qquad (5)$$

From this it is seen that the angular dependence of $A^2_{\text{exp.}}$ comes from both the **l** vector and the scalar g^2 which now reads

$$g=(X^2+Y^2+Z^2)^{1/2} \qquad (6)$$

with

$$\begin{aligned} X&=l_1\,g_{xx}+l_2\,g_{xy}+l_3\,g_{xz}\,,\\ Y&=l_1\,g_{yx}+l_2\,g_{yy}+l_3\,g_{yz}\,,\\ Z&=l_1\,g_{zx}+l_2\,g_{zy}+l_3\,g_{zz}\,. \end{aligned} \qquad (7)$$

Here l_1, l_2 and l_3 are direction cosines of the magnetic field with respect to the x, y, z axes. In order to evaluate the principal values of $\mathbf{A}^2$ experimentally the procedure of rotating the crystal about three perpendicular axes is followed[4]. For convenience a new matrix K^2 is defined as,

$$\mathbf{K}^2 = \mathbf{g}\,\mathbf{A}^2\,\mathbf{g}\,. \tag{8}$$

Then in analogy with the determination of anisotropic g tensor[5] a rotation about the x-axis gives

$$g^2 A_{\text{exp}}^2 = P_1' \cos^2\Theta + Q_1' \sin^2\Theta - 2 R_1' \sin\Theta\cos\Theta \tag{9}$$

where P_1', Q_1' and R_1' are independent of the rotation angle and:

$$\begin{aligned} P_1' &= (K_{xz})^2 + (K_{yz})^2 + (K_{zz})^2\,, \\ Q_1' &= (K_{xz})^2 + (K_{yy})^2 + (K_{yz})^2\,, \\ R_1' &= K_{xy}K_{xz} + K_{yy}K_{yz} + K_{yz}K_{zz}\,. \end{aligned} \tag{10}$$

Similarly rotation about the y and z axes give P_2', Q_2', R_2' and P_3', Q_3', R_3', respectively. In this way experimentally measured P_i', Q_i', R_i' are used to construct the matrix $\mathbf{K}^2$. By using Equation (10):

$$\begin{bmatrix} P_2' & R_3' & R_2' \\ R_3' & P_3' & R_1' \\ R_2' & R_1' & P_1' \end{bmatrix} = \begin{bmatrix} (K^2)_{xx} & (K^2)_{xy} & (K^2)_{xz} \\ (K^2)_{xy} & (K^2)_{yy} & (K^2)_{yz} \\ (K^2)_{xz} & (K^2)_{yz} & (K^2)_{zz} \end{bmatrix} \tag{11}$$

Then the $\mathbf{K}^2$ matrix is converted to give the square of the hyperfine coupling matrix

$$\mathbf{A}^2 = \mathbf{g}^{-1}\,\mathbf{K}^2\,\mathbf{g}^{-1} \tag{12}$$

which we are trying to find. After finding the A^2 matrix, it is diagonalized by a matrix transformation,

$$\mathbf{R}\,\mathbf{A}^2\,\mathbf{R}^{-1} = \mathbf{A}_{\text{diag}}^2\,. \tag{13}$$

R is the transformation matrix from the laboratory axes to the principal axes of A.

In the present case the spin hamiltonian,

$$\mathcal{H} = \beta\,\mathbf{H}\,\mathbf{g}\,\mathbf{S} + \mathbf{S}\,\mathbf{A}^{(1)}\,\mathbf{I}^{(1)} + \mathbf{S}\,\mathbf{A}^{(2)}\,\mathbf{I}^{(2)} \tag{14}$$

describes the above proposed radical. In order to determine the Hamiltonian parameters we followed the following steps.

1) The g-factor was determined as explained in our recent article[5].

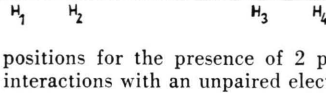


Fig. 5. Line positions for the presence of 2 protons hyperfine interactions with an unpaired electron.

2) For the determination of A's line positions have been indicated as in Figure 5 and from the relations,

$$A^{(1)} = \tfrac{1}{2}(H_e + H_i)\,, \quad A^{(2)} = \tfrac{1}{2}(H_e - H_i)\,. \tag{15}$$

$A^{(1)}$ and $A^{(2)}$ are determined at every direction of the magnetic field for the rotation about the x, y and z axes. Then the squares of these quantities have been plotted against the rotation angle Θ.

3) From the graphs the P_i', Q_i', R_i' parameters were determined and $(\mathbf{K}^{(1)})^2$ and $(\mathbf{K}^{(2)})^2$ matrices were constructed. From these the best fitting values of P, Q, R to the experimental curves were determined by least square computations with an IBM 360.

4) The matrices $(\mathbf{A}^{(1)})^2$ and $(\mathbf{A}^{(2)})^2$ were computed from (12).

5) The matrices $(\mathbf{A}^{(1)})^2$ and $(\mathbf{A}^{(2)})^2$ were diagonalized according to (13) and their principal values and direction cosines were found.

d) Results

For the determination of the g-factor, the experimental points and the best fitting theoretical curves are shown in Figure 6. Similarly experimental $(A^{(1)})^2$ and $(A^{(2)})^2$ points and best fitting curves are shown in Figure 7. The results obtained from these graphs are given in Table 1.

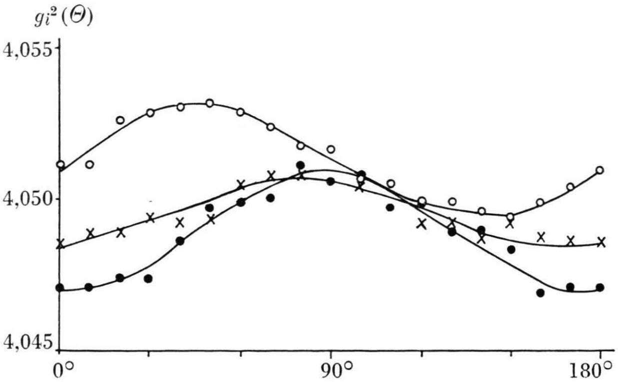
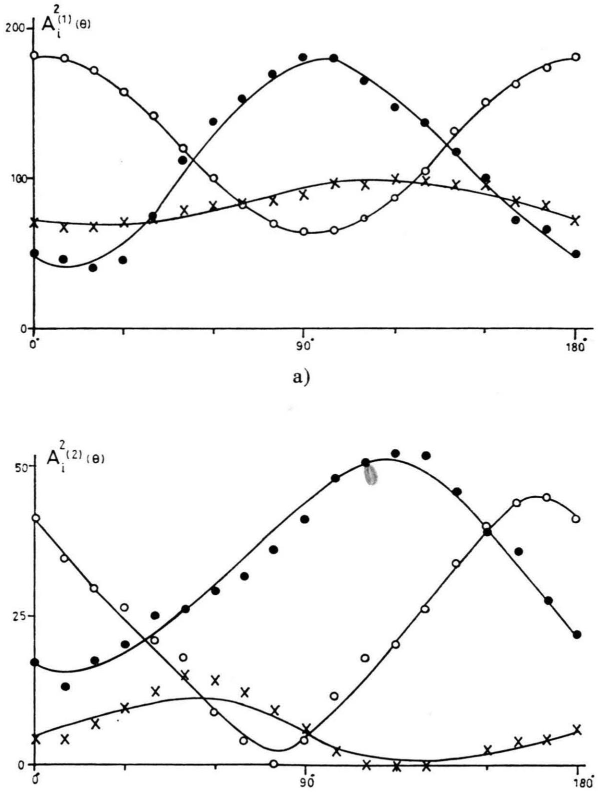


Fig. 6. The experimental and fitting curves for g^2. ○, ● and × represents $g_x^2(\Theta)$, $g_y^2(\Theta)$ and $g_z^2(\Theta)$ respectively. For the rotation about the x, y and z axes the $\Theta=0$ directions correspond to $z\,\|\,H$, $x\,\|\,H$ and $y\,\|\,H$ respectively.

In the average, a g value of 2.0124, can be given with the approximation that it is isotropic within the experimental errors. However the tensors $\mathbf{A}^{(1)}$ and

Table 1. The tensors **g**, $A^{(1)}$, $A^{(2)}$ in the laboratory system, their principal values and direction cosines from the laboratory to the principal axes systems.

Tensor				Principal values	Direction cosines		
$g_{\text{lab.}}$	2.0122	0.0001	−0.0001	$g_{xx} = 2.0122$	0.7508	−0.5453	−0.3727
	0.0001	2.0125	−0.0004	$g_{yy} = 2.0121$	0.6592	0.5826	0.4755
	−0.0001	−0.0004	2.0125	$g_{zz} = 2.0130$	−0.0422	−0.6027	0.7968
$A^{(1)}$	6.64	0.80	1.34	$A^{(1)}_{xx} = 6.01$	0.898	−0.397	−0.188
	0.80	7.99	−0.38	$A^{(1)}_{yy} = 8.35$	0.398	0.917	−0.036
	1.37	−0.38	13.32	$A^{(1)}_{zz} = 13.50$	0.187	−0.142	0.981
$A^{(2)}$	4.25	−0.37	1.03	$A^{(2)}_{xx} = 3.75$	0.907	0.189	−0.376
	−0.37	6.70	0.59	$A^{(2)}_{yy} = 6.45$	−0.384	0.736	−0.557
	1.03	0.59	6.52	$A^{(2)}_{zz} = 7.28$	0.172	0.650	0.740



a)

b)

Fig. 7. The experimental and fitting curves for $(A_i^{(1)})^2$ and $(A_i^{(2)})^2$. For the rotations about the x, y and z axes the $\Theta = 0$ directions correspond to $z \parallel H$, $x \parallel H$ and $y \parallel H$ respectively.

$\mathbf{A}^{(2)}$ with the isotropic values for $\mathbf{A}^{(1)} = 9.27$ and $\mathbf{A}^{(2)} = 5.82$ gauss are quite anisotropic in comparison with the g factor.

3. Discussion

The above explanation has been based upon the radical that we proposed. This is because the $CdC_2O_4 \cdot 3\,H_2O$ crystal should have a center of symmetry as in other oxalates and therefore a four-line pattern cannot be obtained if we propose an OH radical. The isotropic hyperfine values found by several authors for the OH radical are 41.3 [3], 22 [6], 24.1 [7], 29 [8], 23.2 [9]. These do not agree with our results. On the other hand, the $-\dot{H}_2C_2O_3-$ radical proposed by Gordy et al. [1] in urea oxalate could give the observed pattern also in the present case but the g value and the hyperfine values, obtained, do not agree as $A^{(1)} = 16.8$ gauss, $A^{(2)} = 4.9$ gauss and $g = 2.0039$ are quite different from our results in Table 1. However, in order to be 100 percent sure about the proposed radical it is necessary either to deutoerate the crystal or enrich it with ^{13}C.

Acknowledgement

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