ESR of Gamma Irradiated $KHSO_4$ Single Crystal

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Potassium hydrogen sulphate single crystal has been γ-irradiated at room temperature and its electron spin resonance spectrum recorded by changing the H_0 static magnetic field, around an orthogonal axes system. The electron spin resonance spectrum is a single line with a slightly anisotropic g factor. The paramagnetic species has been identified as SO_3^- and the principal values of the g tensor has been determined as $g_1 = g_2 = 2.0060$, $g_3 = 2.0045$. Direction cosines of the principal values of the g tensor with respect to the chosen axes have been determined. The spin-orbit contribution to the g-factor has been explained.

1. Introduction

It is known that sulphur-oxy radicals may be produced by gamma-irradiation [1–5]. Several substances, namely sodium dithionate, sulphamic acid, potassium sulphamate [5], sodium thiosulphate [3] and lithium sulphate [4] were irradiated and studied. All these materials give more than one radical species which makes the identification difficult and the determined properties uncertain. The present paper describes a study of gamma-irradiated potassium hydrogen sulphate single crystal. It was hoped to obtain a new sulphur-oxy radical and to determine its properties or those of a known one more precisely than has been possible before.

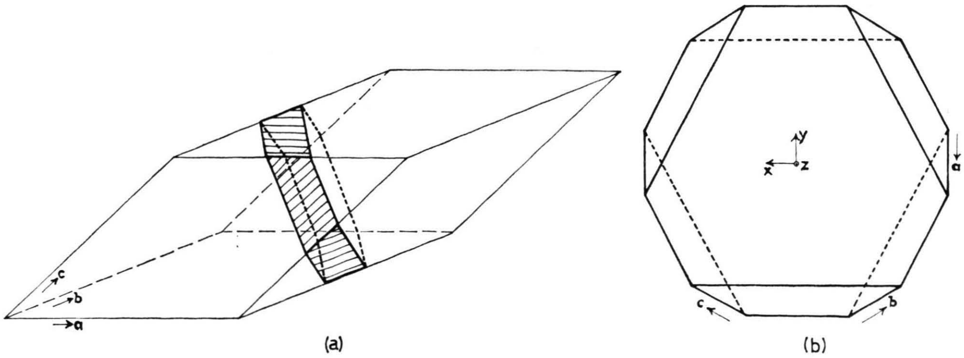
2. Experimental Details and Results

a) Experimental Procedure

Commercial potassium hydrogen sulphate, $KHSO_4$, was crystallized by concentration of an aqueous solution. The crystals were found to be trigonal in symmetry with 16 molecules per unit cell. The crystal axes have been determined by x-ray diffraction experiments. The unit cell dimensions were found to be $a = b = c = 15.5$ Å with $\alpha = \beta = \gamma = 43°$. The crystal axes a, b, c and the rotation axes x, y, z are shown in Figure 1. The z-axis is parallel to the [111] axis, the y-axis is the intersection of the (111) and (111) planes and the x-axies lies in the (111) plane. In appearance the crystals are the middle cut of a trigonal figure as shown in Figure 1.

The samples were irradiated with a Cobalt-60 gamma-ray source (250 c) for 24 hours and the ESR spectra were recorded with a Varian X-band spectrometer at the Hacettepe University of Ankara. During the measurements 2 mW microwave power was used. The crystal was rotated about each of the three orthogonal x, y, z axes and spectra were recorded at 15° intervals. The axis of rotation was kept perpendicular to the H_0 magnetic field in each case.

The recorded ESR spectrum of gamma-irradiated $KHSO_4$ is a single line at all orientations of the rota-



(a) (b)

Fig. 1. a) The crystal shape of $KHSO_4$. b) The crystal axis a, b, c and the rotation axis x, y, z.
Anm. d. Redaktion: In der Fig. 1 b müssen x und y vertauscht werden.

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tion about the x, y, z axes and the line-width is 2.85 gauss. The intensity of the line did not change after a lapse of some days.

Since the line is single and direction dependent the Hamiltonian of the species is

$$\mathcal{H} = \beta \, \boldsymbol{H}_0 \cdot \boldsymbol{g} \cdot \boldsymbol{S} \tag{1}$$

where β is the Bohr magneton, H_0 the static magnetic field, g the spectroscopic splitting tensor and S the electron spin.

b) Determination of the g Tensor

In the x, y, z coordinate system, fixed to the crystal, the g tensor is given by

$$g = (g_{ik}) \; ; \; i, k = x, y, z \, . \tag{2}$$

Instead of the g tensor the g^2 tensor is determined experimentally for the reason which will be obvious in the following. In doing this the Hamiltonian matrix, $\langle i \,|\, \beta \, \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} \,|\, j \rangle$, is written down by using the wave functions $|+\rangle$ for $S_z = \frac{1}{2}$ and $|-\rangle$ for $S_z = -\frac{1}{2}$, and from this Hamiltonian matrix the energies

$$E = \pm \tfrac{1}{2} \beta \, g \, H_0 \tag{3}$$

are obtained, where g has the form

$$g = (X^2 + Y^2 + Z^2)^{1/2} \tag{4}$$

and

$$\begin{aligned} X &= l \, g_{xx} + m \, g_{xy} + n \, g_{xz} \, , \\ Y &= l \, g_{yx} + m \, g_{yy} + n \, g_{yz} \, , \\ Z &= l \, g_{zx} + m \, g_{zy} + n \, g_{zz} \, , \end{aligned} \tag{5}$$

here l, m, and n are the direction cosines of the H_0 magnetic field with respect to the x, y, z axes. Thus, when the magnetic field is in the z-direction $l = m = 0$, $n = 1$, the familiar expression

$$g^2 = g_{xz}^2 + g_{yz}^2 + g_{zz}^2 \tag{6}$$

is obtained [6]. The analogous expressions can be written for H_0 directed along the y and z axes. If the magnetic field is rotated in particular planes such as the $y\,z$ plane; $m = \sin \Theta$, $n = \cos \Theta$,

$$\begin{aligned} g^2(\Theta) &= P_1 \cos^2 \Theta + Q_1 \sin^2 \Theta - 2 \, R \sin \Theta \cos \Theta \\ &= \tfrac{1}{2}(P_1 + Q_1) + \tfrac{1}{2}(P_1 - Q_1) \cos 2 \, \Theta - R_1 \, \mathrm{sni} \, 2 \, \Theta \\ &= \tfrac{1}{2}(P_1 + Q_1) - \tfrac{1}{2} k_1 \sin(2 \, \Theta - \alpha_1) \end{aligned} \tag{7}$$

is obtained. The parameters P, Q and R replace the g_{ij} in the following way

$$\begin{aligned} P_1 &= g_{xz}^2 + g_{yz}^2 + g_{zz}^2 \, , \\ Q_1 &= g_{xy}^2 + g_{yy}^2 + g_{zy}^2 \, , \\ R_1 &= g_{xy} \, g_{zz} + g_{yy} \, g_{yz} + g_{yz} \, g_{zz} \, , \end{aligned} \tag{8}$$

and the parameters k_1 and α_1 are related to P_1, Q_1 and R_1 through the transformation

$$\begin{aligned} k_1 &= [(P_1 - Q_1)^2 + 4 \, R_1{}^2]^{1/2} , \\ \alpha_1 &= \tfrac{1}{2} \tan^{-1} \left(\frac{P_1 - Q_1}{2 \, R_1} \right) . \end{aligned} \tag{9}$$

The constant k_1 is the amplitute, and α_1 is the phase angle for the sinusoidal variation of $g^2(\Theta)$ in the $y\,z$ plane. So, by rotating in three successive planes, perpendicular to each other, we find the P, Q, R which constitute the g^2 tensor. Taking the initial conditions of these three rotations into account, g^2 can be written as

$$\boldsymbol{g}^2 = \begin{bmatrix} [P_2 = Q_3] & R_3 & R_2 \\ R_3 & [P_3 = Q_1] & R_1 \\ R_2 & R_1 & [P_1 = Q_2] \end{bmatrix} . \tag{10}$$

After finding the g^2 matrix it is diagonalized by a matrix transformation,

$$\boldsymbol{R} \, \boldsymbol{g}^2 \, \boldsymbol{R}^{-1} = \boldsymbol{g}^2_{\mathrm{diag.}} \tag{11}$$

R is the transformation matrix from the laboratory axes to the principal axes of g. This method has been followed and the best fitting values of P, Q, R have been determined from the experimental results by a least-squares computation with a computer. Figure 2 shows the g^2 values against the rotational angle Θ, which is the angle between the magnetic field and the chosen axis. $\Theta = 0°$ corresponds to $H_0 \| y$, $H_0 \| z$ and $H_0 \| x$ for the rotation about the z, x, and y axis, respectively.

The g tensor with its principal values and corresponding direction cosines, in the x, y, z axes system, are given in Table 1. The g tensor has cylindrical symmetry with the principal values of $g_1 = g_2 = 2.0060$ and $g_3 = 2.0045$. Due to this cylindrical symmetry the directions indicated with an asterisk have no significance.

3. Discussion

It has been shown that gamma-irradiated potassium, sodium and ammonium thiosulphate powders give similar ESR spectra [1]. Therefore, considering these and the results obtained by Atkins [7] in gamma-irradiated sodium and potassium selenates, the paramagnetic species most likely to be formed in $KHSO_4$ crystals during gamma-irradiation should be sulphur or a kind of sulphur-oxy radical which arise due to partial degradation of the sulphate molecules. The possible sulphur and sulphur-oxy radicals are S_2^-,

g tensor			Principal values	Direction cosines		
2.0062	0.0000	−0.0001	g_1=2.0060	(0.7771	−0.6263	−0.0627)*
0.0000	2.0060	0.0001	g_2=2.0060	(0.6207	0.7790	−0.0890)*
−0.0001	0.0001	2.0047	g_3=2.0045	(0.1046	0.0303	0.9941)

Table 1. The g tensor, its principal values and direction cosines in the x, y, z axis. (Since the tensor has cylindrical symmetry the directions marked with an asterisk have no significance.)

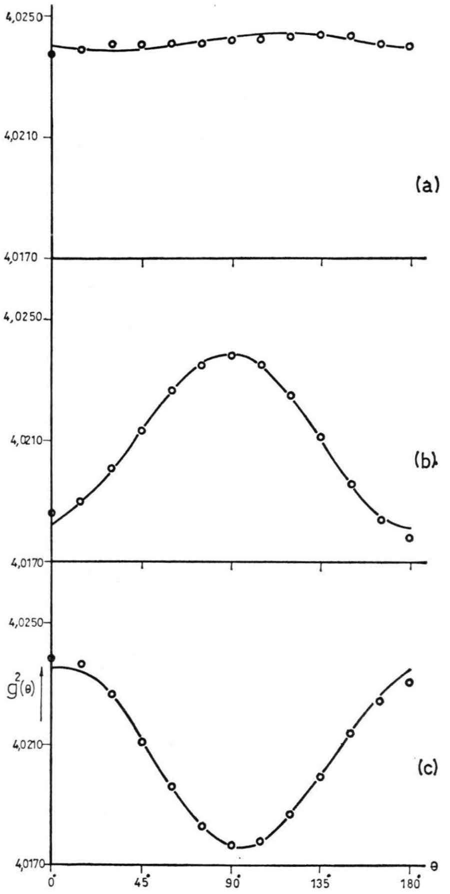

Fig. 2. a–c) Variations of $g^2(\Theta)$ for the rotations about the z, x and y-axes respectively. $\Theta=0°$ directions correspond to $H_0 \parallel y$, $H_0 \parallel z$ and $H_0 \parallel x$ in the order of a, b, c. The dots are experimental points and the solid lines are theoretical curves.

SO, SO_2^+, SO_2^-, SO_3^+, SO_3^- and SO_4^-. S_2^- and SO are most unlikely to be the observed for the following reasons. First, an S_2^- or SO radical would be formed only from a complete or nearly complete degradation of the sulphate ion. Second, an S_2^- radical would have the principal values of g 2.0026, 2.0465, 2.0308 [8]. Finally S_2^- or SO radical has so far not been observed in gamma-irradiated crystals of sodium dithionate, sulphamic acid, potassium sulphamate, potassium amine disulphonate and potassium methane disulphonate [5]. Published ESR data on the g tensor for the SO_2^+ radical found in x-irradiated sodium thiosulphate give the principal g values 2.0079, 2.0105 and 2.0305 [3]. It therefore appears that our species is not SO_2^+. Again ESR data for the radical SO_2^- give the principal values 2.004, 2.0102, 2.0057 [9]; and 2.0047, 2.0095, 2.0070 [3]; and these suggest that SO_2^- is not the paramagnetic species observed. SO_3^+ is isoelectronic with NO_3, which has the principal g values $g_{\parallel}=1.998$, $g_{\perp}=2.029$ [10]; our species does not satisfy these requirements. On the other hand SO_4^- species has the principal values 2.0035, 2.0327, 2.0084 [11], which does not agree with our results.

There remains the radical SO_3^- with a published average g value of 2.004. Since our average g value is 2.0055 and shows cylindrical symmetry we identify the species as SO_3^-. The main isotopes of sulphur and oxygen atoms have zero nuclear spin and therefore the ESR spectrum of $^{32}SO_3^-$ is a single line. The SO_3^- is isoelectronic with PO_3^{-2} and ClO_3. The principal g values of these species and the spin-orbit coupling constants, λ, for P, S and Cl atoms are given in Table 2. Although Walsh [14] predicted that the AB_3 molecules with 25 electrons should be pyramidal with C_{3v} symmetry, it is sufficient to state here that the difference in the g value from the free-spin value depends on the spin-orbit mixing of the excited states into the ground state. Since the sulphur atomic orbitals p_z, $d_{x^2-y^2}$, d_{z^2} and p_x, d_{xz} transform as a_1 and b_1 respectively, the ground state wave function should possess at least some sulphur p and d character. So, if we consider the spin-orbit coupling constants for P, S, Cl atoms in Table 2 and assume that the energy differences between the ground and

Table 2. Comparison of the principal values of the g tensors for PO_3^{-2}, SO_3^-, ClO_3 and spin-orbit coupling constants of P, S and Cl atoms.

Radical	Principal values			λ (cm^{-1})	Ref.
PO_3^{-2}	2.001	2.001	1.999	299	12
SO_3^-	2.0060	2.0060	2.0045	382	
ClO_3	2.0103	2.0103	2.0069	586	2

the appropriate excited states are equal for isoelectronic PO_3^{-2}, SO_3^- and ClO_3 radicals we expect the principal values of g for SO_3^- to be between the principal values of PO_3^{-2} and ClO_3. This is observed.

As in the isoelectronic PO_3^{-2} and ClO_3, the direction of the smallest principal value should be perpendicular to the O_3 plane also in the SO_3^- radical. On the other hand, the direction cosines in Table 2 show that the direction of g_3 is nearly parallel to the [111] axis of the $KHSO_4$ crystal. Clearly the form of the SO_3^- radical should be as in Figure 3.

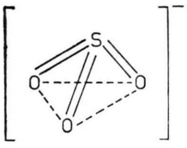

Fig. 3. The SO_3^- radical.

4. Conclusion

Since SO_3^- has been obtained in $KHSO_4$ without any other radicals in comparison with the substances studied by several authors [3, 5, 13] this ESR investigation suggests two conclusions:

a) Different products may be found in different lattices although they have similar forms. Thus we find SO_3^- in $KHSO_4$, Atkins et al. find SO_4^- in $Li_2SO_4 \cdot 2\,H_2O$ [4] and Chandry et al. find SeO_3^- in K_2SeO_4 [7].

b) The stability of the species produced by gamma-irradiation may vary with the crystal matrix. For example SO_3^- is more stable in $KHSO_4$ than in NH_3SO_3 [5] and $K_2NH(SO_3)_2$ [13].

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