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MASTER

ELECTRON PARAMAGNETIC RESONANCE STUDIES OF RADIATION INDUCED
DEFECTS IN SINGLE CRYSTALS OF LITHIUM SULFATE

by

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TABLE OF CONTENTS

	Page
Acknowledgements.	ii
List of Tables.	v
List of Figures	vi
Chapter	
I. Introduction	1
II. Electron Paramagnetic Resonance (EPR).	5
EPR Theory.	5
The Spin Hamiltonian.	11
Data Analysis	15
III. Experimental Apparatus	20
Spectrometer System	20
Microwave Cavity for Work Near 77°K	31
IV. Sample Preparation	37
Crystal Growth.	37
Irradiation	40
V. Electron Irradiated Lithium Sulfate at 77°K.	43
Introduction.	43
Experimental Results and Spin Hamiltonian	43
Discussion.	52
Conclusion.	59
VI. Thermal Decay of the OH Radicals in Electron Irradiated Lithium Sulfate at 77°K	61

TABLE OF CONTENTS (Cont'd.)

Chapter	Page
Introduction	61
Experimental Results and Spin Hamiltonians	63
Discussion	73
Conclusion	83
VII. Neutron Irradiated Lithium Sulfate.	84
Introduction	84
Experimental Results and Spin Hamiltonians	84
Discussion	94
Conclusion	99
Appendix for Chapter VII	100
Appendix	102
List of References	108
Autobiographical Statement	111

LIST OF TABLES

Table		Page
1.	The estimated values of the parameters for the g- and A-tensors.	51
2.	Various interatomic directions of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	55
3.	The spin Hamiltonian data by Wigen and Cowen.	58
4.	The g- and A-tensors for the type A, B, and C centers . . .	62
5.	A- and g-tensor data for O_2H radicals	78
6.	g-tensor data for O_2^- and O_3^- radicals.	81
7.	g-tensor data for type D, E, and F resonances	93
8.	g-tensor data for various oxygen and sulfur oxide radicals	96

LIST OF FIGURES

Figure	Page
1. Energy level diagram of an electron in a magnetic field. . .	7
2. Hyperfine splitting of the resonance line: (A) Effect of a nucleus of spin $1/2$ on the energy levels of an electron in a magnetic field; (B) Splitting of the single resonance line into two components by a nucleus of spin $1/2$	10
3. Direction cosines of the magnetic field referred to the g-tensor principal axis system.	13
4. Typical angular dependencies of the position of the resonance versus an experimental angle: (A) Axial symmetry and $g_{ } > g_{\perp}$; (B) Axial symmetry and $g_{\perp} > g_{ }$; (C) Non-axial symmetry.	16
5. Polar angles of an axially symmetric g-tensor referred back to the crystalline axes	18
6. Block diagram of the Fieldial magnetic field regulator . . .	21
7. Block diagram of the EPR spectrometer.	23
8. Detection of the resonance: (A) Modulation of the external field; (B) Derivative of the power absorption with respect to the magnetic field	26
9. Method of controlling klystron frequency: (A) $f_k = f_c$; (B) $f_c > f_k$; (C) $f_k > f_c$	28
10. Block diagram of the superheterodyne detection system. . .	30
11. Schematic diagrams (drawn to scale) of the liquid nitrogen temperature EPR cavity of cylindrical form and its accessories: (A) The cross section of the assembly; (B) Top view of the cavity; (C) Cross section of the sample holder. A- top plate of the cavity; B- bottom plate of the cavity; C- stainless steel waveguide; D- coupling screw; E- quartz rod; F- E-bend waveguide; G- Teflon rod; H- thumb cap; I- threaded bottom tip; J- stainless steel tubing; K- phosphor bronze strip; L- He gas feedhold; M- Mylar seal; N- plastic cone	32

Figure	Page
12. E- and H- field patterns in a cylindrical cavity (TE ₀₁₁ MODE).	34
13. Crystal growth habit of Li ₂ SO ₄ ·H ₂ O	38
14. A projection of the constituent atoms of Li ₂ SO ₄ ·H ₂ O on the a-c plane. The relative positions and numbering of the O, S, and Li atoms are in accordance with Ziegler's data, ¹⁹ while the positions and numbering of the H atoms are in accordance with the neutron diffraction data of Ozerov et al. ²⁰	39
15. EPR spectrum of Li ₂ SO ₄ containing a mixture of H ₂ O and D ₂ O near 77°K. The sample has been irradiated in a 1 mA beam of 1 MeV electrons near 77°K and kept at the same temperature. The magnetic field is perpendicular to the b-axis and makes an angle of -30° with the a-axis. The field intensity increases from left to right. The + sign indicates the position of the isotropic line centered near the free electron g-value. The two lines (h ₁ and h ₂) are the proton hyperfine lines, and the three lines (d ₁ , d ₂ , and d ₃) are the deuteron hyperfine lines.	45
16. The anisotropy of the EPR spectrum of Fig. 15: (A) Rotation about the b-axis; (B) Rotation about an axis perpendicular to the a-b plane. The position (ΔH) of the hyperfine lines is measured relative to the isotropic line (see Fig. 15). The full and open circles indicate the observed values of ΔH for the proton hyperfine lines, where the open circles imply a certain degree of uncertainty due to poor resolution caused by overlapping lines; the crosses indicate the observed positions of the deuteron hyperfine lines. In (B), for the clarity of the figure, the anisotropy of the deuteron hyperfine lines is not shown (see text). The solid curves represent the theoretical anisotropy	46 & 47
17. The type A spectrum of electron-irradiated Li ⁶ SO ₄ containing a mixture of H ₂ O and D ₂ O at 77°K. The sample has been irradiated at 77°K and stored at 77°K. The magnetic field is perpendicular to the b-axis and makes an angle of -20° with the a-axis. The field intensity increases to the right. The + sign indicates the free electron resonance field	64

18. The thermal decay and growth curves for the types A, B, and C spectra. The ordinate measures the peak-to-peak height of the spectrum in arbitrary units. The abscissa measures the time in minutes that the sample has been held at room temperature. 66

19. The type B and C spectra at 77°K: (A) Spectrum from a sample of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; (B) Spectrum from a sample of $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$. Both samples have been warmed to room temperature for 12 hours. The magnetic field is perpendicular to the b-axis and makes an angle of -20° with the a-axis. The field intensity increases from left to right. The + sign indicates the free electron resonance field . . . . . 67 & 68

20. The angular dependence of the type B spectrum: (A) Rotation about the b-axis ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$); (B) Rotation about the a-axis ($\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$). The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field. The portion of the experimental plot in Fig. 20(A) near 40° was uncertain due to overlapping lines and is therefore left out. In Fig. 20(B), a dot represents an unresolved triplet corresponding to the deuteron hyperfine structure . . . . 71 & 72

21. The angular dependence of the type C spectrum of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$: (A) Rotation about the b-axis; (B) Rotation about the a-axis. The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field . . . . . 74 & 75

22. Spectrum of a neutron-irradiated sample of $^7\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The sample has been irradiated at room temperature and stored at room temperature. The spectra has been taken at 77°K. The magnetic field is perpendicular to the b-axis and makes an angle of -60° with the a-axis. The field intensity increases from left to right. The + sign indicates the free electron resonance field. 86

23. Angular dependence of the type D spectrum: (A) Rotation about the b-axis; (B) Rotation about an axis perpendicular to the a-b plane. The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field . . . . . 87 & 88

24. Angular dependence of the type E and F spectra: (A) Rotation about the b-axis; (B) Rotation about the a-axis. The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field. In (B), the portion of the type F dependence represented by the crosses is uncertain because of overlap. Also, the portion of the type E resonance that is missing above 60° is omitted, because of the complete overlap of this line with other lines of larger amplitude. . . . .

90 & 91

CHAPTER I

INTRODUCTION

The interest shown in radiation-induced defects in materials has been increasing in recent years. The internal structure of the material is altered by the radiation such that any other sample of the same material irradiated in the same manner is damaged in the same way. Crystals, because of their uniformity and order, offer perhaps the best systems in which to investigate these radiation-induced defects. An example of a crystal that is easily damaged by ionizing radiation is lithium sulfate monohydrate. Consequently, this crystal will be the subject of the following work.

One method of studying these radiation induced defects is electron paramagnetic resonance (EPR). This is a sensitive technique used to probe the local environment of a defect. Utilizing the knowledge of the local environment, it is then possible to understand the position and nature of the defect.

Recent experimental studies of electron-irradiated lithium sulfate at 77°K by Wigen and Cowen¹ have revealed a resonance containing several components. One of the components, an isotropic line, has been proposed to arise from a trapped electron. The other portion of the resonance has been observed to be anisotropic and contain either two lines or a partially resolved triplet of lines depending upon whether the crystal water of hydration was H_2O or D_2O . The data for this latter

portion of the spectrum has been fitted to Hamiltonian of the form:

$$\mathcal{H} = \beta \vec{S} \cdot \vec{g} \cdot \vec{H} + \vec{S} \cdot \vec{A} \cdot \vec{I} \quad (1)$$

where β is the Bohr magneton, $\vec{g}$ is the g-tensor, $\vec{S}$ is the vector electron spin operator, $\vec{H}$ is the magnetic field, $\vec{A}$ is the hyperfine tensor, and $\vec{I}$ is the vector nuclear spin operator. Wigen and Cowen found the g-tensor to be axially symmetric and the hyperfine tensor to deviate from axial symmetry and to have a z-axis different from the symmetry axis of the g-tensor. The proposed model to describe the anisotropic component consisted of a modified bond localized on that oxygen of the sulfate group that is hydrogen bonded to the crystal water of hydration. The deviation of the A-tensor from axial symmetry was attributed to an additional hyperfine interaction of the unpaired electron with a neighboring lithium nucleus of spin 3/2.

Ovenall,² however, disputed the proposed lithium interaction by stating "the [nuclear] spin states of such a nucleus [lithium] would be independent of the spin states of the proton and, to a very good approximation, the additional hyperfine interaction would merely split or broaden each line of the original doublet". He then further proposed that the observed resonance was due to an unpaired electron localized in a π orbit on the oxygen atom of a radical of the form OH. In order to account for the deviation of the hyperfine tensor from axial symmetry, as would be expected for an OH radical, Ovenall proposed that the two nonbonding electrons located in a p-orbit on the oxygen atom must have

a fixed spatial orientation. This fixed orientation could possibly arise from an additional hydrogen bond to a neighboring water molecule.

Reference was made to a similar radical observed by Wyard and Smith³ in an ultraviolet irradiated mixture of H_2O and H_2O_2 . This radical has been speculated to be either an O_2H or an OH radical, but identification was not certain.

Further confusion occurred when Symons⁴ suggested that the radical observed by Wigen and Cowen could not be an SO_4^- radical because of the different properties expected for this radical. He agreed with Ovenall that the hyperfine interaction was due to a hydrogen atom that was attached directly to the oxygen atom containing the unpaired electron. However, he believed that the radical observed by Wyard and Smith was an O_2H radical, and therefore, the radical observed in lithium sulfate was probably an O_2H radical. Furthermore, this radical is expected to exhibit a hyperfine tensor that is non-axial. Symons had hoped to carry out an experiment to determine the number of O atoms involved. This experiment consisted of substituting ^{17}O for the naturally occurring oxygen isotope in the crystal and then looking for a hyperfine splitting. No further progress has been reported about this phase of the work.

Because of the preceeding disagreements, the work discussed in this paper has been carried out. The main purpose, initially, was to determine whether the lithium nucleus had an effect on the anisotropy of the spectra in an attempt to clear up the disagreement concerning the lithium hyperfine interaction.

The first group of samples had been neutron irradiated and the observed spectra was quite complex and did not correspond to the spectra observed by Wigen and Cowen. Subsequently, other samples have been irradiated by electrons and gamma rays at 77°K in order to produce the Wigen and Cowen spectra. From the data obtained from the electron irradiated samples, it was then possible to identify some of the stronger resonance lines in the neutron irradiated samples.

The following text is divided into several chapters as follows: Chapter II contains the simple theory of EPR and its application to the present work; Chapter III contains the essential equipment used in the experiment and the manner in which it functions; Chapter IV discusses the sample preparation; Chapters V, VI, and VII contain the data and results of the experiments on the electron irradiated samples (V and VI) and the neutron and gamma irradiated samples (VII). An appendix is included to show the origin of the Hamiltonian used in this work.

CHAPTER II

ELECTRON PARAMAGNETIC RESONANCE (EPR)

EPR Theory

The detailed general theory of EPR has been given elsewhere.^{5,6} Therefore, all that will be included here will be a simple introduction. When a magnetic moment is placed in a static magnetic field, the Hamiltonian for the moment in the field is given by⁵

$$\mathcal{H} = - \vec{\mu} \cdot \vec{H}$$

where $\mathcal{H}$ is the Hamiltonian, $\vec{\mu}$ is the magnetic moment, and $\vec{H}$ is the applied field. In order to consider the effect of a magnetic field on an electron it is necessary to give the magnetic moment of the electron which is⁷

$$\vec{\mu} = - \frac{g\beta}{\hbar} \vec{S}$$

where g is the electronic g -factor (2.002319 for a free electron)⁸, β is the Bohr magneton, $\hbar$ is Planck's constant divided by 2π , and $\vec{S}$ is the spin angular momentum of the electron. The g -factor is a physical property of the electron and represents the proportionality constant relating the magnetic moment and the angular momentum. Using this value of $\vec{\mu}$, the Hamiltonian for an electron in an external field is given by

$$\mathcal{H} = \frac{g\beta}{\hbar} \vec{S} \cdot \vec{H}$$

The electron can have only two possible orientations in the magnetic

field corresponding to the values of $m_s = \pm \frac{1}{2}$. This gives the energy level scheme (Zeeman levels) of a free electron as a function of H , which is shown in Fig. 1. In the figure, m_s is the spin quantum number representing the component of $\vec{S}$ along the magnetic field direction. The magnetic moment of the electron also precesses about the static magnetic field with a frequency given by⁹

$$\omega = \frac{g\beta}{\hbar} H$$

This phenomenon is known as Larmour precession. In an EPR experiment, the sample is not only placed in a static magnetic field but is also placed in an oscillating magnetic field that is perpendicular to the static field. The frequency of this magnetic field is approximately 9.5 KMHz., when a static field of approximately 3500 gauss is utilized. A resonance condition occurs when the rotating part of the oscillating field is identical to the Larmour precessional frequency. At resonance, a torque is applied to the spin magnetic moment which causes it to "flip" to the opposite energy state (see Fig. 1). This can be expressed by the simple relation,¹⁰

$$h\nu = g\beta H \quad (2)$$

This states that when the energy of a quantum, $h\nu$, of the oscillating field is equal to the separation of the magnetic energy levels, transitions will occur. Because of the Boltzmann distribution the $m_s = -\frac{1}{2}$ state has a larger population than the $m_s = +\frac{1}{2}$ state.

Fig. 1   Energy level diagram of an electron in a magnetic field.

Therefore, at resonance there will be a net transfer of spins from the $-1/2$ state to the $1/2$ state resulting in an absorption of energy from the oscillating field. The absorption of power is recorded in the form of a graph. This graph plots the derivative, with respect to the magnetic field, of the absorption of power as a function of the magnetic field (see Chapter III for details). This graph will be referred to as an EPR spectrum (or simply spectrum) in the following.

If EPR experiments only measured transitions involving free electrons in a magnetic field, the information gained would be small. Fortunately, there are many factors that contribute to the observed spectra. One of these factors is the spin-orbit coupling that produces a variation of the observed g -value from that of a free electron. This variation depends upon the direction of the magnetic field relative to a set of axes in the crystal.¹¹ This interaction, when combined with the free electron g -value, produces the so-called g -tensor. For a further discussion of this phenomenon see the appendix.

Another effect of interest is the hyperfine interaction between the electron and a nucleus of spin I . This can best be understood by imagining that the electron "feels" the effect of an alteration of the external field by the presence of the nucleus. For the case of a nucleus of spin $1/2$, the electron is under the effect of one of two different fields corresponding to the $m_I = 1/2$ and $m_I = -1/2$ (m_I is the component of I along the magnetic field direction) orientations of the nucleus in the field. This can be represented analytically as an

additional term in the Hamiltonian of the form¹²

$$\mathcal{H}_{\text{H.F.S.}} = A \vec{S} \cdot \vec{I}$$

where A is the hyperfine coupling constant. The effect that this additional interaction has on the energy level structure of the electron is shown in Fig. 2(A). Here each of the Zeeman levels is split by the nucleus of spin 1/2 into two components. Because the perturbation consists of a single frequency, ν , during an electronic transition, the nucleus remains fixed in space. (The nuclear transitions would occur at a frequency approximately 2,000 times lower than the electronic transition frequency.) Thus, the nuclear selection rule of $\Delta m_I = 0$ is found to be obeyed. The spectra that would be observed for this energy level scheme is shown in Fig. 2(B). Here the separation of the two lines is the hyperfine coupling constant, A. In general, however, the hyperfine coupling will also depend upon the direction of the static magnetic field relative to a set of axes in the crystal.¹¹ Therefore, the hyperfine coupling can also be expressed as a tensor. Thus

$$\mathcal{H}_{\text{H.F.S.}} = \vec{S} \cdot \vec{A} \cdot \vec{I} \quad .$$

Most of the electrons in materials do not give EPR spectra. The reason for this is that most of the electrons are paired. Therefore, any transition by an electron from the $m_s = -1/2 \rightarrow m_s = +1/2$ state must be accompanied by a transition of its paired electron from the $m_s = +1/2 \rightarrow m_s = -1/2$ state in order to obey the Pauli exclusion

Fig. 2 Hyperfine splitting of the resonance line:
 (A) Effect of a nucleus of spin $1/2$ on the energy levels of an electron in a magnetic field; (B) Splitting of the single resonance line into two components by a nucleus of spin $1/2$.

principle.¹³ Thus, even if a transition does occur, no energy can be absorbed. For this reason, only materials with unpaired electrons can be studied by EPR techniques. These unpaired electrons can occur naturally in the substance, such as in transition elements or free radicals, or they can be produced artificially by irradiation of the samples with x-rays, charged particles, or neutrons. The resonances that are observed in the present work are all attributable to defects which have been artificially induced.

The Spin Hamiltonian

Electron paramagnetic resonance data is usually fitted to a spin Hamiltonian. This consists of a Hamiltonian containing all the interactions involving the electron (both spin dependent and orbital), where the orbital contributions have been averaged over the orbital wave functions, thus leaving only spin dependent operators. A detailed method showing the procedure used is given in the appendix. Taking, then, just the spin Hamiltonian needed for this paper,¹¹

$$\mathcal{H} = \beta \vec{S} \cdot \vec{g} \cdot \vec{H} + \vec{S} \cdot \vec{A} \cdot \vec{I} \quad ,$$

it is necessary to convert this into a form that is usable in interpreting data.

In the case of lithium sulfate, all but one of the observed g- and A-tensors have been found to be axially symmetric. Therefore, it will be assumed in the following derivation that this condition exists. A further assumption to be made is that the g- and A-tensors are diagonal

in the same coordinate system. Then, the two tensors can be written in the following form:

$$\vec{g} = \begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix}$$

$$\vec{A} = \begin{pmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\parallel} \end{pmatrix}$$

Looking at the Zeeman term in the Hamiltonian $\beta \vec{S} \cdot \vec{g} \cdot \vec{H}$, and referring to Fig. 3, the portion $\vec{g} \cdot \vec{H}$ can be written as

$$\begin{aligned} \vec{g} \cdot \vec{H} &= \begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix} \begin{pmatrix} \cos \alpha \\ \cos \beta \\ \cos \gamma \end{pmatrix} H \\ &= \begin{pmatrix} g_{\perp} \cos \alpha \\ g_{\perp} \cos \beta \\ g_{\parallel} \cos \gamma \end{pmatrix} H = \vec{H}' \end{aligned}$$

Therefore, defining $\vec{g} \cdot \vec{H}$ as a new magnetic field $\vec{H}'$, and assuming $\vec{S}$ to be quantized along this direction, the Zeeman part of the Hamiltonian can be written as

$$\mathcal{H} = \beta \vec{S} \cdot \vec{H}'$$

Fig. 3 Direction cosines of the magnetic field referred to the g-tensor principal axis system.

Thus, the solution of $\hat{H}\psi = E\psi$, where ψ is the spin wave function of the electron, gives¹⁴

$$E_Z = \beta m_s |H^*|$$

$$\begin{aligned} E_Z &= \beta m_s H \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \gamma} \\ &= \beta m_s g H \end{aligned} \quad (3)$$

Where $g = \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \gamma}$ is called the spectroscopic g-factor.

Since $\vec{S}$ is quantized along the direction

$$\frac{\vec{g} \cdot \vec{H}}{gH},$$

the term $\vec{S} \cdot \vec{A} \cdot \vec{I}$ can be written as

$$m_s \frac{\vec{g} \cdot \vec{H}}{gH} \cdot \vec{A} \cdot \vec{I}.$$

If a new magnetic field is defined as

$$\vec{H}'' = m_s \frac{\vec{g} \cdot \vec{H} \cdot \vec{A}}{gH},$$

then $\vec{S} \cdot \vec{A} \cdot \vec{I} = \vec{H}'' \cdot \vec{I}$.

The energy eigenvalues are known for this expression, if $\vec{I}$ is quantized along $\vec{H}''$. They are¹⁴

$$E_{H.F.S.} = \frac{m_I m_s}{gH} |\vec{g} \cdot \vec{H} \cdot \vec{A}|.$$

Therefore,

$$E_{\text{H.F.S.}} = \frac{m_I m_s}{g} \sqrt{g_{\perp}^2 A_{\perp}^2 + (g_{\parallel}^2 A_{\parallel}^2 - g_{\perp}^2 A_{\perp}^2) \cos^2 \gamma} .$$

Combining the Zeeman and Hyperfine terms together, the result is

$$E_{\text{TOTAL}} = \beta m_s H \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \gamma} + \frac{m_I m_s}{g} \sqrt{g_{\perp}^2 A_{\perp}^2 + (g_{\parallel}^2 A_{\parallel}^2 - g_{\perp}^2 A_{\perp}^2) \cos^2 \gamma} . \quad (4)$$

These energies predict the way that a single orbital level will split under the effect of an external magnetic field and under the effect of a hyperfine interaction.

Data Analysis

Now that the expression for the level splitting (Eq. (4)) has been calculated, it will be necessary to apply this information to the recorded spectra. Normally a plot is made of the position of the resonance line in units of gauss versus the direction (or angle) of the magnetic field relative to a set of axes in the crystal. In general, three mutually perpendicular axes must be chosen, for the rotation axes, and a plot of position versus angle is made for each of the three axes. However, if, after making plots for two axes, axial symmetry is apparent, then the plot for the third axis can be neglected or used for verification. The question then arises as to how the axial symmetry is determined from the data. Figure 4 illustrates the three possible situations. Figure 4(A) illustrates data for rotations about two

Fig. 4 Typical angular dependencies of the position of the resonance versus an experimental angle: (A) Axial symmetry and $g_{||} > g_{\perp}$; (B) Axial symmetry and $g_{\perp} > g_{||}$; (C) Non-axial symmetry.

mutually perpendicular axes when axial symmetry occurs and $g_{\parallel} > g_{\perp}$. Figure 4(B) illustrates data for rotations about two mutually perpendicular axes when axial symmetry occurs and $g_{\perp} > g_{\parallel}$. Figure 4(C) illustrates data for rotations about two mutually perpendicular axes when axial symmetry is not present. The way that the curves indicate axial symmetry and the relative magnitudes of $g_{\parallel}$ and $g_{\perp}$ can best be understood by the illustration in Fig. 5. The axes a, b, and c' represent a coordinate system fixed in the laboratory. The $g_{\parallel}$ is the z axis of the coordinate system in which the g-tensor is diagonal. The circle represents the plane containing $g_{\perp}$ which is perpendicular to the z axis. As can easily be observed, if the magnetic field direction is varied on any of the planes c'b, c'a, or ab (as is done in a typical experiment), at some angle the magnetic field vector will intersect the $g_{\perp}$ plane. At this point, the magnetic field is perpendicular to the $g_{\parallel}$ axis and thus $\cos \gamma = 0$ in Eq. (3). This implies that, if axial symmetry exists, then a g-value corresponding to $g_{\perp}$ will be repeated somewhere in the data from the rotations about two mutually perpendicular axes. The dashed lines in Figs. 4(A) and (B) illustrate this point. Determining the relative magnitudes of $g_{\parallel}$ and $g_{\perp}$ requires writing down the equation relating ν , H, and g. This can be done by referring back to Eq. (4) which gives the total energy of the various levels. Taking just the Zeeman term $E_Z = m_s \beta H \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \gamma}$, and remembering that the transition occurs for $\Delta m_s = \pm 1$, the desired expression is:

Fig. 5 Polar angles of an axially symmetric g -tensor referred back to the crystalline axes.

$$h\nu = \beta H \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \gamma} \quad (5)$$

In this equation, if $g_{\parallel} > g_{\perp}$ then $g_{\perp}$ occurs at the highest field. If $g_{\perp} > g_{\parallel}$ then $g_{\perp}$ occurs at the lowest field. These two cases are represented in Figs. 4(A) and (B), respectively. A similar analysis of the hyperfine splitting, where the separation of the resonance lines versus angle is plotted, will yield similar information concerning the hyperfine tensor. However, the hyperfine interaction would then have to be included in Eq. (5).

Once $g_{\perp}$ is determined and axial symmetry has been found, it is a relatively simple matter to calculate the tensor axis direction relative to the laboratory system and also the value of $g_{\parallel}$. The simplest and most direct way of obtaining this information is by taking several points from the angular dependence plot. The best points to choose are the peak or minimum of the curve (corresponding to the points B in Fig. 4) and two other points intermediate between point B and $g_{\perp}$. These points should be taken from the data of two different rotation axes. These three points can then be inserted into Eq. (5) to give three equations for the unknowns $g_{\parallel}$ and the polar angles (θ, ϕ) of the symmetry axis of the g-tensor. Obviously, γ must be expressed in terms of θ and ϕ , and the direction of $\vec{H}$. This transformation has not been carried out in this example because the relationship is different for each rotation.

CHAPTER III
EXPERIMENTAL APPARATUS
Spectrometer System

An EPR spectrometer has to perform three important functions. First, the spectrometer has to provide the correct conditions for resonance, that is, a static magnetic field, H , and an oscillating microwave field of frequency ν , such that the condition $h\nu = g\beta H$ is satisfied as earlier discussed. Second, the spectrometer must provide a means of detecting the small absorption of power by the sample. Third, a means must be provided to display the resonance so that the information gathered can be studied at a different time. All of these functions will be discussed in the following.

The magnet system used to provide the static magnetic field consisted of a Varian Associates twelve inch rotating magnet with a Varian model V-FR2501 field regulated power supply. The advantage realized in this type of magnet system is a well regulated supply with a constant sweep rate over wide ranges that approach the limit of the magnet and supply. This is accomplished through the use of a Hall effect probe placed in the magnet gap. A block diagram of the control circuits is shown in Fig. 6. The oscillator supplies a current at a frequency of approximately 40kHz by way of the field sensing circuits to the sensing probe located on one of the magnet pole faces. A Hall voltage of the same frequency and of amplitude depending upon the

Fig. 6 Block diagram of the Fieldial magnetic field regulator.

strength of the field returns to the sensing circuit and combines with an additional signal from the sweep and field controls. This combined "error" signal is amplified and phase detected utilizing a portion of the oscillator output that has been amplified in the reference amplifier. The DC output voltage from the phase detector is amplified and applied to the pass bank transistors. The function of the pass bank is to control the magnitude of the current supplied to the magnet by the power supply rectifiers. The amount of current that is allowed to flow through the magnet is determined by the position of the fine and coarse field controls on the front panel. The extent of the variation of the field is determined by the setting of the sweep control also on the front panel.

The strength of the magnetic field has been measured by using a Varian Associates Nuclear Fluxmeter. A Hewlett-Packard model 524C frequency counter has been used to measure the frequency of the fluxmeter oscillator. This frequency can then be converted to magnetic field. Points have then been inserted on the graph paper corresponding to known values of the field obtained from utilization of the fluxmeter.

The actual system for supplying the microwave power and for detecting the resonance consisted of a Varian Associates 4500 series EPR spectrometer utilizing 400 Hz. magnetic field modulation. Complete operating details are described elsewhere.¹⁵ Therefore only a brief description will be given here. A block diagram of the system is given in Fig. 7.

The sample is contained in a specially designed microwave cavity

Fig. 7 Block diagram of the EPR spectrometer.

(to be described later) located in the center of the magnet gap. The purpose of the cavity is to concentrate the microwaves at the sample and provide the rotating magnetic field which becomes the perturbation required to cause transitions between the various electron states. The microwaves are generated by a reflex klystron located inside a water cooled oil bath which is kept at a constant temperature of 60°F. Changing of the frequency of the oscillator is accomplished mechanically or electrically. The microwaves then pass through an isolator and an attenuator on their way to arm 1 of a magic tee. Here the power splits into arms 2 and 3. Arm 3 is resistance terminated while arm 2 connects to the sample cavity located in the magnet gap. Initially the klystron is tuned to a frequency that exactly matches the resonant frequency of the cavity. When this condition is accomplished, no microwave power is reflected from the cavity toward the magic tee. However, as the static magnetic field is varied through the resonance condition, the sample upsets this delicate balance and a small portion of the microwave power is reflected back from the cavity. This power enters arm 2 and splits equally between arms 1 and 4. The power passing back toward the klystron is dissipated in the isolator. The power in arm 4 falls upon a diode detector which terminates this arm. Therefore, the DC output voltage of this detector can then be related to the absorption of power by the sample during resonance. Electronically, it would be very difficult to amplify this signal and display it on a recorder. Therefore, a different method is employed. Beside the static magnetic

field which is slowly varied through resonance, there is also a small oscillating field of frequency 400 Hz. parallel to the static magnetic field. This modulation field is supplied by the 400 Hz. oscillator and sweep amplifier. The purpose of this modulation is to cross over a resonance point many times per second. This effectively modulates the microwave power reflected to the detector located in arm 4. The output of this detector now consists of a DC component and also an AC component. This AC signal passes on to a preamp and narrow band amplifier. The signal is then phase detected at 400 Hz. The resultant DC signal passes through an integrator which averages out most of the random noise still present. The final signal is then displayed on a recorder. The actual recorded signal is not the absorption curve but the derivative of the absorption curve. This can be understood by looking at Fig. 8(A). As the magnetic field is varied through the resonance field H_0 the modulation field H_1 goes back and forth across a small portion of the resonance. The crystal detector sees a small fluctuation of power that is representative of the derivative, $\frac{dP}{dH}$, of the absorption curve. This is represented in Fig. 8(B).

Presentation of the pure absorption derivative is not as simple as described above. One complicating factor is that the cavity tends to change its resonant frequency as the sample goes through resonance. Thus, a dispersion curve will emerge corresponding to the derivative of the shift of the cavity resonance versus magnetic field. In order to

Fig. 8

Detection of the resonance: (A) Modulation of the external field; (B) Derivative of the power absorption with respect to the magnetic field.

avoid this complication, the klystron must change its frequency simultaneously with the cavity. This can be accomplished by the use of an automatic frequency control (AFC). Referring back to Fig. 7, it can be seen how this is accomplished. The 10 KHz. oscillator modulates the reflector voltage applied to the klystron. The modulation of the reflector voltage frequency modulates the klystron. Thus, at the detector crystal in arm 4 of the magic tee, there also appears the AFC information. The nature of this information can be understood by referring to Fig. 9. Fig. 9(A) shows the detector output when the klystron and cavity have the same resonant frequency. Fig. 9(B) shows the detector output when the cavity frequency is higher than the klystron frequency, while Fig. 9(C) shows the detector output when the cavity frequency is lower than the klystron frequency. The overall shape of the curve is produced by plotting the absorption of power of the cavity versus frequency. The symbols, f_c and f_k , correspond to the cavity frequency and the klystron frequency, respectively. When the two frequencies are identical, the output of the crystal is a frequency of 20 KHz. The origin of this frequency doubling is apparent from the drawing. When the cavity frequency is higher than the klystron frequency, the output contains a 10 KHz. fundamental that is out of phase with the modulation. When the cavity frequency is below that of the klystron, the output at the crystal contain a 10 KHz. fundamental that is in phase with the modulation. This signal representing the position of the cavity resonance with respect to the klystron frequency

Fig. 9 Method of controlling klystron frequency:
 (A) $f_k = f_c$; (B) $f_c > f_k$; (C) $f_k > f_c$.

is amplified and separated in the preamp and is then phase detected at 10 KHz. The resulting DC voltage is then applied with the correct polarity to the reflector voltage power supply of the klystron. This error voltage changes the klystron frequency so that it always corresponds to the resonant frequency of the cavity.

In order to improve the sensitivity of the present EPR spectrometer, a superhetrodyne adapter has been constructed. When performing EPR experiments where 100 KHz. modulation can be utilized, a factor of approximately 16 can be realized as an improvement in signal to noise ratio as compared to 400 Hz. modulation. This phenomenon occurs because the crystal detector in the bridge has a noise figure that depends upon the frequency that it passes. A superhetrodyne adapter enables one to utilize 400 Hz. modulation and still obtain, theoretically, a factor of 16 in signal to noise ratio improvement. The way that this is accomplished is illustrated in Fig. 10. Microwave power of a frequency that is ± 30 MHz. from that of the signal klystron is supplied by the local klystron through a directional coupler. The power from this klystron mixes with the reflected power from the sample cavity at the crystal and produces a 30 MHz. beat. The 400 Hz. signal information from the cavity appears as an amplitude modulation on this beat frequency. The crystal then detects and passes a 30 MHz. signal, thus producing the optimum signal to noise ratio. This signal is then immediately amplified at the bridge by a preamp and further amplified externally by a 30 MHz. I.F. amplifier. The detected output

Fig. 10

Block diagram of the superheterodyne detection system.

from the I.F. amplifier then goes to the narrow band amplifier of Fig. 7 where it is amplified and then phase detected at 400 Hz., the frequency used to modulate the magnetic field.

Microwave Cavity for Work Near 77°K*

A cylindrical X-band cavity and its accessories have been successfully constructed and employed in order to facilitate prolonged EPR studies near 77°K with little electrical noise due to nitrogen bubbling.

Figure 11 is a scale drawing of the cavity system. The cavity is made of polished brass with dimensions 4.77 cm. i.d. and 2.96 cm. long. A Teflon tape gasket is used to electrically isolate the top A and bottom B of the cavity from its sidewall. In so doing, the undesirable TM_{011} mode is suppressed. The coupling of the cavity to the stainless steel waveguide C is accomplished by using a coupling screw D fashioned after one designed by Andrews and Kim.¹⁷ The screw is fastened to the end of a quartz rod E whose other end protrudes from the broad side of an E-bend F. The sample holder (Fig. 11(C)) consists of a Teflon rod G, a thumb cap H, and a threaded sample tip I. A hole runs all the way through the axis of the rod for holding glass tubes. The thumb cap tightens the tube in place. The sample holder itself is held in place

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* The content of this section has recently been published by this author and Y.W. Kim in the Review of Scientific Instruments.¹⁶

Fig. 11 Schematic diagrams (drawn to scale) of the liquid nitrogen temperature EPR cavity of cylindrical form and its accessories; (A) The cross section of the assembly; (B) Top view of the cavity; (C) Cross section of the sample holder. A- top plate of the cavity; B- bottom plate of the cavity; C- stainless steel waveguide; D- coupling screw; E- quartz rod; F- E-bend waveguide; G- Teflon rod; H- thumb cap; I- threaded bottom tip; J- stainless steel tubing; K- phosphor bronze strip; L- He gas feedhold; M- Mylar seal; N- plastic cone.

by a phosphor bronze strip K located in a support J soldered to the cavity top plate.

During the experiment the cavity is immersed in a Dewar of liquid nitrogen. The dimensions of the Dewar are 5.78 cm. i.d., 7.25 cm. o.d., and 26.5 cm. long. Its liquid capacity is approximately 0.7 liter. Liquid nitrogen is kept out of the cavity by applying a low pressure helium gas through the feedhole L. The end of the E bend is sealed with a Mylar gasket M to prevent the escape of the helium gas. All other connecting joints are sealed by O-rings.

In order to prevent the formation of large bubbles of nitrogen gas on the bottom of the cavity, a plastic cone N is screwed to the bottom of the cavity. Thus nitrogen bubbles rise to the surface before they attain any appreciable size, and contribute practically no noise to the operation of the cavity system. After attaching the cavity to the bridge, it has been observed that several cavity resonances occur. These extra resonant modes are to be expected and must be sorted out. The mode that is desired¹⁸ is shown in Fig. 12. This mode, TE_{011} , concentrates the magnetic field at the center of the cavity. If a dielectric probe in the form of an L is introduced through the sample hole, a probing of the cavity during the time microwave power is applied will identify this cylindrically symmetric mode. By monitoring the reflected power as the rod is moved vertically, it should show a maximum at the top and bottom of the cavity and a minimum at the center. The center produces the minimum because at this point the electric field

Fig. 12

E- and H-field patterns in a cylindrical cavity (TE_{011} MODE).

is a minimum, and it is the electric field that interacts with the dielectric. A final check as to the mode present is to rotate the rod at a fixed height. There should be no variation of the reflected power (cylindrical symmetry). When these two conditions are satisfied, the proper mode has been obtained.

A cavity of three times the length of the previously mentioned cavity has also been constructed. The purpose of this particular form was to provide a means of observing simultaneously two resonance lines from two different samples that normally have the same g -value. This is accomplished by putting one sample in the top mode positioned at the center of the magnet gap and putting the other sample in the bottom mode of the three mode cavity. The bottom cavity is in the fringe field of the magnet and thus appears at a higher field on the chart paper. This particular cavity was used in the temperature dependent studies, where the bottom mode contained a reference sample.

The cavity and Dewar system as described here operates for approximately two hours without refilling with liquid nitrogen. The rate of nitrogen evaporation with the cavity immersed is approximately 0.07 liters/hour. The cavity can accommodate samples of approximately 1.9 cm^3 . Temperatures above 77°K can be obtained by increasing the pressure of the helium gas, which then leaks around the sample rod. The chief advantages of a cavity of cylindrical form as described above are:

- (i) The magnet can be rotated about the sample, thus keeping the Q of the cavity constant so that any amplitude

fluctuations are really due to the sample.

- (ii) The cylindrical cavity offers a higher Q factor than rectangular cavities normally used. This higher Q means an increase in sensitivity.
- (iii) Sample volumes can be larger in a cylindrical cavity. This also means, in a sense, an increase in sensitivity.
- (iv) Since nitrogen is not allowed inside the cavity, the change in dielectric constant as the nitrogen boils will not affect the cavity.

CHAPTER IV
SAMPLE PREPARATION

Crystal Growth

Since single crystals of lithium sulfate are not commercially available, it has been necessary to grow the crystals used in the present work. Initially, normal lithium sulfate (93% ^7Li) was used to make saturated solutions. Since the solubility of lithium sulfate is greater in ice water than at room temperature, solutions were made in an ice bath and then allowed to warm to room temperature. The supernate was removed to a clean jar leaving behind the undissolved lithium sulfate. The jar containing the saturated solution was then set aside open to the atmosphere and allowed to evaporate. This process produced very small crystals that were then used as a seed in new solutions until a crystal of approximately 1cm. x 1/2cm. x 3/4cm. was obtained. The crystal growth habit is shown in Fig. 13. All crystals had easily distinguishable faces with the b-axis being the longest dimension. The crystal belongs to the monoclinic class¹⁹ with a space group C_2^2 . This means a two-fold screw symmetry axis identified as the longest dimension or b-axis by Zeigler.¹⁹ Laue X-ray diffraction patterns have been taken to verify this two-fold axis. Figure 14 illustrates the position of the atoms in the unit cell as determined by Zeigler¹⁹ and Ozerov²⁰ (see Chapter V).

Deuteration of the crystals was performed by baking the lithium

Fig. 13 Crystal growth habit of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The b -axis is the two-fold axis of the monoclinic system and perpendicular to the a -axis.

Fig. 14 A projection of the constituent atoms of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ on the a - c plane. The relative positions and numbering of the O, S, and Li atoms are in accordance with Ziegler's data,¹⁹ while the positions and numbering of the H atoms are in accordance with the neutron diffraction data of Ozerov et al.²⁰

sulfate powder at 250°C for twenty-four hours to drive off any H₂O and then redissolving the powder in pure D₂O. The above process of crystallization was then performed except that the evaporating D₂O was collected. The growth habit of the deuterated crystals has been found to be the same as for the hydrated crystals.

Crystals containing an enrichment to 95% of the ⁶Li isotope have also been grown. The enrichment has been obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. Both hydrated and deuterated crystals of this enriched isotope mixture have been grown. The growth habit, as expected, was the same for all combinations of isotopes.

Irradiation

After the crystals had been cut to size, they were then irradiated by electrons, gamma rays, and neutrons. The electron irradiations have been carried out at the Agricultural Engineering Department, Michigan State University, East Lansing, Michigan. The irradiations were performed at liquid nitrogen temperatures using a General Electric resonant transformer accelerator. The time of the irradiation was from two to four minutes. The electron beam was directed straight down with an energy of 1MeV and a beam current of 1Ma. The apparatus for holding the sample consisted of a Virtus insulated 1 liter stainless steel Dewar fitted with a protective aluminum plate on the top edge, a styrofoam float, and a copper plate with sample wells milled in the surface. Nitrogen bubbled into the sample wells and turned the samples so that the beam hit them on all

sides. The samples were then immediately transferred to a storage Dewar and kept at 77°K until the data was taken.

The gamma irradiations were performed at the Phoenix Memorial Laboratory located at the University of Michigan, Ann Arbor, Michigan. The irradiation facility consisted of an eighteen foot well filled with water at the bottom of which the cobalt 60 source was located. After personnel left the irradiation room, the source was raised out of the water to irradiate samples left in the room. The lithium sulfate crystals were located in a position where the flux was approximately 100,000 roentgens/hour. The samples had been contained in small vials lowered into liquid nitrogen. Every hour, the nitrogen in the Dewar was changed in order to minimize the possibility of explosion. Irradiation times of from one to eight hours have been used. After the irradiation, the samples were stored in a Dewar at 77°K.

The neutron irradiations were performed in the swimming pool type reactor of the University of Michigan, Ann Arbor, Michigan. The samples were sealed in polyethylene tubes and lowered into the water. The samples rested against the reactor face where the temperature was supposedly 25°C. However, it was difficult to keep the sample temperature at 25°C. Temperatures in excess of 85°C were noticed. In attempts to keep the samples cooler, they were incased in aluminum foil, glycerine, and mineral oil. All these materials aid in the prevention of the heating of the samples by providing a better thermal contact between the sample and the pool water.

The samples, after irradiation and storage, then needed to be

fastened to the sample rod previously described. Sample tips were cut with specific angles that would grip certain faces of the crystals so that a rotation study could be performed about the b- or a-axes or about an axis perpendicular to the ab-plane. Attachment to the rod has been accomplished by means of a small amount of Dow Corning Silicone Vacuum Grease. In the case of the neutron irradiated samples, they have been attached at room temperature. However, in the case of the gamma and electron irradiated samples, the attachment has been performed at liquid nitrogen temperatures using the grease. Great care was exercised so that the samples did not become warmer during the attachment at 77°K. All the spectra reported in this work have been recorded at 77°K using the cavity previously described.

CHAPTER V

ELECTRON IRRADIATED LITHIUM SULFATE AT 77°K*

Introduction

The work described in this chapter concerns the EPR spectra of electron irradiated lithium sulfate. As previously mentioned (see Chapter I), Wigen and Cowen¹ have recently investigated the EPR spectra of electron irradiated lithium sulfate. Subsequently, however, Ovenall² and Symons⁴ have disputed Wigen and Cowen's model for the anisotropic spectra, as well as their postulation of a lithium hyperfine interaction being responsible for the non-axiality of the observed hyperfine tensor.

This situation has motivated the work described in this chapter. In particular, a possible contribution of the lithium hyperfine interaction has been investigated by labeling the lithium isotopes.

Experimental Results and Spin Hamiltonian

Single crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ with controlled relative concentrations of the Li-isotopes (^7Li and ^6Li) have been grown from liquid solutions of the salt at room temperature. Subsequently, these samples have been irradiated in a 1-mA beam of 1 MeV electrons near 77°K for 2 min. in a General Electric Resonant Transformer Accelerator,

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* The content of this chapter has been recently published by this author and Y.W. Kim in the Journal of Physics and Chemistry of Solids.²¹

Michigan State University, East Lansing, Michigan, and kept at the same temperature. EPR spectra of the irradiated samples have been investigated at 77°K without warming. The regular Varian Associates 100 kc/s multi-purpose cavity has been replaced with a cylindrical cavity specially designed for the purpose of this work (see Chapter III). The first derivative (simply spectrum) of the EPR absorption has been recorded.

Figure 15 illustrates a typical EPR spectrum obtained from a sample of ${}^6\text{Li}_2\text{SO}_4$ containing a mixture of H_2O and D_2O . The magnetic field is perpendicular to the b-axis of the sample, and makes an angle of -30° with the a-axis. The magnitude of the magnetic field H increases from left to right in the figure. The two lines of same intensity, labeled as h_1 and h_2 are to be seen only from the monohydrated samples, while the three lines of same intensity, labeled as d_1 , d_2 , and d_3 , are characteristic of the monodeuterated samples. This indicates very strongly that the doublet and the triplet constitute the hyperfine structure of the proton of spin $1/2$ and the deuteron of spin 1 , respectively. Indeed the measured ratio of the separation between the h_1 and h_2 lines to that between the d_1 and d_3 lines is close to the ratio (approximately 3) of the proton nuclear magnetic moment to the deuteron nuclear magnetic moment. See Fig. 15. The isotropic line observed by Wigen and Cowen has also been observed in the present work, but its intensity is weak. In Fig. 15 it is masked by the h_2 line and marked with the + sign. The observed angular dependence of the doublet (h_1 and h_2) and the triplet (d_1 , d_2 , and d_3) is illustrated in Fig. 16.

Fig. 15

EPR spectrum of Li_2SO_4 containing a mixture of H_2O and D_2O near 77°K . The sample has been irradiated in a 1 mA beam of 1 MeV electrons near 77°K and kept at the same temperature. The magnetic field is perpendicular to the b-axis and makes an angle of -30° with the a-axis. The field intensity increases from left to right. The + sign indicates the position of the isotropic line centered near the free electron g-value. The two lines (h_1 and h_2) are the proton hyperfine lines, and the three lines (d_1 , d_2 , and d_3) are the deuteron hyperfine lines.

Fig. 16

The anisotropy of the EPR spectrum of Fig. 15: (A) Rotation about the b-axis; (B) Rotation about an axis perpendicular to the a-b plane. The position (ΔH) of the hyperfine lines is measured relative to the isotropic line (see Fig. 15). The full and open circles indicate the observed values of ΔH for the proton hyperfine lines, where the open circles imply a certain degree of uncertainty due to poor resolution caused by overlapping lines; the crosses indicate the observed positions of the deuteron hyperfine lines. In (B), for the clarity of the figure, the anisotropy of the deuteron hyperfine lines is not shown (see text). The solid curves represent the theoretical anisotropy. (Figure is continued on next page.)

Fig. 16 (Continued.)

The doublet and the triplet lines are identified by a set of circles (either filled or open) and a set of crosses respectively. The open circles in Fig. 16(B) indicate some degree of uncertainty in the experimental determination of the position of the doublet lines, which is due partly to an accidental overlapping of the doublet lines and the isotropic line among themselves. The position of the doublet and the triplet for each angle of rotation is measured in units of G relative to the isotropic line (the $+$ sign of Fig. 2). Thus, the relative position, ΔH , of a line becomes either negative or positive depending upon whether the line lies on the lower field side or higher field side of the isotropic line. The position of the isotropic line is indicated by OG in Fig. 16. In the case of the rotation of Fig. 16(B), there are in general six lines due to the triplet for each angle of rotation. For the benefit of clarity of the figure, however, their anisotropy is not shown. The pairs of solid curves will be discussed later. The observed anisotropy of the spectra shown in Fig. 16 leads to the following conclusion: There are two possible sites per unit cell for the paramagnetic defects responsible for the spectra. The two sites are equivalent only with regard to the b -axis rotation. This is consistent with the fact that the single h_1 line of Fig. 16(A), pertaining to the two equivalent sites, splits into two h_1 lines of Fig. 16(B), corresponding to the inequivalence of the two sites.

The anisotropy of the doublet and the triplet, and their positions relative to the isotropic line have been found to be the same for all

combinations of the H-isotopes and the Li-isotopes. The only noticeable effect of the Li-isotopes on the doublet and the triplet is that the width of the doublet lines and the triplet lines of the ^6Li -doped samples is narrower than the width of the corresponding lines of the ^7Li -doped samples. Thus, for example, the resolution of the triplet in Fig. 15 has been found to become much poorer, if ^7Li -doped samples are used instead of ^6Li -doped samples. The same effect of the Li-isotopes on the isotropic line has also been observed.

This means that the hyperfine interaction of the unpaired electron spin of the defect with the lithium isotopes constitutes a perturbation of higher order than the perturbation due to the proton hyperfine interaction. Accordingly, the spin Hamiltonian to describe the resolved hyperfine structure and its anisotropy does not have to contain the Li-hyperfine interaction.

The most convenient form of the spin Hamiltonian is then given by equation (1), where the hyperfine tensor $\vec{A}$ pertains only to the proton or deuteron depending upon the H-isotope labeling. In the present case, the effective electron spin S is given by $1/2$, and the g -factor by²²

$$g = \{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \lambda\}^{1/2} \quad (6)$$

where $g_{\parallel}$ and $g_{\perp}$ are the "parallel" and "perpendicular" components of an axially symmetric g -tensor respectively and λ is the angle between H and the axis of the g -tensor. As an approximation, the hyperfine tensor A

is also assumed to be axially symmetric and to possess its symmetry axis parallel to that of the g-tensor. Then, the position of a hyperfine line corresponding to the magnetic nuclear spin quantum number M_I can be given by the following expression:²²

$$H = \frac{h\nu}{g\beta} + M_I \frac{\{g_{\perp}^2 A_{\perp}^2 + (A_{\parallel}^2 g_{\parallel}^2 - A_{\perp}^2 g_{\perp}^2) \cos^2 \lambda\}^{1/2}}{\{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \lambda\}^{1/2}} \quad (7)$$

where h , ν , $A_{\parallel}$ and $A_{\perp}$ are Planck's constant, the fixed microwave resonance frequency, the "parallel" and the "perpendicular" components of the A-tensor respectively. If the difference between $g_{\parallel}$ and $g_{\perp}$ is very small, then, the g-components in the second term of equation (7) may be cancelled out and equation (7) can be simplified as follows:

$$H = h\nu/g\beta + M_I \{A_{\perp}^2 + (A_{\parallel}^2 - A_{\perp}^2) \cos^2 \lambda\}^{1/2} \quad (8)$$

The common direction of the g- and A-tensors, the two components of the g-tensor, and the two components of the A-tensor are determined in such a way that a satisfactory fit of the observed anisotropy (Fig. 16) by means of equation (6) and equation (8) is obtained. The tensor direction is specified in terms of the polar and azimuthal angles (θ, ϕ) measured from the b- and a-axes respectively.

The determined values of the parameters of the spin Hamiltonian are listed in Table 1. The pair of solid curves for the proton of $I = 1/2$ of Fig. 16 illustrates the calculated anisotropy. In view of

TABLE 1. THE ESTIMATED VALUES OF THE PARAMETERS FOR
THE g- AND A-TENSORS

	g-tensor	A-tensor
Components	$g_{ } = 2.064$ $g_{\perp} = 2.005$	$ A_{ } = 10.4 \text{ G}$ $ A_{\perp} = 42 \text{ G}$
Polar angle, θ	75°	75°
Azimuthal angle, ϕ	37°	37°

simple approximations pertaining to equation (8), the agreement between the observed and calculated anisotropies is satisfactory.

Discussion

The results described in the preceding indicate clearly that the defect responsible for the observed anisotropic spectra contains a single proton (or deuteron) for the hydrated samples (or deuterated samples), and can be described satisfactorily in terms of a spin Hamiltonian given by equation (1), where the g-tensor and the A-tensor are practically axially symmetric and possess parallel axes of symmetry. Also, the hyperfine interaction of the electron spin with neighboring Li atoms is not needed to describe the observed anisotropy of the spectra, except for its effect on the width of individual hyperfine lines. Furthermore, the unit cell should contain two possible sites for the defect, which are equivalent with regard to the b-axis rotation, and non-equivalent otherwise.

The only possible source of a single proton for the defect under consideration is the (crystal) water molecule. It is known¹⁹ that a unit cell of the crystal contains two water molecules which satisfy the equivalence condition mentioned above. Then, the following processes for the formation of the defect are conceivable:

Case i: One of the two H-atoms is severed off the molecule by some mechanism in the course of the electron irradiation. This process would provide two simple types of defects, each consisting of a single proton: (a) an OH radical, and (b) a radical containing the severed H

atom. The simplest of the latter is an interstitial atomic hydrogen, isolated from the neighboring atoms and molecules. The equivalence requirement seems to favor the type (a), simply because the possible sites of the OH radical are all symmetry-related, while the type (b) is probably not.

Case ii: Somehow, a "hole" is produced on a molecule neighboring an H_2O molecule by the irradiation, and the hole interacts with one of the two H-atoms of the water molecule. The most likely neighboring molecule for this case is the $SO_4^{=}$ group, which is believed to be hydrogen bonded to its nearest-neighbor water molecule. In this case the hole would interact primarily with the proton which participates in the hydrogen bonding.

In order to examine the two possible cases, the direction of the g- and A-tensors determined in the present work (Table 1) have to be compared with various crystallographic directions for the lithium sulfate. This comparison necessitates the knowledge of the relative positions of the heavy atoms (O, S) and light atoms (H, Li) in the unit cell of the crystal system. Unfortunately, however, there are in existence two sets of crystallographic data which appear to be in disagreement with regard to the relative position of some of the constituent atoms of the unit cell. One of these has been provided by Ziegler¹⁹ and the other by Larson and Helmholtz.²³ In particular, the relative position of water molecules seem to be significantly different between the two sets of data. Since both sets of the data are referred to in recent works on

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$,^{1,24-26} the present discussion will use both of them for the purpose of comparison. Figure 14 illustrates schematically the projection of the constituent atoms (S, Li, O, and H) on the a-c plane in accordance with Ziegler's data and with recent neutron diffraction data.²⁰ The numbering of individual atoms except for the H-atoms is consistent with that adopted in Fig. 2 of Ziegler's paper. The directions of the lines joining (i) O_5 to O_1 , (ii) O_5 to O_2 , (iii) O_5 to O_3 , (iv) O_5 to O_4 , (v) O_5 to S, (vi) H_1 to S, and (vii) H_1 to O_2 have been calculated by using Ziegler's data and the data of Larson and Helmholtz, separately. The results are compared in Table 2. A careful survey of Table 1 and Table 2 would yield the following observations: First of all, the directions (ii), (iii), (vi), and (vii) are definitely inconsistent with the experimental data, regardless of which one of the two sets of crystallographic data is more reliable than the other. This rules out the possibility (Case ii above) that the H_1 atom might be interacting with a hole belonging to the sulfate group, which is hydrogen-bonded via the H_1 -atom to the water molecule. Accordingly, Case i becomes more favorable for the formation of the defect under consideration. Secondly, of the remaining directions (i), (iv), and (v), the direction (iv) is the closest to the experimental direction, provided that Ziegler's data are the correct ones. The next closest directions are given by (i) and (v), but the agreement is rather poor.

Repeated search for proton hyperfine structures other than the one described in the present work by means of the isotope labeling has

TABLE 2. VARIOUS INTERATOMIC DIRECTIONS OF
 $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (see text)

Angles (i) O_5-O_1 (ii) O_5-O_2 (iii) O_5-O_3 (iv) O_5-O_4 (v) O_5-S (vi) H_1-S (vii) H_1-O_2												
	L&H†	Z†	L&H	Z	L&H	Z	L&H	Z	L&H	Z	Z*	Z*
θ	55°	52°	28°	36°	44°	45°	68°	75°	50°	50°	71°	53°
ϕ	35°	38°	53°	62°	6°	-2°	8°	30°	30°	30°	18°	60°

* Calculated in terms of the neutron diffraction data by Ozerov et al.,²⁰ who favored Ziegler's data.

† L&H and Z stand for Larson & Helmholtz and Ziegler respectively.

turned out to be futile. This failure indicates that there is no detectable concentration of paramagnetic defects, each consisting of single proton, which are different in nature from the defect under consideration. This observation supports the view that most of those H-atoms to be produced by the severance (see Case i in the preceding) turn into non-magnetic configurations.

The configuration of the defect responsible for the anisotropic spectra thus appears to be very similar to an OH radical which is to be formed by the severance of one of the two H-atoms of a water molecule, and which is oriented close to the direction of O_5 to O_4 (Ziegler's data). If there is any bonding of O_5 in this radical to one of the neighboring molecules, the bonding must be not too significant. Otherwise, the observed axial symmetry of the A-tensor would be probably reduced.²⁷ This model of the defect appears to be similar to the one proposed by Ovenall (see Introduction) except for the speculated degree of the bonding of the radical to its neighbors. If possible hydrogen bonding of the present radical to the O_4 atom is taken seriously, then it is not impossible to view the configuration of the radical as that of an O_2H radical speculated by Symon.⁴

When compared with the spectra observed by Wigen and Cowen, the results of the present work indicate certain similarities as well as some discrepancies. The similarity lies in the observation of the proton and deuteron hyperfine structures, and of the isotropic line. The general behavior of the hyperfine structures with regard to the

angle of rotation seems to be similar. The discrepancies, however, lie in the quantitative aspect of the spectra. Comparing Table 3 containing the data by Wigen and Cowen¹ with Table 1, it can be seen that the principal values of the g- and A-tensors and tensor directions differ noticeably. According to Wigen and Cowen, who apparently employed the crystal data of Larson and Helmholtz,²³ the A-tensor direction is close to the direction of the line joining the O₅ atom to the O₂ atom. Secondly, the deviation from the axial symmetry of the A-tensor is practically insignificant in the present work, while it is noticeable in the Wigen and Cowen work (see Introduction). Thirdly, the separation between the two proton hyperfine lines in the present work is approximately 2 times larger than that of the corresponding separation in the Wigen and Cowen work. The same is also true with regard to the deuteron hyperfine structure. Fourth, the Li-hyperfine interaction is not significant in the present experiment (see Introduction of this Chapter). These discrepancies are rather puzzling in view of the fact that the present experiment has been performed practically in the same way as the Wigen and Cowen experiment with regard to the electron irradiation by using the same radiation facilities, time, and beam intensity at liquid nitrogen temperature. The only apparent difference in the experiment seems to lie in the growth of the single crystals. The samples in the present experiment are grown from liquid solutions of the salt near room temperature, while those of the Wigen and Cowen experiment appear to have been grown from similar liquid solutions of the salt near 50°C. The

TABLE 3. THE SPIN HAMILTONIAN DATA BY WIGEN AND COWEN⁽¹⁾

	g-tensor	A-tensor
Components	$g_{ } = 2.040 \pm 0.001$ $g_{\perp} = 2.002 \pm 0.001$	$A_{zz} = -4 \pm 1$ (G) $A_{yy} = -16 \pm 1$ $A_{xx} = -21 \pm 1$
Polar Angle,* θ	69.3°	77°
Azimuthal Angle,* ϕ	30°	43.5°

* Converted to the frame of reference used in the present work.

results of the present experiment are very satisfactorily reproducible. Therefore, it is possible that the difference in the crystal growth may have something to do with the apparent discrepancies. It is also possible that the proton defect investigated by Wigen and Cowen happens to be quite different in nature from that investigated in the present experiment, even though the experimental conditions are basically similar. Further efforts are being made with regard to these points of concern.

Conclusion

Single crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ have been grown with labeled Li- and H-isotopes near room temperature, and irradiated in 1 MeV electron beams near 77°K. EPR studies of the irradiated samples have also been conducted near 77°K, without warming the samples. The anisotropic spectra with resolved proton (or deuteron) hyperfine structure are satisfactorily described in terms of a spin Hamiltonian consisting of a Zeeman term and a proton (or deuteron) hyperfine interaction term where both the g-tensor and the hyperfine tensor are axially symmetric. The Li-hyperfine interaction, if any, is not needed to describe the observed anisotropy, and its only noticeable effect is on the width of individual hyperfine lines.

The defect of axial symmetry responsible for the spectra is probably an OH radical with insignificant bonding to its neighbor. If Ziegler's crystallographic data are taken to be correct, the defect is oriented very closely to the direction of $\text{O}_5\text{-O}_4$.

However, further efforts will be necessary in order to clarify the existing discrepancies among the two sets of crystallographic data and the difference between the crystals grown at elevated temperatures and those at room temperature.

CHAPTER VI

THERMAL DECAY OF THE OH RADICALS IN ELECTRON IRRADIATED LITHIUM SULFATE AT 77°K*

Introduction

In the previous chapter, the electron paramagnetic resonance (EPR) absorption of lithium sulfate electron-irradiated near 77°K was investigated. The absorption center responsible for the observed anisotropic spectrum with a resolved proton hyperfine structure was attributed to an OH radical which has little or no bonding to its neighbors. This center will be referred to as the type A center in the following. The spin Hamiltonian for the type A center was found to be of the form:

$$\mathcal{H} = \beta(\vec{S} \cdot \vec{g} \cdot \vec{H} + \vec{S} \cdot \vec{A} \cdot \vec{I}) \quad (9)$$

where the g - and A -tensors are both axial about a common axis (see Table 4).

Upon warming to room temperature, this center has been found to decay, while two new centers have been observed to grow. The behavior and properties of these new centers and their relationship to the original center are investigated in the present paper.

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* The content of this chapter has been approved for publication in the Journal of Physics and Chemistry of Solids.

TABLE 4
THE g- AND A-TENSORS FOR TYPE A, B, AND C CENTERS

	Type A	Type B	Type C
$g_{\perp}$	2.005	2.006	2.002
$g_{\parallel}$	2.064	2.033	2.088
θ	75°	79°	57°
ϕ	37°	-65°	-34°
$A_{\text{isotropic}}$	20.9 gauss	12 gauss	*
$A_{\text{anisotropic}}$	10.5 gauss	~ 0	*

*
See Text.

Experimental Results and Spin Hamiltonians

Single crystals of lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) and monodeuterate ($\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$) have been grown with Li and H isotope-labeling and subsequently electron-irradiated near 77°K as described in the previous chapter. The crystals are monoclinic in structure.^{19,23} The (EPR) spectra of the irradiated samples have been taken using a Varian model 4500 EPR spectrometer (X-band) utilizing the specially designed X-band microwave cavity previously described. The first derivative (simply spectrum in the following) of the EPR absorption curve has been recorded. The separation between the two peaks of the spectrum is measured in units of the magnetic field, and referred to as the width of the spectrum in the following.

A recorded OH(OD) radical spectrum from a sample of $^6\text{Li}_2\text{SO}_4$ containing a mixture of H_2O and D_2O is shown in Fig. 17. The two lines labeled h are from the OH radical while the three lines labeled d are from the OD radical. The line labeled I is isotropic and was previously attributed to a trapped electron by Wigen and Cowen.¹ Here the magnetic field is perpendicular to the b-axis and makes an angle of -20° with the a-axis. The + sign corresponds to $g = 2.0023$.

Studies of the thermal decay of this type A center and the creation of the new centers have been complicated by the fact that their (EPR) absorptions are only observable at 77°K. Therefore, the following procedure has been successfully used. The type A spectra of the newly irradiated crystals have been first taken at 77° without warming. Then,

Fig. 17 The type A spectrum of electron-irradiated Li_2SO_4 containing a mixture of H_2O and D_2O at 77°K . The sample has been irradiated at 77°K and stored at 77°K . The magnetic field is perpendicular to the b-axis and makes an angle of -20° with the a-axis. The field intensity increases to the right. The + sign indicates the free electron resonance field.

the EPR cavity containing the sample has been removed from the liquid nitrogen Dewar, and nitrogen gas (approximately 20 l/min.) has been fed into the cavity in place of the helium gas. During this process, the cavity has also been warmed with a heat gun. This procedure warms the cavity to room temperature in approximately two minutes. The sample has then been held at room temperature for a controlled time period and subsequently returned to 77°K in order to investigate the spectra again. The observed decay curve for the type A spectrum is labeled A in Fig. 18. The ordinate measures the peak-to-peak height of the spectrum (one of the proton hyperfine lines) in arbitrary units, while the abscissa denotes the time the sample has been held at room temperature. Also shown in the figure are the growth curves (B and C) corresponding to the two new centers, type B and C, which grow in the warming process. The detailed description of these two centers will be given in a later paragraph. It is seen that the type A spectrum decays appreciably in 10 minutes at room temperature. Its decay rate is neither exponential nor proportional to any power of the time. The tail of the decay curve persists for quite a long time so that a time of approximately 12 hours at room temperature is necessary to make the concentration of the type A centers reach a level at which the peak-to-peak height of the type A spectrum is well below that of the other centers.

Figure 19(A) shows an observed spectrum of a sample of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ after being kept at room temperature for 12 hours. The I points out the

Fig. 18

The thermal decay and growth curves for the types A, B, and C spectra. The ordinate measures the peak-to-peak height of the spectrum in arbitrary units. The abscissa measures the time in minutes that the sample has been held at room temperature.

Fig. 19 The type B and C spectra at 77°K . (A) Spectrum from a sample of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. (B) Spectrum from a sample of $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$. Both samples have been warmed to room temperature for 12 hours. The magnetic field is perpendicular to the b -axis and makes an angle of -20° with the a -axis. The field intensity increases from left to right. The + sign indicates the free electron resonance field. (continued on the next page.)

Fig. 19 (continued.)

previously mentioned isotropic line. As in Fig. 17, the magnetic field increases to the right, is perpendicular to the b-axis, and makes an angle of -20° with the a-axis. The + sign indicates $g = 2.0023$. The spectra of the type B and C centers are labeled B and C, respectively. Fig. 19(B) is of a deuterated sample. There now appears one line instead of two for the type B center. It is noticed that the width of the type B resonance of Fig. 19(B) is about 0.3 times the peak-to-peak separation of the proton doublet structure in Fig. 19(A). This ratio of 0.3 is close to the ratio of the deuteron magnetic moment to the proton magnetic moment. The I in the figure points out the previously mentioned isotropic line. It should be noted here that a substantial increase of the spectrometer gain was necessary in order to obtain the spectra of Fig. 19.

The type B spectrum has been found to consist of a well-resolved doublet in the case of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ but an unresolved triplet in the case of $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$. The degree of resolution is much better for the Li-labeled crystals. However, no resolved deuteron hyperfine structure was observed. These observations lead to the following two conclusions:

- (i) The type B center consists of a proton of spin $1/2$ (or deuteron of spin 1), whose hyperfine structure is expected to exhibit 2 (or 3) lines,
- and (ii) The hyperfine interactions of the center with neighboring Li nuclei constitute a higher order perturbation than that of the proton (or deuteron). The angular dependence of the type B spectrum for a sample of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ for the b-axis rotation is given by the dots in

Fig. 20(A). The abscissa represents the angle in degrees measured from the a-axis, while the ordinate measures the separation (in gauss) of the spectral position from the free-electron resonance field ($g = 2.0023$) corresponding to zero on the ordinate axis. In this figure, data at angles of 30° , 40° , and 50° have not been included. This is due to an overlap of the type B and type C spectra, which then obscures the spectral positions. Figure 20(B) illustrates the angular dependence of the spectra of a sample of $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ for a rotation about the a-axis, each dot representing an unresolved triplet of deuterium hyperfine lines. The results indicate that a unit cell of the sample contains two possible sites of equal probability for the type B center, which are related by the two-fold symmetry about the b-axis. The observed angular dependences have been best described by means of a spin Hamiltonian of the form of Eq. 9, where the g-tensor has been found to be axially symmetric and the hyperfine tensor $\hat{A}$ pertaining to the proton (or deuteron) appears to be almost isotropic, exhibiting little variation over the range of angles. The magnitude of the variation was not sufficient to calculate with any accuracy the A-tensor axis direction. Table 4 lists the data for the g-tensor and the average isotropic value of $\hat{A}$, which have yielded the solid curves in Fig. 20. The agreement is satisfactory.

The type C spectrum grew at approximately the same rate as the type B spectrum (see Fig. 18), and exhibited no resolved structure. Its peak-to-peak width exhibited a dependence on both the lithium and hydrogen

Fig. 20 The angular dependence of the type B spectrum: (A) Rotation about the b-axis ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$); (B) Rotation about the a-axis ($\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$). The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field. The portion of the experimental plot in Fig. 20(A) near 40° was uncertain due to overlapping lines and is therefore left out. In Fig. 20(B), a dot represents an unresolved triplet corresponding to the deuteron hyperfine structure. (Figure is continued on next page.)

Fig. 20 (Continued.)

isotopes. The contribution of the lithium hyperfine broadening seems to be comparable with that of the hydrogen hyperfine broadening. The line width was a maximum for samples labeled with H- and ^7Li -isotopes and was the narrowest for D- and ^6Li -labeled samples. This may be taken as indicating that the type C centers interact with neighboring Li and H nuclei, but the interaction is much weaker than in the case of the type B center. The observed angular variation of the type C spectrum is illustrated by the dots in Figs. 21(A) and 21(B) for the b-axis and a-axis rotations, respectively. The ordinates and abscissas are measured as in Fig. 20. It should be noticed that the single resonance line in Fig. 21(A) splits into two resonance lines in Fig. 21(B). This indicates the existence of two sites per unit cell that are equivalent for the b-axis rotation. The spectra have been fitted to a spin Hamiltonian of form of Eq. 9 with an axial g-tensor but without the hyperfine term. The data of the g-tensor are given in Table 4. The solid curves in Fig. 21 represent the calculated angular dependence.

Discussion

The experimental results pertaining to the type B spectrum seem to be attributable to a defect center of spin $1/2$, which undergoes a major hyperfine interaction with a single proton. There are two distinct sites of this center per unit cell, which are related by the two-fold symmetry of the monoclinic lattice.^{19,23}

The type B centers could be formed in two ways: (i) Isolated H-atoms that had been severed from crystal waters and trapped in the

Fig. 21 The angular dependence of the type C spectrum of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$: (A) Rotation about the b-axis; (B) Rotation about the a-axis. The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field. (Figure is continued on next page.)

(B)

Fig. 21 (Continued.)

lattice during the initial irradiation at 77°K migrate upon warming and form radicals with neighboring atoms. (ii) The original type A centers have been transformed into type B centers. The first possibility is ruled out by the experimental failure of detecting EPR spectra of the isolated H-atoms at 77°K before warming. This strongly suggests that the type B center is a transformation of the type A center.

However, the type B center seems to be more complex, less symmetric, and larger in size than the type A center. Several mutually consistent evidences may be given in support of this. First, $\Delta g = g_{||} - g_{\perp}$ is smaller for the type B center than for the type A center. Second, the isotropic part of the A-tensor is less for the type B center and also the anisotropic part of the A-tensor is almost negligible for the type B center. Both of these changes are consistent with a proton radical, which is larger and less symmetric than the type A center. The formation of the larger and less symmetric complex can effectively reduce the isotropic hyperfine coupling by reducing the s-character of the wave function and also quench the orbital angular momentum, thereby reducing Δg .^{28,29}

Table 4 indicates that the g-tensor axis direction of the type B center is definitely different (in azimuthal angle ϕ) from that of the type A center. The observed g-tensor axis direction does not correspond to any known crystallographic direction containing a single proton, but it is very close to the S-O₃ direction shown in Fig. 14. It is not believed, however, that the H-atom could place itself in a position of a

sulfur atom or the O_3 atom, or any other O-atom of the $SO_4^{=}$ group. Therefore, it is proposed that the axis of the g-tensor just happens to be parallel to the S- O_3 axis.

The decay rate of the type A center (see Fig. 18), which exhibited no obvious functional dependence on time, rules out a simple interaction between OH radicals, in favor of a several-step reaction process. Due to the covalent nature of the bonding in the crystal, the migration of an atom or molecule along most directions in the lattice would be difficult.³⁰ Consequently, the migration of the original OH radicals is probably along the water molecule columns which are hydrogen bonded. Attachment or interactions of the OH radicals with neighboring atoms can then take place with atoms making up the walls of these columns or with atoms and molecules in the column itself. However, these participating atoms except for the hydrogen atom in the original OH radical exhibit no resolved hyperfine interaction and therefore are most likely oxygen atoms.

The simplest possible radical that seems consistent with the data is an O_2H radical. Two supporting evidences may be mentioned as follows: First, the observed g-values and proton hyperfine structure of the type B center are very close to the corresponding quantities pertaining to O_2H radicals investigated independently by Kaitmazov and Prokhorov,³¹ and by Wyard and Smith.³

Table 5 compares the corresponding quantities as measured by these authors. A comparison of Table 4 and 5 would indicate a close agreement

TABLE 5
A- & g-TENSOR DATA FOR O_2H RADICALS

	Ref. 31	Ref. 3
$g_{\perp}$	*	$2.0002 \pm .0007$
$g_{\parallel}$	*	$2.0419 \pm .004^{\dagger}$
$A_{\text{isotropic}}$	12 gauss	13.5 ± 3 gauss

*

Not given.

†

Changed to 2.039 in a more recent paper.³²

among the three sets of experiments. Secondly, though less pertinent, recent independent investigations of O_2F radicals³³⁻³⁵ (which are similar in structure to O_2H radicals) have indicated that the isotropic hyperfine interaction of the unpaired electron of the radical with the nucleus (of spin 1/2) of the fluorine is approximately thirteen gauss, which is very close to that of the radical under consideration in the present paper. The fluorine nucleus and the proton both have a nuclear spin of 1/2 and a nuclear moment of comparable magnitude. Since in both radicals the unpaired electron is in a π -orbital on the O-O portion of the molecule,^{2,33} the observed proton hyperfine splitting can be understood in terms of an exchange interaction between the unpaired spin and the σ bonding orbital on the H atom.³⁶ This σ orbital then contributes to the isotropic hyperfine coupling.

The type C center also is formed from some reaction involved in the decay of the type A center, for the type C center grows simultaneously with the type B center with approximately the same growth rate. Since the radical exhibits no resolved hyperfine structure due to Li- and/or H-atoms, these atoms are not an integral part of the radical. Therefore, the radical is most likely made up of oxygen. Lithium or hydrogen atoms may be neighbors to this type C center. Any hyperfine interaction of the type C center with the neighboring hydrogen and lithium atoms corresponds to a higher order perturbation and merely affects the absorption width by means of unresolved hyperfine interactions. The observed g-shift is positive (see Table 4). The variation in g-value for this

center is the largest of all. This may be taken as indicating that the type C center is the most symmetric in shape.^{28,29} Any positive configurational identification of this radical seems hopeless, mainly because of its lack of hyperfine structure and the fact that the observed g-tensor axis direction does not correspond to any known lattice direction (see Table 4).

If one is allowed to speculate on possible models for the type C center, then the observed values of the g-tensor favor an O_2^- or an O_3^- radical. Table 6 lists previously observed^{4,37,38} g-tensor components for O_2^- and O_3^- . Because the g-tensor components of O_3^- indicate a large non-axiality, which has not been observed in the type C center, the radical, O_3^- , will not be considered. This leaves only an O_2^- responsible for the type C center. According to a recent work by Känzig and Cohen³⁷ on O_2^- radicals trapped in a rhombic field:

$$g_z = g_e + 2\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2}$$

$$g_x = g_e \left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\lambda}{E} \left[-\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} + 1 \right]$$

$$g_y = g_e \left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\lambda}{E} \left[\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - 1 \right]$$

where g_e is the free electron g-value (2.0023), z is measured along the molecular axis, Δ is the crystal field splitting of the degenerate $p\pi_g$ orbital (see Fig. 2 of Ref. 37), E is defined in the same figure of Ref. 37 and λ is the spin orbit coupling constant. Thus the g-tensor does not

TABLE 6
g-TENSOR DATA FOR O_2^- AND O_3^- RADICALS

	O_2^-	O_2^-	O_3^-
g_x	2.00*	1.9512 ⁺	2.0025 ⁺⁺
g_y	2.00	1.9551	2.0174
g_z	2.175	2.4359	2.0113

* See Ref. 4.

⁺ See Ref. 37.

⁺⁺ See Ref. 38.

exhibit axial symmetry. The amount of nonaxiality found by Känzig and Cohen was $|g_x - g_y| = .0039$. In making a comparison of this data with the data in the present experiment, two major factors must be considered:

(i) Because of the covalent nature of the bonding in lithium sulfate³⁸ the crystal field splitting of the degenerate $p\pi_g$ levels is expected to be larger in the present work than in the case of KCl. (ii) The spin-orbit coupling constant is probably reduced since the wave functions are more spread out and overlapped in the covalent environments.^{39,40}

Thus, assuming the rhombic field to be responsible for the type C center, $\frac{\lambda}{\Delta}$ and consequently $\frac{\lambda}{E}$ are expected to be much less in the type C center. In this sense, the above equations can be approximated for the type C center by

$$g_z = g_e + 2 \frac{\lambda}{\Delta}$$

$$g_x = g_e - \frac{\lambda}{E} \left(-\frac{\lambda}{\Delta} \right) \approx g_e$$

$$g_y = g_e + \frac{2\lambda}{E} \quad .$$

Therefore, if $2 \frac{\lambda}{E}$ is less than .001 (the estimated accuracy for the determination of g-values in the present work), the g-tensor for the type C center would show an apparent axial symmetry.

On the other hand, in the case of ClO, a molecule isoelectronic with O_2^- , P.W. Atkins et al.³⁸ have found the g-tensor to be axially symmetric with components $g_{\perp} = 1.9909$ and $g_{\parallel} = 2.0098$. This molecule was trapped in an H_2SO_4 matrix at 77°K. These g-values correspond to a

large crystal field splitting of the degenerate $p\pi_g$ orbitals.³⁸ Therefore, the apparent lack of non-axiality of the g-tensor for the type C center does not necessarily exclude the O_2^- model.

Conclusion

Single crystals of lithium sulfate have been grown with labeled Li and H isotopes and irradiated in a 1 MeV electron beam at 77°K. After warming to room temperature and again returning to 77°K, the previously reported OH radical spectrum disappears and two new types (B and C) of spectra are observed.

The type B spectrum can be explained by an axially symmetric Hamiltonian containing a Zeeman term and an isotropic proton hyperfine interaction term. This spin Hamiltonian is assigned to a modification of the original OH radical, forming an O_2H radical. The type C spectrum can be explained by an axially symmetric Hamiltonian containing only a Zeeman term, and is attributed to an O_2^- radical produced simultaneously with the type B center.

CHAPTER VII
NEUTRON IRRADIATED LITHIUM SULFATE*

Introduction

- The EPR studies of electron irradiated lithium sulfate at 77°K discussed in Chapter V have produced an EPR spectrum identified as being due to an OH radical (type A) with little or no bonding to its neighbors. In Chapter VI it has been discussed that, upon warming to room temperature for 24 hours and again investigating the spectrum at 77°K, the original OH radical had disappeared and two new species of paramagnetic centers have been produced. One (type B) has been identified as a modification of the original OH radical. The other (type C) has been attributed to be an oxygen-radical of the form O_2^- formed simultaneously with the O_2H radical. Gamma irradiation has produced similar results. However, neutron-irradiated samples at room temperature not only produced the type B and C spectra but also three new spectra. It is these spectra which are discussed in the present Chapter.

Experimental Results and Spin Hamiltonians

Single crystals of lithium sulfate monohydrate with controlled concentrations of ^6Li , ^7Li , H and D isotopes have been grown as previously described. The crystals were subsequently irradiated in beams

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* The content of this chapter is being submitted to the Journal of Physics and Chemistry of Solids.

of thermal neutrons in the Phoenix Memorial Laboratory of the University of Michigan, Ann Arbor, Michigan, U.S.A. Thermal neutron doses of 10^{15} nvt to 10^{17} nvt were used.

Figure 22 illustrates a spectrum obtained from a sample of ${}^7\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ at 77°K . The magnetic field increases to the right and makes an angle of -60° with the a-axis of the monoclinic crystal.¹⁹ The observed resonance lines are labeled I, B, C, D, E, and F. The type I line has been speculated by Wigen and Cowen¹ as being due to a trapped electron. The lines labeled B and C are due to an O_2H radical and an O_2^- radical, respectively. The lines D, E, and F are new spectral lines characteristic to neutron-irradiated samples.

The angular variation (of the center of resonance) of the type D line for a rotation about the two-fold b-axis is given by the dots in Fig. 23(A) and the variation for a rotation about an axis perpendicular to the a-b plane is given by the dots in Fig. 23(B). The position of the line is measured relative to $g = 2.0023$ in units of gauss. The angle is measured in degrees. The splitting of the single line for the rotation about the b-axis into two lines for the rotation about the axis perpendicular to the a-b plane suggests the existence of two sites per unit cell that are equivalent for the rotation about the two-fold b-axis.¹⁹ The width of the absorption line depends upon the hydrogen isotope used in the water of hydration, being wider for H_2O and narrower for D_2O .

Fig. 22

Spectrum of a neutron-irradiated sample of ${}^7\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The sample has been irradiated at room temperature and stored at room temperature. The spectra has been taken at 77°K . The magnetic field is perpendicular to the b-axis and makes an angle of -60° with the a-axis. The field intensity increases from left to right. The + sign indicates the free electron resonance field.

Fig. 23 Angular dependence of the type D spectrum: (A) Rotation about the b-axis; (B) Rotation about an axis perpendicular to the a-b plane. The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field. (Figure is continued on next page.)

(B)

Fig. 23 (Continued.)

The dots in Fig. 24(A) show the angular dependence of the type E and type F lines for a rotation about the b-axis, while the dots in Fig. 24(B) illustrate their angular dependence for a rotation about the a-axis. The measurements of the magnetic field and the angle are made as in the case of Fig. 23. The single line observed for each of the type E and F centers in Fig. 24(A) separates into two lines in Fig. 24(B). This again suggests the existence of two sites per unit cell that are equivalent for the rotation about the b-axis. In Fig. 24(B), data around $\Delta H = 0$ is inaccurate because of the overlap between various resonance lines. The extent of the error for the type F resonance was approximately ± 3.5 gauss, which would correspond to an error of approximately $\pm .002$ in the calculation of the g-tensor element, $g_{\perp}$, in this region of angles. The uncertain points are indicated with crosses in Fig. 24(B). In this same figure, the data for the type E resonance is missing for all angles above 60° , because of substantial overlap of the type E resonance in this region with other lines of larger amplitude. The amplitude and width of the type E and F lines depend on the labeling of Li isotopes: The type E resonance appeared with a larger amplitude in the ^6Li samples than in the ^7Li samples, while the type F line appeared with a larger amplitude in the ^7Li samples than in the ^6Li samples. The extent of this variation in amplitude for the two centers was as much as a factor of 10. The widths of both lines from the ^7Li samples were also wider than their corresponding widths from the ^6Li samples.

The data for the type D line has been fitted to a spin Hamiltonian

Fig. 24 Angular dependence of the type E and F spectra: (A) Rotation about the b-axis; (B) Rotation about the a-axis. The observed spectral position (represented by a dot), ΔH , is measured relative to the free electron resonance field. In (B), the portion of the type F dependence represented by the crosses is uncertain because of overlap. Also, the portion of the type E resonance that is missing above 60° is omitted, because of the complete overlap of this line with other lines of larger amplitude. (Figure is continued on next page.)

Fig. 24 (Continued.)

of the form:

$$\mathcal{H} = \beta \vec{S} \cdot \vec{g} \cdot \vec{H} \quad (10)$$

where the spin, S , is $1/2$ and the g -tensor is axially symmetric. The calculated values of the g -tensor components are given in Table 7. The polar angles θ and ϕ indicate the direction of the symmetry axis of the g -tensor and are measured from the b - and a -axes, respectively. The results of this fitting are illustrated by the solid curves in Fig. 23. The results are seen to be satisfactory.

The data for the type E center has been fitted to a spin Hamiltonian of the form of Eq. 10. As previously mentioned, the data in the region between 60° and 90° for the a -axis rotation were obscured. It was determined, however, that the range of g -values that could occur in this region of angles is $2.002 < g_x < 2.005$. If the resonance occurred outside this region it would no longer be obscured. On this basis, the g -tensor has been found to be non-axial. For simplicity in plotting, however, the calculated fit was made assuming an axial symmetry with $g_{\perp} = g_x = g_z = 2.008$ and $g_{\parallel} = g_y = 2.033$ (see Appendix at end of this Chapter). The results of this approximation are illustrated by the solid curves in Fig. 24. The observed and calculated data are shown in Table 7. The polar angles θ and ϕ refer to the direction of the largest g -tensor component, g_y , measured from the b - and a -axes respectively. The other directions could not be determined because of the overlap problem previously mentioned. The fit is as good

TABLE 7
g-TENSOR DATA FOR THE TYPE D, E, AND F RESONANCES

	D	E	F
g_x	2.004	~ 2.002 to 2.005 (Experimental)	2.005
g_y	2.004	2.033 (Calculated)	2.005
g_z	2.100	~ 2.008 (Experimental)	2.107
θ	38°	84°	83°
ϕ	47°	90°	90°

as would be expected under the simplification.

The data for the type F center has also been fitted to a spin Hamiltonian of the form given above. The calculated g-tensor is axial within the error of $\pm .002$ as previously mentioned and tabulated in Table 7. The polar angles are measured as in the type D case. The calculated fit to the data is given by the solid curves in Fig. 24. This fit is quite satisfactory. It is interesting to notice that the g-tensor symmetry axis of the type F center is practically parallel to the direction of the maximum g-tensor axis of the type E center (see Table 7).

Discussion

Assigning the observed resonances D, E, and F to specific defects is a difficult task because of two complicating factors. (i) The observed resonance lines have no resolved hyperfine structure, which would give a clue to the number and kinds of atomic nuclei involved. (ii) The observed tensor axis for the type D resonance does not exactly correspond with any known lattice directions. However, if one is allowed to speculate on possible models, the most logical choices would be oxygen and/or sulfur oxide radicals. The reasons favoring these radicals are: (i) The crystal is predominately composed of oxygen atoms with sulfur atoms attached to most oxygens. (ii) The spectra exhibited no resolved hyperfine structure due to an atom with a non-vanishing nuclear moment (Li and H).

Consider first the type D resonance. This resonance exhibits a positive shift in g-value from $g = 2.0023$ for a free electron (Table 7),

and therefore, primary attention is given to those oxygen and sulfur radicals that are known to exhibit such positive g-shifts. Table 8 lists those radicals which are known to exhibit this property.^{4,37,38,41-43} A comparative survey of Table 7 and Table 8 would indicate that the data of the O_2^- radical of Ref. 4 corresponds closely to the type D data. Känzig and Cohen³⁷ have shown that if the degenerate $p\pi_g$ ground state of O_2^- is split by a rhombic field, the g-tensor should be non-axial. In comparing the g-tensor data for the Type D center with that of O_2^- radicals investigated by Känzig and Cohen, it is necessary to consider the following information. (i) The crystal field splitting of the degenerate ground state is larger for the type D center, because of the covalent bonding.³⁸ (ii) The spin orbit coupling constant will be also reduced because of the covalent nature of the bonding.^{39,44} Utilizing this information, the g-tensor expressions for O_2^- by Känzig and Cohen can be approximated with the following:

$$g_z = g_e + \frac{2\lambda}{\Delta}$$

$$g_x = g_e - \frac{\lambda}{E} \left(-\frac{\lambda}{\Delta} \right) \approx g_e$$

$$g_y = g_e + \frac{2\lambda}{E}$$

where g_e is the free electron g-value (2.0023); Δ is the crystalline field splitting of the degenerate ground state as illustrated in Fig. 2 of Ref. 37, E is also defined in the same figure and is larger than Δ ; and λ is the spin orbit coupling constant. If $2\lambda/E$ is less than .001 (the estimated

TABLE 8

g-TENSOR DATA FOR VARIOUS OXYGEN AND SULFUR OXIDE RADICALS

	O_2^-	O_2^-	O_3^-	SO_2^-	SO_3^-	SO_4^{*-}	SO_4^-
g_x	2.00	1.9551	2.0025	2.0024	2.004	2.0035	2.0037
g_y	2.00	1.9512	2.0174	2.0102	2.004	2.0327	2.0486
g_z	2.175	2.4359	2.0113	2.0057	2.003	2.0084	2.0082
Ref.	4	37	38	38	41	42	43

* See Ref. 46.

accuracy of the measurement for the type D data), the g -tensor would exhibit an apparent axial symmetry. On the other hand, ClO , a molecule isoelectronic with O_2^- , has been found³⁸ to exhibit axial symmetry with g -tensor components $g_{\perp} = 1.9909$ and $g_{\parallel} = 2.0098$. These g -values correspond to a large crystal field splitting of the degenerate π_g orbitals. Therefore it seems that an O_2^- radical with an increased ground state splitting is responsible for the type D spectrum. Furthermore, this radical must be trapped in a position close to the water molecule column or in the column itself. Then, the absorption width can be affected by unresolved hyperfine interactions with the protons in the crystal water, as observed.

Consider next the type E center. A comparison of Table 7 with Table 8 indicates that the data for the type E center is the closest to the data for an SO_4^- radical of Ref. 42. Morton et al.⁴³ have stated that the largest g -tensor component lies along an O-O bond. When compared with known lattice directions of the crystal,¹⁹ the direction O_3-O_1 ($\phi = 114^\circ$ and $\theta = 87^\circ$) is in close agreement with the direction of the largest g -tensor component of the type E line. On the other hand, recently several workers^{43,45} have reported observing SO_3^- radicals simultaneously with SO_4^- radicals. The g -tensor of SO_3^- is almost isotropic around $g = 2.003$. Therefore a search was made for the four hyperfine lines due to ^{33}S (.7% abundant, $I = 3/2$) in SO_3^- at the expected positions (approximately ± 50 and ± 150 gauss from the isotropic line).^{43,45} The expected four lines appear to be present in the samples investigated

here. However, the extremely poor signal to noise ratio of the hyperfine structure makes the results of the search favorable but not positive for the SO_3^- radical. A by-product of this search is that the isotropic line at $g = 2.003$ is probably not a single line as previously speculated by Wigen and Owen,¹ but rather a compound line, containing partly the line from SO_3^- radicals. An SO_4^- radical would certainly be consistent with the observed effects of Li on the line widths, because of the physical position of the sulfate groups next to lithium atoms. Considering all these, it is suggested that the type E resonance is due to an SO_4^- radical (see Ref. 46).

Before a possible model for the type F center is considered, several pieces of experimental evidence should again be pointed out. (i) The symmetry axis of the g -tensor for the type F center is parallel to the direction of the maximum g -tensor component axis for the type E center; (ii) The line widths of both lines are affected similarly by unresolved Li hyperfine interactions; (iii) Both lines occur together with different relative amplitudes, which are governed by the lithium isotope labeling. These evidences would lead one to believe that perhaps both spectra are produced by the same type of radicals trapped in two different environments. This difference in environments could then result in a relative shift in the orbital levels of SO_4^- . This could cause the observed difference in the apparent symmetry of the g -tensor for the type F versus the type E center as well as the change in the g -tensor components. In support of this, the other SO_4^- radical in Table 8

(Ref. 43) also shows an increase in $g_{||}$ (as does the type F center) from the SO_4^- radical of reference 42. Thus it would seem reasonable that the type F resonance is produced by an SO_4^- radical trapped in an environment different from the radical responsible for the type E resonance.

Conclusion

Single crystals of lithium sulfate monohydrate have been grown with labeled lithium and hydrogen isotopes and have been irradiated by thermal neutrons. The resulting EPR spectra have yielded those lines which have been discussed previously in Chapters V and VI, as due to O_2H and O_2^- radicals observed in electron irradiated samples. However, three new spectra are characteristic to the neutron irradiated samples. One of these (type D) can be described by an axially symmetric Hamiltonian containing only the Zeeman term. This center has been assigned to an O_2^- radical. The other two spectra (type E and F) are attributed to SO_4^- radicals trapped in different environments. The isotropic line at $g = 2.003$ is probably not a single line as previously speculated by Wigen and Cowen¹ but rather a compound line, containing partly the line from SO_3^- radicals.

APPENDIX FOR CHAPTER VII

A generalization of the results of Chapter II gives for the spectroscopic g-factor the following expression:

$$g_n = \sqrt{g_x^2 \cos^2 \alpha + g_y^2 \cos^2 \beta + g_z^2 \cos^2 \gamma}$$

where g_n represents the g-factor for non-axial symmetry. The corresponding g-factor for an axially symmetric case can be expressed as (Chapter II)

$$g_a = \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \beta}$$

The difference between these two g-values can be expressed as

$$g_n - g_a = \sqrt{g_x^2 \cos^2 \alpha + g_y^2 \cos^2 \beta + g_z^2 \cos^2 \gamma} - \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \beta}$$

Since the actual directions of g_x and g_z are not known, the g-values actually taken from the data of Fig. 24 will be used for g_n . Therefore, the difference, $g_n - g_a$, can be expressed in the following form:

$$g_n - g_a = g_n - \sqrt{g_{\perp}^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \beta}$$

For a rotation about the b-axis, the following differences can be calculated.

(i) Angle of rotation; 0° ($\beta = 90^\circ$, minimum g-value)

$$g_n - g_a = 2.008 - 2.008 = 0$$

(ii) Angle of rotation; 90° ($\beta = 6^\circ$, maximum g-value)

$$g_n - g_a = 2.032 - 2.033 = - .001$$

For a rotation about the a-axis the following differences can be calculated.

(i) Angle of rotation; 6° ($\beta = 0^\circ$, maximum g-value)

$$g_n - g_a = 2.033 - 2.033 = 0$$

(ii) Angle of rotation; 90° ($\beta = 84^\circ$, minimum g-value)

$$g_n - g_a = (2.002 \text{ to } 2.005) - 2.008 = -(.003 \text{ to } .006)$$

For the b-axis rotation, the difference between g_n and g_a is insignificant at both the minimum and maximum g-value angles. This is the reason that the axial g-tensor approximation for the b-axis rotation in Fig. 24(A) is so satisfactory. For a rotation about the a-axis, the corresponding difference is again insignificant at the maximum g-values angle, yielding a satisfactory fit to the data near 0° in Fig. 24(B). At 90° of the same a-axis rotation, the difference $g_n - g_a$ is relatively large. However, any effect of this difference on the fitting near 90° in Fig. 24(B) can not possibly be assessed because one does not have reliable experimental data in this region, due to the overlapping of lines.

APPENDIX

DERIVATION OF THE SPIN HAMILTONIAN

The interactions responsible for observed EPR spectra are traceable to many sources. However, the discussion here will include only those interactions that directly affect the spin Hamiltonian of Eq. 1. The interactions that must be included are:⁴⁷

- (1) Magnetic interactions of the electrons with the field

$$V_H = \sum_k \beta (\vec{l}_k + 2\vec{s}_k) \cdot \vec{H}$$

- (2) Interactions of the spins with their orbital motions

$$V_{LS} = \lambda \vec{L} \cdot \vec{S}$$

- (3) Interaction of a nucleus with the electrons

$$V_N = 2\gamma \beta \beta_N \sum_K \left\{ \frac{(\vec{l}_k - \vec{s}_k) \cdot \vec{I}}{r_k^3} + \frac{3(\vec{r}_k \cdot \vec{s}_k)(\vec{r}_k \cdot \vec{I})}{r_k^5} + \frac{8\pi}{3} \delta(r_k) \vec{s}_k \cdot \vec{I} \right\}$$

where

β is the Bohr magneton

$\vec{l}_k$ is the angular momentum of the k^{th} electron

$\vec{s}_k$ is the spin angular momentum of the k^{th} electron

$\vec{H}$ is the magnetic field applied to the sample

λ is the spin orbit coupling constant

β_N is the nuclear magneton

γ is the nuclear gyromagnetic ratio

$\vec{I}$ is the nuclear angular momentum

$\vec{r}$ is the radius vector of the electron relative to the nucleus.

In order to arrange these potentials into a more usable form, a transformation is necessary. The I_z term of

$$\left[\left(\frac{3\vec{r}_k \cdot \vec{s}_k}{r_k^5} \right) (\vec{r}_k \cdot \vec{I}) - \frac{\vec{s}_k \cdot \vec{I}}{r_k^3} \right]$$

is

$$\frac{3\vec{r}_k \cdot \vec{s}_k}{r_k^5} (r_{kz} I_z) - \frac{s_{kz} I_z}{r_k^3} .$$

This I_z term can then be written as

$$I_z \left[s_{kz} \left(\frac{3r_{kz}^2}{r_k^5} - \frac{1}{r_k^3} \right) + s_{kx} \left(\frac{3r_{kx} r_{kz}}{r_k^5} \right) + s_{ky} \left(\frac{3r_{ky} r_{kz}}{r_k^5} \right) \right] .$$

Let $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$, then the I_z term can be written with the sum sign included as

$$I_z \sum_k \left[s_{kz} \left(\frac{3z_k^2}{r_k^5} - \frac{1}{r_k^3} \right) + s_{kx} \left(\frac{x_k z_k}{r_k^5} \right) + s_{ky} \left(\frac{y_k z_k}{r_k^5} \right) \right] .$$

In an angular momentum space where $\vec{S}$ is a constant, this equals⁵⁰

$$I_z \tau \left[S_z \sum_k \left(\frac{3z_k^2 - r_k^2}{r_k^5} \right) + S_{xk} \sum_k \frac{z_k x_k}{r_k^5} + S_{yk} \sum_k \frac{z_k y_k}{r_k^5} \right]$$

where τ is a constant of proportionality and S_z , S_x , and S_y are components of the total spin $\vec{S}$ in this angular momentum space. Factoring out a $\left(\frac{1}{r^3} \right)$, the result is⁵⁰

$$I_z \tau \left(\frac{1}{r^3} \right) \left[S_z \sum_k \left(\frac{3z_k^2 - r_k^2}{r_k^2} \right) + S_{xk} \sum_k \frac{z_k x_k}{r_k^2} + S_{yk} \sum_k \frac{z_k y_k}{r_k^2} \right] .$$

Using the table given by Bleaney,⁵⁰ this equals

$$\propto I_z \tau \left(\frac{1}{r^3} \right) \{ S_z [3L_z^2 - L(L+1)] + \frac{S_x}{2} (L_z L_x + L_x L_z) + \frac{S_y}{2} (L_z L_y + L_y L_z) \}$$

where α is another constant.

Similarly the I_y component is proportional to

$$\{ S_y [3L_y^2 - L(L+1)] + \frac{S_x}{2} (L_x L_y + L_y L_x) + \frac{S_z}{2} (L_x L_z + L_z L_x) \}$$

and the I_x component is proportional to

$$\{ S_x [3L_x^2 - L(L+1)] + \frac{S_y}{2} (L_x L_y + L_y L_x) + \frac{S_z}{2} (L_x L_z + L_z L_x) \} .$$

Combining these three components, the result is

$$\propto \tau \left(\frac{1}{r^3} \right) [L(L+1) \vec{S} \cdot \vec{I} - \frac{3}{2} (\vec{L} \cdot \vec{S})(\vec{L} \cdot \vec{I}) - \frac{3}{2} (\vec{L} \cdot \vec{I})(\vec{L} \cdot \vec{S})] .$$

It can therefore be seen that all the interactions can be written in terms of angular momentum operators. After doing this, the results are

$$V_N = \left(\frac{1}{r^3} \right) 2\gamma\beta\beta_N [\vec{L} \cdot \vec{I} + \xi \{ L(L+1)(\vec{S} \cdot \vec{I}) - \frac{3}{2} (\vec{L} \cdot \vec{S})(\vec{L} \cdot \vec{I}) - \frac{3}{2} (\vec{L} \cdot \vec{I})(\vec{L} \cdot \vec{S}) - \kappa \vec{S} \cdot \vec{I} \}] ,$$

$$V_{LS} = \lambda \vec{L} \cdot \vec{S} ,$$

and

$$V_H = \beta \vec{H} \cdot (\vec{L} + 2\vec{S})$$

where $\xi = \alpha \tau$.

Collecting all potentials, the Hamiltonian is now given by the following equation;

$$\begin{aligned} \mathcal{H} &= \lambda \vec{L} \cdot \vec{S} + \beta \vec{H} \cdot (\vec{L} + 2\vec{S}) + P[\vec{L} \cdot \vec{I} + \vec{S} \cdot \vec{I} (\xi L(L+1) - \kappa) \\ &\quad - \frac{3}{2} \xi (\vec{L} \cdot \vec{S})(\vec{L} \cdot \vec{I}) - \frac{3}{2} \xi (\vec{L} \cdot \vec{I})(\vec{L} \cdot \vec{S})] \end{aligned}$$

where

$$P = \left(\frac{1}{r^3} \right) 2\gamma\beta\beta_N .$$

Consider now the case of an orbital singlet. To first order in the perturbation all terms of the form $\langle 0|L|0 \rangle$ are zero.⁵¹ Therefore, to first order,

$$\mathcal{H}_s^{(1)} = 2\beta \vec{H} \cdot \vec{S} - P(\kappa \delta_{ij} + \frac{3}{2} \xi l_{ij}) S_i I_j$$

where the term $-(\kappa \delta_{ij} + \frac{3}{2} \xi l_{ij})$ comes from the sum $\langle 0|a+b+c|0 \rangle$, and

$$a = [\xi L(L+1) - \kappa] \vec{S} \cdot \vec{I} = [\xi L(L+1) - \kappa] S_i I_j \delta_{ij} ,$$

$$b = -\frac{3}{2} \xi (\vec{L} \cdot \vec{S})(\vec{L} \cdot \vec{I}) = -\frac{3}{2} \xi L_i S_i L_j I_j = -\frac{3}{2} \xi L_i L_j S_i I_j ,$$

$$c = -\frac{3}{2} \xi (\vec{L} \cdot \vec{I})(\vec{L} \cdot \vec{S}) = -\frac{3}{2} \xi L_j I_j L_i S_i = -\frac{3}{2} \xi L_j L_i S_i I_j .$$

Now,

$$\langle 0|b+c|0 \rangle = -\frac{3}{2} S_i I_j \xi \left[\frac{2}{3} L(L+1) \delta_{ij} + l_{ij} \right]$$

where

$$l_{ij} = \langle 0|L_i L_j + L_j L_i|0 \rangle \quad \text{for } i \neq j .$$

Thus,

$$\langle 0|a+b+c|0 \rangle = \left[-\frac{3}{2} l_{ij} \xi - \kappa \delta_{ij} \right] S_i S_j .$$

To second order in the perturbation, the terms which do not contain L will

give no contribution since $\langle 0|n\rangle = 0$ if $n \neq 0$.⁵² Therefore, rewriting $\mathcal{H}$ with only those terms that contain L ,

$$\mathcal{H} = \lambda \vec{L} \cdot \vec{S} + \beta \vec{H} \cdot \vec{L} + P[\vec{L} \cdot \vec{I} - \frac{3}{2} \xi (\vec{L} \cdot \vec{S})(\vec{L} \cdot \vec{I}) - \frac{3}{2} \xi (\vec{L} \cdot \vec{I})(\vec{L} \cdot \vec{S})]$$

In subscript notation

$$\mathcal{H} = \lambda L_i S_i + \beta H_i L_i + P[L_i I_i - \frac{3}{2} \xi S_i I_j (L_i L_j + L_j L_i)]$$

The second order perturbation is of the form⁵³

$$\mathcal{H}^{(2)} = - \sum_n \frac{\langle 0|H|n\rangle \langle n|H|0\rangle}{E_n - E_0}$$

Taking only the terms involving $H_i S_j$ and $S_i I_j$ and neglecting all terms of P^2 and ξ^2 which are smaller than the remaining terms,

$$\begin{aligned} \mathcal{H}_s^{(2)} = & - 2\lambda\beta \sum_n \frac{\langle 0|L_i|n\rangle \langle n|L_j|0\rangle}{E_n - E_0} S_i H_j \\ & - 2\lambda P \sum_n \frac{\langle 0|L_i|n\rangle \langle n|L_j|0\rangle}{E_n - E_0} S_i I_j \\ & - (-\frac{3}{2}) P \xi \lambda [i \epsilon_{lij} S_l] I_k \sum_n \frac{\langle 0|L_i|n\rangle \langle n|L_j L_k + L_k L_j|0\rangle}{E_n - E_0} \end{aligned}$$

Defining

$$\Lambda_{ij} = \sum_n \frac{\langle 0|L_i|n\rangle \langle n|L_j|0\rangle}{E_n - E_0}$$

and

$$U_{lk} = \frac{1}{2} i \epsilon_{lij} \sum_n \frac{\langle 0|L_i|n\rangle \langle n|L_j L_k + L_k L_j|0\rangle}{E_n - E_0}$$

the result for $\mathcal{H}_s^{(2)}$ can be written as

$$\mathcal{H}_s^{(2)} = -2\lambda\beta\Lambda_{ij}S_iH_j - 2\lambda P\Lambda_{ij}S_iI_j + 3P\xi\Lambda U_{\ell k}S_\ell I_k \quad .$$

Combining $\mathcal{H}_s^{(1)}$ and $\mathcal{H}_s^{(2)}$,

$$\mathcal{H}_s = 2(\beta\delta_{ij} - \lambda\beta\Lambda_{ij})S_iH_j - P[\kappa\delta_{ij} + \frac{3}{2}\xi\ell_{ij} + 2\lambda\Lambda_{ij} - 3\xi\lambda U_{ij}]S_iI_j \quad .$$

In practice, the tensor elements above are grouped together in the form

$$\mathcal{H}_s = 2\beta g_{ij}S_iH_j + A_{ij}S_iI_j$$

where g_{ij} and A_{ij} constitute the g-tensor and the hyperfine coupling tensor, respectively.

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