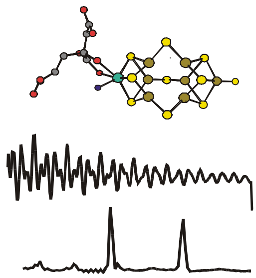
# *Basic Theory and Applications of EPR*

***Applications of EPR for Geology***




이홍인

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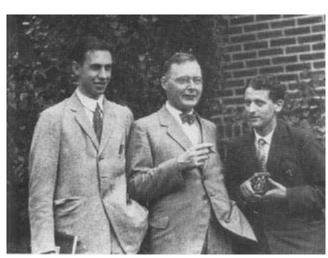
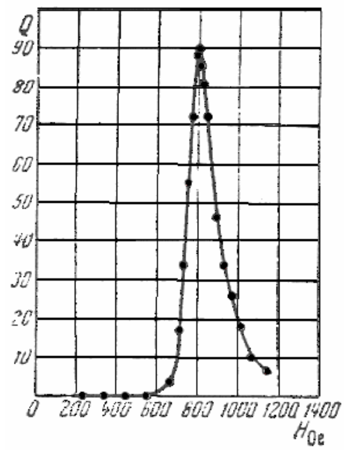
***"But don't you see what this implies? It means that there is a fourth degree of freedom for the electron. It means that <u>the electron has spin, that it rotates</u>."***

*- George Uhlenbeck to Samuel Goudsmit in 1925 on hearing of the Pauli principle -*






Zavoisky가 1944년에 얻은 최초의 EPR 스펙트럼
(시료: $CuCl_2.2H_2O$, 자장의 세기: 47.6G, 전자기파의 주파수: 133MHz)

*"**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 balence 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 -*

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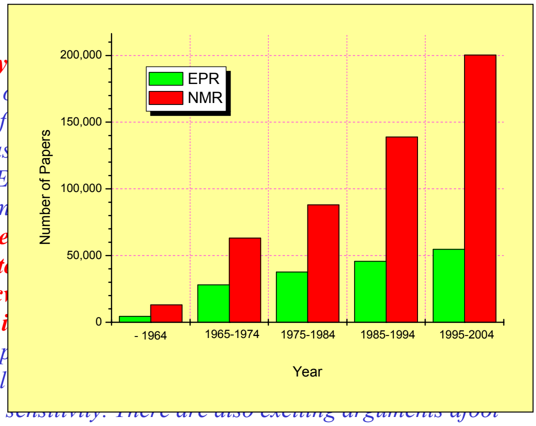


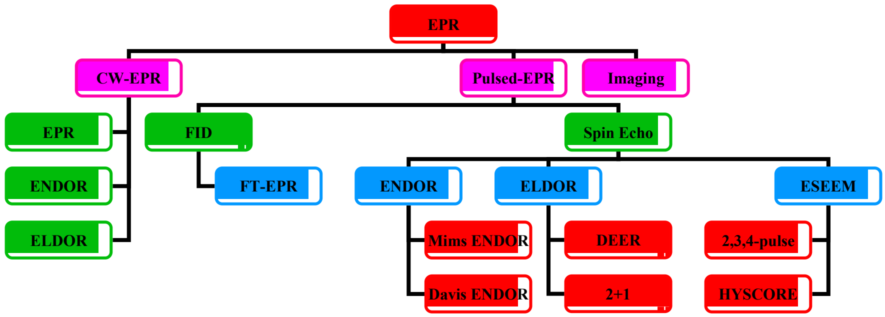

the ultimate in detection sensitivity. There are also exciting arguments afoot among physicists concerning the very nature of the electron, (New Scientist, 14th October 2000, pp25), **Humphrey Maris of Brown University says he thinks he can cut an electron in two!** "

- John Maher -

# Applications

Anthropology, Archeology, Biochemistry, Biology, Chemical Reactions, Clusters, Colloids, Coal, Dating, Dosimetry, Electrochemistry, EPR Imaging, Excitons, Ferromagnets, Forensic Science, Gases, Gemmology, Geography, **Geology**, Glass, History, **Inorganic Radicals**, Materials Science, Medicine, Metal Atom Chemistry, Metalloproteins, Microscopy, **Mineralogy**, **Organic Radicals**, Organometallic Radicals, Paleontology, Photochemistry, Photosynthesis, **Point Defects**, Polymers, Preservation Science, Quantum Mechanics, Radiation Damage, Semiconductors, Spin Labels, Spin Traps, **Transition Metals**, Zoology

# EPR Methodologies

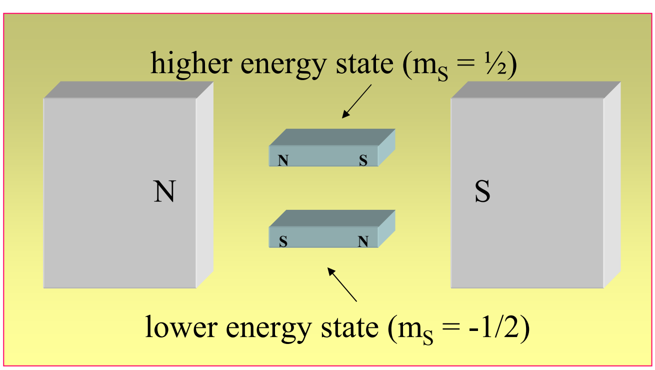



*These are just scratches of modern EPR techniques.*

# What is EPR ?

*Electron Pramagnetic Resonance (EPR)*
*Electron Spin Resonance (ESR)*
*Electron Magnetic Resonace (EMR)*

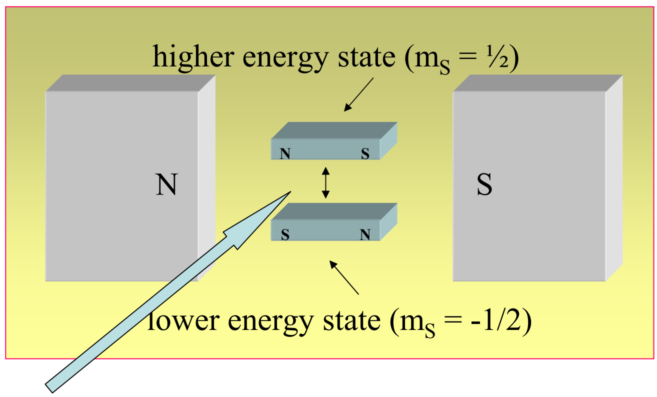
*EPR ~ ESR ~ EMR*




"Electron Zeeman Interaction"

# *What is EPR ?*

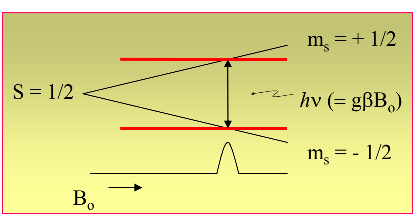
*EPR is the resonant absorption of microwave radiation by paramagnetic systems in the presence of an applied magnetic field.*




**hν (microwave)**

"Electron Zeeman Interaction"

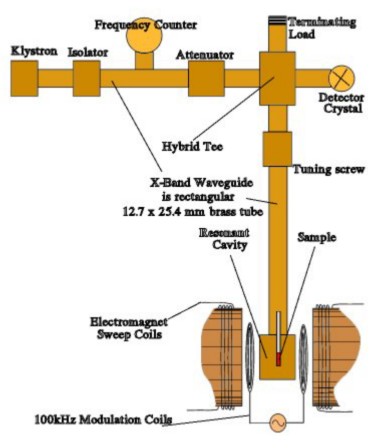
# *What is EPR ?*




- ***h*** Planck's constant ($6.626196 \times 10^{-27}$ erg.sec)
- **ν** frequency (GHz or MHz)
- **g** g-factor (approximately 2.0)
- **β** Bohr magneton ($9.2741 \times 10^{-21}$ erg.Gauss$^{-1}$)
- **$B_o$** magnetic field (Gauss or mT)

$$H = \beta \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H}$$

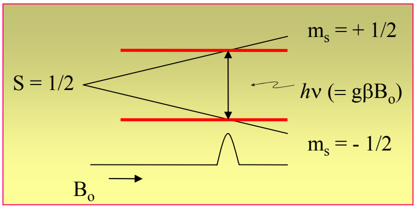
Selection Rule
$\Delta M_S = \pm 1$




Conventional CW EPR spectrometer Arrangement

"Electron Zeeman Interaction"

# What is EPR ?

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Bruker EMX EPR spectrometer

"Electron Zeeman Interaction"

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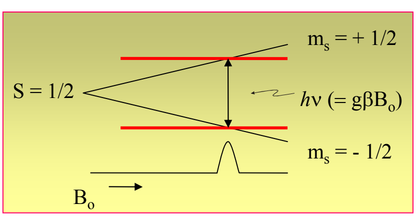


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경북대학교

"Electron Zeeman Interaction"

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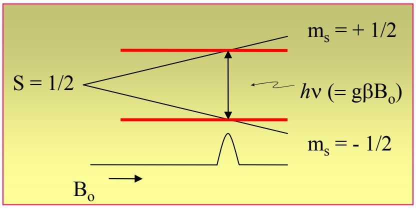


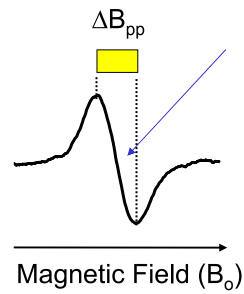


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$\mathbf{B_o}$ magnetic field (Gauss or mT)

$H = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H}$

$\mathbf{g} = h\nu/\beta B_o$

Selection Rule
$\Delta M_S = \pm 1$

"Electron Zeeman Interaction"

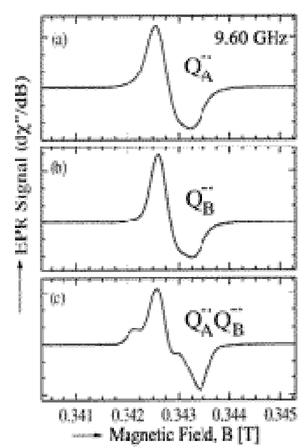
# What is g ?

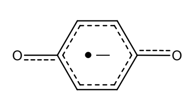
It is an inherent property of a system containing an unpaired spin.

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 ± 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?***

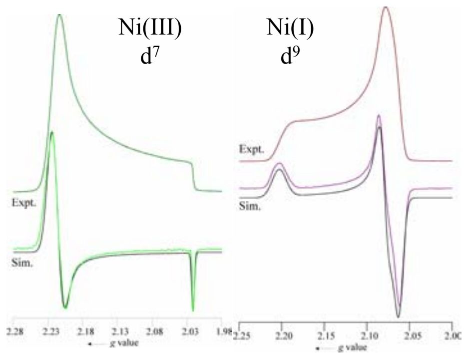
This is due to ***spin orbit*** coupling which determines both the value of ***g and its anisotropy*** (how far the 3 g values are from $g_{av}$. ***The g value can often be calculated and the value is characteristic for a particular spin system.***

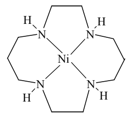


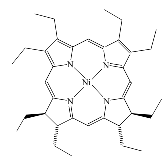
π-radical

# *What is g ?*

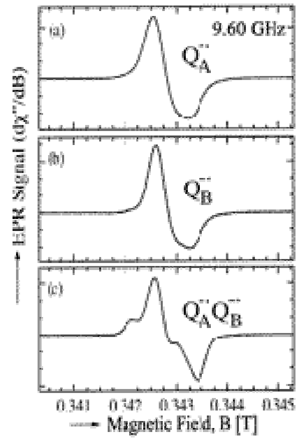


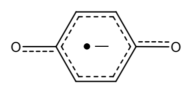



$[Ni(cyclam)]^{3+}$



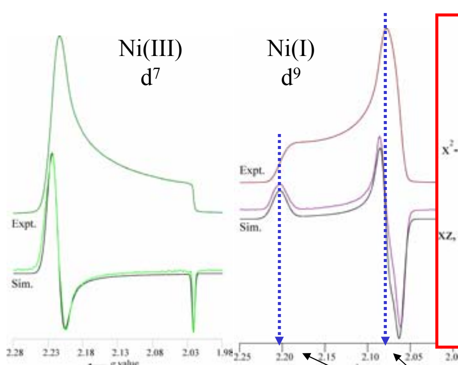
*tct*-Ni(OEiBC)$^-$

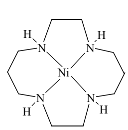


π-radical

# *What is g ?*



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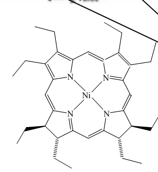

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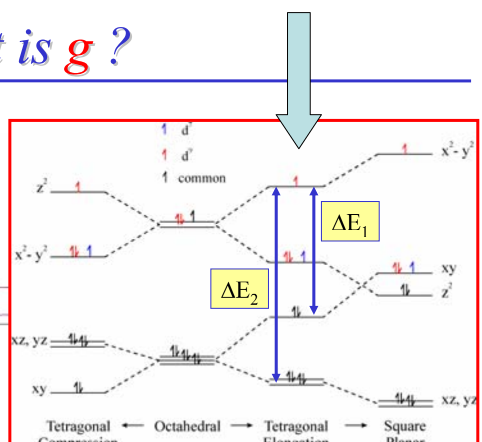



MO Scheme for Low-Spin $d^{7,9}$ Complexes

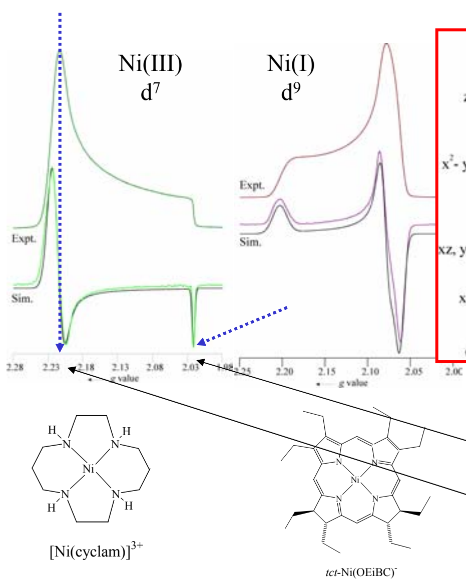
for $d^9$,

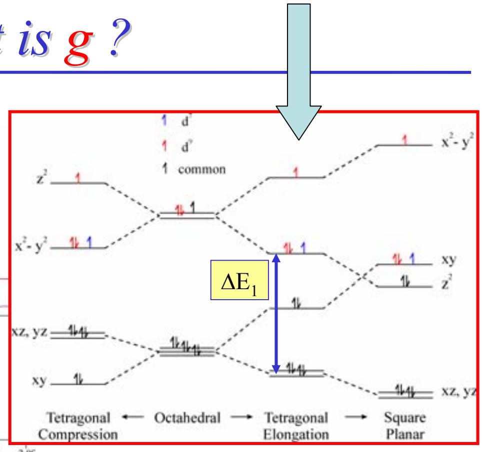
$g_z = g_e [1 + 8\lambda / \Delta E_1] = g_{\parallel}$

$g_{x,y} = g_e [1 + 2\lambda / \Delta E_2] = g_{\perp}$

λ: spin-orbit coupling constant

# What is g ?




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

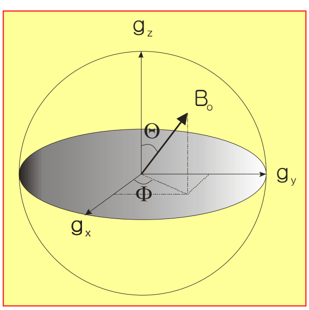
for $d^7$,

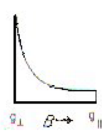
$g_z \sim g_e = g_{\parallel}$

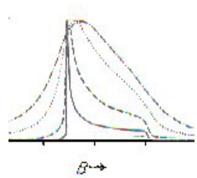
$g_{x,y} = g_e\,[1 + 6\lambda / \Delta E_1] = g_{\perp}$

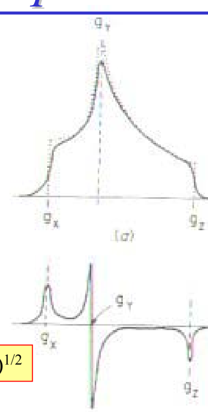
$\lambda$: spin-orbit coupling constant

# Powder Patterns of EPR Spectra

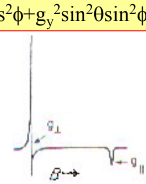







$g_{eff} = (g_x^2\sin^2\theta\cos^2\phi + g_y^2\sin^2\theta\sin^2\phi + g_z^2\cos^2\theta)^{1/2}$



Rhombic $\boldsymbol{g}$: $g_x \neq g_y \neq g_z$

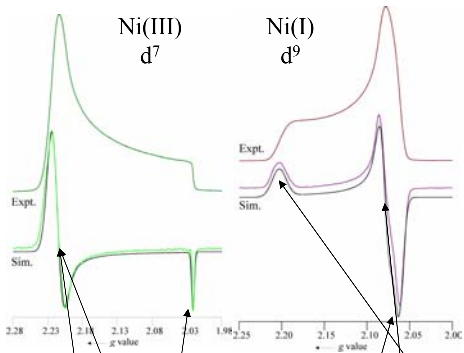
Isotropic $\boldsymbol{g}$: $g_x = g_y = g_z$

*Even though we talk about* ***$g_x$, $g_y$, and $g_z$,*** *the values should be more properly called* ***$g_1$, $g_2$, and $g_3$*** *unless we have evidence for the nature of the g tensor relative to the* ***molecular axes****.*

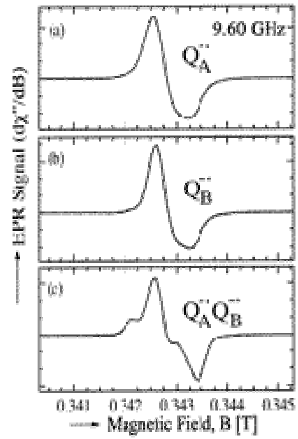
***Powder****: randomly oriented samples such as frozen solutions, powders*

Axial $\boldsymbol{g}$: $g_x = g_y \neq g_z$

# Powder Patterns of EPR Spectra

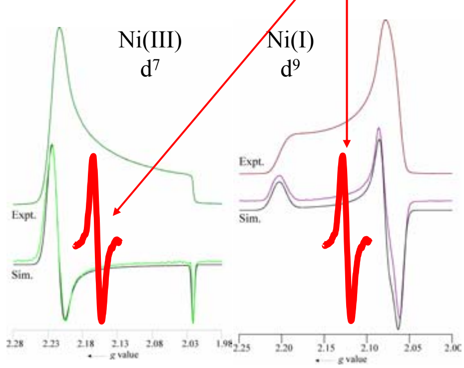


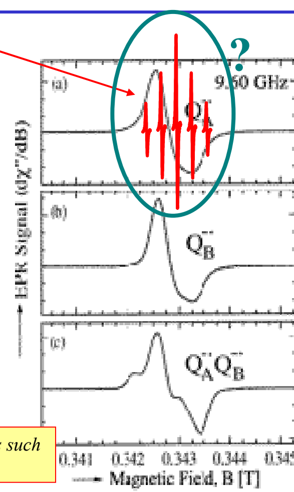

Axial : $g_x = g_y \neq g_z$ Rhombic: $g_x \neq g_y \neq g_z$

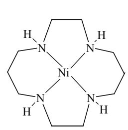



Near isotropic

# Solution EPR



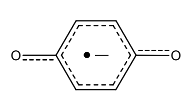




$[Ni(cyclam)]^{3+}$

*Powder: randomly oriented samples such as frozen solutions, powders*

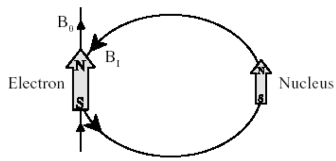
***In solution**: when molecules are rapidly tumbling (within microwave time scale), **g-anisotropy is averaged out.***

*tct*-Ni(OEiBC)$^-$

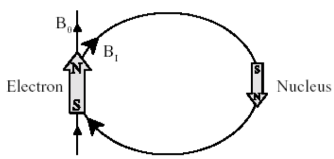


π-radical

# Electron spin – Nuclear spin Interaction




$B_{eff} = B_0 - B_{Ind}$

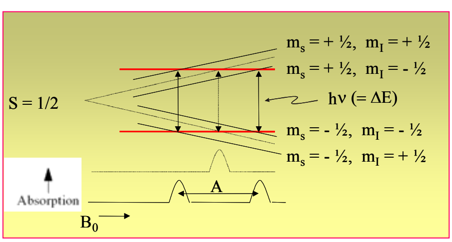



$B_{eff} = B_0 + B_{Ind}$

| Isotope | Nuclear Spin ($I$) | % Abundance |
|---|---|---|
| $^{1}H$ | 1/2 | 99.9 |
| $^{2}H$ | 1 | 0.02 |
| $^{12}C$ | 0 | 98.9 |
| $^{13}C$ | 1/2 | 1.1 |
| $^{14}N$ | 1 | 99.6 |
| $^{15}N$ | 1/2 | 0.37 |
| $^{16}O$ | 0 | 99.8 |
| $^{17}O$ | 5/2 | 0.037 |
| $^{32}S$ | 0 | 95.0 |
| $^{33}S$ | 3/2 | 0.76 |
| $^{51}V$ | 7/2 | 99.8 |
| $^{55}Mn$ | 5/2 | 100 |
| $^{56}Fe$ | 0 | 91.7 |
| $^{57}Fe$ | 1/2 | 2.19 |
| $^{59}Co$ | 7/2 | 100 |
| $^{58}Ni$ & $^{60}Ni$ | 0 | 68 & 26 |
| $^{61}Ni$ | 3/2 | 1.19 |
| $^{63}Cu$ & $^{65}Cu$ | 3/2 | 69 & 31 |
| $^{95}Mo$ & $^{97}Mo$ | 5/2 | 16 & 9 |
| $^{183}W$ | 1/2 | 14.4 |

"Hyperfine Interaction"

# Electron spin – Nuclear spin Interaction

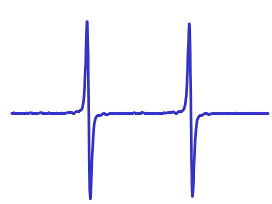



$H = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$

Selection Rule
$\Delta M_S = \pm 1; \Delta M_I = 0$

S=½;
I=½
Doublet

hfc (=A)

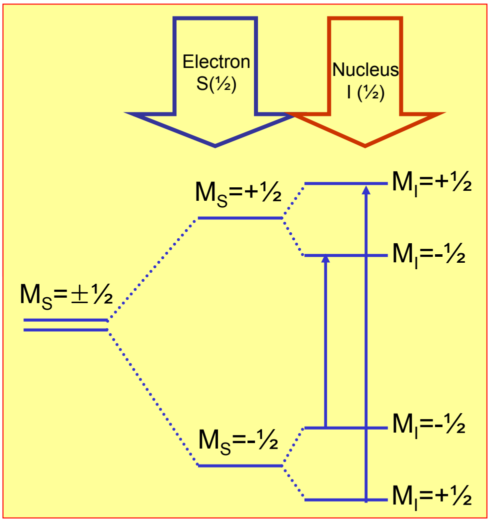


Magnetic Field →

hfc: hyperfine coupling constant

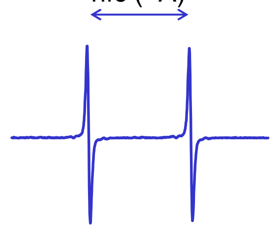
"Hyperfine Interaction"

# *Electron spin – Nuclear spin Interaction*




S=½;
I=½
Doublet

hfc (=A)



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"Hyperfine Interaction"

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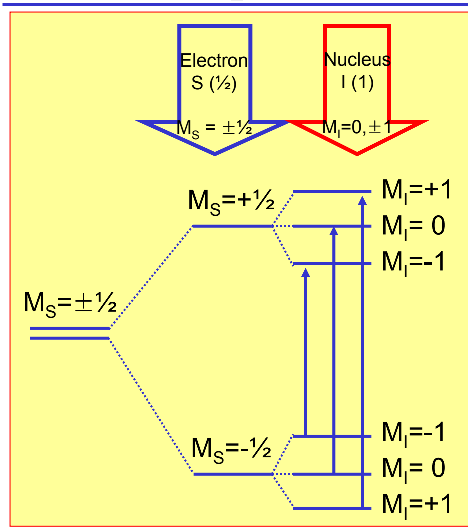
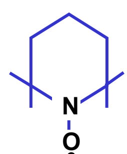
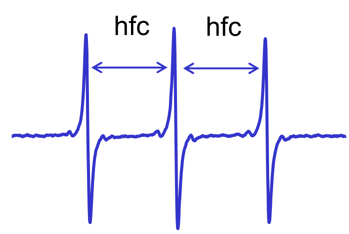



S=½;
I=1
Triplet

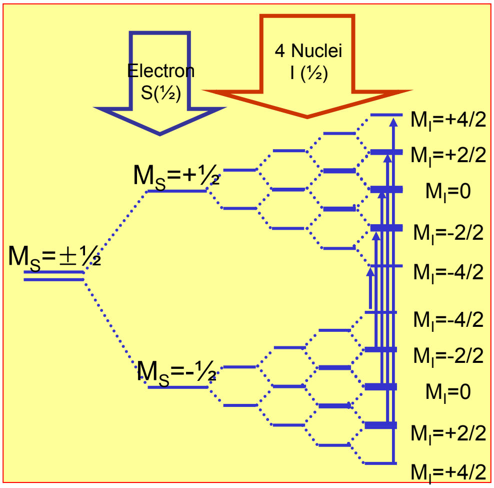


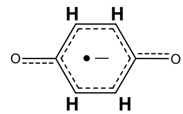

Magnetic Field →

Selection Rule
$\Delta M_S = \pm 1$; $\Delta M_I = 0$

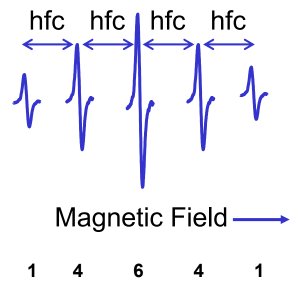
"Hyperfine Interaction"

# Electron spin – Nuclear spin Interaction




S=½;
I=1/2 x 4
Quintet



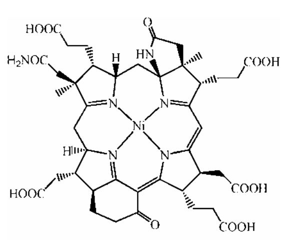

**Pascal's triangle**

***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

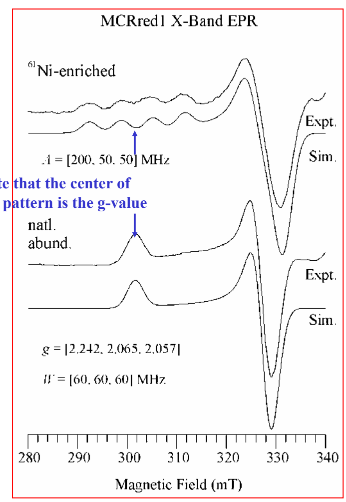
For $^{61}$Ni, I = 3/2, so you expect (and see) 4 lines.

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




$F_{430}$

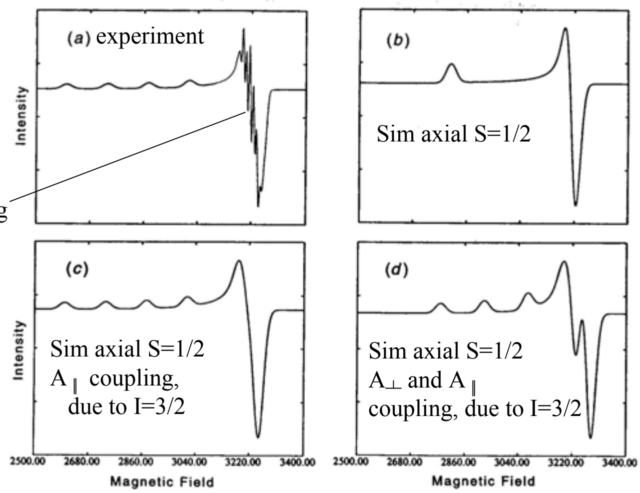
Ni(I)
$d^9$



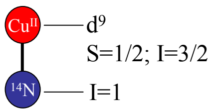

**Note that the center of the pattern is the g-value**

***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

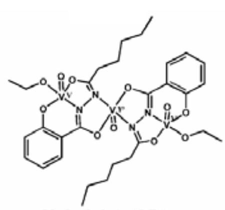



Superhyperfine Splitting

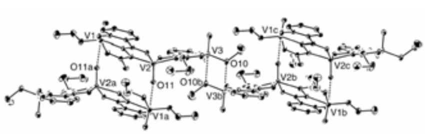


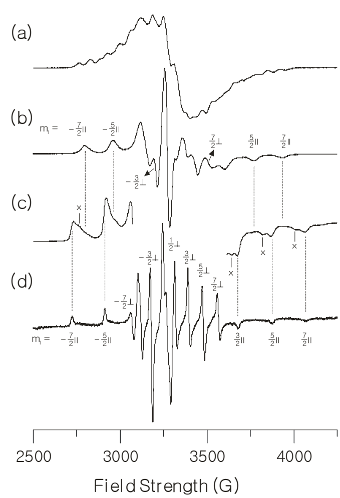

“Hyperfine Interaction”

# Electron spin – Nuclear spin Interaction



$V_3O_3(hshz)_2(OEt)_2$






“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:* $\mathbf{H = D\,[S_z^2 - 1/3\,S(S+1)\;\; + E/D\,(S_x^2 - S_y^2)] + g_o \beta S\, H}$

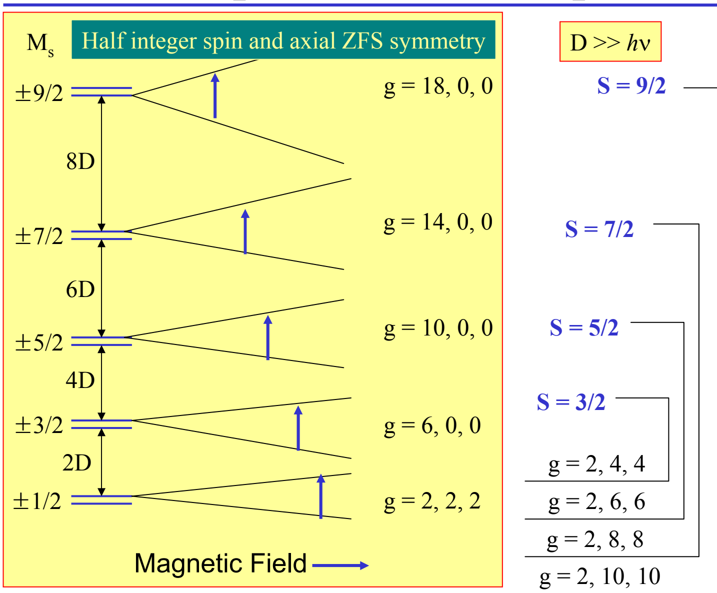
*The new terms are D and E/D. D is called the* ***zero-field splitting (ZFS) parameter****; E/D is the* ***rhombicity*** *(the ratio between D, the axial splitting parameter, and E, the rhombic splitting parameter, at zero field). The minimum value of E/D is 0 for an axial system. The maximum value is 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),* $H = D\,[S_z^2 - 1/3\,S(S+1)] + g_o \beta S\, H$

*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* $S_z = -3/2, -1/2, 1/2,$ *and* $3/2$.

*The energy for the + or -3/2 level will be: D[9/4-1/3(3/2*5/2)]= D[9/4-5/4]= D*
*The energy for the + or - 1/2 level will be: -D.*

# Electron spin – Electron spin Interaction




*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

$$\boxed{H = \beta \mathbf{S\cdot g\cdot H} + \mathbf{S\cdot A\cdot I} + \mathbf{D[S_z^2 - 1/3\ S(S+1) + E/D(S_x^2 - S_y^2)]}}$$

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 interation can also be detacted.

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

# Applications – Minerals

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Spectrochimica Acta Part A 60 (

EPR, optical, infrared and Raman spe

N.O. Gopal, K.V. Naray

Department of Physics, Sri Venkateswara

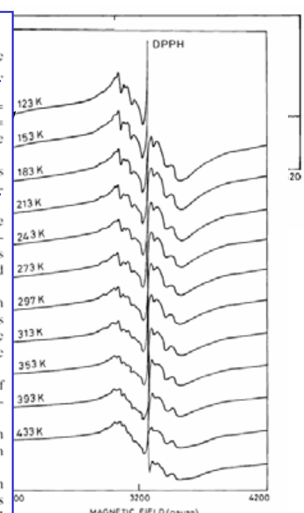
Received 3 October 2003; accep

**1. Introduction**

Natural minerals have been sorption spectroscopic investiga chemical compositions. Genera sition ions such as $Fe^{3+}$, $Cr^{3+}$ a natural minerals. Electron para optical absorption, infrared an minerals provide useful inform istry of transition metal ions erals [1–6]. For most transitio that are present only in small a site), EPR is the most powerful ous information about the vale EPR studies have been perform [7–12].

**5. Conclusions**

1. The preliminary chemical analysis of the Actinolite mineral reveals the presence of iron, manganese, cobalt, nickel and chromium.
2. The EPR spectrum exhibits two resonance signals at $g$ = 2.0 and 4.3. The well resolved hyperfine pattern at $g$ = 2.0 is attributed to $Mn^{2+}$ ions, whereas the resonance signal at $g$ = 4.3 is attributed to $Fe^{3+}$ ions.
3. The magnitude of hyperfine splitting constant $A$ indicates that the bonding between $Mn^{2+}$ and its surrounding ligands is moderately ionic.
4. The temperature variation EPR studies reveal that the variation of number of spins with temperature is in accordance with Boltzmann law. The activation energy has been calculated from log $N$ versus $1/T$ graph and is found to be 0.0082 eV.
5. The variation of susceptibility with temperature is in accordance with the Curie's law. Form the $1/\chi$ versus temperature graph, the Curie constant and the Curie temperature have been evaluated and are found to be 0.175 emu/mol and 77 K, respectively.
6. The optical absorption spectrum reveals the presence of iron both in trivalent and divalent states and also an intervalence charge transfer band ($Fe^{2+}-Fe^{3+}$).
7. The optical band gap energy has been calculated from the ultraviolet absorption edge of the optical absorption spectrum and is found to be 3.14 eV.
8. The infrared spectrum reveals the presence of metal ion hydroxyl vibrations. The Raman spectrum exhibits bands characteristic of the Si–O–Si stretching and Mg–OH translation modes.




he EPR spectra of polycrystalline Actinolite mineral observed at temperatures for the resonance signal at $g$ = 2.0.

# Applications – Minerals

*Radiation Effects & Defects in Solids*
March 2004, Vol. 159, pp. 141–147

## OPTICAL AND EPR INVESTIGATIONS ON SMITHSONITE MINERALS

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*(Received 1 September 2003; In final form 20 January 2004)*

### 1 INTRODUCTION

The mineral smithsonite has the chemical formula $ZnCO_3$. It belongs to the trigonal crystal system with the $D^6_{3d} - R\bar{3}c$ group. It is isostructural with the calcite type with the unit cell parameters $a = 0.466$ nm, $c = 1.498$ nm, $\alpha = 1.625$, $\gamma = 1.850$ and $Z = 6$ [1]. The Zn(II) ions are accordingly in the octahedral coordination of oxygen ions, belonging to the apexes of the triangular anions $[CO_3]^{2-}$ as in the analogous crystals [2]. Transition metal ions such as Cu(II), Mn(II), Fe(II), Co(II) may easily substitute Zn(II). Smithsonite is used as bio-mineral, because it is very effective to eliminate toxins from the body [3] and it is also used as flotation mineral [4]. It has wide applications in the field of microwaves [5]. The present investigations are aimed at having a comprehensive view of the effect of transition metal impurities in the mineral by optical absorption and EPR studies. Two samples of the naturally occurring mineral smithsonite, one from Graphic Mines, Kelly, New Mexico, USA (Sample No. BM 81038) and another from the Westernhope Mine, Weardale, Durham County, UK (Sample No. RV 5/1080) are chosen for the study.

### 5 CONCLUSIONS

From the optical absorption spectra, the main impurity present in the two samples is attributed to a Cu(II) ion in the tetragonally distorted octahedral site suggesting the isomorphous replacement of Cu(II) for Zn(II) in smithsonite. EPR spectra of Cu(II) in these samples support the same conclusion. Further EPR spectra of the samples indicate the presence of Mn(II) in traces. However, the concentration of Mn(II) is too small to exhibit any optical absorption bands.

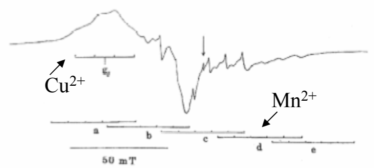


FIGURE 3 EPR spectrum of the USA sample at room temperature. The arrow indicates DPPH signal as a standard. The multiple transitions are designated by a–e.

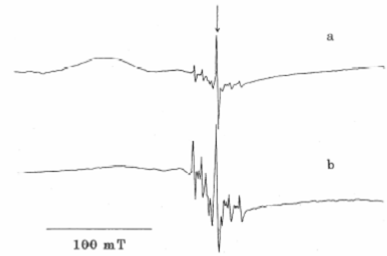


FIGURE 4 EPR spectra of the UK sample at room temperature (a) and 77 K (b). The arrow indicates the DPPH signal as a standard.

# Applications – Minerals

## Electron Paramagnetic Resonance of Rhyolite and $\gamma$-Irradiated Trona Minerals

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Reprint requests to Prof. F. K.; Fax: +90-362-457 6081; E-mail: koksalf@omu.edu.tr

Z. Naturforsch. **58a**, 293 – 298 (2003); received January 2, 2003

### 1. Introduction

Various kinds of stones, geothermal samples and lava systems have been investigated by electron paramagnetic resonance (EPR) [1, 2]. The samples studied were either natural state or in their $\gamma$-irradiated [3 – 14]. These studies revealed the presence of various kinds of sulphur oxy and carboxy radicals in these substances. Around the Erciyes mountain in inner Anatolia, and its neighbouring province Nevşehir, the mostly encountered remnants are various kinds of stones or tuffs. One of these stones is rhyolite, locally named 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 Erciyes, which was active earlier. Due to it is use in house construction, this stone is important in that region. To our knowledge there exists no investigation of this mineral with EPR. Also trona, which is widely used in soda and glass production, seemed interesting to study with EPR. Rhyolite and trona were first studied in their natural states, and then their $\gamma$-irradiated states were considered. Before $\gamma$-irradiation the results indicated the

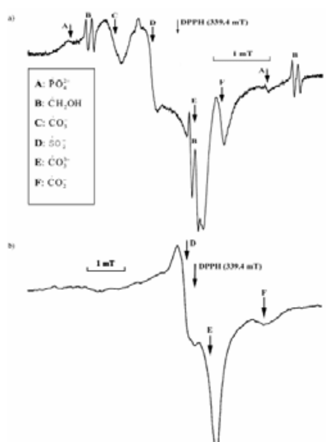


Fig. 2. a) EPR spectrum of rhyolite from the Yellow Stone of Nevşehir at ambient temperature, and b) at 113 K.

# *Applications – Minerals*

**Electron Paramagnetic Resonance of Rhyolite and $\gamma$-Irradiated Trona Minerals**

F. Köksal, R. Köseoğlu[a], and E. Başaran[b]

Physics Department, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey
[a] Physics Department, Faculty of Arts and Sciences, Niğde University, Niğde, Turkey
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Fig. 3. a) Low field part of the EPR spectrum of rhyolite from the "Yellow Stone" at ambient temperature, and b) at 113 K.

# *Applications – Minerals*

**Electron Paramagnetic Resonance of Rhyolite and $\gamma$-Irradiated Trona Minerals**

F. Köksal, R. Köseoğlu[a], and E. Başaran[b]

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Rhyolite from the "Yellow Stone of Nevşehir" and $\gamma$-irradiated trona from the Ankara Mine have been investigated by electron paramagnetic resonance at ambient temperature and at 113 K. Rhyolite was examined by X-ray powder diffraction and found to consist mainly of $SiO_2$. Before $\gamma$-irradiation, the existing paramagnetic species in rhyolite were identified as $\dot{P}O_4^{2-}$, $\dot{C}H_2OH$, $\dot{C}O_3^-$, $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$ free radicals and $Fe^{3+}$ at ambient temperature. At 113 K $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$ radicals and $Fe^{3+}$ were observed. The $\gamma$-irradiation produced neither new species nor detectable effects on these free radicals. The disappearance of some of the radicals at 113 K is attributed to the freezing of their motions. Before $\gamma$-irradiation, the trona mineral shows only $Mn^{2+}$ lines, but after $\gamma$-irradiation it indicated the inducement of $CO_3^{3-}$ and $CO_2^-$ radicals at ambient temperature, 113 K, in addition to the $Mn^{2+}$ lines. The $g$ and $a$ values of the species were determined.

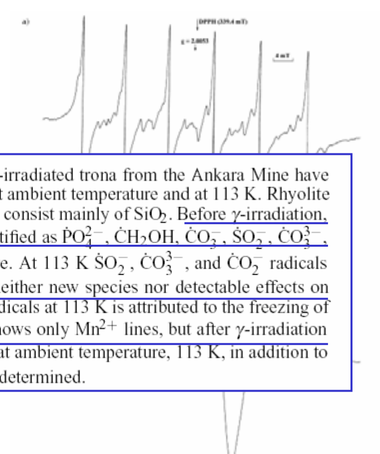


Fig. 4. a) EPR spectrum of trona from the "Ankara Trona Mine" at ambient temperature before the $\gamma$-irradiation, and b) after the $\gamma$-irradiation.

# 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 PARAMAGENTIC RESONANCE

CARBON BASED ELECTRONICS A NATIONAL CONSORTIUM

ELECTRICALLY ACTIVE DEFECTS AND CARRIER TRAPPING IN SEMICONDUCTING DIAMOND

HIGH PRESSURE HIGH TEMPERATURE MATERIALS PR

DIAMOND RESEARCH ON INTERFACES FOR VERSATIL

PhD studentships available for September 2006 - contact Mark

# Applications – Diamonds

J. Phys.: Condens. Matter 14 (2002) 13751–13760 PII: S0953-8984(02)52099-3

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

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### 1. Introduction

The unique physical properties of diamond and the substantial success of high-pressure–high-temperature (HPHT) synthesis of diamond using transition metal solvent/catalysts make this material very attractive for numerous applications, from electronic to mechanical purposes. Depending on the growth conditions and the solvent/catalysts used, these synthetic diamond crystals contain various types of impurity-related defect, that can significantly alter their properties. Therefore, considerable effort is addressed to identify and characterize the different centres found in as-grown and annealed diamonds. The most common of these, nitrogen, is known to be present in isolated substitutional sites, either in the paramagnetic neutral state ($N_s^0$; P1 electron paramagnetic resonance (EPR) centre [1, 2]) or positively charged diamagnetic state [3], and also in aggregated forms (*A* and *B* aggregates [30]), especially after annealing of the crystals. When Ni or Ni alloys are used as solvent catalysts, Ni is incorporated into the diamond lattice in the form of dispersed atoms, giving rise to several EPR and optical spectra. The relative intensities of these signals are dependent on the nitrogen concentration in the sample. Diamonds with higher nitrogen content (>50 ppm) exhibit typically optical centres

with zero-phonon lines (ZPLs) at 1.885 and 2.5 eV [4]. Besides, the well known P1 centre and the single substitutional nickel $Ni_s^-$, which gives rise to the EPR line at $g = 2.0319$ (W8 EPR centre with spin $S = 3/2$ [5]), are also observed. Furthermore, several paramagnetic defects with strong evidence of nickel participation have been found by EPR in recent years [6–13]. Among these centres the AB1–AB6 [6–8] and NE1–NE8 [13] defects are detected in nitrogen-

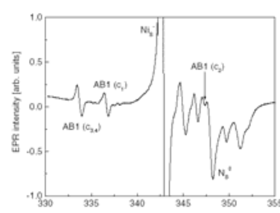


**Figure 2.** X-band ($f = 9.7507$ GHz) EPR spectrum of an as-grown diamond sample from Novosibirsk for $B \parallel \langle 100 \rangle + 66°$ in a {110} crystal plane, obtained at $T = 110$ K and high microwave power.

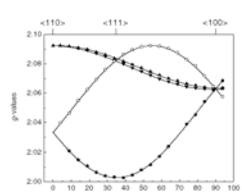


**Figure 3.** Angular dependence of the AB1 (NE4) EPR lines for rotation of the magnetic field *B* in a slightly misaligned {110} crystal plane. The symbols represent the experimental data for the four centre orientations and the solid curves are the angular dependences calculated using the fitted values $g_\parallel = 2.0027$, $g_\perp = 2.0923$. The line splitting (▲, ▼) between both centre orientations perpendicular to the rotation plane is caused by a small misorientation of the ⟨110⟩-rotation axis of $\Delta\theta = 0.3°$, $\Delta\varphi = 1.2°$ ([1.0207, 0.9788, 0.0074]).

# Applications – Diamonds

J. Phys.: Condens. Matter 14 (2002) 13751–13760 PII: S0953-8984(02)52099-3

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

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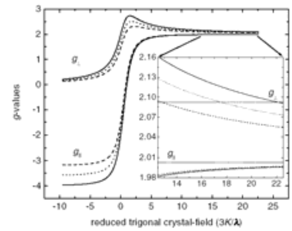


**Figure 4.** Plot of the $g$-values $g_\parallel$ and $g_\perp$ against the reduced trigonal crystal field ($3K/\lambda$) for a $^2T_2$ state resulting from a $d^9$ configuration in a nearly tetrahedral environment for different orbital quenching factors $k$. Contributions from the excited $^2E$ state and outside the $^2E+^2T_2$ manifold are ignored. Appropriate for a single $d^9$ hole the spin-orbit parameter $\lambda$ has been taken to be negative.

### 4. Conclusions

The EPR spectrum of the trigonal NE4 centre, which has been observed in as-grown and annealed synthetic HPHT diamond crystals grown by the split-sphere technique [15] by Nadolinny *et al* [11, 12], was never detected in as-grown and annealed HPHT diamond samples synthesized at the NIRIM [9]. A re-analysis of the published data has led to a more accurate determination of the spin Hamiltonian parameters describing the anisotropy of the NE4 EPR spectrum. The analysis clearly indicates that the latter spectrum is in fact due to the trigonal AB1 centre. Such inference could be confirmed by EPR studies of synthetic diamonds with the same origin as the crystals at which the NE4 EPR spectrum has been detected. The proof of the identity of the AB1 and NE4 centres also corroborates the proposed assignment of the doublet of lines at 1.72 eV found by ODEPR (MCDA) investigations to AB1 paramagnetic defects. The calculation of the $g$-values within the framework of crystal-field theory shows that among the proposed models for the AB1 (NE4) centre only the models of a nickel ion at the centre of the double semivacancy $(C_3VNiVC_3)^-$ with a $d^5$ ($t_{2g}^5$) configuration in a trigonal distorted strong octahedral field and of substitutional nickel $Ni_s^+$ ($3d^9$) with an associated defect (vacancy or an impurity ion) can explain the experimental $g$-values.

# Applications – Diamonds

J. Phys.: Condens. Matter 15 (2003) 2493–2505 PII: S0953-8984(03)57431-8

## Photoexcitation electron paramagnetic resonance studies on nickel-related defects in diamond

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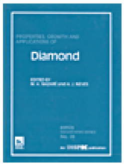
**Abstract**

Measurements of the electron paramagnetic resonance (EPR) upon photoexcitation are reported on Ni defects in diamonds grown with Ni-containing solvent/catalysts. The temperature dependence of the W8 EPR spectrum photoquenching shows that the relaxation of substitutional $Ni_s^-$ upon electron ionization is very small, corroborating the interpretation that the previously reported photoinduced effects with thresholds at 2.5 and 3.0 eV correspond to two complementary photoionization transitions involving $Ni_s$. Photoinduced behaviour of the NIRIM1 EPR centre favours the interstitial $Ni_i^+$ model for this defect and suggests that the $Ni_i^{0/+}$ level is located at 1.98±0.03 eV below the conduction band. In N-doped diamond, $Ni_i$ is more likely to appear in the neutral state, undetectable by EPR, whereas at substitutional sites $Ni_s^-$ is revealed. Observation of a strong AB2 EPR signal photoquenching and simultaneous detection of different spectral dependencies of the EPR intensity for other defects determine an electron photoionization energy of 1.67±0.03 eV

# 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

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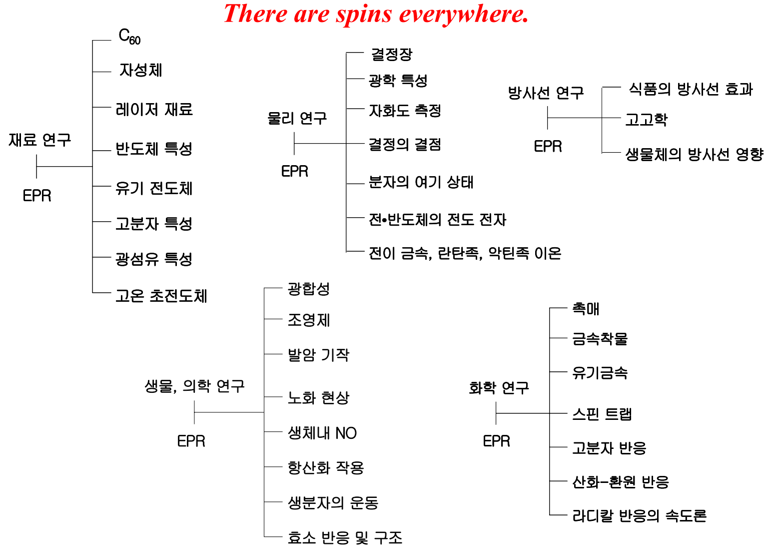
A7. Properties of Defects in Diamond: Vacancy and Self-Interstitial

A7.2 Theory of the Self-Interstitial in Diamond

# Applications

***There are spins everywhere.***



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