ESR spectroscopy of catalytic systems - a primer

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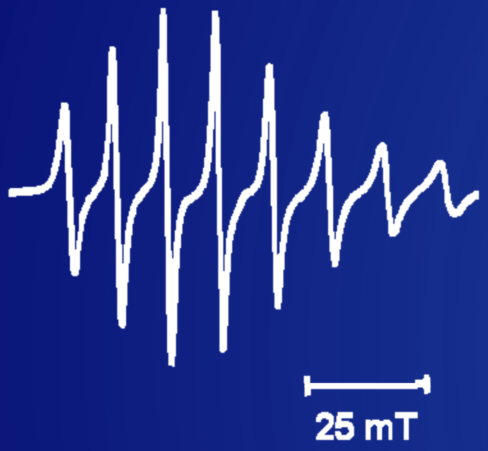
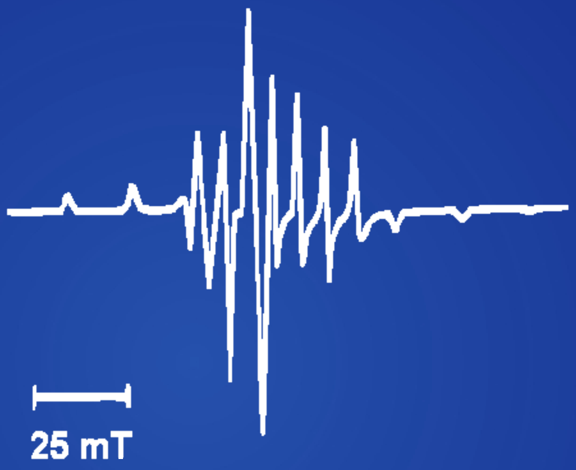
ESR spectroscopy

Solid vs. solution

Colloidal solution of nanoparticles
(in water at 300 K)



Colloidal solution of nanoparticles
(in ice at 120 K)



- What is the nature of the paramagnetic center?
- Which interactions determine the observed spectra?
- Where does the difference between solution and solid come from?

Outline:

- Introduction
- Magnetic interactions of an unpaired electrons
    - Zeeman interaction
    - interactions with other electron spins (group spins and zero field splitting)
    - hyperfine interaction
- dynamics and line shape
- experimental aspects
- transition metal ions
    - electronic states and spin orbit coupling
    - ions in crystal or ligand fields
    - some examples (Ti^{3+},VO^{2+} (d^1), Mn^{2+} (d^5), Co^{2+} (d^7), Cu^{2+} (d^9))

Introduction

references

ESR spectroscopy

J.A. Weil, J.R. Bolton, J.E. Wertz, *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*, Wiley, New York, 1994.

N.M. Atherton *Principles of Electron Spin Resonance*, Ellis Horwood, New York 1993.

W.Gordy, *Theory and Applications of Electron Spin Resonance*, Wiley, New York, 1980.

A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Dover Publ. 1970.

Practical Aspects

C.P. Poole, *Electron Spin Resonance*, Dover, Mineola, 1996.

Basics of Magnetic Resonance

C. P. Slichter *Principles of Magnetic Resonance*, Springer Series in Solid State Sciences, 3rd Ed., Springer, Berlin, 1996.

R.R. Ernst, G. Bodenhausen and A.Wokaun, *Principles of NMR in one and two Dimensions*, Oxford University Press, Oxford, 1993.

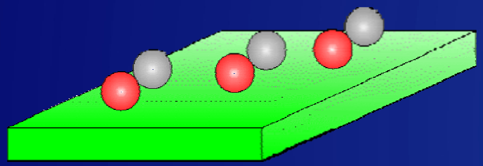
A. Abragam, Principles of Nuclear Magnetic Resonance, Clarendon, Oxford, 1983.

Introduction

What kind of systems?

molecules, atomic species:

(diamagnetic)
paramagnetic



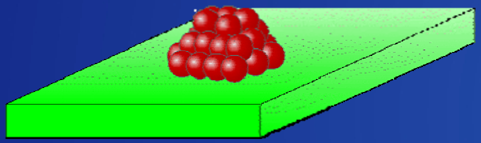
radicals: NO, O_2, NO_2

reaction intermediates

transition metal ions

metals:

(diamagnetic)
paramagnetic
ferromagnetic
antiferromagnetic

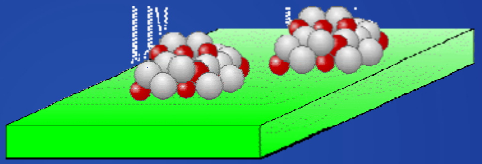


usually ferromagnetic metals e.g. Fe, Co, Ni

conduction band ESR for small particles

compounds:

(diamagnetic)
paramagnetic
ferromagnetic
antiferromagnetic



e.g. oxides, nitrides
defects

ESR spectroscopy

Zeeman interaction

Interaction of an angular momentum with a magnetic field:

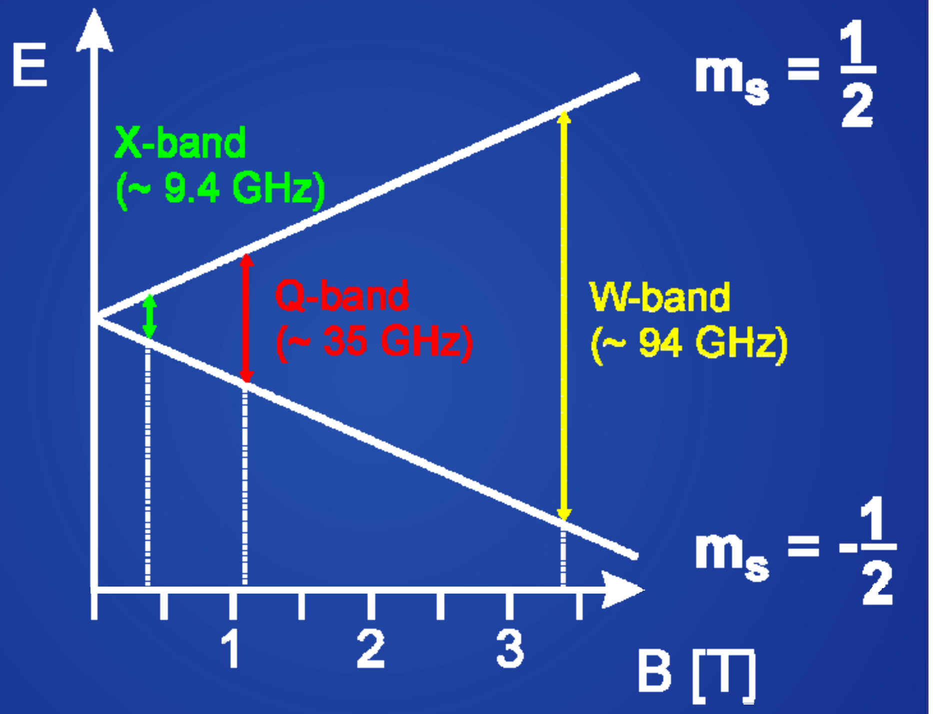
classically: $E = - \underline{\mu}\ \underline{\mathbf{B}}$

translation to QM $H = \mu_B\, g\, \underline{\mathbf{J}}\ \underline{\mathbf{B}}$

if field is in z-direction: $H = \mu_B\, g\, J_z\, B_0$

eigenvalues: $E = \mu_B\, g\, B_0\, M_J$

for $M_J = \pm 1/2$: $\Delta E = h\nu = \mu_B\, g\, B_0$



ESR spectroscopy

Zeeman interaction

isotropic case: $H = \mu_B\, g\, \underline{\mathbf{J}}\, \underline{\mathbf{B}}$

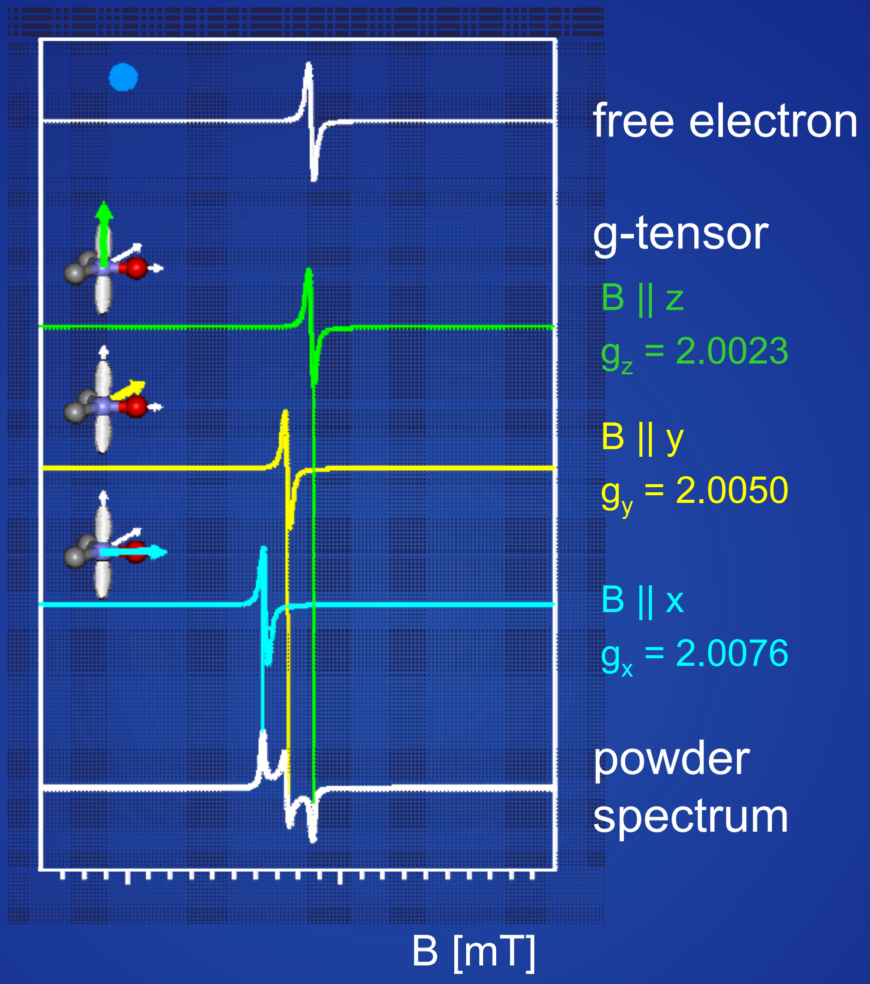
anisotropic case: $H = \mu_B\, \underline{\mathbf{J}}\, \underline{\boldsymbol{g}}\, \underline{\mathbf{B}}$

g is a symmetric (3x3) matrix
=> always possible to diagonalize
principal components g_x, g_y, g_z

eigenvalues: $E = \mu_B\, g(\theta,\phi)\, B_0\, m_J$

with: $g(\theta,\phi) = [\, \sin^2(\theta) \cos^2(\phi)\, g_x^2 + \sin^2(\theta) \sin^2(\phi)\, g_y^2 + \cos^2(\theta)\, g_z^2]^{1/2}$

θ and ϕ describe the orientation of the static magnetic field in the g-matrix coordinate system



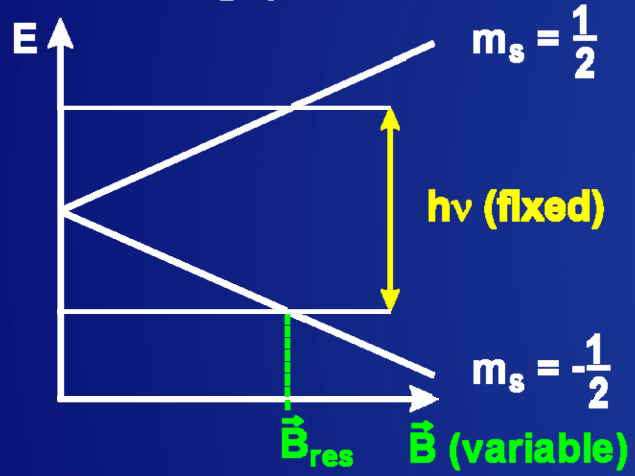
ESR spectroscopy

hyperfine interaction

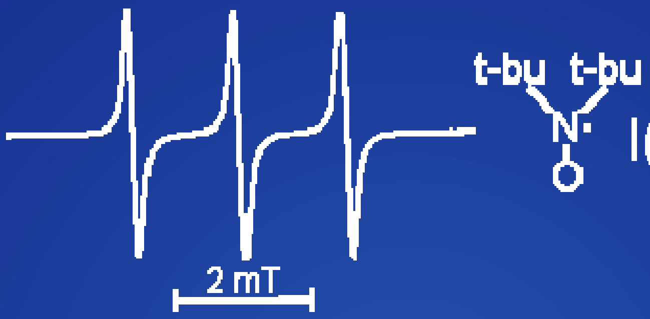
Max-Planck-Gesellschaft

isotropic case

$$H = \mu_B g_e \vec{S}\vec{B}$$

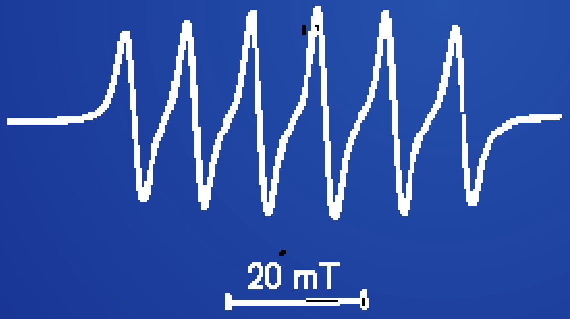


DTBN in toluene (300 K)



$I(^{14}N) = 1$

$MnCl_2$ in water (300 K)



Mn^{2+} I = 5/2

reason: hyperfine interaction; (2I+1)-states

ESR spectroscopy

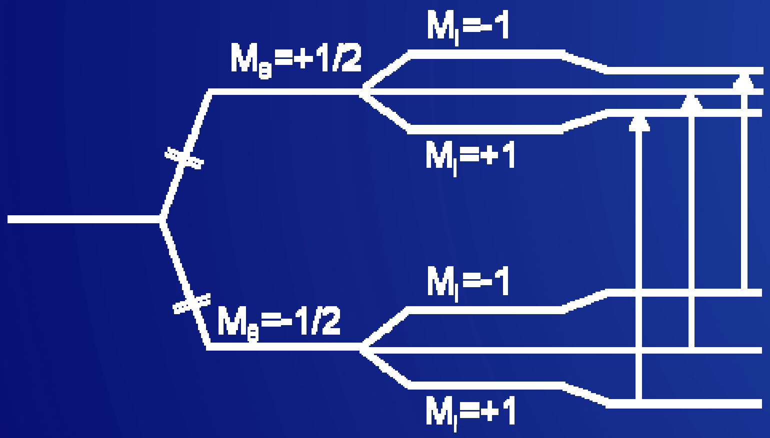
hyperfine interaction

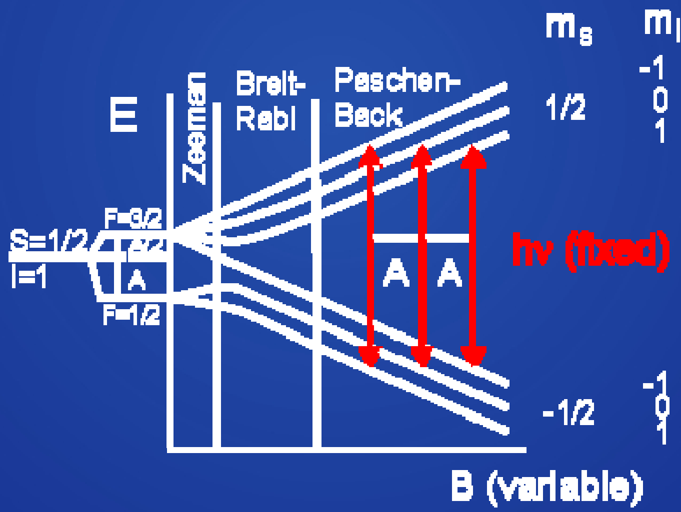
What is hyperfine interaction?

interaction of an electron spin with a nuclear spin

isotropic, high field case

$$H = \underbrace{\mu_B\, g\, S_z\, B_0}_{\text{el. Zeeman}} - \underbrace{\gamma_n\, B_0\, I_z}_{\text{nuc. Zeeman}} + \underbrace{a_{iso}\, I_z\, S_z}_{\text{hyperfine interaction}}$$





ESR spectroscopy

hyperfine interaction

in general: two contributions

1. dipole-dipole interaction:

$$H = \underline{S}\,\boldsymbol{T}\,\underline{I}$$

T is the anisotropic interaction matrix

traceless => integral over a sphere vanishes

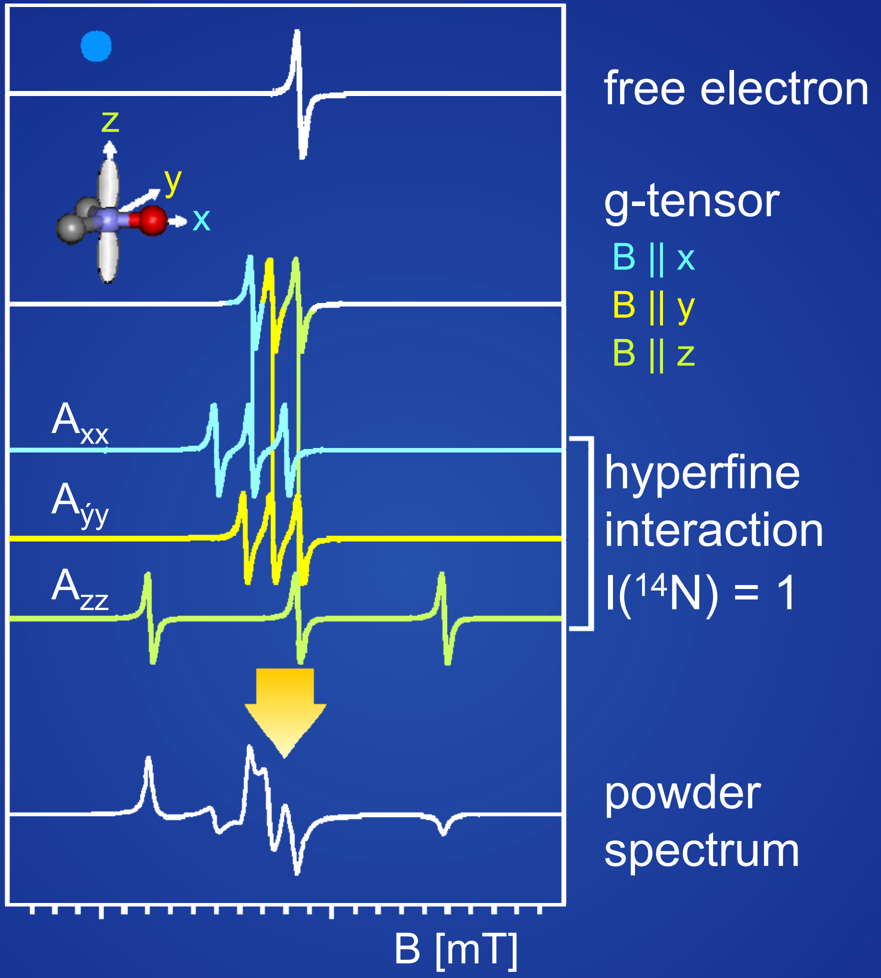
2. Fermi-contact interaction:

$$H = a_{iso}\,\underline{S}\,\underline{I}$$

isotropic, depend on the probability to find an electron at the position nucleus

$$H_{hfi} = \underline{S}\,\boldsymbol{A}\,\underline{I}$$

with $\boldsymbol{A} = \boldsymbol{T} + a_{iso}\,\mathbf{1}$ $\mathbf{1}$: unit matrix



ESR spectroscopy

hyperfine interaction

Max-Planck-Gesellschaft

Solution:

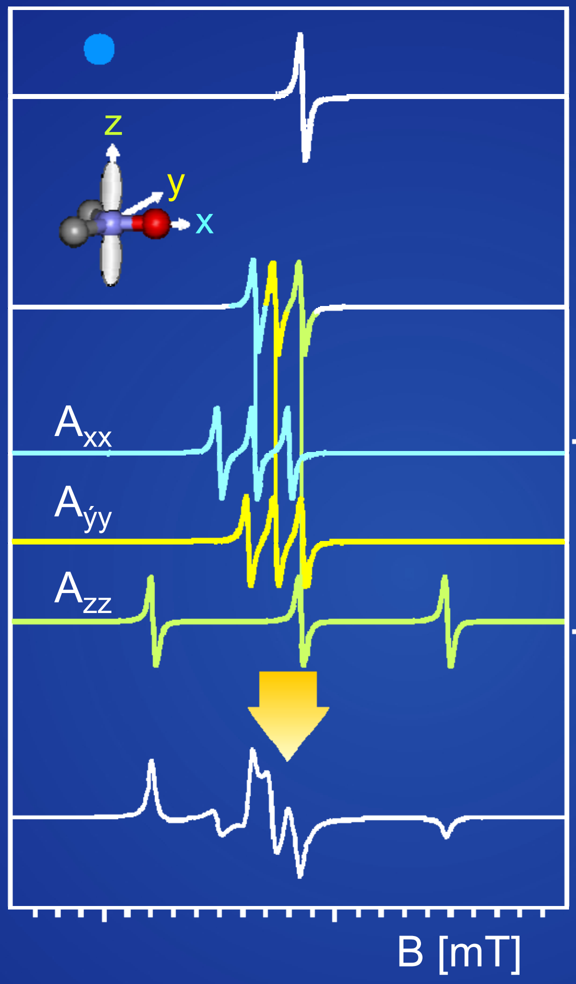
1. High field approximation:

($m_s = \pm ½$)

$$E(\theta,\phi) = \pm ½ g(\theta,\phi)\mu_B B \pm ½ m_I A(\theta,\phi)$$

with: $$g(\theta,\phi) = [\ \sin^2(\theta)\cos^2(\phi)\, g_x^2 + \sin^2(\theta)\sin^2(\phi)\, g_y^2 + \cos^2(\theta)\, g_z^2]^{1/2}$$

$$A(\theta,\phi) = [\ \sin^2(\theta)\cos^2(\phi)\, A_x^2 + \sin^2(\theta)\sin^2(\phi)\, A_y^2 + \cos^2(\theta)\, A_z^2]^{1/2}$$



free electron

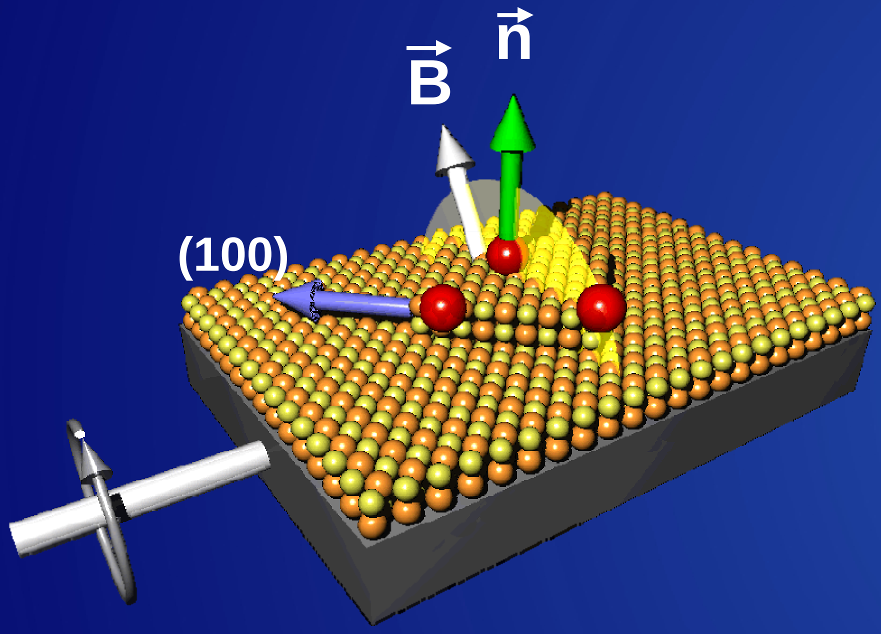
g-tensor
B || x
B || y
B || z

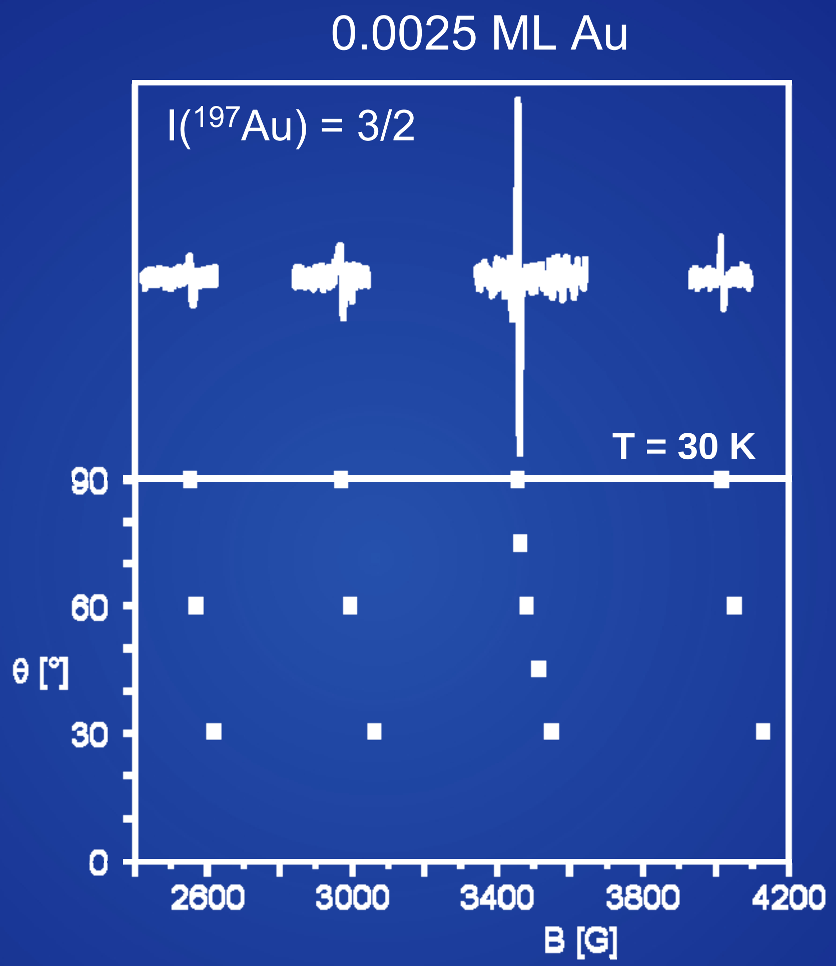
hyperfine interaction $I(^{14}N) = 1$

powder spectrum

MgO(001)/Mo(001)

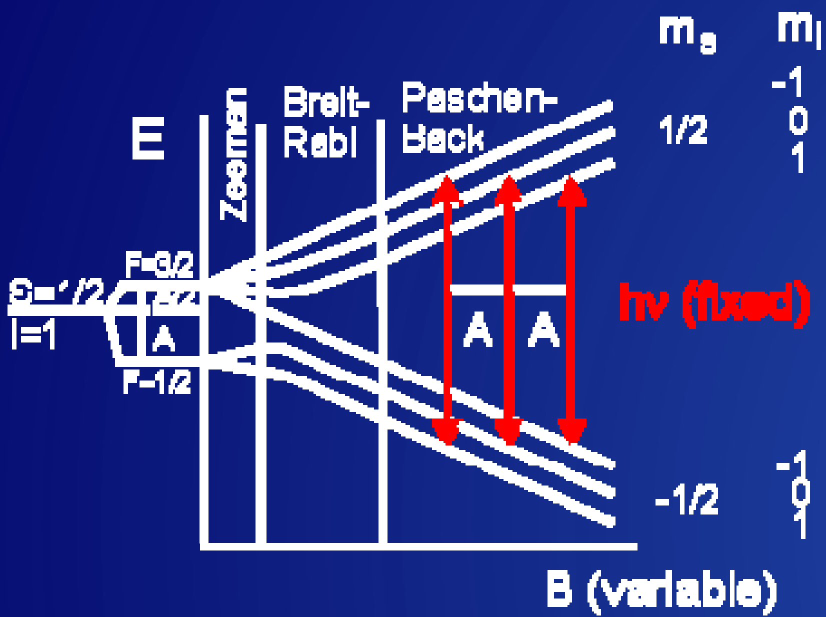
EPR of Au atoms

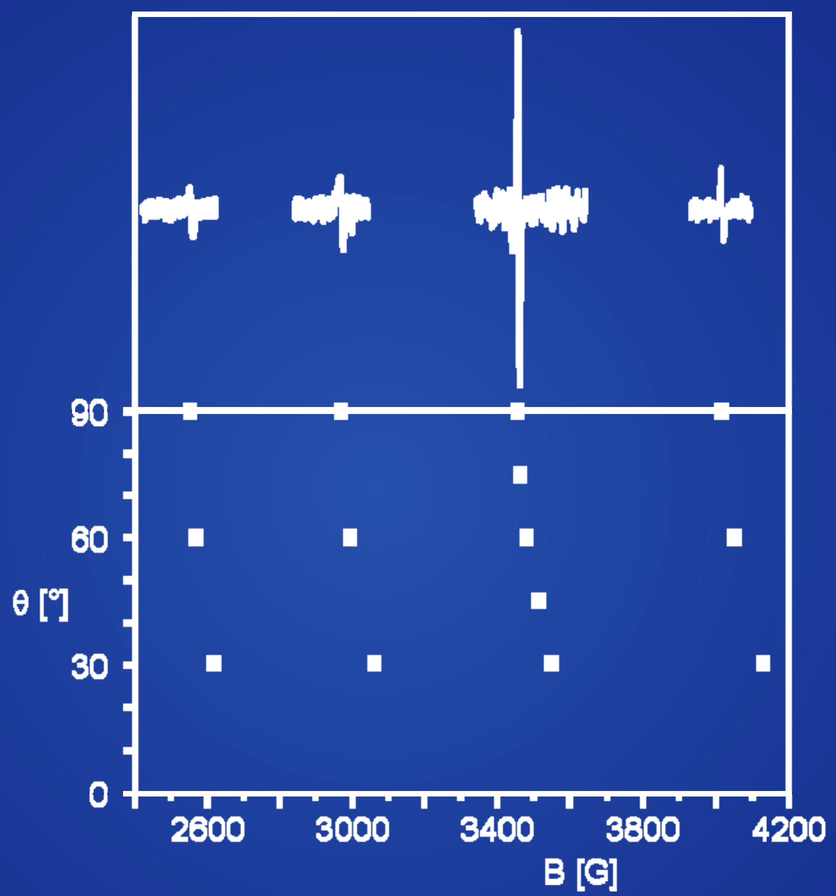




MgO(001)/Mo(001)

EPR of Au atoms





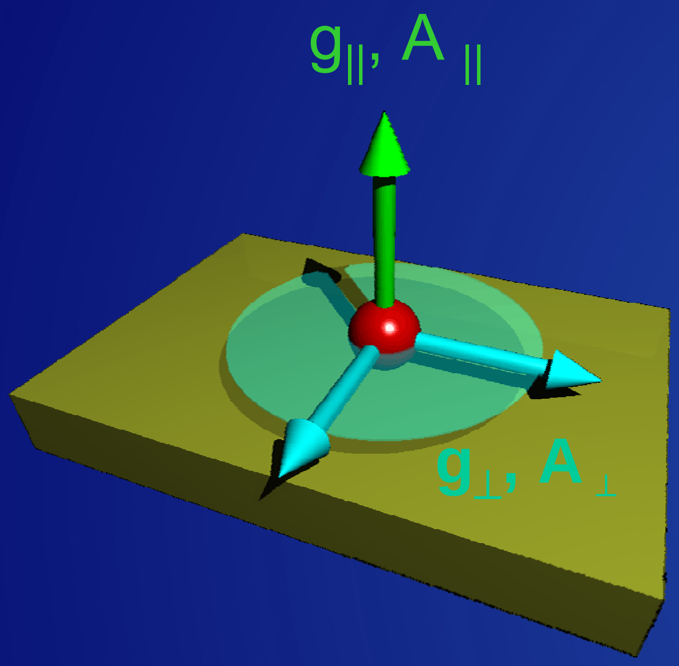
High limit inappropriate

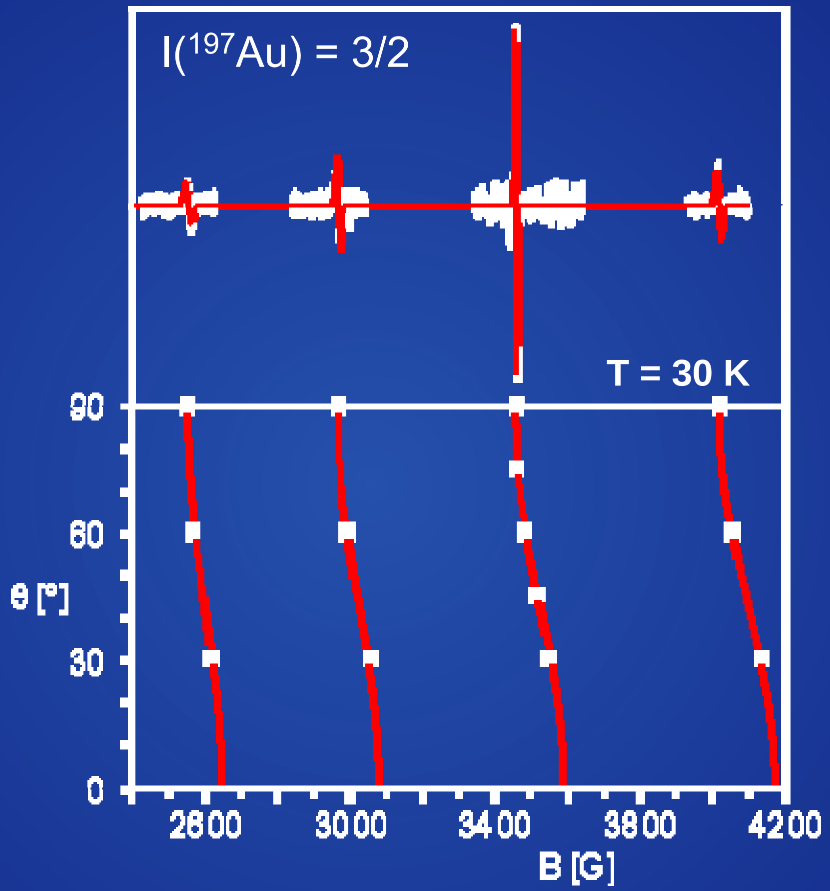
hyperfine interaction only factor 4 smaller than Zeeman interaction

=> Breit Rabi region

MgO(001)/Mo(001)

EPR of Au atoms





$g_{||}$ = 1.9904

$A_{||}$ = 1410 MHz

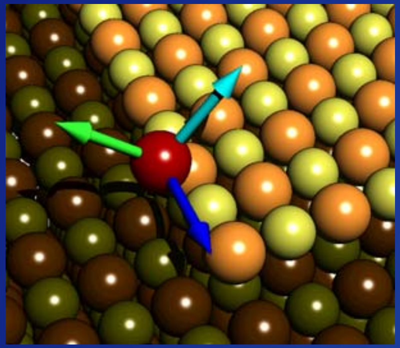
$g_{\perp}$ = 2.0652

$A_{\perp}$ = 1402 MHz

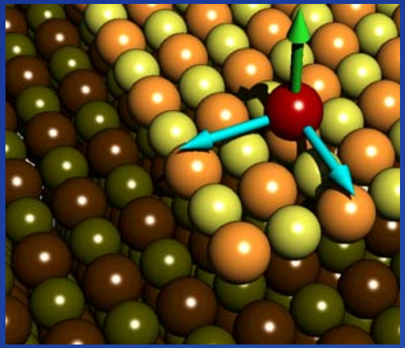
MgO(001)/Mo(001)

EPR of Au atoms

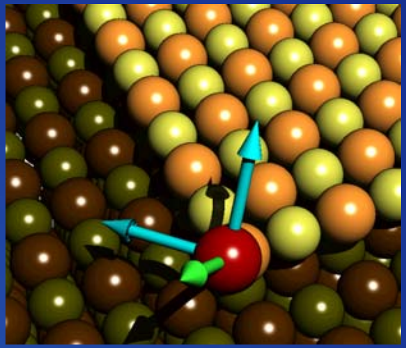
edge

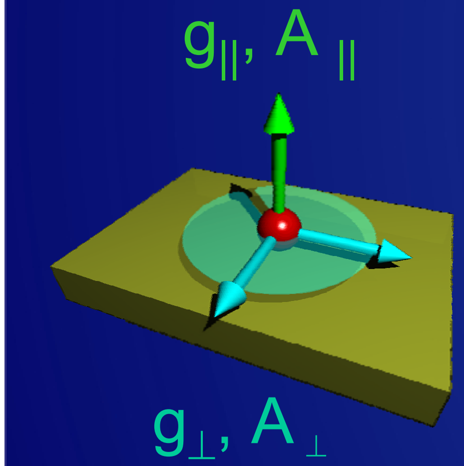


terrace



corner





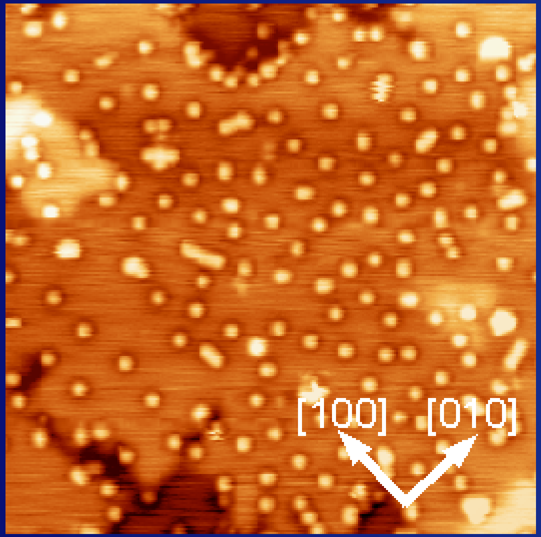
From symmetry considerations:

=> Au atoms nucleate on terrace sites

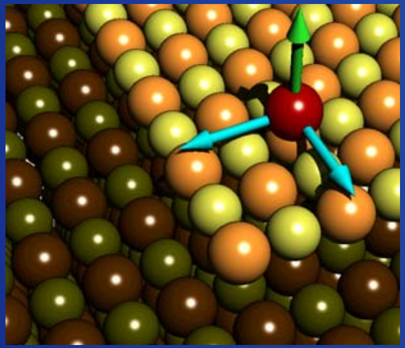
Au on MgO(001) films

Comparison EPR and STM

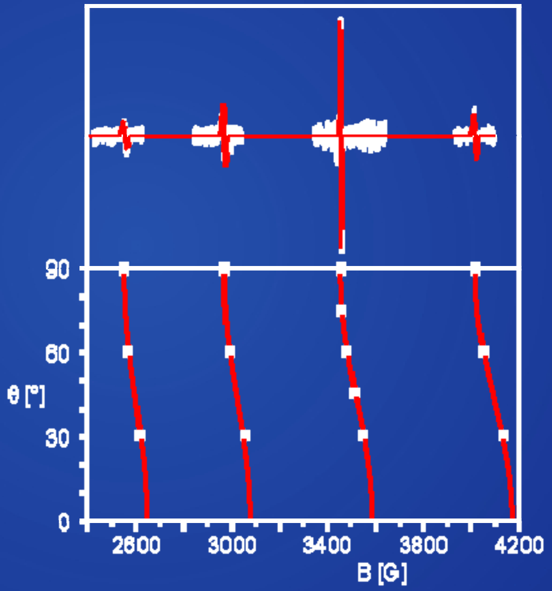
6 ML MgO(001)/Ag(001)
+ 0.005 ML Au



terrace



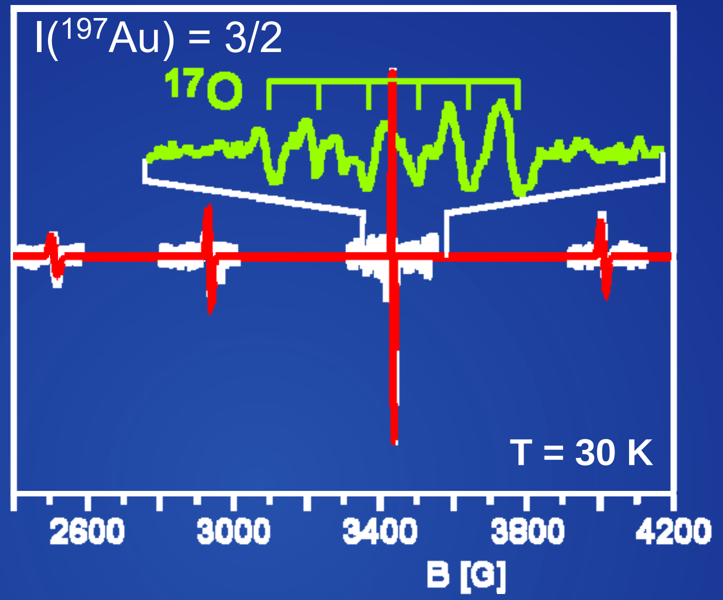
20 ML MgO(001)/Mo(001)
0.0025 ML Au



MgO(001)/Mo(001)

EPR of Au atoms

surface



interaction to one oxygen in the MgO lattice:

=> on-top of oxygen

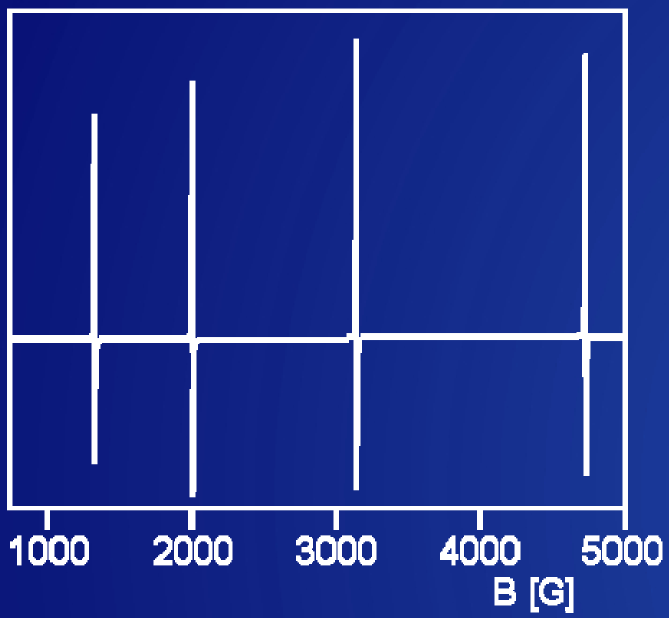
M. Yulikov et al. Phys. Rev. Lett. **96**, 146804 (2006).

MgO(001)/Mo(001)

EPR of Au atoms

Max-Planck-Gesellschaft

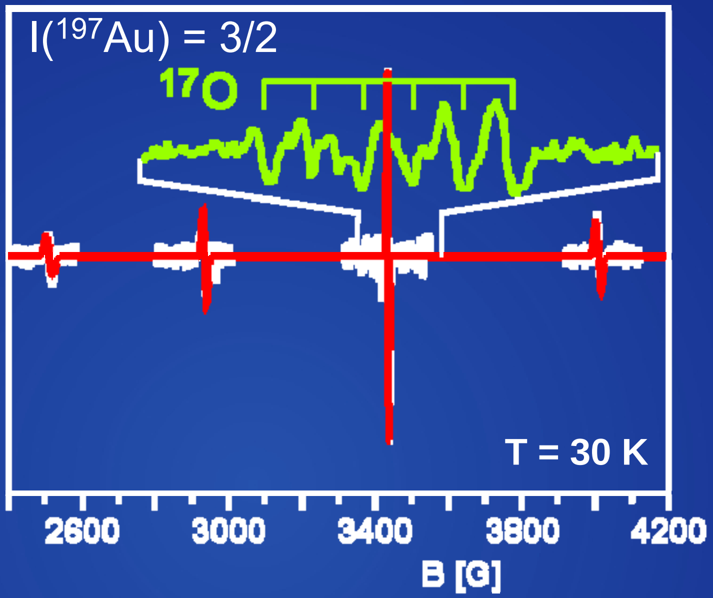
Ne-matrix[1]



a_{iso} = 3136 MHz

T_{dip} = 1.9 MHz

surface



a_{iso} = 1405 MHz

T_{dip} = 2.7 MHz

$A_{\perp}$ (^{17}O) = 56 MHz

[1] P. H. Kasai and J. D. McLeod, J. Chem. Phys. **55**, 1566 (1971).

MgO(001)/Mo(001)

EPR of Au atoms

Isotropic hyperfine constant

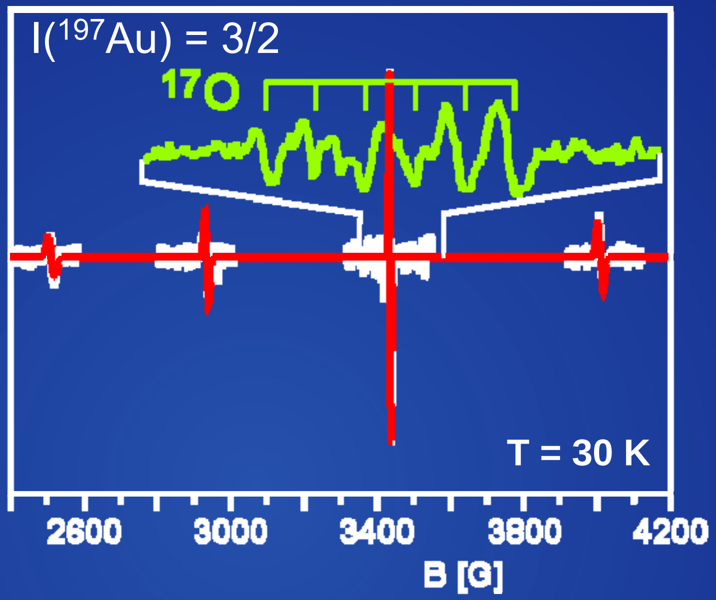
=> Fermi-contact interaction:

depend on the probability to find an electron at the position nucleus

Question:

Why is the spin density at the nucleus reduced as compared to the matrix?

surface



a_{iso} = 1405 MHz

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MgO(001)/Mo(001)

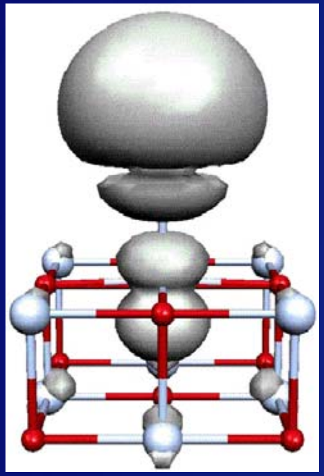
EPR of Au atoms

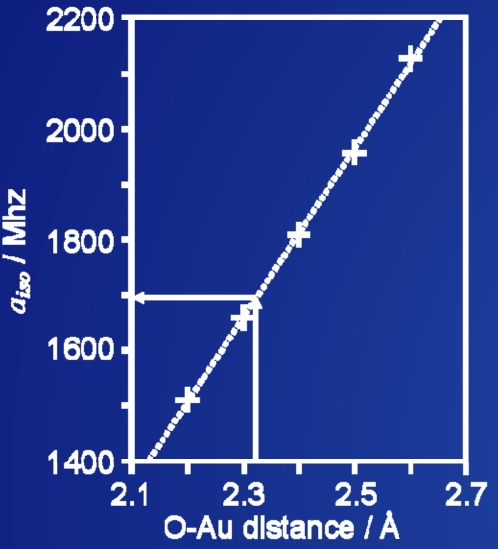
Max-Planck-Gesellschaft

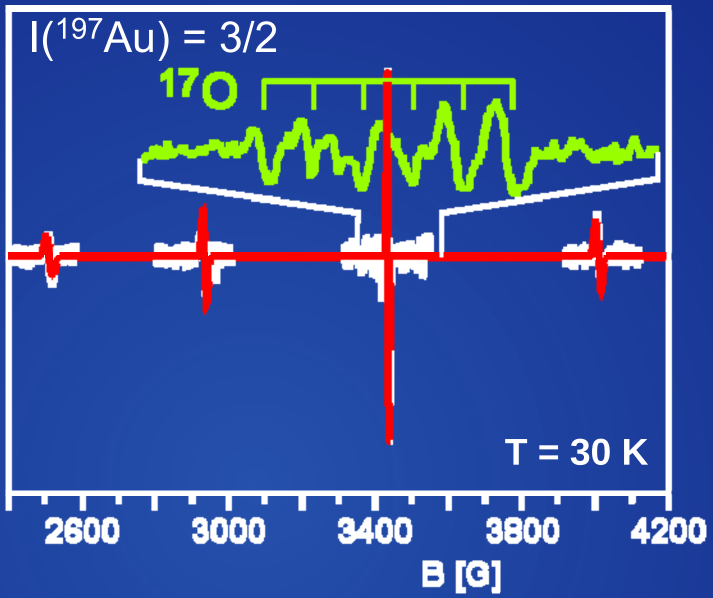
Theory

Experiment

spin density[1]







a_{iso} = 1704 MHz

T_{dip} = 7.3 MHz

$A_{\perp}$ (^{17}O) = -46 MHz

Result:

No electron transfer;
essentially neutral Au atoms

a_{iso} = 1405 MHz

T_{dip} = 2.7 MHz

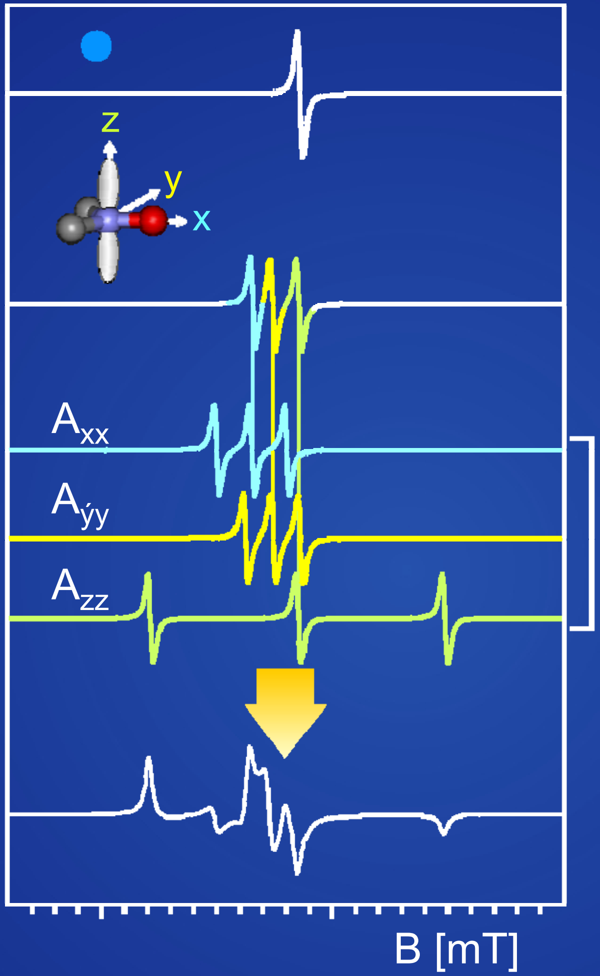
$A_{\perp}$ (^{17}O) = 56 MHz

[1] A. Del Vitto et al., J. Phys. Chem. B **109**, 8040 (2005).

M. Yulikov et al. Phys. Rev. Lett. **96**, 146804 (2006).

ESR spectroscopy

basic considerations



free electron

g-tensor

B || x

B || y

B || z

hyperfine interaction $I(^{14}N) = 1$

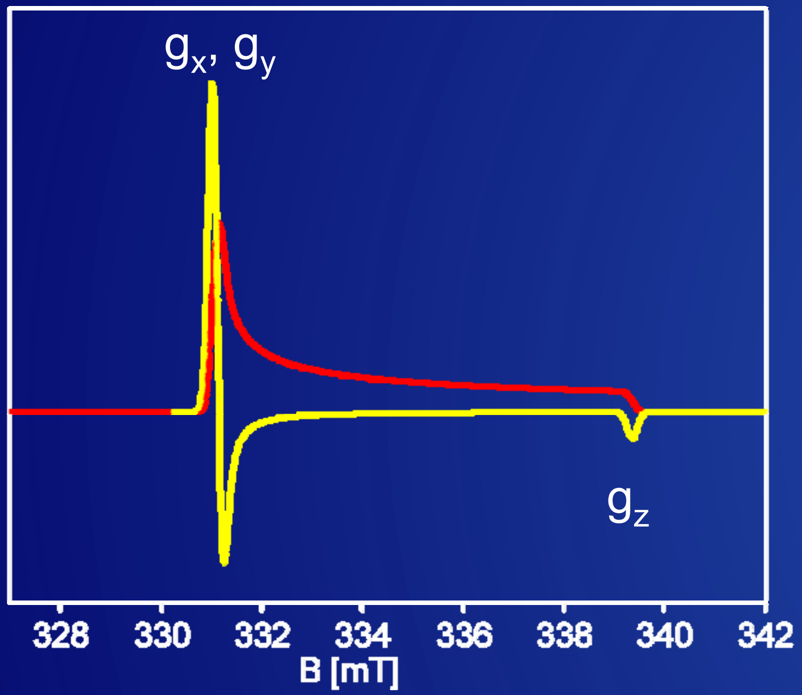
powder spectrum

ESR spectroscopy

line shapes for powders

Max-Planck-Gesellschaft

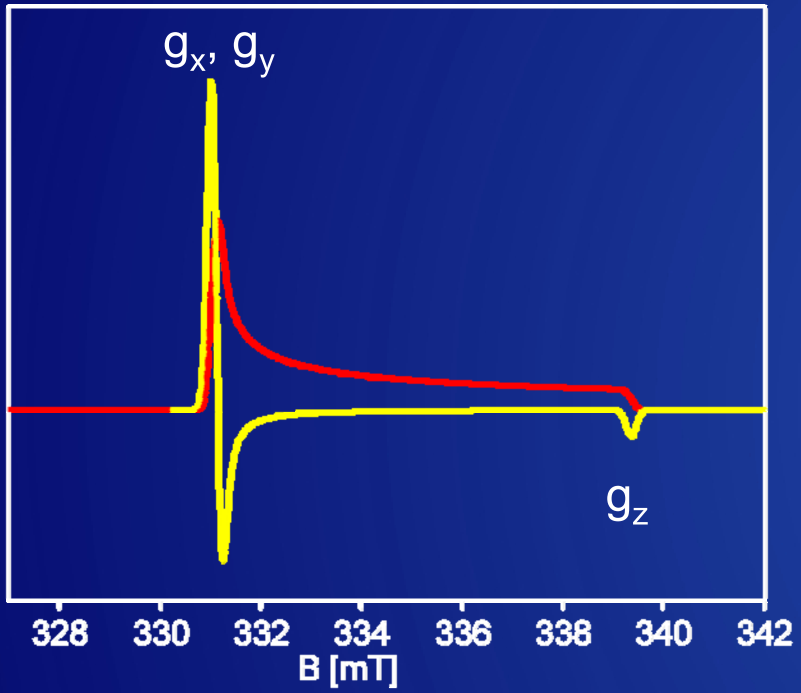
axial g matrix ($g_x = g_y \neq g_z$)



ESR spectroscopy

line shapes for powders

axial g matrix ($g_x = g_y \neq g_z$)



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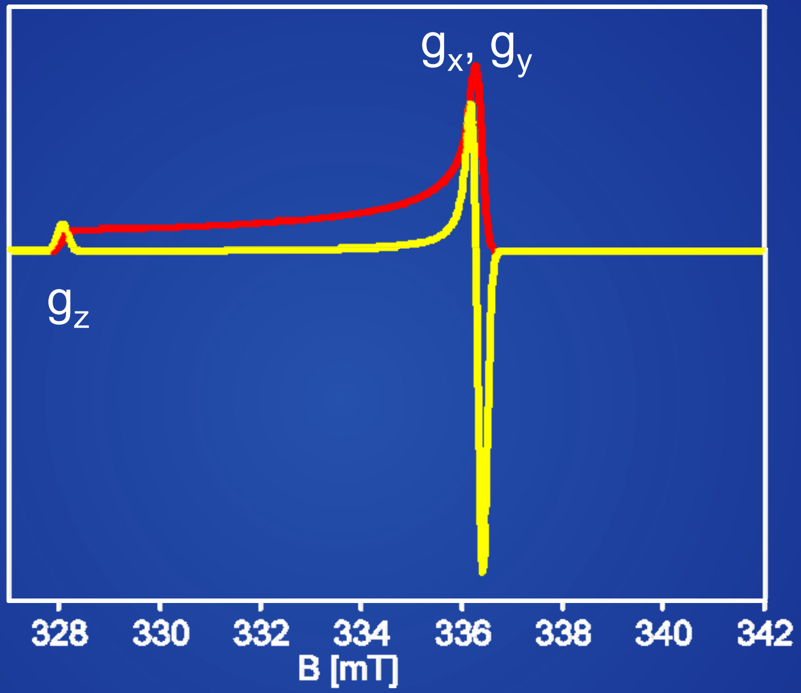
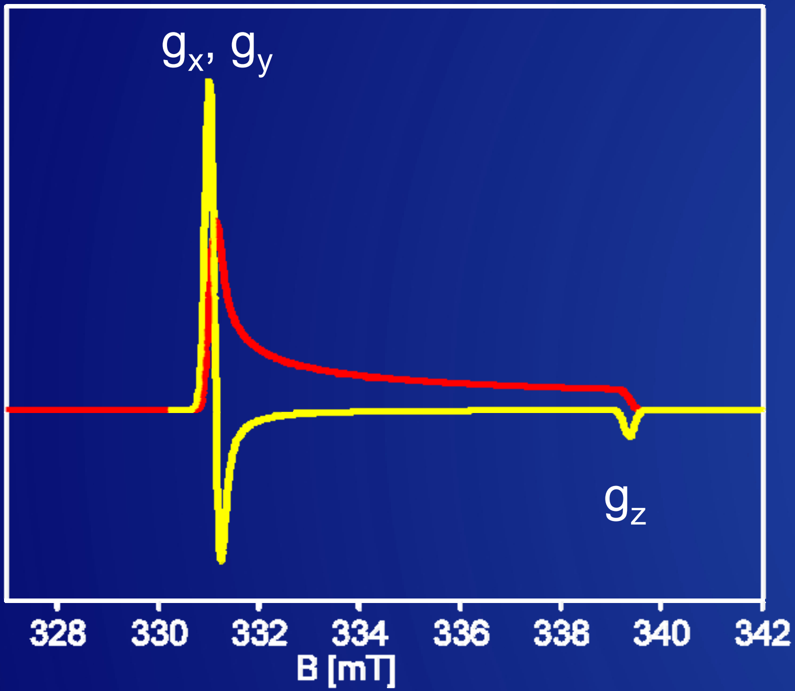


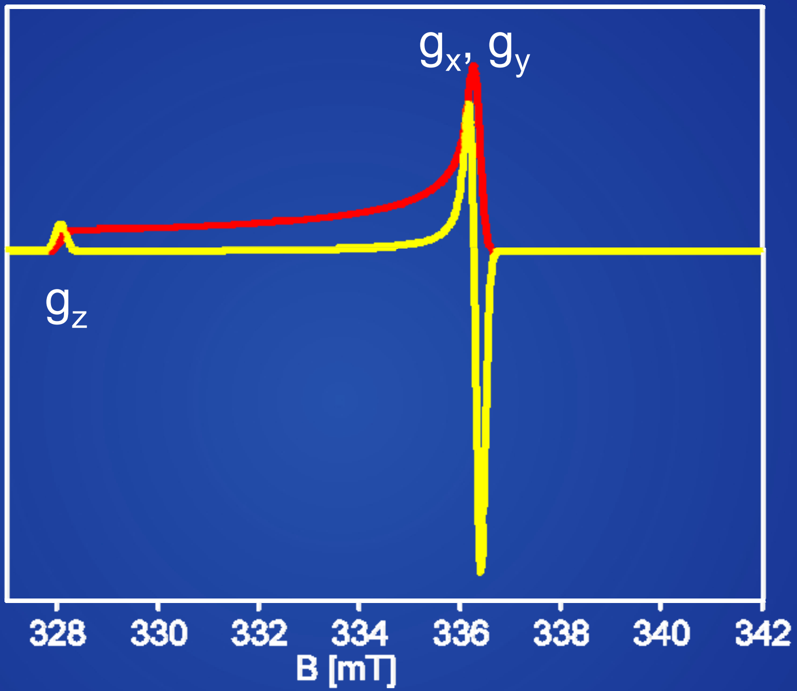
ESR spectroscopy

line shapes for powders

axial g matrix ($g_x = g_y \neq g_z$)



axial g matrix ($g_x = g_y \neq g_z$)



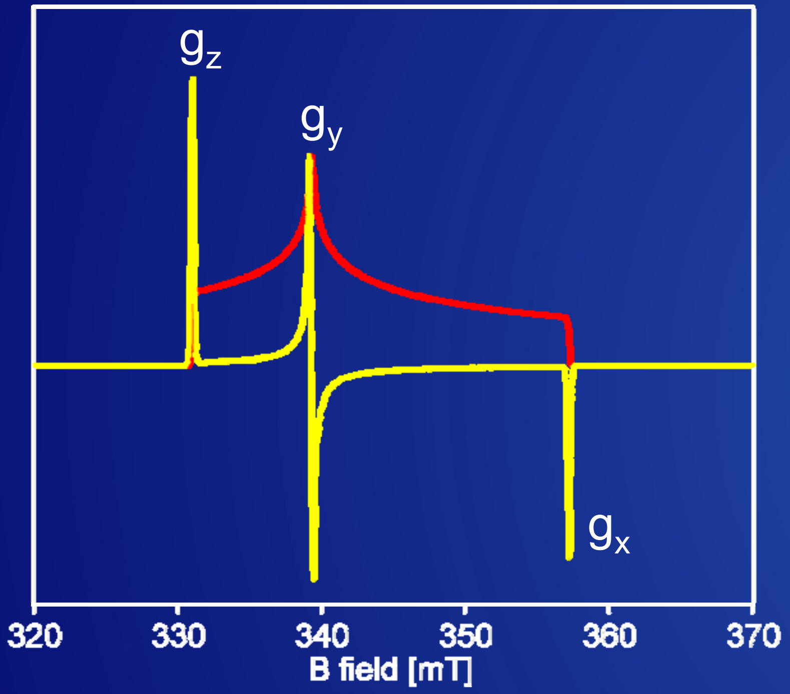
ESR spectroscopy

line shapes for powders

Max-Planck-Gesellschaft

orthorhombic g matrix

$(g_x \neq g_y \neq g_z)$

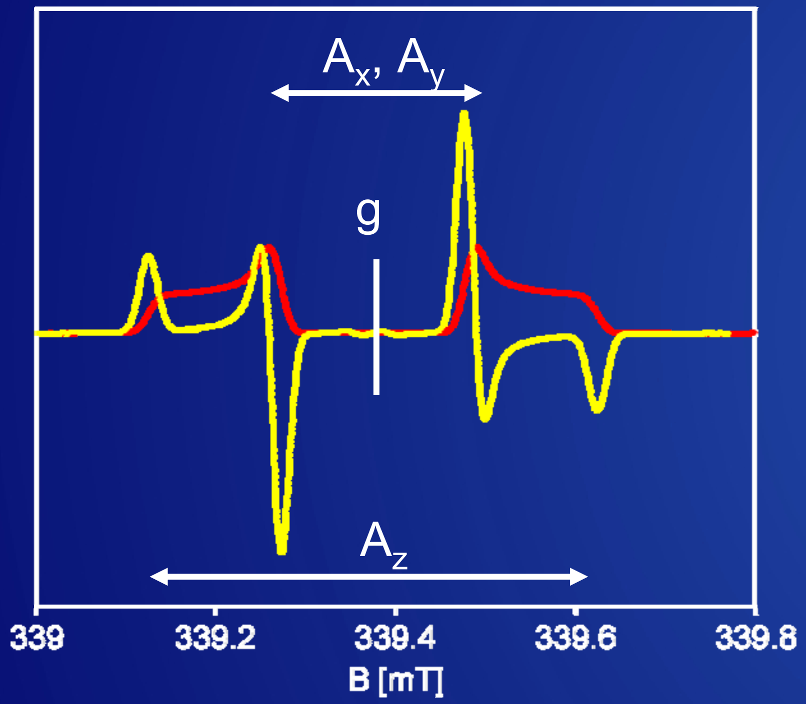


ESR spectroscopy

line shapes for powders

isotropic g

axial A matrix ($A_x = A_y \neq A_z$)

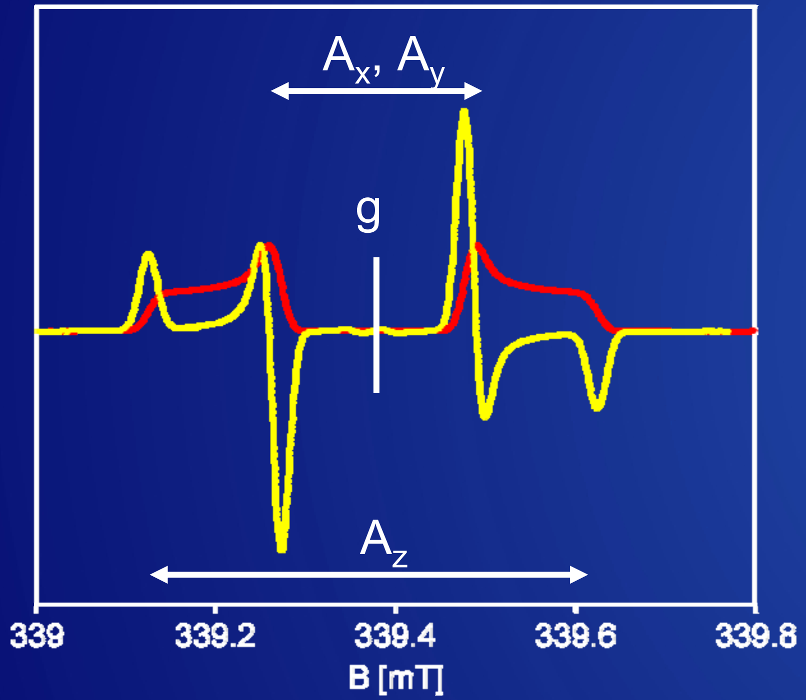


ESR spectroscopy

line shapes for powders

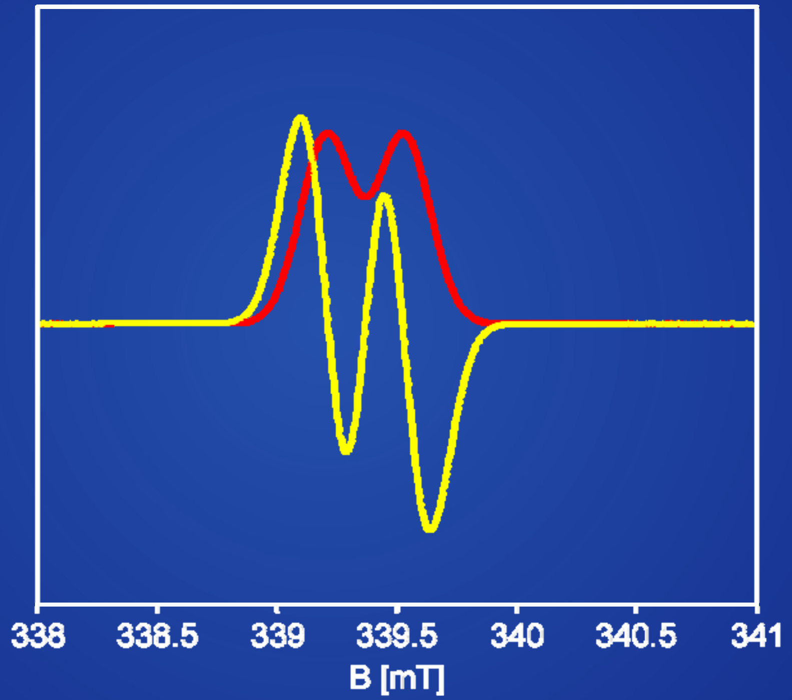
isotropic g

axial A matrix ($A_x = A_y \neq A_z$)



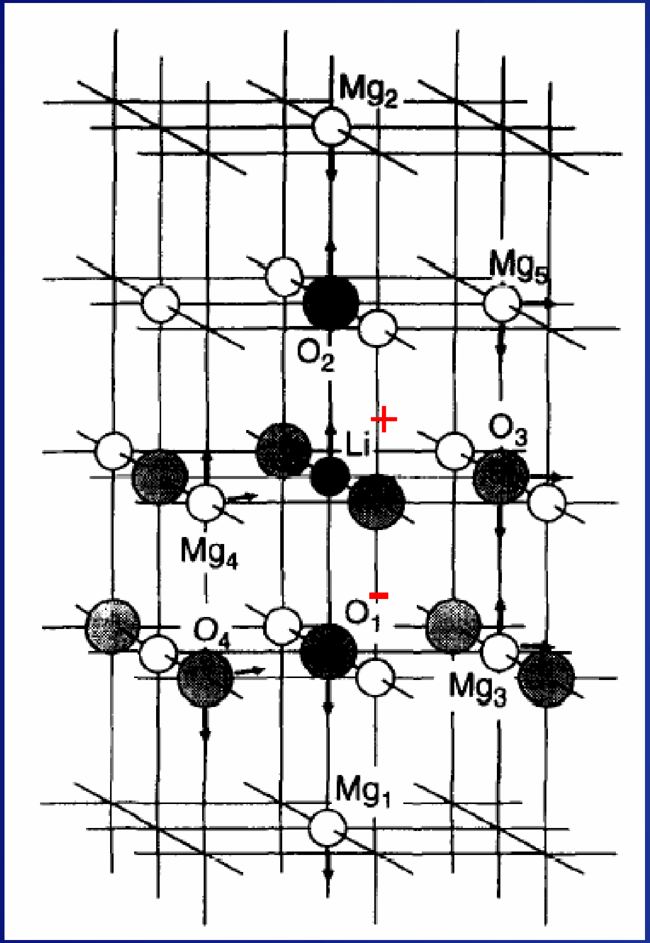
Same g and A parameter

BUT linewidth x10



Li in MgO

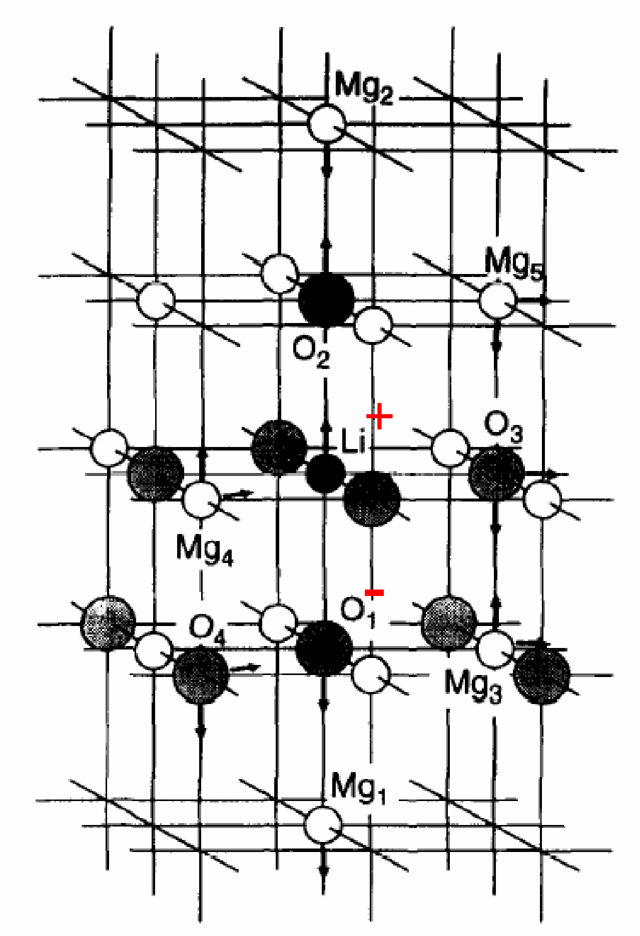
a simple example



What to expect?

Li in MgO

a simple example



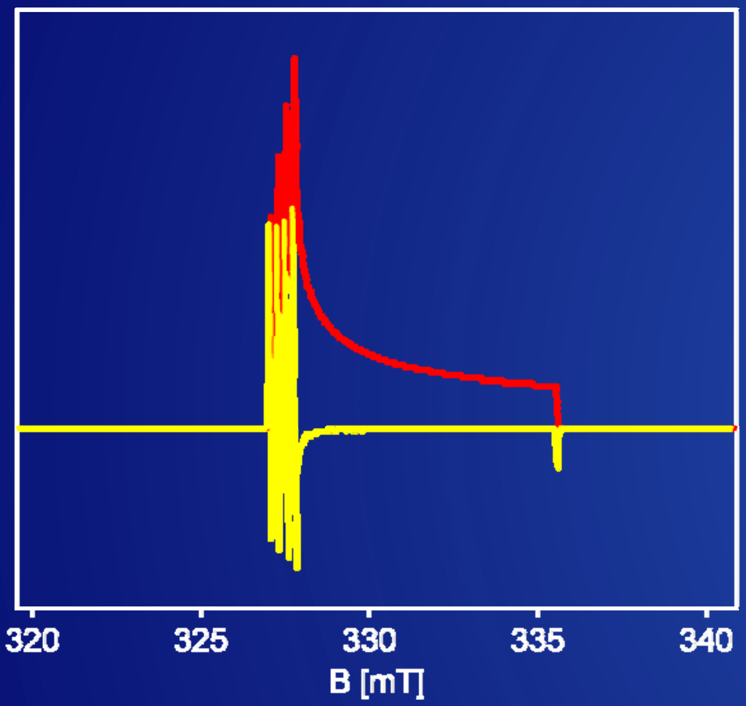
What to expect?

- paramagnetic signal from an O^- species
- local c_4 axis => axial g-tensor
- hyperfine coupling to 1 Li ion (I = 5/2) => 6 lines
- local c_4 axis => axial A-tensor

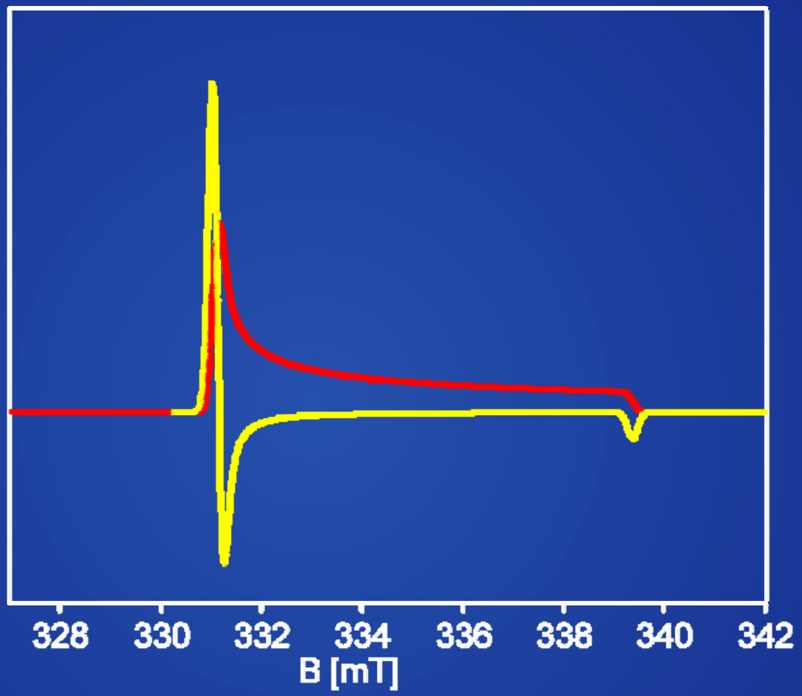
Li in MgO

a simple example

axial g + axial A



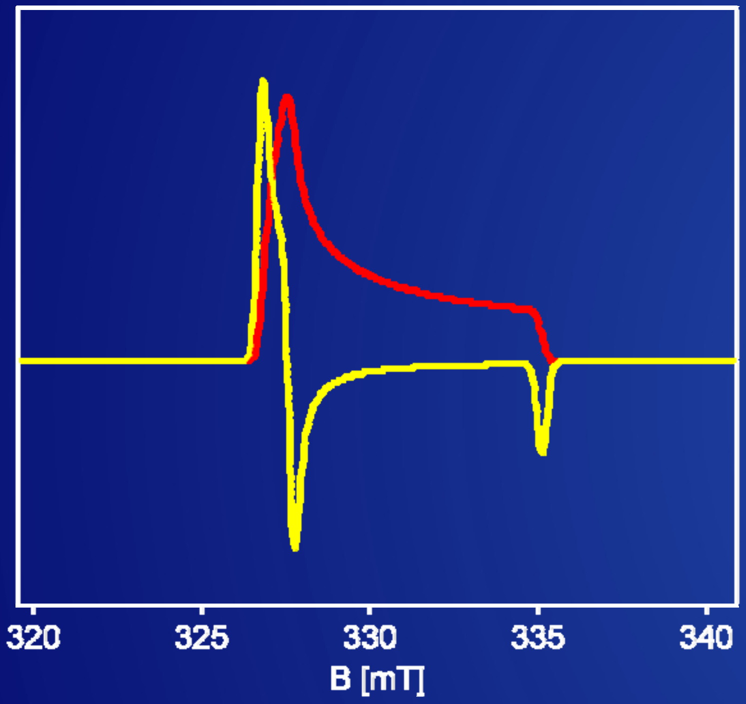
pure g

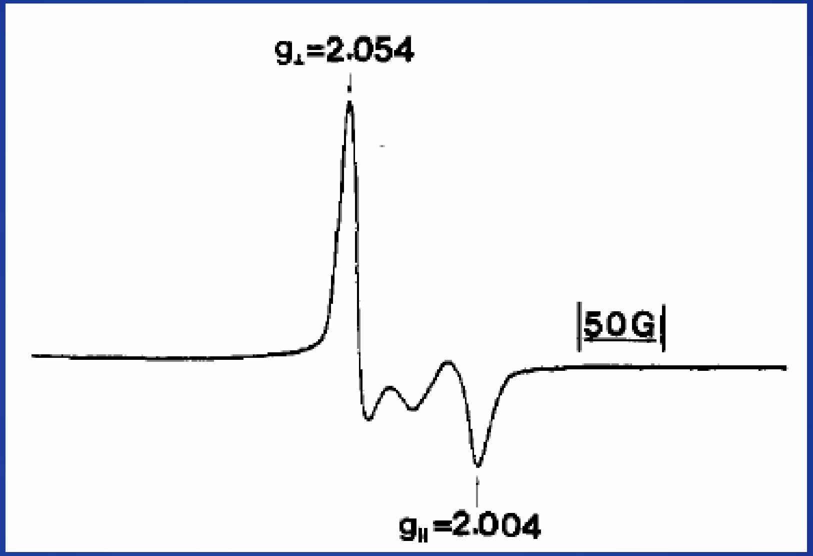


Li in MgO

a simple example

axial g + axial A

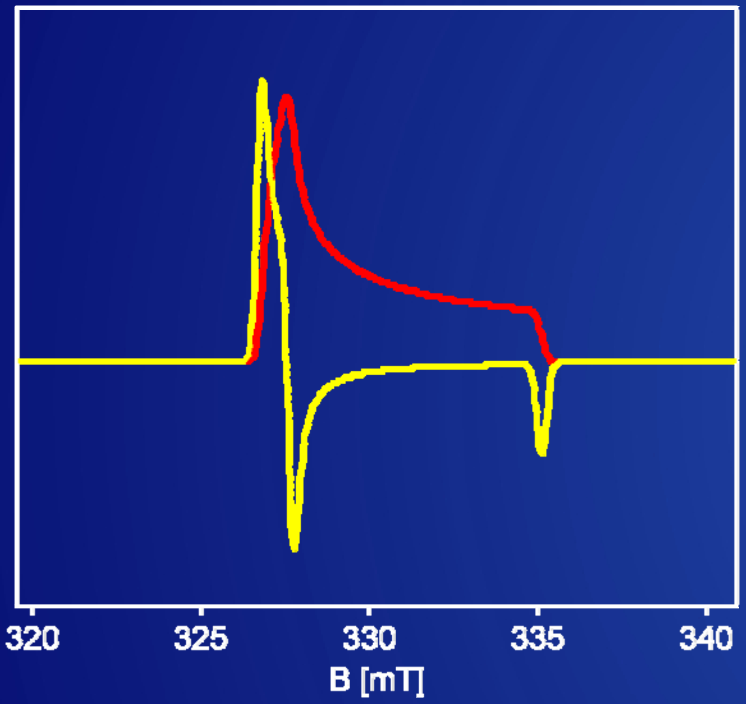


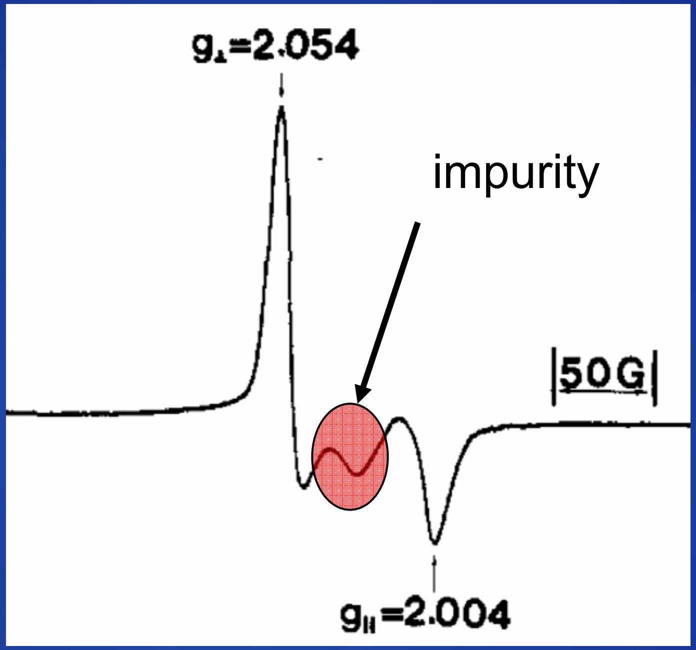


Li in MgO

a simple example

axial g + axial A



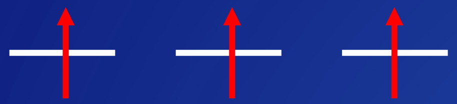


J. X. Wang and J. H. Lunsford, J. Phys. Chem. **90**, 5883 (1986).

ESR spectroscopy

group spins and zero field splitting

Hund’s rule: more than one energetically degenerate orbital:
first fill one electron in each orbital



$S = s_1+s_2+s_3 = 3/2$

this results in a total spin S, also called group spin
in short this group spin is often called electron spin S > ½

there is an important consequence:

These system show an interaction which is mediated by the spin orbit interaction and is formally equivalent to the dipole interaction:

$$H_{zfs} = \underline{\mathbf{S}}\ \boldsymbol{D}\ \underline{\mathbf{S}}$$

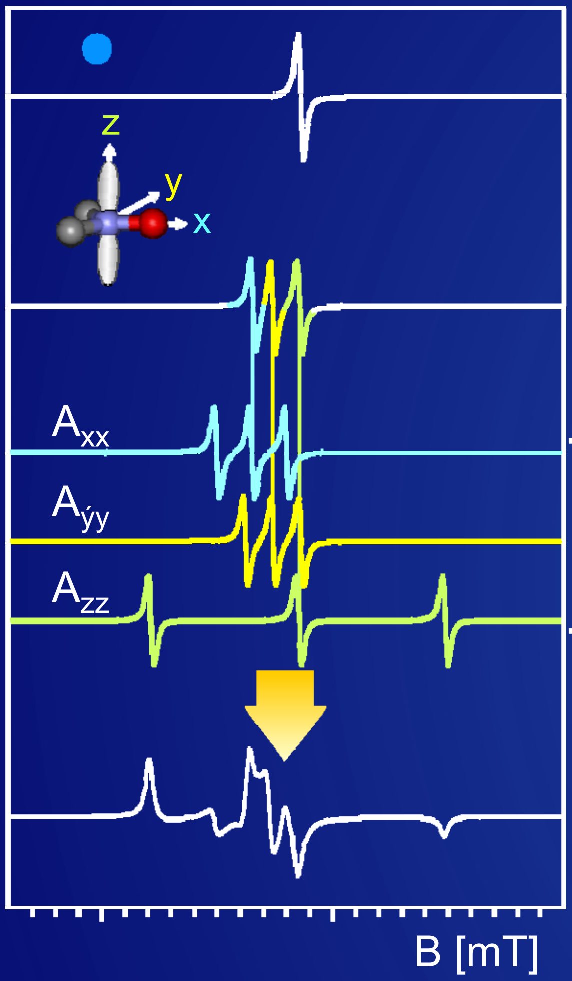
the interaction is independent of the field. This is also true for the hyperfine interaction, or the dipolar interaction but the zero field splitting is usually the leading term!

size of the effect can vary dramatically: from small for slightly distorted systems to very large such that no ESR signal can be observed

ESR spectroscopy

effect of rotational motion

rigid limit



free electron

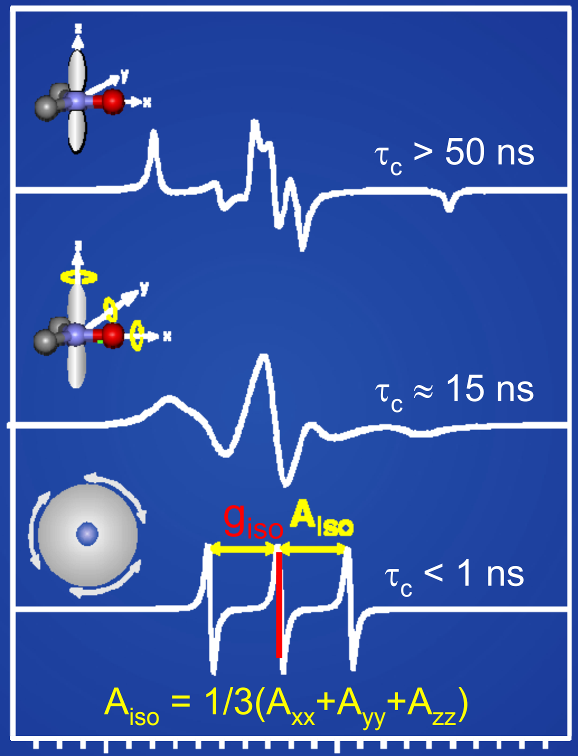
g-tensor
B || x
B || y
B || z

hyperfine
interaction
$I(^{14}N) = 1$

powder
spectrum

rotational motion

isotropic rotation



$A_{iso} = 1/3(A_{xx}+A_{yy}+A_{zz})$

rigid
limit

slow
motion

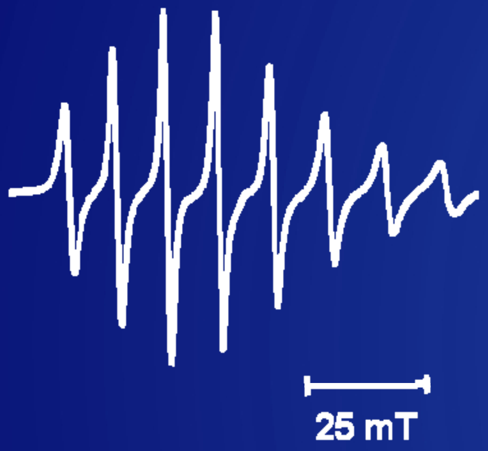
fast
motion

$g_{iso} = 1/3(g_x+g_y+g_z)$

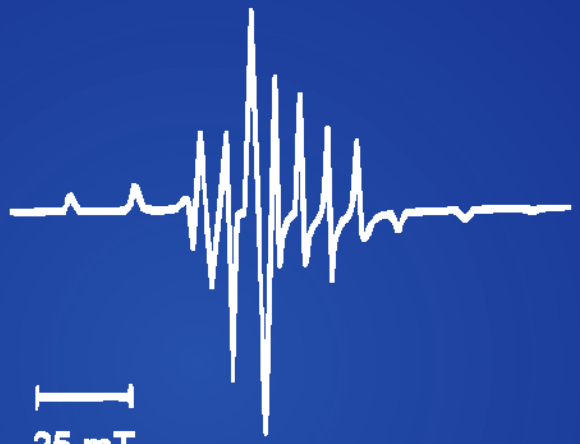
ESR spectroscopy

Solid vs. solution

Colloidal solution of nanoparticles
(in water at 300 K)

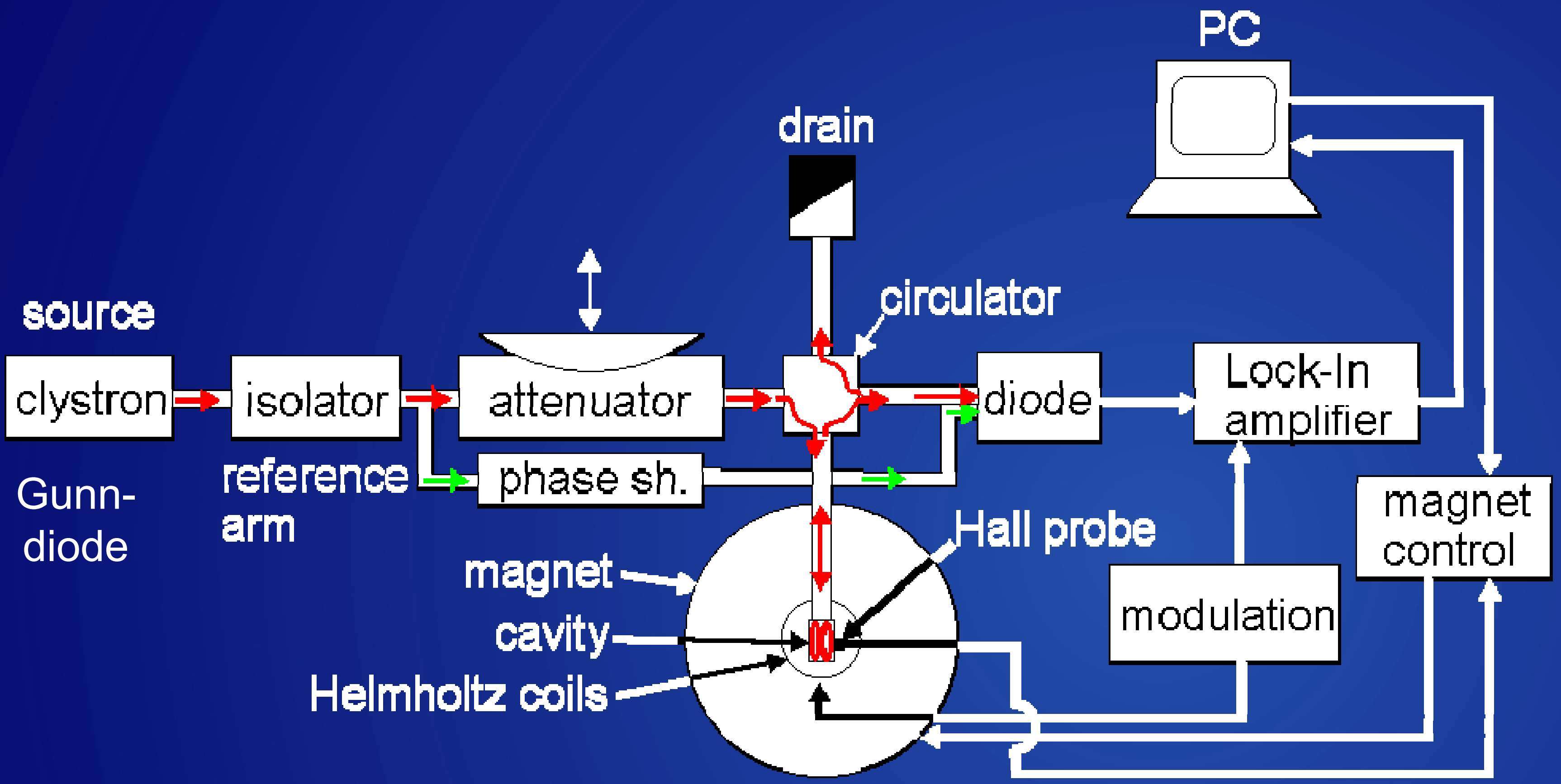


Colloidal solution of nanoparticles
(in ice at 120 K)



experimental aspects

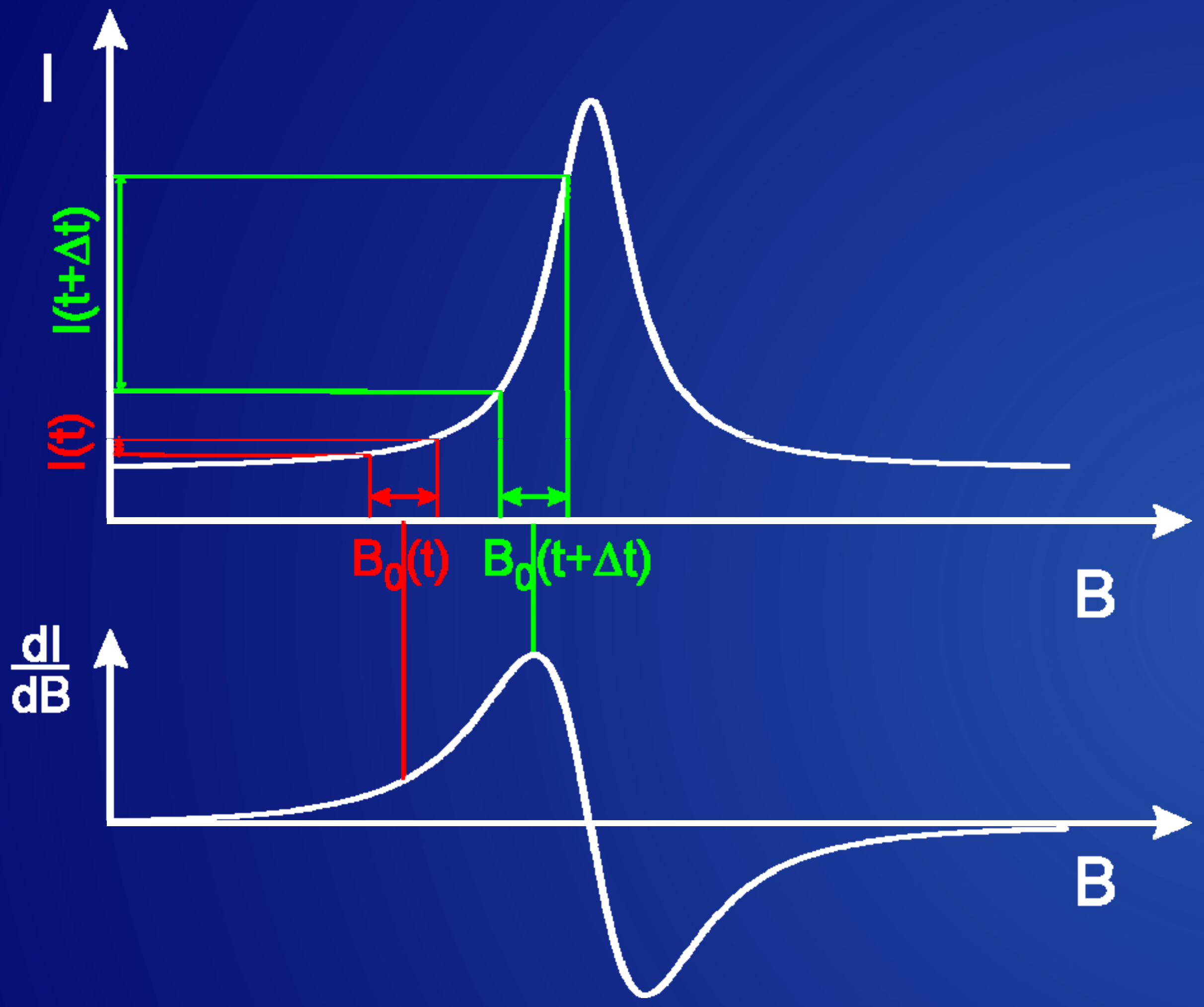
cw set-up at 10 GHz



experimental aspects

consequence of lock-in detection

Max-Planck-Gesellschaft



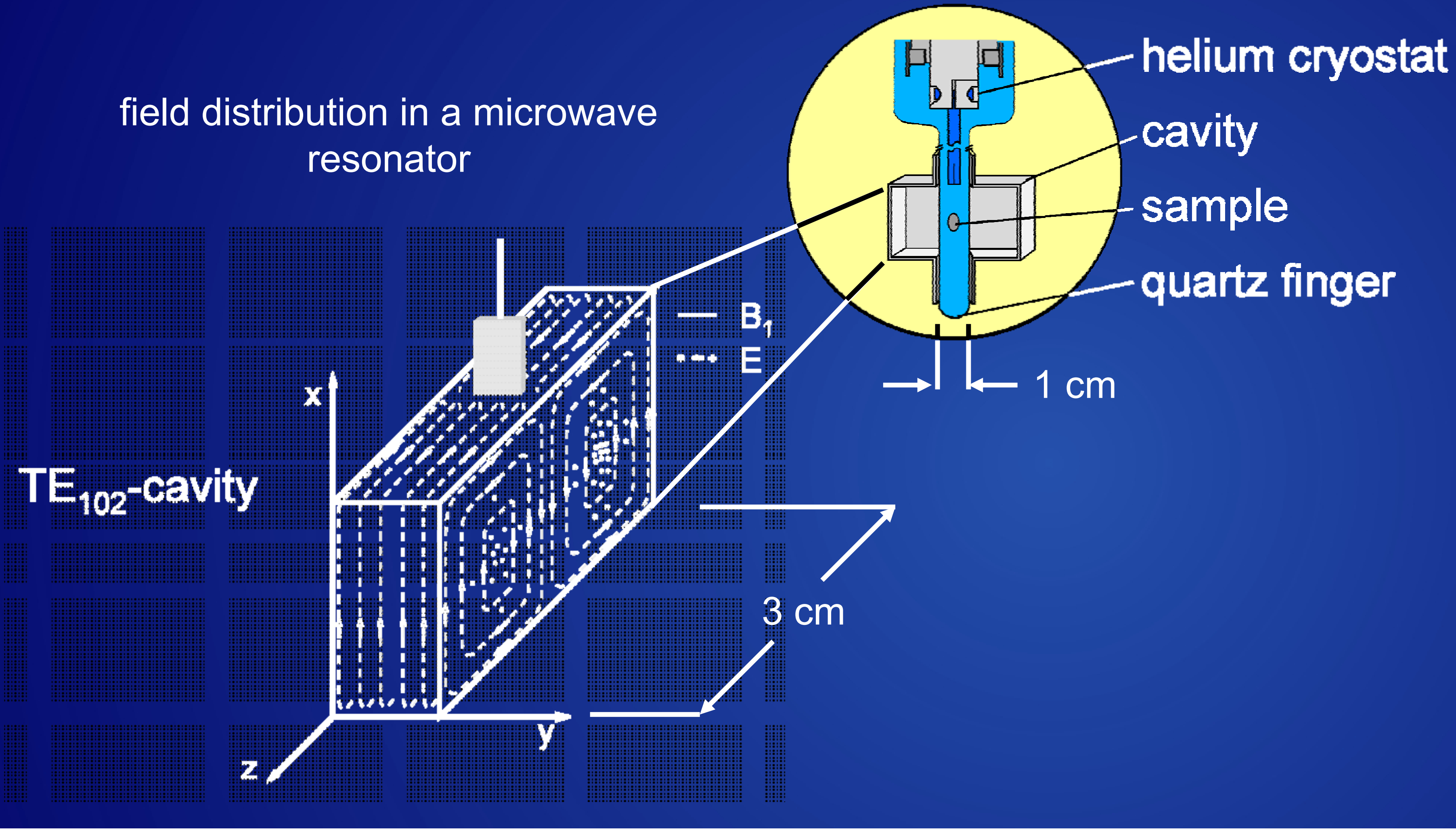
1. lock-in detection gives 1. derivative of the absorption line

2. holds only true if modulation amplitude is small as compared to line width

experimental aspects

resonators or cavities

field distribution in a microwave resonator



experimental aspects

intensity of ESR spectra

What determines the signal intensity?

1. transition probabilities (calculated from quantum mechanics)
2. absorbed microwave power

$$\overline{P} = \frac{1}{2}\omega_0 H_1^2 \chi''$$

χ'' = complex part of the high frequency susceptibility

obeys Curie's law => I(ESR Signal) ~ 1/T

H_1 = oscillating magnetic field (perpendicular to the static magnetic field)

depends on the quality factor Q of the resonator

rectangular cavity: $$H_1^2 = \frac{\mu H_0^2 Q_L (1 - |\Gamma_0|^2) P_{inc}}{4\pi\nu_0 \mu'^2}$$

Γ_0: reflection coefficient

μ,μ': mag. perm. waveguide and cavity

experimental aspects

intensity of ESR spectra

What does this mean?

ESR is quantitative, but…

- relative numbers of spins in the sample: easy
- absolute numbers of spins in the sample: difficult

  (one needs a calibration standard which is measured under exactly the same conditions (including sample shape and size, temperature, microwave settings etc.)
- fraction of paramagnetic species as compared to the total number of species: very difficult

  only possible with detailed knowledge of the paramagnetic species (transition probabilities, relaxation properties, coupling situation), an internal standard of known concentration, and the total number of sites in the sample

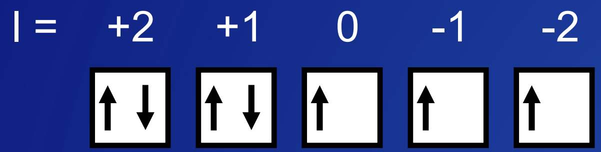
transition metal ions

electronic states and spin orbit coupling

We need the electronic ground state:

construction according to Hund's rules and Pauli principle

example: Co^{2+} ($3d^7$) for the ground state configuration see literature



L = 3, S = 3/2 (assuming LS coupling)

^4F

no fields: degeneracy: $(2S + 1)(2L + 1) = 28$

if LS coupling is exactly correct: L = const. => $g = g_e$

spin orbit coupling lifts the degeneracy of states with equal L and S but different J

two contribution: 1. changes the splitting between states (m_S, m_{S+1}), shift of g_{iso}

2. depends on m_s^2 (only important for S > ½) no contribution to g_{iso}

often neither LS nor jj coupling correct. The correction to the LS case can be made by the so-called Racah coefficients B and C which are tabulated

transition metal ions

crystal or ligand field

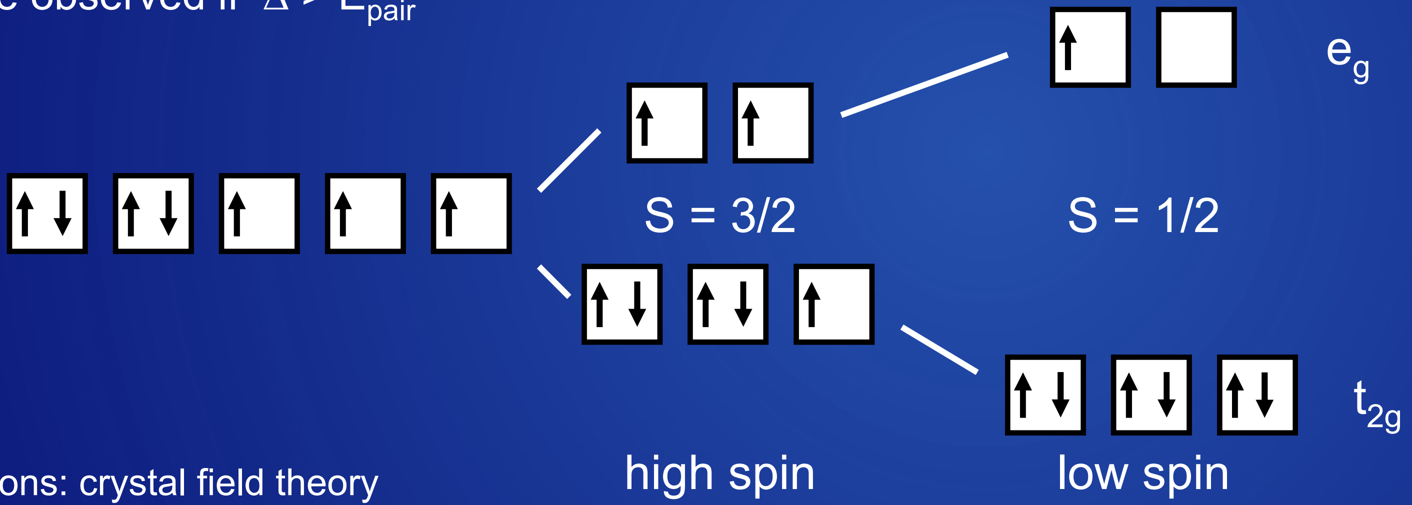
no fields: degeneracy: (2S + 1)(2L + 1)

degeneracy is lifted partly by external electric fields

the external electric field can due to neighboring ions or ligands

lifting the degeneracy will lead to a partial decoupling of spin and orbit, thus the Racah coefficient are slightly small than in the free ion

drastic effects are observed if $\Delta > E_{pair}$



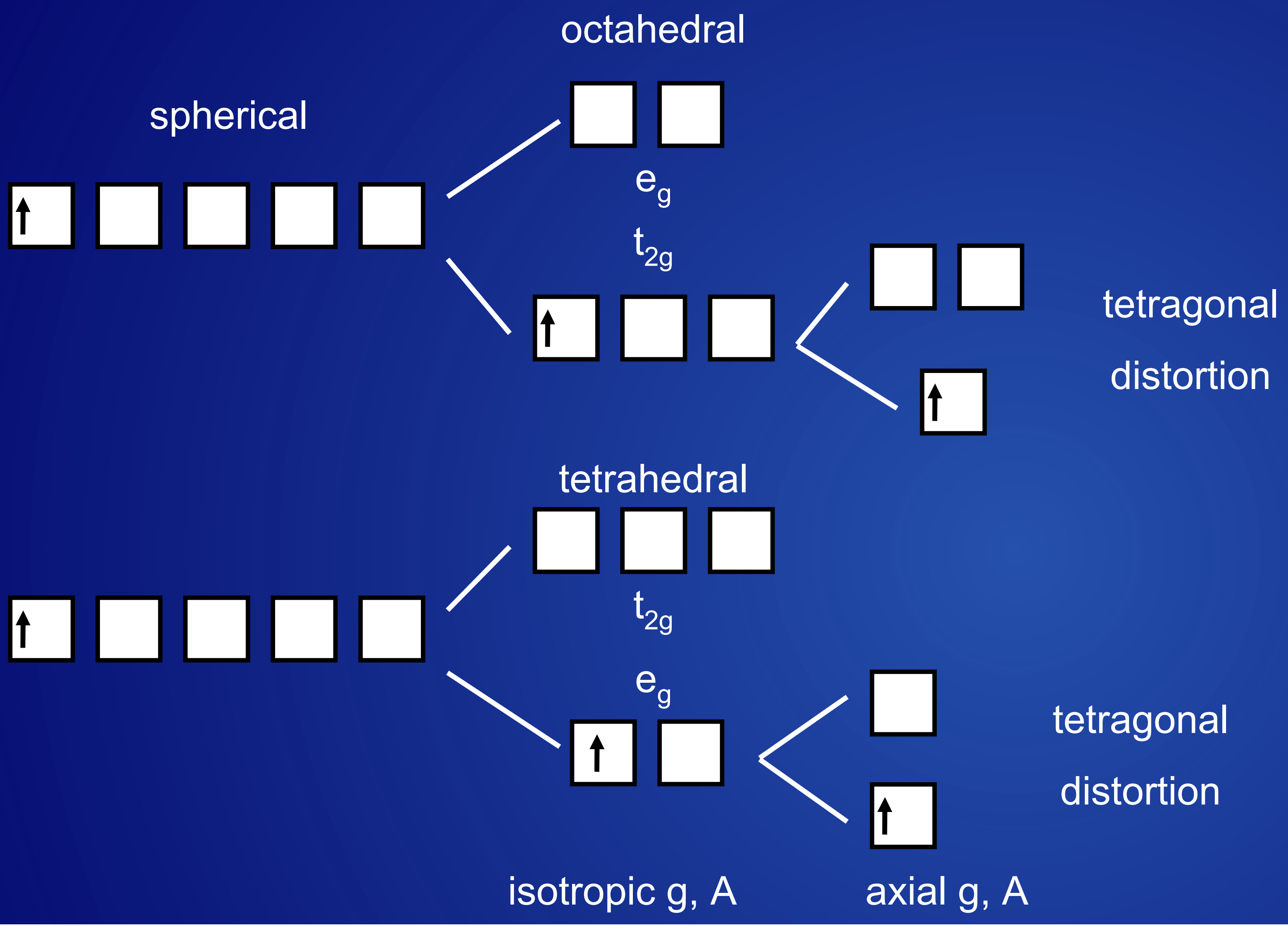
pure ionic interactions: crystal field theory

including covalency: ligand field, MO theory

transition metal ions

symmetry reduction

Max-Planck-Gesellschaft



octahedral

spherical

e_g

t_{2g}

tetragonal

distortion

tetrahedral

t_{2g}

e_g

tetragonal

distortion

isotropic g, A

axial g, A

transition metal ions

Fe^{3+}, Mn^{2+} (d^5)

Fe^{3+}: ground state ^6S, high-spin (S=3/2), low-spin (S=1/2)

in cubic symmetry: $g_{iso} \approx 2$

low symmetry: large zero-field splitting (only transitions within Kramers-Dubletts) large g-anisotropies $g_{||} = 2$, $g_{\perp} = 6$

97.8% of the isotopes have no nuclear moment
=> almost no hf-satallites

Mn^{2+} isoelectronic to Fe^{3+}; just high spin systems of importance

small g-anisotropy, much smaller zero-field splitting rf. Fe (a few GHz) transition between different Kramers multipletts possible

^{55}Mn (100%; I =5/2) => characteristic hyperfine pattern; usually well resolved because of small g-tensor anisotropy

transition metal ions

Mn^{2+} (d^5)

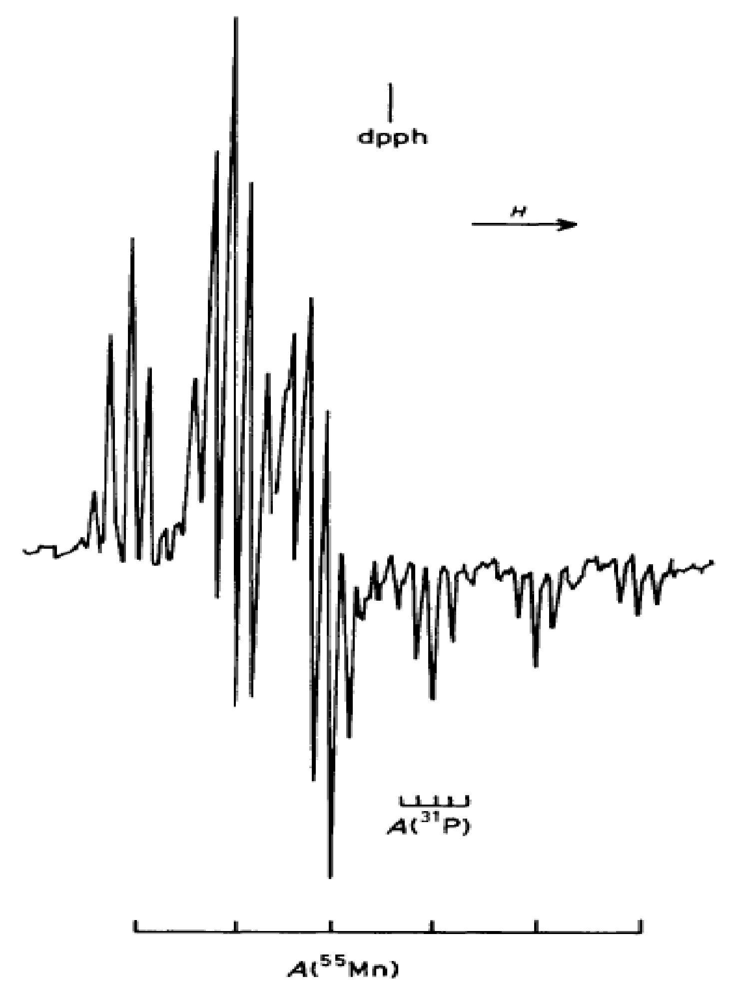
$[Mn\,(dppm)_2(CO)(CNBu^t)]^{2+}$

dppm: Ph_2-P-CH_2-P-Ph_2

What to expect?

1. Mn (I = 5/2) => 6 groups
2. coupling to 4 ^{31}P(I=1/2)

   (1 : 4 : 6 : 4 : 1)



G. A. Carriedo J. Chem. Soc., Dalton Trans. 1769 (1987).

transition metal ions

Mn^{2+} (d^5)

$[Mn\,(dppm)_2(CO)(CN)]^+$

dppm: Ph_2-P-CH_2-P-Ph_2

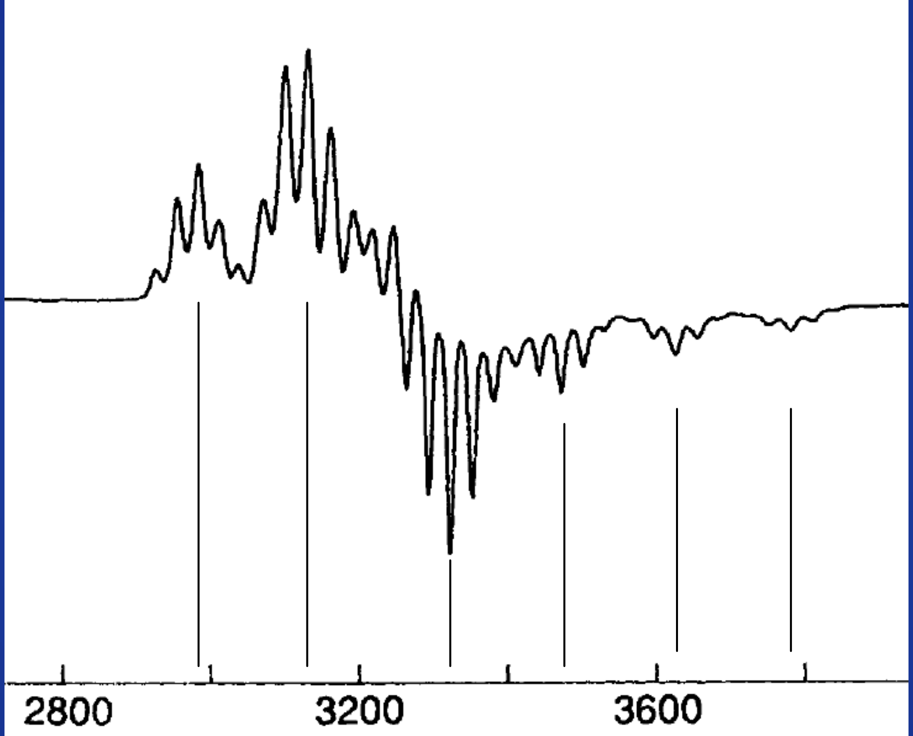
What to expect?

1. Mn ($I = 5/2$) => 6 groups
2. coupling to 4 $^{31}P(I=1/2)$

   (1 : 4 : 6 : 4 : 1)

What is unexpected?

Splitting between



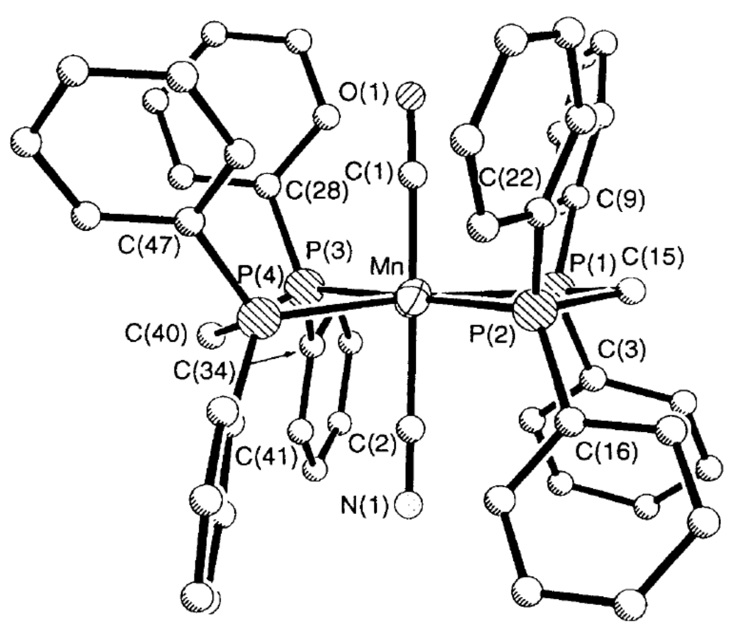
G. A. Carriedo J. Chem. Soc., Dalton Trans. 3103 (1993).

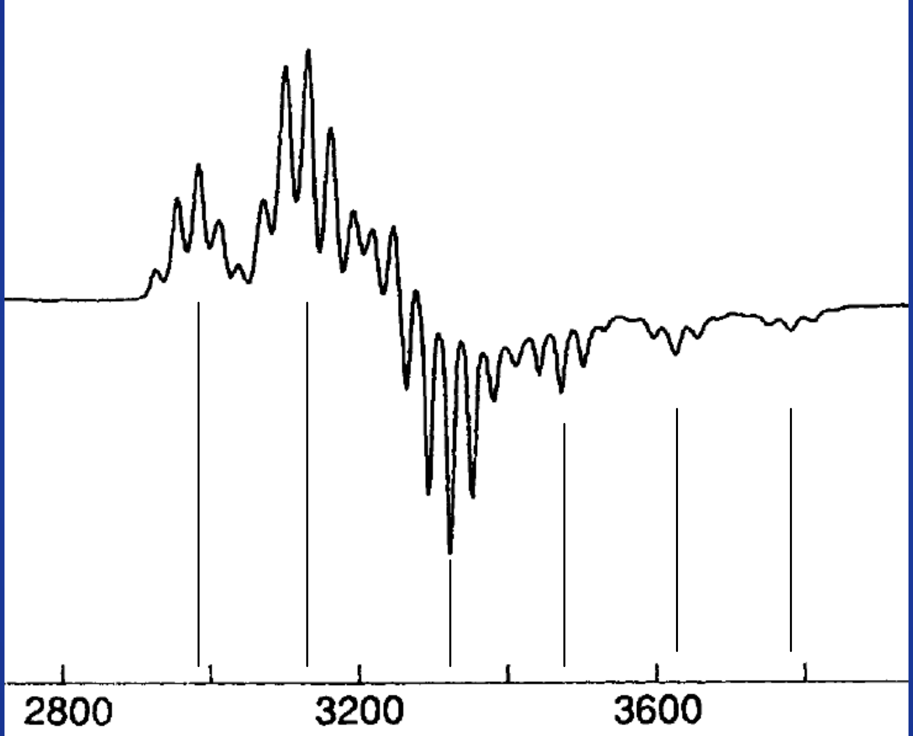
transition metal ions

Mn^{2+} (d^5)

$[Mn(dppm)_2(CO)(CN)]^+$

dppm: Ph_2-P-CH_2-P-Ph_2





G. A. Carriedo J. Chem. Soc., Dalton Trans. 3103 (1993).

transition metal ions

Ti^{3+}, VO^{2+} (d^1)

Ti^{3+}: typically 6 fold coordination in distorted octahedral symmetry

often axial symmetric tensor ($g_x = g_y \neq g_z$) $g \approx 1.85 - 2$

87% of the isotopes have no nuclear moment

^{47}Ti (7.4 %; I=5/2) and ^{49}Ti (5.4%; I =7/2)

=> intense pattern due to g-anisotropy just weak satellites from hf-interaction

V^{4+}, VO^{2+}

isoelectronic to Ti^{3+}, mostly VO^{2+}

typical g-values: $g_{||} = 1.94$, $g_{\perp} = 1.98\text{-}1.99$

^{51}V (99.75%; I =7/2) => characteristic hyperfine pattern;
usually well resolved because of small g-tensor anisotropy

transition metal ions

Cu^{2+} (d^9)

Cu^{2+}: ground state ^2D, $S=1/2$

usually distorted octahedral ligand field (tetragonal symm.)

=> axial symmetric tensor: $g = 2 – 2.2$; usually $g_{||} < g_{\perp}$

distorted tetrahedral ligand field (tetragonal symm.)

$g_{||} > g_{\perp}$ is usually found

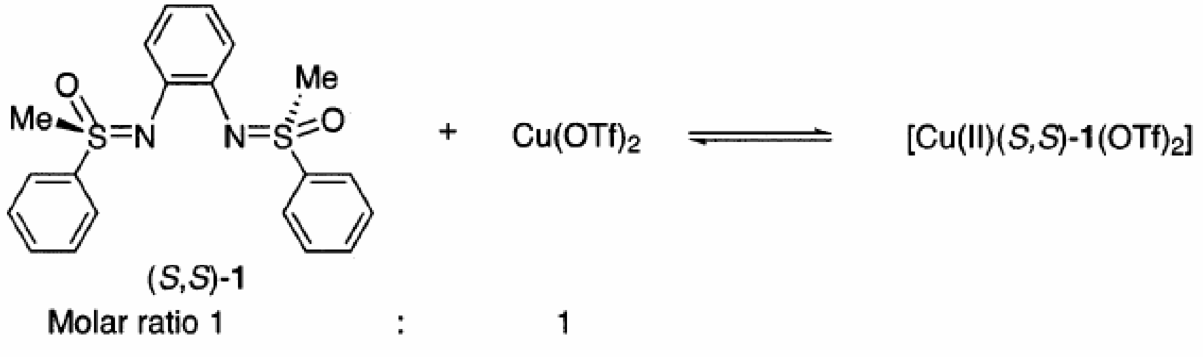
^{63}Cu (69.2%; $I = 3/2$); ^{65}Cu (30.8%; $I = 3/2$);

almost equal gyromagnetic ratio => strongly overlapping hyperfine multipletts

transition metal ions

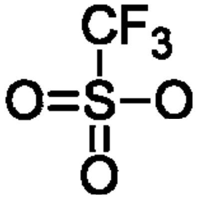
Cu^{2+} (d^9)

Max-Planck-Gesellschaft

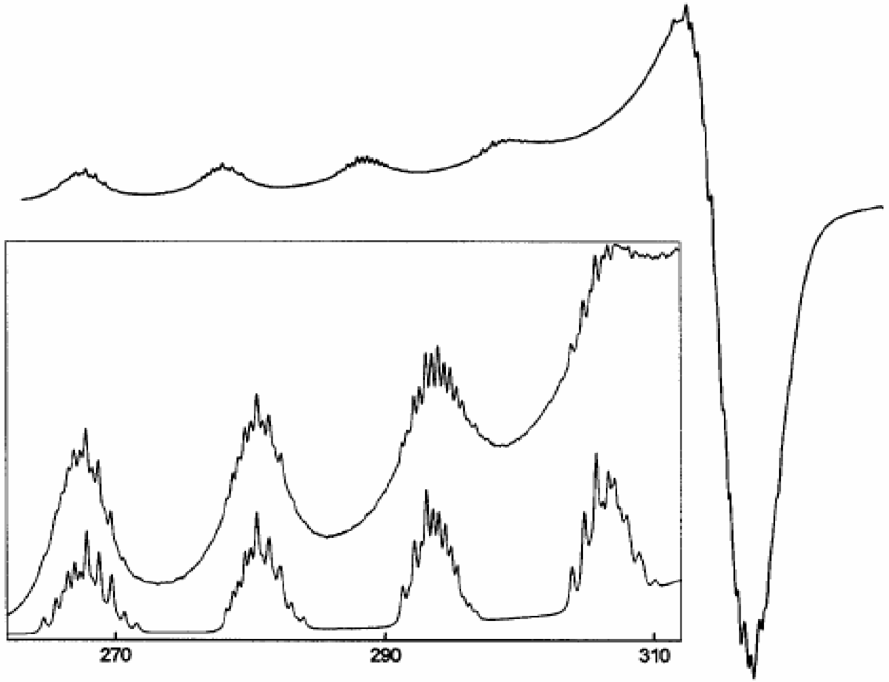


(*S*,*S*)-**1** + $Cu(OTf)_2$ ⇌ [Cu(II)(*S*,*S*)-**1**$(OTf)_2$]

Molar ratio 1 : 1



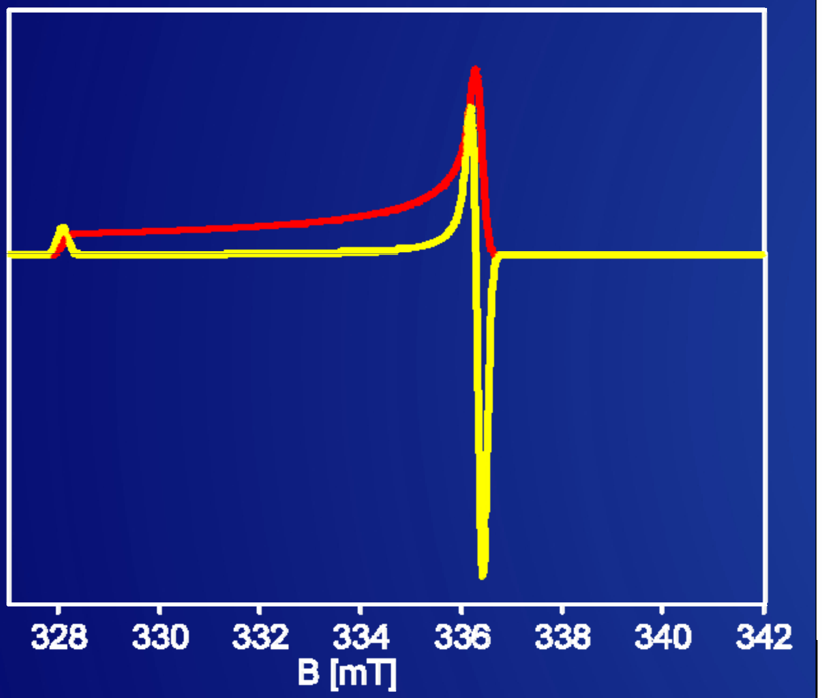
OTf

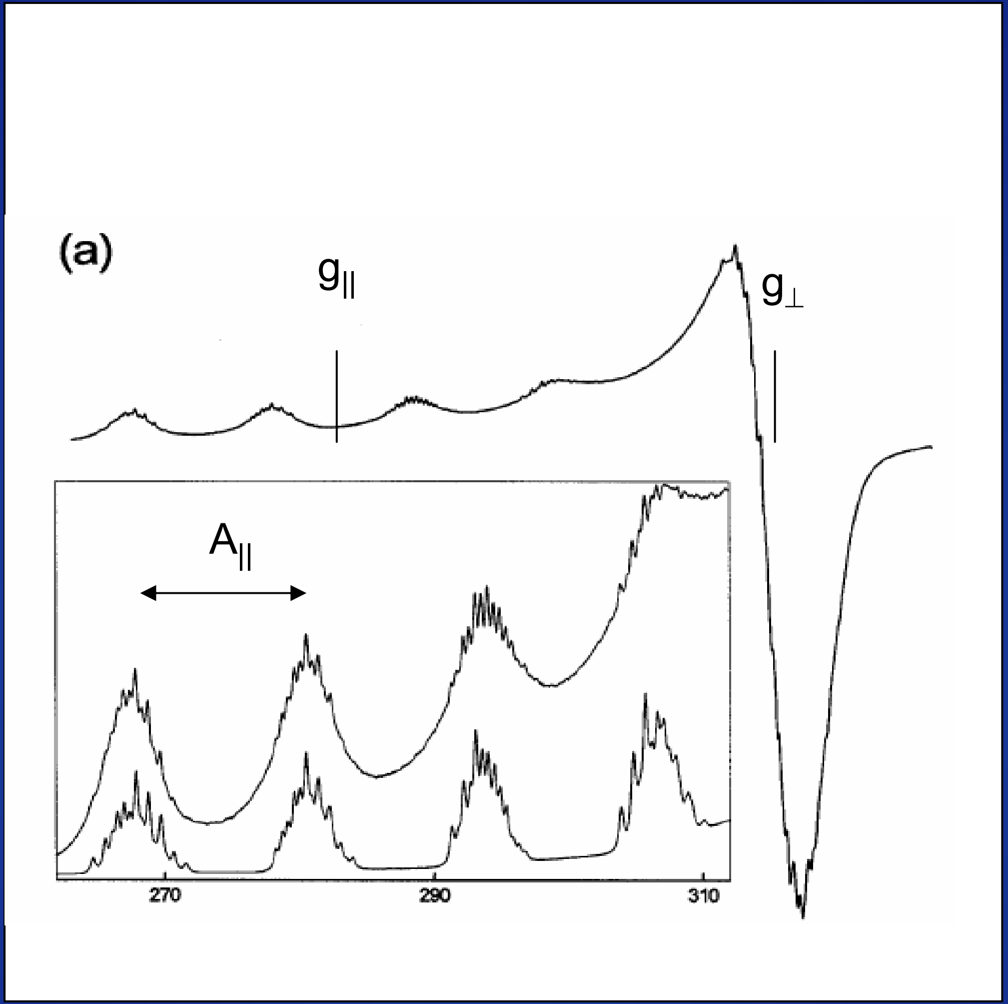


C. Bolm et al., *J. Am. Chem. Soc.* **125**, 6222 (2003).

transition metal ions

Cu^{2+} (d^9)



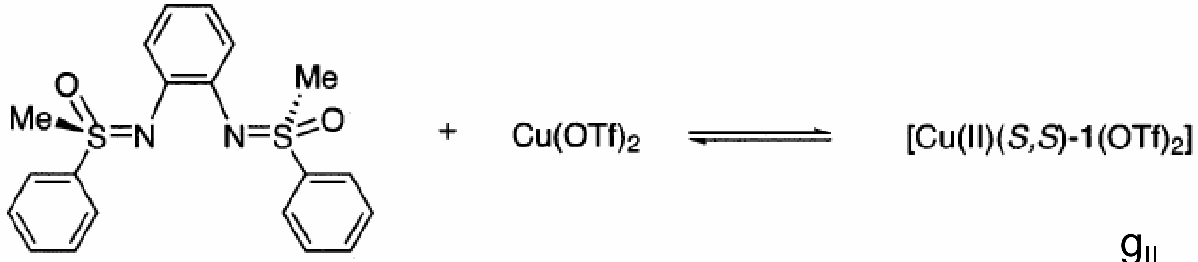


C. Bolm et al., *J. Am. Chem. Soc.* **125**, 6222 (2003).

transition metal ions

Cu^{2+} (d^9)

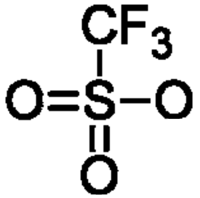
Max-Planck-Gesellschaft



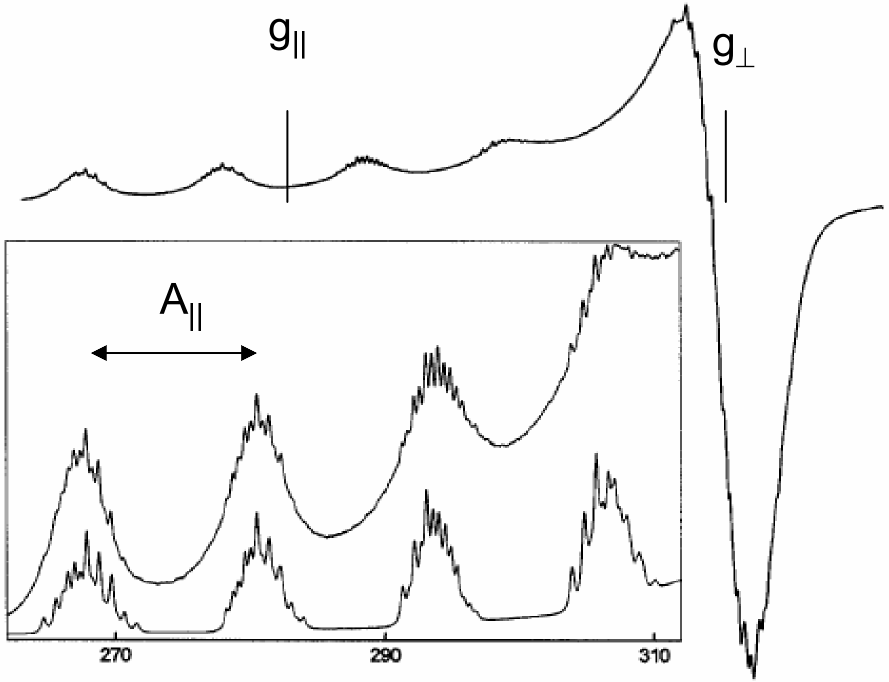
$+ \ Cu(OTf)_2 \rightleftharpoons [Cu(II)(S,S)\text{-}\mathbf{1}(OTf)_2]$

(*S*,*S*)-**1**

Molar ratio 1 : 1



OTf



$g_\perp$	$g_\parallel$	$A_\perp(^{63}Cu)$	$A_\parallel(^{63}Cu)$
2.06	2.357	23 MHz	410 MHz

C. Bolm et al., *J. Am. Chem. Soc.* **125**, 6222 (2003).

transition metal ions

Co^{2+} (d^7)

Co^{2+}: ground state ^{4}F, high-spin (S=3/2), low-spin (S=1/2)

octahedral and tetrahedral ligand field are usually distored

perfect octahedral symmetry: $g_{iso} = 4.3$

small distortion: g from 1.5 to 7; however, g_{iso} often close 4.3

in tetrahedral symmetry smaller deviations from g_e

low symmetry: large zero-field splitting (usually not possible to observe a spectrum in solution, require low temperatures)

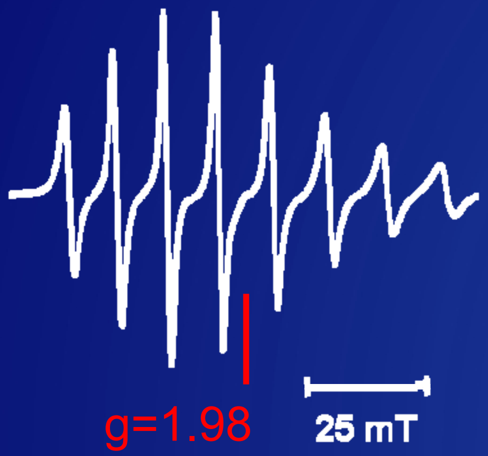
^{59}Co (100%; I =7/2) => eight line spectrum

ESR spectroscopy

transition metal ions

Max-Planck-Gesellschaft

Colloidal solution of nanoparticles
(in water at 300 K)



isotropic spectrum consist of 8 lines

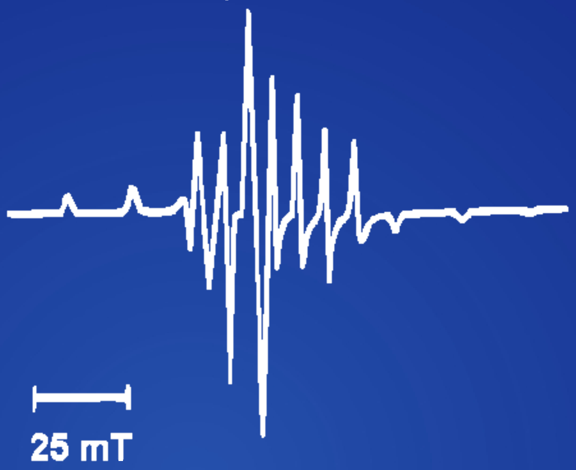
=> hyperfine interaction: I = 7/2

no line in the center

=> all nuclei carry a spin of 7/2

three possibilities: ^{51}V, ^{59}Co, ^{181}Ta

Colloidal solution of nanoparticles
(in ice at 120 K)



- moderate hyperfine anisotropy

($A_z \approx 20$ mT, $A_x = A_y \approx 8$ mT) $a_{iso} \approx 12$ mT

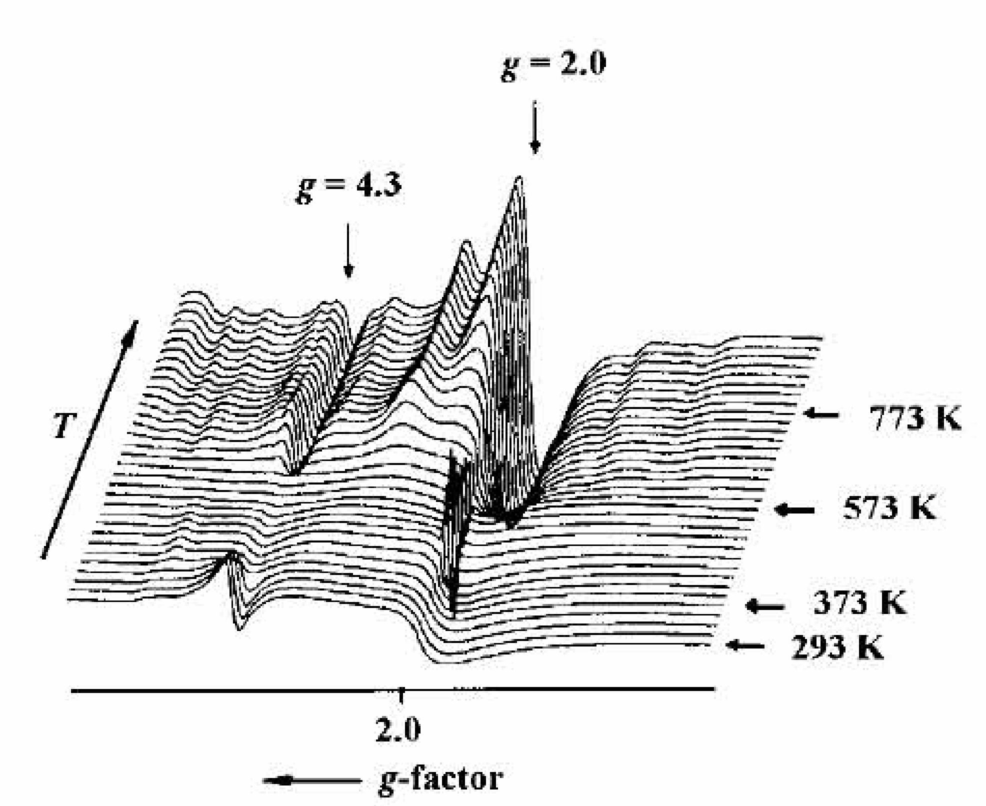
- almost isotropic g-value

$\Rightarrow$no Co;

Ta and V have similar electronic structures however, the spin orbit coupling plays a much bigger role for Ta.

ESR spectroscopy

transition metal ions



Fe in $AlPO_4$-5

two species: 1. $g \approx 2$

2. $g \approx 4.3$

1. species: octahedral coordinated Fe^{3+} on lattice positions
2. species: extra lattice Fe^{3+} in a distorted tetrahedral environment

strong redistribution of sites upon heating. At high temperature minimal 3 different sites occupied by Fe^{3+}. Regular lattice sites account for approx. 45% of the sites.

A. Brückner, U. Lohse, H. Mehner Microporous Mesoporous Mater. 20, 207 (1998).

Conclusions

Max-Planck-Gesellschaft

EPR

- Can be done at elevated pressures (materials with dielectric losses are problematic; water, metals etc)
- Can be done at elevated temperature (in-situ experiments possible)
- Quantification of absolute amounts is in general difficult! Relative amounts are easier
- Spin physics can hamper the detection of signals

g- and A-matrices

- Information on site symmetry
- Information on electronic structure
- Information on neighboring atoms