"But don't you see what this implies? It means that there is a fourth degree of freedom for the electron. It means that the electron has spin, that it rotates."

- George Uhlenbeck to Samuel Goudsmit in 1925 on hearing of the Pauli principle -
"There are spins everywhere" is now a well known quote amongst EMR spectroscopists. It is born out by the huge list of topics at the right hand side. In some of these the use of EMR techniques is obviously minimal, history for example, in others such as biochemistry EMR's influence has been seminal. In topics such as imaging EMR is advancing at a rapid pace, particularly with recent advances in instrumentation and computing power. For at least the next ten years we will see EMR following in the footsteps of NMR in instrumentation - moving to higher field/frequency machinery, and with a move from continuous wave (cw) to fourier transform (ft) measurements, possibly even eclipsing the former in time. This will extend the list of topics even further. Another crumb from the physicist's plate will shortly be available - the use of force balance methods will enable the measurement of single spins on surfaces - the ultimate in detection sensitivity. There are also exciting arguments afoot among physicists concerning the very nature of the electron, (New Scientist, 14th October 2000, pp25). Humphrey Maris of Brown University says he thinks he can cut an electron in two!”

- John Maher -
"There are spins everywhere. It is born out by the huge list of topics at the right hand side. In some of these the use of EMR techniques is obviously minimal, history for example, in others such as biochemistry EMR’s influence has been seminal. In topics such as imaging EMR is advancing at a rapid pace, particularly with recent advances in instrumentation - moving from continuous wave (cw) to fourier transform (ft) measurements, possibly even eclipsing the former in time. Another crumb from the physicist’s plate will shortly be available - the use of force balance methods will the ultimate in detection sensitivity. There are also exciting arguments afoot among physicists concerning the very nature of the electron. (New Scientist, 14th October 2000, pp25), Humphrey Maris of Brown University says he thinks he can cut an electron in two!"

- John Maher -

**Applications**

**EPR Methodologies**

These are just scratches of modern EPR techniques.

**What is EPR?**

*Electron Paramagnetic Resonance (EPR)*
*Electron Spin Resonance (ESR)*
*Electron Magnetic Resonance (EMR)*

Electron Zeeman Interaction
What is EPR?

EPR is the resonant absorption of microwave radiation by paramagnetic systems in the presence of an applied magnetic field.

“Electron Zeeman Interaction”

Conventional CW EPR spectrometer Arrangement

“Electron Zeeman Interaction”
What is EPR?

$EPR \rightarrow \text{Electron Zeeman Interaction}$

$S = \frac{1}{2}$

$m_s = +\frac{1}{2}$

$h\nu = g\beta B_0$

$m_s = -\frac{1}{2}$

$\hbar$ Planck’s constant ($6.626196 \times 10^{-27}$ erg.sec)

$\nu$ frequency (GHz or MHz)

$g$ g-factor (approximately 2.0)

$\beta$ Bohr magneton ($9.2741 \times 10^{-21}$ erg.Gauss$^{-1}$)

$B_0$ magnetic field (Gauss or mT)

$H = \beta S g H$

Selection Rule

$\Delta M_s = \pm 1$

Bruker EMX EPR spectrometer

“Electron Zeeman Interaction”
What is EPR?

$S = 1/2$

$m_s = +1/2$

$m_s = -1/2$

$\Delta B_{pp}$

$\Delta MS = \pm 1$

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$B_o$ magnetic field (Gauss or mT)

$H = \beta S g H$

Selection Rule

“Electron Zeeman Interaction”

What is $g$?

It is an inherent property of a system containing an unpaired spin.

Similar to the chemical shift observed in an NMR spectrum.

The g value for a single unpaired electron (free electron) has been calculated and experimentally determined. It is $2.0023192778 \pm 0.0000000062 (= g_e)$. The g value for an $S = 1/2$ system is usually near $g_e$, but it is not exactly at $g_e$. Why not?

This is due to spin orbit coupling which determines both the value of $g$ and its anisotropy (how far the 3 g values are from $g_e$. The g value can often be calculated and the value is characteristic for a particular spin system.
What is $g$?

Similar to the chemical shift observed in an NMR spectrum. The $g$ value for a single unpaired electron (free electron) has been calculated and experimentally determined. It is $2.0023192778 \pm 0.0000000062 (=g_e)$. The $g$ value for an $S = 1/2$ system is usually near $g_e$, but it is not exactly at $g_e$. Why not? This is due to spin orbit coupling which determines both the value of $g$ and its anisotropy (how far the 3 $g$ values are from $g_{av}$). The $g$ value can often be calculated and the value is characteristic for a particular spin system.

MO Scheme for Low-Spin $d^{7,9}$ Complexes

$g_2 = g_e \left(1 + \frac{8 \lambda}{\Delta E_1}\right) = g_1$
$g_{x,y} = g_e \left(1 + \frac{2 \lambda}{\Delta E_2}\right) = g_{\perp}$

$\lambda$: spin-orbit coupling constant
**What is $g$?**

For $d^7$, $d^9$ complexes:

- $g_0 - g_e = g_1$
- $g_{x,y} = g_0 \left[1 + \frac{6\lambda}{\Delta E_1}\right] = g_2$

$\lambda$: spin-orbit coupling constant

**MO Scheme for Low-Spin $d^{7,9}$ Complexes**

**Powder Patterns of EPR Spectra**

- **Isotropic $g$:** $g_x = g_y = g_z$
- **Axial $g$:** $g_x \neq g_y \neq g_z$
- **Rhombic $g$:** $g_x \neq g_y \neq g_z$

Even though we talk about $g_x$, $g_y$, and $g_z$, the values should be more properly called $g_0$, $g_1$, and $g_2$, unless we have evidence for the nature of the $g$ tensor relative to the molecular axes.

**Powder:** randomly oriented samples such as frozen solutions, powders
The g value for a single unpaired electron has been calculated and experimentally determined. It is an inherent property of a system containing an unpaired spin.

Similar to the unpaired spin, near isotropic powder patterns of EPR spectra are observed in an NMR chemical shift of Ni(II).

Near isotropic

For Ni(III) and Ni(I), the g values are from gav.

Axial: $g_x = g_y \neq g_z$
Rhombic: $g_x \neq g_y \neq g_z$

The g value for a single unpaired electron is usually near $g_e$, but it is not exactly at $g_e$. Why not?

In solution: when molecules are rapidly tumbling (within microwave time scale), g-anisotropy is averaged out.

Powder: randomly oriented samples such as frozen solutions, powders

π-radical
**Electron spin – Nuclear spin Interaction**

\[ B_{\text{eff}} = B_0 - B_{\text{Ind}} \]

\[ B_{\text{eff}} = B_0 + B_{\text{Ind}} \]

**Selection Rule**

\[ |\Delta M_S| = 1; \Delta M_I = 0 \]

**Isotopes**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Nuclear Spin</th>
<th>% Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1/2</td>
<td>99.9</td>
</tr>
<tr>
<td>N</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>98.9</td>
</tr>
<tr>
<td>O</td>
<td>1/2</td>
<td>1.1</td>
</tr>
<tr>
<td>Ne</td>
<td>1</td>
<td>99.6</td>
</tr>
<tr>
<td>Ne</td>
<td>1/2</td>
<td>0.37</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>99.8</td>
</tr>
<tr>
<td>O</td>
<td>1/2</td>
<td>0.037</td>
</tr>
<tr>
<td>Mg</td>
<td>0</td>
<td>95.6</td>
</tr>
<tr>
<td>Mg</td>
<td>1/2</td>
<td>0.74</td>
</tr>
<tr>
<td>Si</td>
<td>3/2</td>
<td>99.2</td>
</tr>
<tr>
<td>Na</td>
<td>5/2</td>
<td>100</td>
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<tr>
<td>Mg</td>
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<td>91.7</td>
</tr>
<tr>
<td>Fe</td>
<td>1/2</td>
<td>2.19</td>
</tr>
<tr>
<td>Cu</td>
<td>7/2</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>68 &amp; 26</td>
</tr>
<tr>
<td>Ni</td>
<td>1/2</td>
<td>1.19</td>
</tr>
<tr>
<td>Cu &amp; Ni</td>
<td>7/2</td>
<td>69 &amp; 31</td>
</tr>
<tr>
<td>Na &amp; Ni</td>
<td>5/2</td>
<td>16 &amp; 9</td>
</tr>
<tr>
<td>Al</td>
<td>1/2</td>
<td>14.4</td>
</tr>
</tbody>
</table>

**H = βSgH + SA**

**S=½; I=½**

**Doublet**

**Hyperfine Interaction**

**Magnetic Field**

hfc: hyperfine coupling constant
Electron spin – Nuclear spin Interaction

**Doublet**

- $S = \frac{1}{2}$
- $I = \frac{1}{2}$
- $hfc (= A)$

**Selection Rule**

- $\Delta M_S = \pm 1$
- $\Delta M_I = 0$

- $M_S = \pm \frac{1}{2}$
- $M_I = \pm \frac{1}{2}$

- Magnetic Field

**Nuclear Spin Interaction**

- $M_S = \pm \frac{1}{2}$
- $M_I = \pm \frac{1}{2}$

**“Hyperfine Interaction”**

Electron spin – Nuclear spin Interaction

**Triplet**

- $S = \frac{1}{2}$
- $I = 1$
- $hfc$ (hyperfine coupling constant)

**Selection Rule**

- $\Delta M_S = \pm 1$
- $\Delta M_I = 0$

- $M_S = \pm \frac{1}{2}$
- $M_I = \pm 1$

- Magnetic Field

**“Hyperfine Interaction”**
Electron spin – Nuclear spin Interaction

So far, we have considered the cases of hyperfine interactions in solutions or in the samples with very narrow $g$-anisotropy. How about powder samples?

For $^{61}$Ni, $I = 3/2$, so you expect (and see) 4 lines.

But the hyperfine splitting is unresolved in the $g_{\perp}$ direction.

So far, we have considered the cases of hyperfine interactions in solutions or in the samples with very narrow $g$-anisotropy. How about powder samples?
**Electron spin – Nuclear spin Interaction**

Superhyperfine Splitting

Cu$^{II}$ $d^9$

S=1/2; I=3/2

14N I=1

Superhyperfine Splitting

“Hyperfine Interaction”

**Electron spin – Nuclear spin Interaction**

V$_3$O$_7$(bsh)$_2$(OE)$_2$

“Hyperfine Interaction”
**Electron spin – Electron spin Interaction**

When there is more than one unpaired electron ($S > 1/2$), the interaction between the spins must be considered. This term can be very large. The Hamiltonian for a system with a spin $> 1/2$ is: 

$$H = D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + \frac{E}{D} \left[ S_x^2 - S_y^2 \right] + g_s \beta S H$$

The new terms are $D$ and $E/D$. $D$ is called the zero-field splitting (ZFS) parameter; $E/D$ is the rhombicity (the ratio between $D$, the axial splitting parameter, and $E$, the rhombic splitting parameter, at zero field). The minimum value of $E/D$ is 0 for an axial system. The maximum value is 1/2 for a rhombic system. The strength of the ZFS is determined by the nature of the ligands.

So for a completely axial system ($E/D = 0$), 

$$H = D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + g_s \beta S H$$

Consider a case where $S = 3/2$, i.e., 4 unpaired electrons. These spins can interact to give a total spin moment, referred to as a system spin. There will be four sublevels for $m_s$, where $S_z = -3/2, -1/2, 1/2, \text{ and } 3/2$.

The energy for the $+3/2$ level will be: 

$$D \left[ \frac{9}{4} - \frac{1}{3} \left( \frac{3}{2} \times \frac{5}{2} \right) \right] = D \left[ \frac{9}{4} - \frac{5}{4} \right] = D$$

The energy for the $-1/2$ level will be: 

$$-D$$

The magnitude of the ZFS can be determined by EPR. The populations of each of the doublet has a Boltzmann distribution. By lowering the temperature to the same energy range as the ZFS and by measuring the EPR amplitude of each doublet, a value of the ZFS can be obtained. Or we can measure $\Delta M_s = \pm 1$ transitions, such as $+5/2 \leftrightarrow +3/2$, at higher fields.
Interactions measured by EPR

\[ H = g_S H + S \cdot I + D(S^2 - I^2/3) S(S+1) + E/D(S_x^2 - S_y^2) \]

- Electron Zeeman interaction (interaction of the spin with the applied field)
- Spin orbit coupling
- Hyperfine and superhyperfine interactions (electron spin-nuclear spin interaction)
- Spin-spin interaction

* Nuclear quadrupole interaction can also be detected.

- High sensitivity (<1 µM to 0.1 mM)
- No background
- Definitive and Quantitative

Applications – Minerals

1. Introduction

Natural minerals have been investigated for their magnetic properties.

2. Chemical compositions: General information on minerals such as FeO, MgO, and MnO.

3. Optical absorption: Infrared and Raman spectroscopy provide useful information on transition metal ions.

4. EPR: This paper discusses EPR for minerals.

5. Conclusions

5.1. Preliminary chemical analysis of the sample

5.2. Interactions measured by EPR

5.3. Applications

- Minerals: Mn2+, Fe3+, etc.
Applications – Minerals

Electron Paramagnetic Resonance of Rhyolite and \( \gamma \)-Bromated Tera Minerals

I. Kızılağaoğlu, O. Kızılağaoğlu, and E. Babaş

Abstract: The research focuses on the examination of the electron paramagnetic resonance (EPR) properties of rhyolite and \( \gamma \)-bromated tera minerals using EPR spectroscopy. The study aims to understand the interaction between the sample's mineralogy and the EPR signal.

1. Introduction

Various types of rhyolite, geological samples, and low levels have been investigated for electron paramagnetic resonance (EPR) properties. This research examines the relationship between the mineralogy of rhyolite and the EPR signal using various techniques such as EPR spectroscopy.

These results reveal the presence of various types of minerals in the rhyolite, and these minerals are crucial in understanding the geological setting. The interaction between the sample's mineralogy and the EPR signal is crucial in understanding the geological environment.
Applications – Minerals

Electron Paramagnetic Resonance of Rhyolite and \gamma-irradiated Taconite Minerals

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Physics Department, Faculy of Arts and Sciences, Selçuk University, Konya, Turkey
E-mail: kili@selcuk.edu.tr

1. Introduction

Various kinds of stones, geothermal samples and other samples have been investigated by electron paramagnetic resonance (EPR) [1,2]. The samples studied were from natural and artificial ones, especially from natural [1,2].

These studies revealed the presence of various kinds of oxide- and carbonates, the same phases, and the same minerals in these stones. Rhyolite, the Deyaz mountain in Inner Anamur, and its neighboring province Nevşehir, the mostly anomalous materials were various kinds of stones [3]. One of these stones is known as Yellow Stone of Nevşehir. It was investigated in this study. We expected to detect paramagnetic centers in rhyolite due to the thermal effects of the close mountain Deyaz, which has active faults. Due to the high temperature and structural deformation, this stone is important in that region. To our knowledge, there exists no investigation of this mineral with EPR. After these, we studied men's teeth and glass production, which is interesting to study with EPR. These studies were the first-time studies with natural and artificial stones, and the first EPR studies were considered. Before \gamma-irradiation, the results indicated the
Applications – Diamonds

http://www2.warwick.ac.uk/fac/sci/physics/research/condensedmatt/diamond/

EPR and Diamond Research Group

Our research group specialises in the development of Electron Paramagnetic Resonance (EPR) and optical spectroscopic methods, and applies these techniques in the study of diamond and other materials/systems.

Current Research activities include:

**HIGH PRESSURE ELECTRON PARAMAGNETIC RESONANCE**

**CARBON BASED ELECTRONICS A NATIONAL CONSORTIUM**

**ELECTRICALLY ACTIVE DEFECTS AND CARRIER TRAPPING IN SEMICONDUCTING DIAMOND**

**HIGH PRESSURE HIGH TEMPERATURE MATERIALS PROCESSING**

**DIAMOND RESEARCH ON INTERFACES FOR VERSATILE ELECTRONICS**

PhD studentships available for September 2006 - contact Mark Newton

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Applications – Diamonds

1. Introduction

The unique site and properties of diamond make it offers substantial opportunities for advanced technology. Its semi-conductive properties allow for the development of new electronic devices, and its unique bonding structure may also offer new opportunities for materials science. These opportunities are an active area of research within the EPR and Diamond Research Group.

The use of high pressure and high temperature processes for the production of diamond and other advanced materials are also areas of active research within the group.

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The identity of the A1B and NE4 electron paramagnetic resonance spectra in high-pressure-high-temperature diamond

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Received 7 August 2002
Published 4 December 2002

Abstract

The identification of the A1B and NE4 electron paramagnetic resonance spectra in high-pressure-high-temperature diamond is described. The spectra were obtained for samples of type-IIa diamond, which was grown in a high-pressure-high-temperature environment.

The spectra are characterized by a strong magnetic dipole interaction, which leads to a splitting of the electron spin levels. The splitting is caused by the strong electric field gradient at the centre of the diamond lattice.

The A1B spectrum is due to a single paramagnetic centre, while the NE4 spectrum is due to a group of closely related centres.

The results of this study provide new insights into the electronic properties of high-pressure-high-temperature diamonds.

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*Figures:*

- Figure 1: A1B and NE4 electron paramagnetic resonance spectra in high-pressure-high-temperature diamond.
- Figure 2: The magnetic field dependence of the A1B and NE4 spectra in high-pressure-high-temperature diamond.
- Figure 3: The temperature dependence of the A1B and NE4 spectra in high-pressure-high-temperature diamond.

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*References:

3. W. Goldhahn, unpublished work.
Applications – Diamonds

The identity of the AB1 and NE4 electron paramagnetic resonance spectra in high-pressure-high-temperature diamond

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Received 14 March 2002
Published 6 December 2002

1. Introduction

The unique optical properties of diamond and its potential for commercial applications make it important to study its mechanical and spectroscopic properties. The improved understanding of these properties is of great interest for the development of optical and electronic devices based on diamond.

2. Experimental

High-pressure-high-temperature diamond was grown in a pressure-temperature cell at 15 kbar and 2000°C. A series of three experiments were performed: (i) the measurement of the EPR spectra of the AB1 spectrum in different pressure-temperature conditions; (ii) the measurement of the EPR spectra of the NE4 spectrum in different pressure-temperature conditions; and (iii) the measurement of the EPR spectra of the AB1 and NE4 spectra in the same sample.

3. Results

The EPR spectra of the AB1 and NE4 spectra were measured at different pressure-temperature conditions. The results showed that the AB1 and NE4 spectra are not affected by the pressure-temperature conditions.

4. Conclusion

The EPR spectra of the AB1 and NE4 spectra were measured under different pressure-temperature conditions. The results showed that the AB1 and NE4 spectra are not affected by the pressure-temperature conditions. The improved understanding of these properties is of great interest for the development of optical and electronic devices based on diamond.
Applications – Diamonds

Properties, Growth and Applications of Diamond
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A7.4 EPR Measurements on the Negatively Charged, Neutral and Positively Charged Vacancies and the Nearest Neighbour Divacancies in Diamond
A5.8 Hydrogen in CVD Diamond: EPR
A6.1 Optical and EPR Properties of Transition Metals in Diamond
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