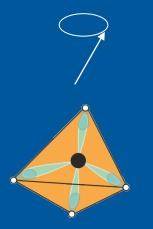


# **Tool to investigate Paramagnets**

Jürgen Lindner Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf



Electron Spin Resonance (ESR) – Basic Idea, Theory, Detection

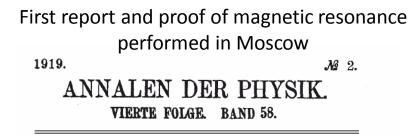
ESR of ions in crystal - crystal fields



#### Ferromagnetic Resonance (FMR)



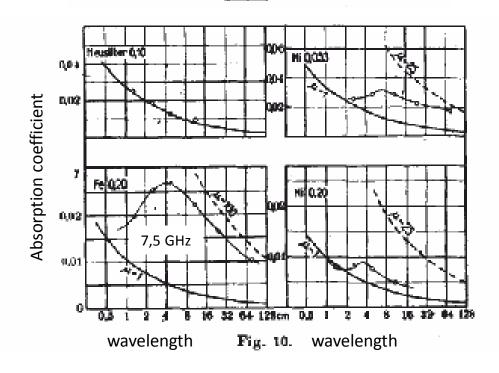
#### Magnetic Resonance - a Russian Discovery



1. Über die Absorption elektromagnetischer Wellen an nwei parallelen Drähten; von W. Arkadiew. Key paper:

Quantitative theory: Landau-Lifshitz-equation

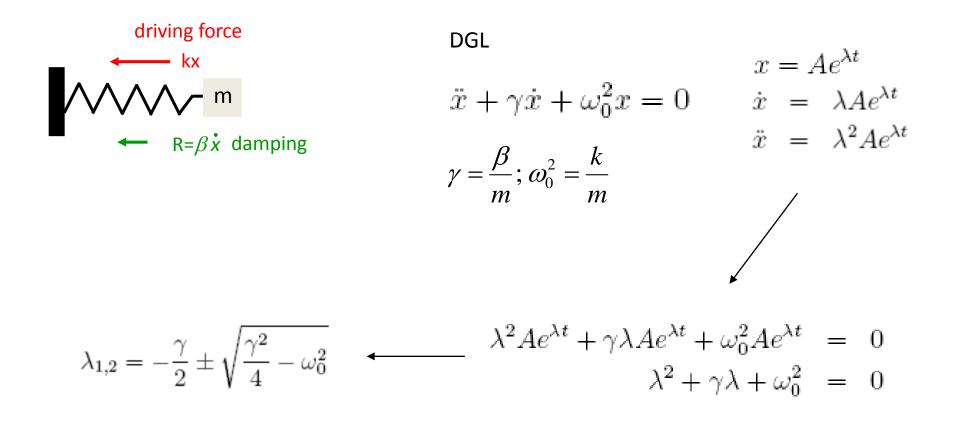
L. Landau, E. Lifshitz, Physik. Zeits. Sowjetunion 8, 153 (1935)





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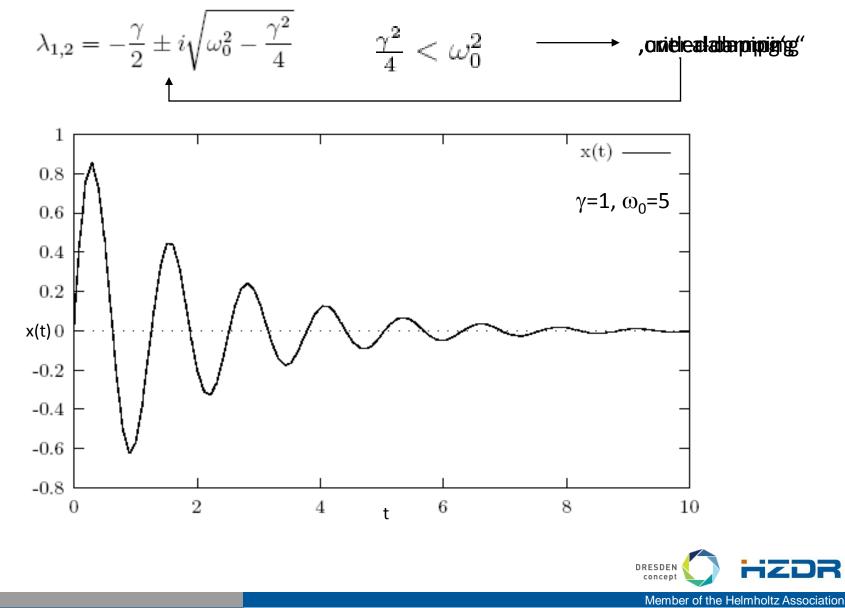
#### Recapitulation: Damped harmonic oscillator I





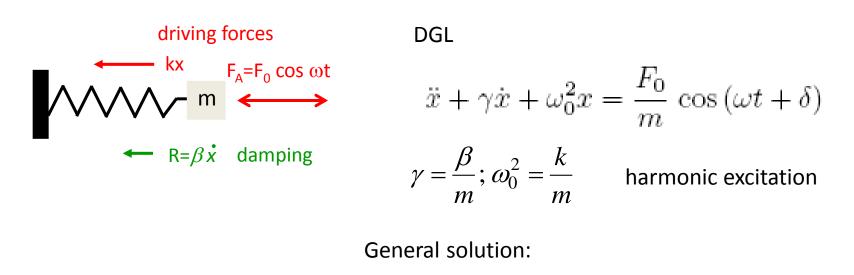
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### Recapitulation: Damped harmonic oscillator II



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### Recapitulation: Externally excited damped harmonic oscillator I



$$x = x_{\rm H} + x_{\rm S}$$

 $\ddot{z} + \gamma \dot{z} + \omega_0^2 z = \frac{F_0}{m} e^{i(\omega t + \delta)}$ Real part of solution of komplex DGL is solution of original DGL Solution of homogeneous DGL Plus particular solution of inhomogeneous DGL  $\downarrow$   $F_{\rm A} = F_0(\cos(\omega t + \delta) + i\sin(\omega t + \delta)) = F_0 e^{i(\omega t + \delta)}$ 



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### Recapitulation: Externally excited damped harmonic oscillator II

$$\ddot{z} + \gamma \dot{z} + \omega_0^2 z = \frac{F_0}{m} e^{i(\omega t + \delta)} \rightarrow F' = \frac{F_0}{m} e^{i\delta} \rightarrow \ddot{z} + \gamma \dot{z} + \omega_0^2 z = F' e^{i\omega t}$$

$$z_{\rm S} = A' e^{i\omega t}$$

$$z_{\rm S} = A' e^{i\omega t}$$

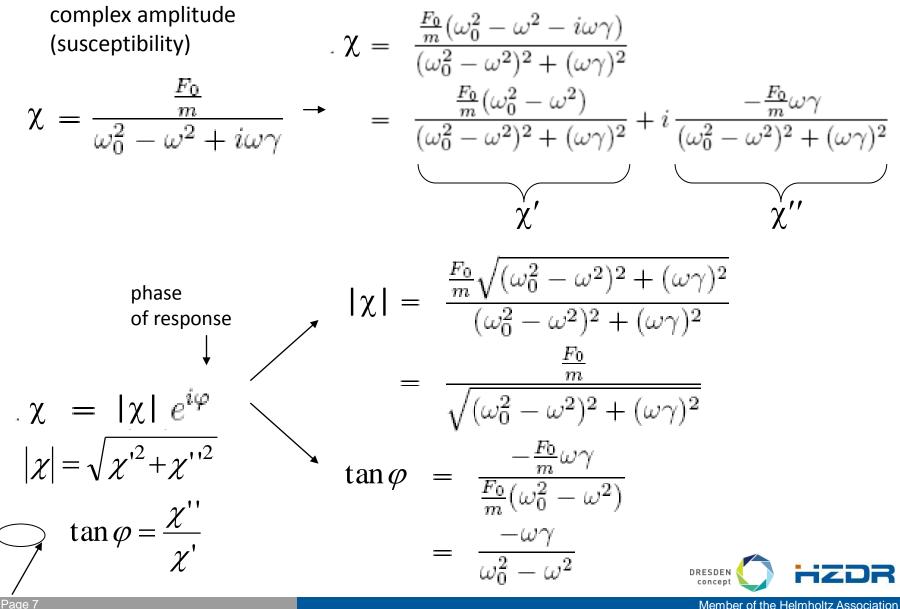
$$\dot{z}_{\rm S} = i\omega A' e^{i\omega t}$$

$$\dot{z}_{\rm S} = -\omega^2 A' e^{i\omega t}$$

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Recapitulation: Externally excited damped harmonic oscillator III



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Recapitulation: Externally excited damped harmonic oscillator IV

 $x = x_{\rm H} + x_{\rm S}$ 

stationary solution

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$$z_{\rm S} = A'e^{i\omega t} = \chi e^{i\delta}e^{i\omega t} = |\chi|e^{i\varphi}e^{i\delta}e^{i\omega t} = |\chi|e^{i(\omega t + \varphi + \delta)}$$

$$z_{\rm S} = \frac{\frac{F_0}{m}}{\sqrt{(\omega_0^2 - \omega^2)^2 + (\omega\gamma)^2}} e^{i(\omega t + \arctan\left(\frac{-\omega\gamma}{\omega_0^2 - \omega^2}\right) + \delta)}$$

$$|x_{\rm S} = \operatorname{Re}[z_{\rm S}]$$

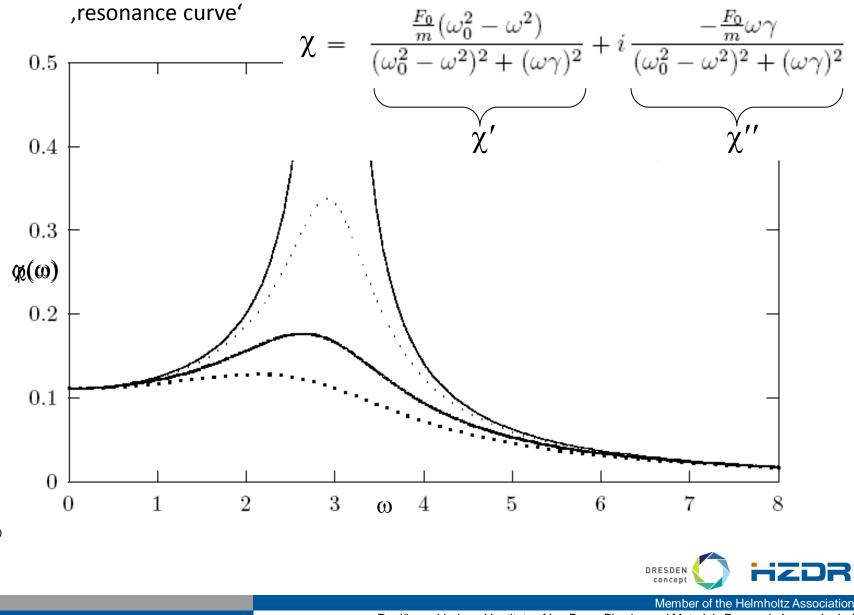
$$= \frac{\frac{F_0}{m}}{\sqrt{(\omega_0^2 - \omega^2)^2 + (\omega\gamma)^2}} \cos\left(\omega t + \arctan\left(\frac{-\omega\gamma}{\omega_0^2 - \omega^2}\right) + \delta\right)$$

oscillation with driving frequency plus phase shift that changes sign depending on whether  $\omega < \omega_0 \text{ or } > \omega_0$ 



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Recapitulation: Externally excited damped harmonic oscillator V

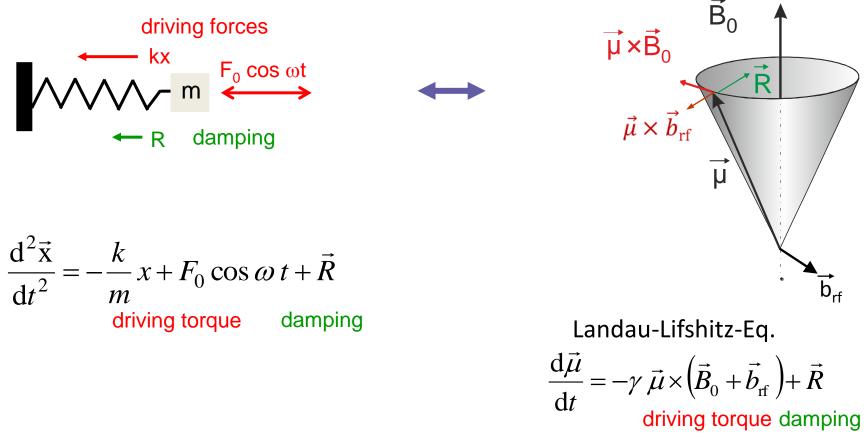


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# Comparison: Mechanical Oscillator vs. Electron Spin Resonance (ESR)

Mechanical system

Magnetic moment





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### Spin in magnetic field – Quantum mechanical treatment I

Classical physics (spin  $\frac{\hbar}{2}$  leads to magnetic moment  $\mu_{\rm B}$ )

$$\vec{\mu} = -\gamma \, \vec{s} \qquad \qquad \gamma = g_{\rm e} \, \frac{\mu_{\rm B}}{\hbar}$$

magnetic moment

electron spin gyromagnetic ratio

Energy of magnetic moment in external magnetic field:

Pauli spin matrices

 $E = -\vec{\mu} \cdot \vec{B}_0$ Quantum mechanics Schrödinger Equation

$$\gamma \vec{B}_0 \cdot \hat{\mathbf{s}} \varphi_i = \gamma \left( B_x \hat{\mathbf{s}}_x + B_y \hat{\mathbf{s}}_y + B_z \hat{\mathbf{s}}_z \right) \varphi_i = E \varphi_i$$

$$\hat{s}_{x} = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$
$$\hat{s}_{y} = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$
$$\hat{s}_{z} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$



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### Spin in magnetic field – Quantum mechanical treatment II

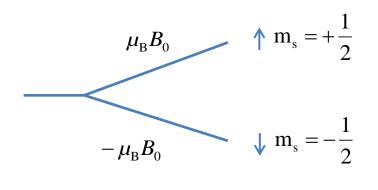
$$\gamma \vec{B}_0 \cdot \hat{\mathbf{s}} \,\varphi_i = \gamma \left( B_x \hat{\mathbf{s}}_x + B_y \hat{\mathbf{s}}_y + B_z \hat{\mathbf{s}}_z \right) \varphi_i = E \varphi_i$$

field along z-direction  $(0,0,B_0)$ 

$$\gamma B_0 \hat{s}_z \varphi_i = E \varphi_i = \pm g_e \frac{\mu_B}{\hbar} B_0 \frac{\hbar}{2} \varphi_i = \pm \mu_B B_0 \varphi_i$$

$$\longrightarrow E = \pm \mu_{\rm B} B_0 \left( + \operatorname{für} \varphi_{\uparrow}, - \operatorname{für} \varphi_{\downarrow} \right)$$

expectation values of Hamilton-Operator



$$\hat{s}_{z} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
$$\varphi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \varphi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
$$\hat{s}_{z} \varphi_{i} = \hbar m_{s} \varphi_{i}$$
$$m_{s} = \pm 1/2$$



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### Spin in magnetic field – Quantum mechanical treatment III -

### time dependent behavior

Time dependent Schrödinger Equation

field along z-direction  $(0,0,B_0)$ 

$$\gamma B_0 \hat{s}_z \ \varphi = i\hbar \frac{d\varphi}{dt}$$

solution:

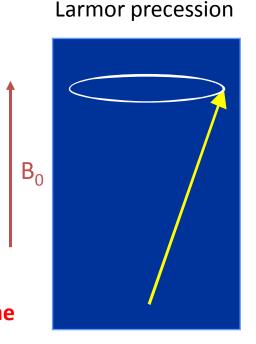
$$\varphi(t) = a \mathrm{e}^{-i\omega_0 t/2} \varphi_{\uparrow} + b \mathrm{e}^{i\omega_0 t/2} \varphi_{\downarrow} = \alpha \varphi_{\uparrow} + \beta \varphi_{\downarrow}$$

with  $\omega_0 = \gamma B_0$ 

Interpretation (expectation value of  $\hat{s}_i$ , *i.e.*  $\langle \phi^* \hat{s}_i \phi \rangle$ ):

$$\hat{\mathbf{s}}_{z} \varphi = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \alpha \\ -\beta \end{pmatrix}$$
$$< \hat{\mathbf{s}}_{z} >= \varphi^{*} \hat{\mathbf{s}}_{z} \varphi = \begin{pmatrix} \alpha^{*} \\ \beta^{*} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} \alpha \\ -\beta \end{pmatrix} = \frac{\hbar}{2} \left( |\alpha|^{2} - |\beta|^{2} \right) = \frac{\hbar}{2} \left( a^{2} - b^{2} \right)$$
$$\xrightarrow{\text{constant in time}}$$

. .



 $\langle \hat{s}_x \rangle = ab\hbar \cos \omega_0 t$   $\langle \hat{s}_y \rangle = ab\hbar \sin \omega_0 t$  rotating with  $\omega_0$  in x/y-plane

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# Spin in magnetic field – Classical treatment

Landau-Lifshitz-Eq. 
$$\frac{d\vec{\mu}}{dt} = -\gamma \vec{\mu} \times \vec{B}_0$$
  
Time dep. Torque  
of angular in external  
momentum magnetic  
field

Ansatz(harmonic oscillator):

Page '

$$\vec{\mu} = \begin{pmatrix} \mu_x \vec{e}_x + \mu_y \vec{e}_y + \mu_z \vec{e}_z \end{pmatrix} e^{i\omega t} + |\mu| \vec{e}_z \text{ und } \vec{B}_0 = B_0 \vec{e}_z$$
time dep. constant
$$i\omega\mu_x = -\gamma B_0\mu_y$$

$$\Rightarrow \quad i\omega\mu_y = \gamma B_0\mu_x$$

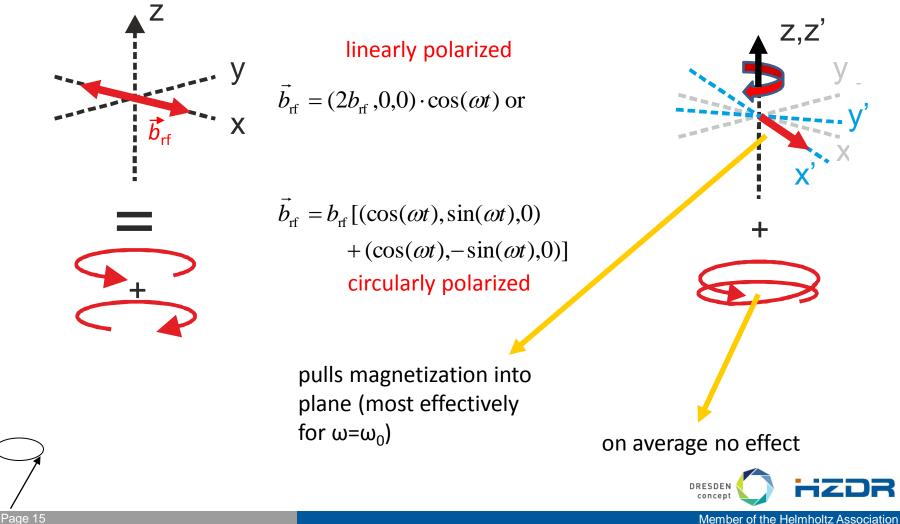
$$i\omega\mu_z = 0$$

$$\Rightarrow \quad \mu(t) = (\mu_x \vec{e}_x - i\mu_x \vec{e}_y) e^{i\omega_0 t} + |\mu| \vec{e}_z$$
with  $\omega_0 = \gamma B_0$  (Larmor frequency)

### Influence of rf-field on magnetization precession I

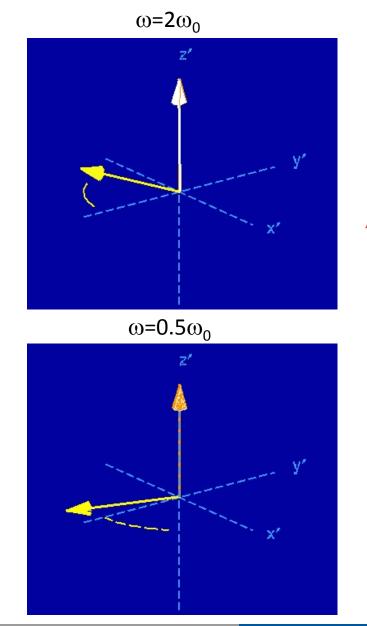
Laboratory system

system that rotates with rf-field

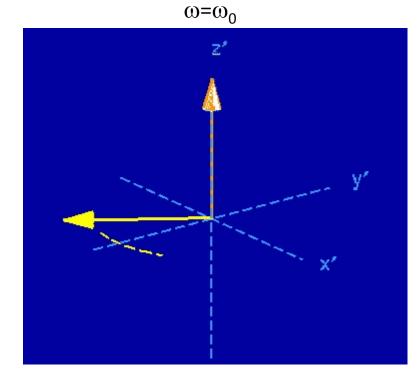


### Influence of rf-field on magnetization precession II

B<sub>o</sub>



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rf-field opens precession cone for  $\omega{=}\omega_{0}$ 



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### **Conventional ESR detection III**

$$\widetilde{m} = \widetilde{\chi} \cdot \widetilde{h}$$

$$= (\chi' - i\chi'') \cdot \widetilde{h}$$

$$\widetilde{h}(t) = ae^{i\omega t} = a(\cos \omega t + i\sin \omega t) \longrightarrow m(t) = \operatorname{Re}(\widetilde{m}(t)) = a\left[\chi' \cos \omega t + \chi'' \sin \omega t\right]$$

$$\operatorname{Re}(\widetilde{h}(t)) = a\cos \omega t$$

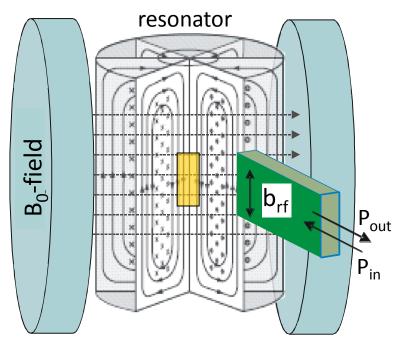
$$P(t) = \mu_0 h \cdot \frac{\mathrm{d}m}{\mathrm{d}t} = \mu_0 a^2 \omega \cos \omega t \left(-\chi' \sin \omega t + \chi'' \cos \omega t\right)$$

$$\begin{split} \langle P \rangle_T &= \frac{\langle w \rangle_T}{T} = \frac{\mu_0 \omega}{2\pi} \int h \cdot \frac{\mathrm{d}m}{\mathrm{d}t} \\ &= \frac{\mu_0 \omega}{2\pi} \int_0^{2\pi/\omega} a^2 \omega \chi'' \cos^2 \omega t \mathrm{d}t \\ &= \frac{\mu_0 \omega^2}{2\pi} a^2 \chi'' \left[ \frac{1}{2} t + \frac{1}{4\omega} \sin 2\omega t \right]_0^{2\pi/\omega} = \frac{1}{2} \mu_0 \omega \chi'' a^2 \end{split}$$

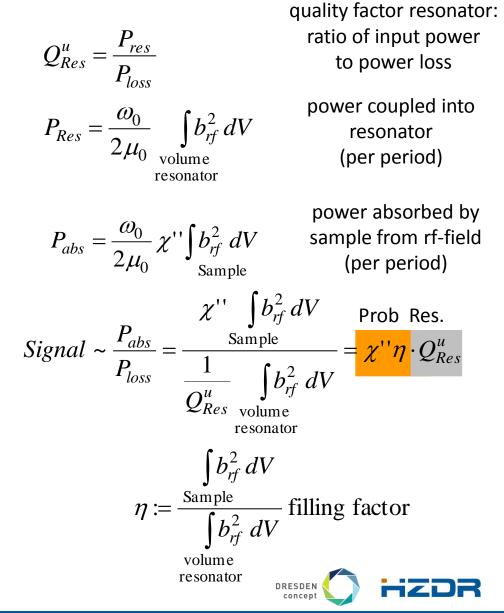
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### Experimental detection of ESR (conventional method)

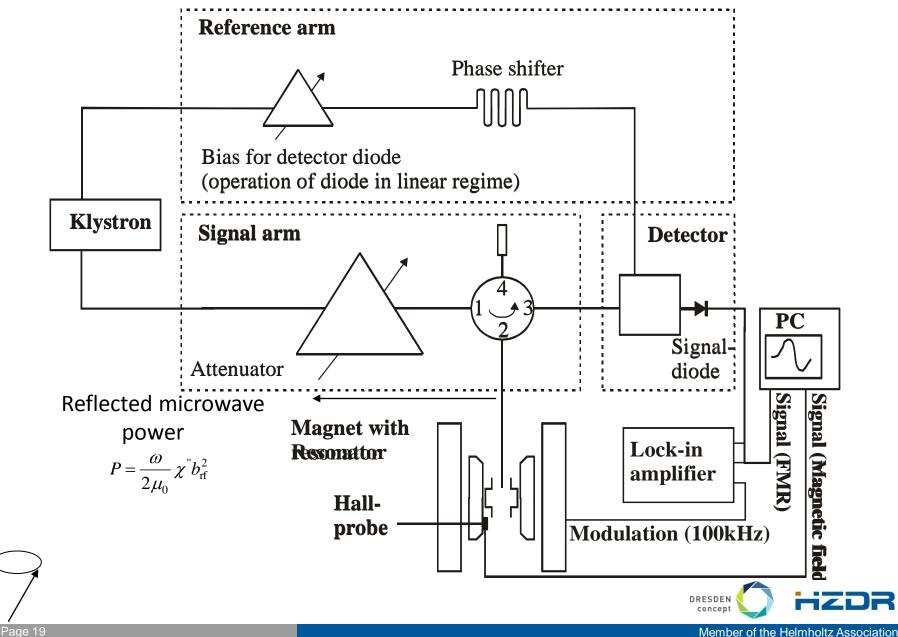


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# **Conventional ESR detection I**



#### Paramagnetic ion in a crystal

Hamilton-Operator for electrons of paramagnetic ion (no external field):

$$\hat{H} = \left\{ \left( \hat{p}_i^2 / 2m \right) - \left( Ze^2 / r_i \right) + \left( e^2 / r_{ij} \right) + \lambda_{ij} \hat{l}_i \cdot \hat{s}_i + a_i \hat{j}_i \cdot \hat{I} - e_i \Phi_c(\vec{r}_i) \right\}$$

Kinetic energy of ion

ergy Coulomb repulsion between electron pairs Coulomb attraction between electrons

and nucleus

Magnetic Crystal field interaction Interaction between electrons and nucleus with nuclear spin *I* 

Spin-orbit interaction between electrons





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#### **Reminder: Cubic Harmonics I**

Solution of Schrödinger Equation for H-Atom

 $\Psi_{n,l,m}(r,\vartheta,\varphi) = R_{n,l}(r) Y_{l,m}(\vartheta,\varphi)$  Hydrogen wavefunctions

#### **Radial part**

Angular dependent part

n = 1	l = 0	$R_{1,0}(r) = 2\left(\frac{Z}{a}\right)^{\frac{3}{2}}e^{-\frac{Zr}{a}}$	l = 0		$Y_{0,0}(\vartheta,\varphi) = \frac{1}{\sqrt{4\pi}}$
<i>n</i> = 2	l = 0	$R_{2,0}(r) = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a}\right) e^{-\frac{Zr}{2a}}$	<i>l</i> = 1	m = 0	$Y_{1,0}(\vartheta,\varphi) = \sqrt{\frac{3}{4\pi}\cos\vartheta}$
		$R_{2,1}(r) = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \frac{Zr}{a} e^{-\frac{Zr}{2a}}$		$m = \pm 1$	$Y_{1,\pm 1}(\vartheta,\varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin \vartheta \ e^{\pm i\varphi}$
<i>n</i> = 3	l = 0	$R_{3,0}(r) = \frac{2}{81\sqrt{3}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(27 - 18\frac{Zr}{a} + 2\left(\frac{Zr}{a}\right)^{2}\right) e^{-\frac{Zr}{3a}}$	<i>l</i> = 2	m = 0	$Y_{2,0}(\vartheta,\varphi) = \sqrt{\frac{5}{16\pi}} (3\cos^2\vartheta - 1)$
	l = 1	$R_{3,1}(r) = \frac{2}{81\sqrt{6}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(6\frac{Zr}{a} - \left(\frac{Zr}{a}\right)^{2}\right) e^{-\frac{Zr}{3a}}$			$Y_{2,\pm 1}(\vartheta,\varphi) = \mp \sqrt{\frac{15}{8\pi}} \sin \vartheta \cos \vartheta \ e^{\pm i\varphi}$
	l = 2	$R_{3,3}(r) = \frac{2}{81\sqrt{30}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(\frac{Zr}{a}\right)^2 e^{-\frac{Zr}{3a}}$			$Y_{2,\pm 2}(\vartheta,\varphi) = \sqrt{\frac{15}{8\pi} \cdot \frac{1}{2} \sin^2 \vartheta} e^{\pm 2i\varphi}$

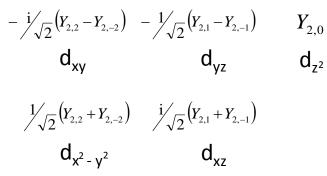


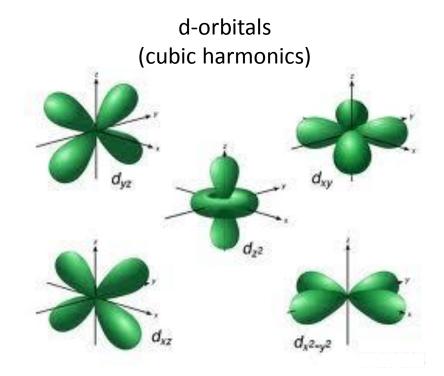
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#### **Reminder: Cubic Harmonics II**

Schrödinger Equation is a linear equation If  $\Psi 1$  and  $\Psi 2$  are solutions, then  $\Psi 3 = a\Psi 1 + b\Psi 2$  is solution, too.

One obtains REAL solutions for:





Example:

$$Y_{2,\pm 2} = \sqrt{\frac{15}{8\pi} \frac{1}{2} \sin^2 \mathcal{G} \cdot e^{\pm 2i\varphi}} \longrightarrow \frac{1}{\sqrt{2}} (Y_{2,2} + Y_{2,-2}) \sim \sin^2 \mathcal{G} \cos 2\varphi = (\sin \mathcal{G} \cos \varphi)^2 - (\sin \mathcal{G} \sin \varphi)^2$$

With (unit sphere, i.e. r=1)  $\sin \vartheta \sin \varphi = x$ ,  $\sin \vartheta \sin \varphi = y$ ,  $\cos \vartheta = z$ 

$$\longrightarrow \frac{1}{\sqrt{2}} (Y_{2,2} + Y_{2,-2}) \sim x^2 - y^2$$



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Crystal field interaction I

$$\hat{H} = \left\{ \left( \hat{p}_i^2 / 2m \right) - \left( Ze^2 / r_i \right) + \left( e^2 / r_{ij} \right) + \lambda_{ij} \hat{l}_i \cdot \hat{s}_i + a_i \hat{j}_i \cdot \hat{l} - e_i \Phi_c(\vec{r}_i) \right\}$$

Assumption: Crystal field creates electrostatic potential at the site of the ion Symmetry of this field is determined by symmetry of the crystal

Weak crystal field:	Crystal field weaker than spin-orbit interaction
	Rare earth ions with low lying f-shell

Intermediate crystal field:Crystal field stronger than spin-orbit interaction3d group ions with outer shell 3d electrons

Strong crystal field:Covalent bonding to neighbored ions or atoms<br/>Crystal field theory not applicable, since<br/>sources of crystal field are not outside of ion<br/>under consideration

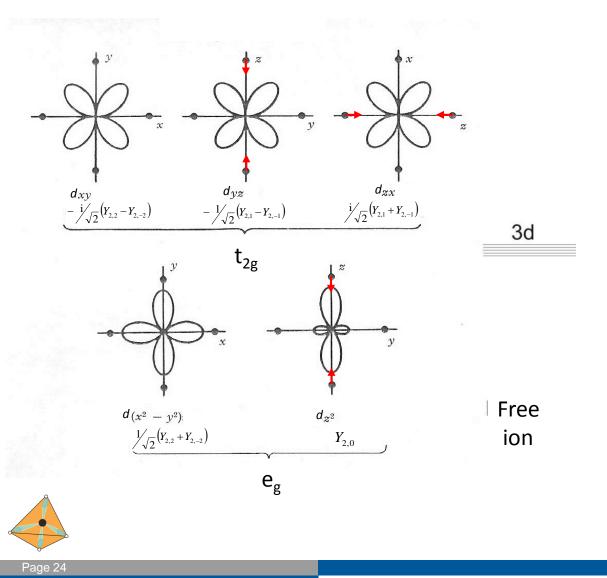




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#### Crystal field interaction II -

Instructive example: d-orbitals in cubic/tetragonal crystal field



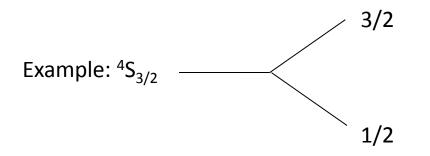


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## Zero-field splitting (influence of spin-orbit coupling)

Removal spin microstate degeneracy for systems with S > 1/2 in absence of an applied field.

Reason are spin-spin interactions like dipolar interaction or spin-orbit interaction between different electrons





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### Example I: Fe<sup>3+</sup>- and Mn<sup>2+</sup>-impurities in ZnO

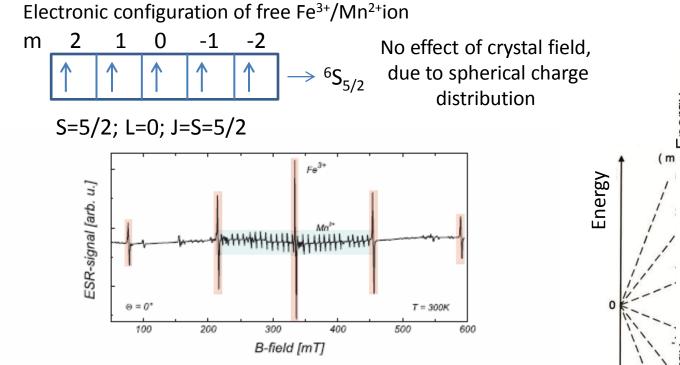
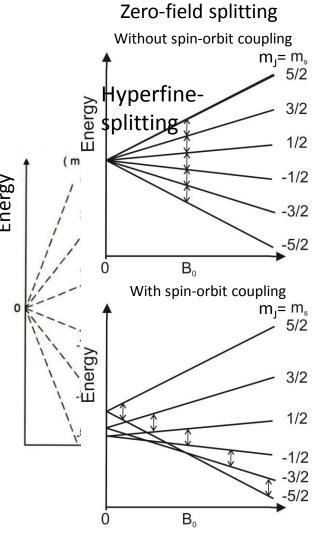


Figure 3.3: Fe<sup>3+</sup>(red bars) and Mn<sup>2+</sup>(blue bar) impurities in ZnO measured by ESR at  $\nu = 9.3$  GHz. The magnetic field is oriented parallel to the crystal c-axis (0001). Both ions have a fivefold fine structure due to S =  $\frac{5}{2}$ . Contrary to the Fe lines the Mn resonances are sixfold hyperfine split by the nuclear moment  $I_{Mn} = \frac{5}{2}$  leading to a spectrum of in total 30 lines.

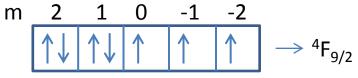
#### T. Kammermeier, PhD thesis Uni Duisburg-Essen (2010)





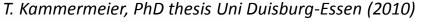
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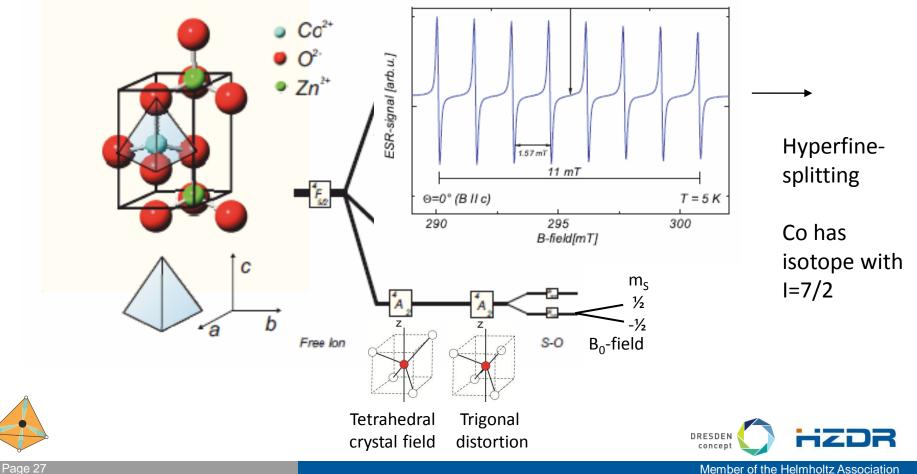
### Example II: Co<sup>2+</sup> in ZnO





S=3/2; L=3; J=L+S=9/2

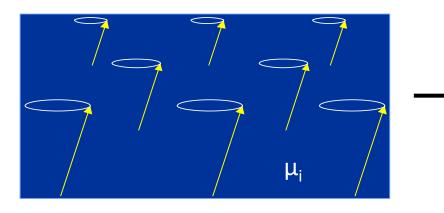




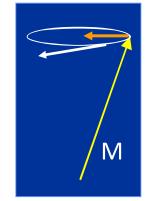
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### Magnetic Resonance in Ferromagnets (coupled spin system)

#### Ensemble of coupled spins



#### Macrospin model

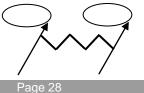


B<sub>eff</sub>: Anisotropy field, dipolar fields exchange fields etc.

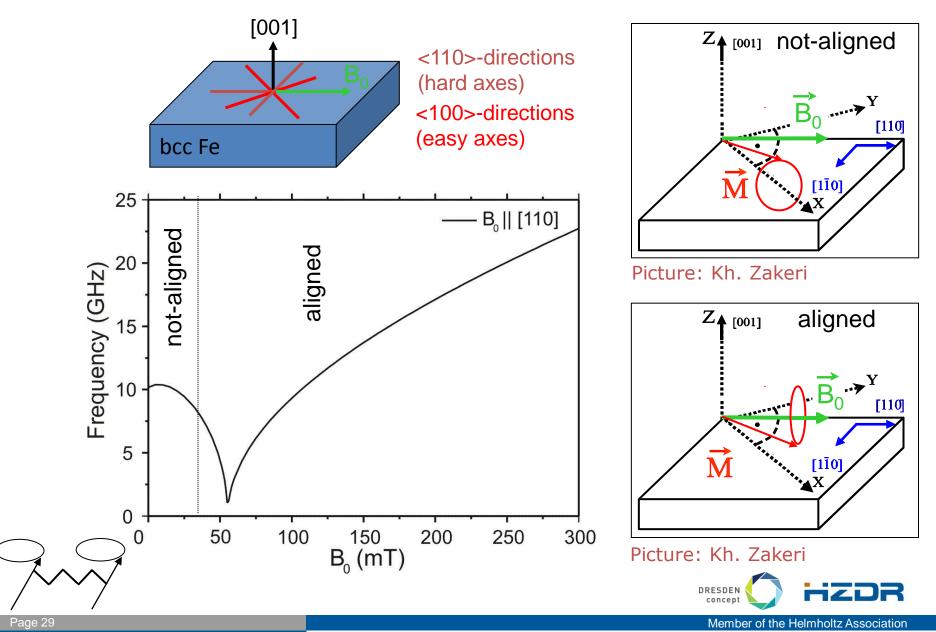
Magnetisation in effective field + damping



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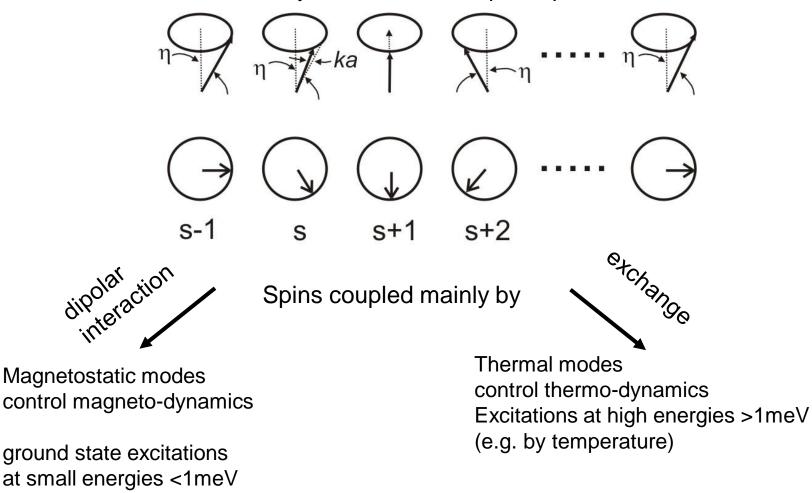


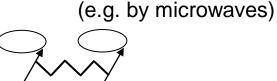
### FMR: Uniform mode - Influence of magnetic anisotropy



#### FMR: Spinwave excitations due to coupling of spins (non-uniform modes) I





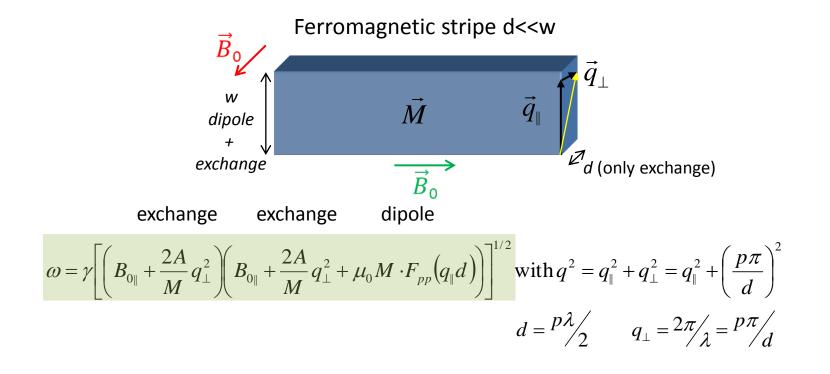


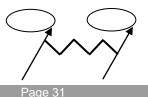
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### FMR: Spinwave excitations due to coupling of spins (non-uniform modes) II

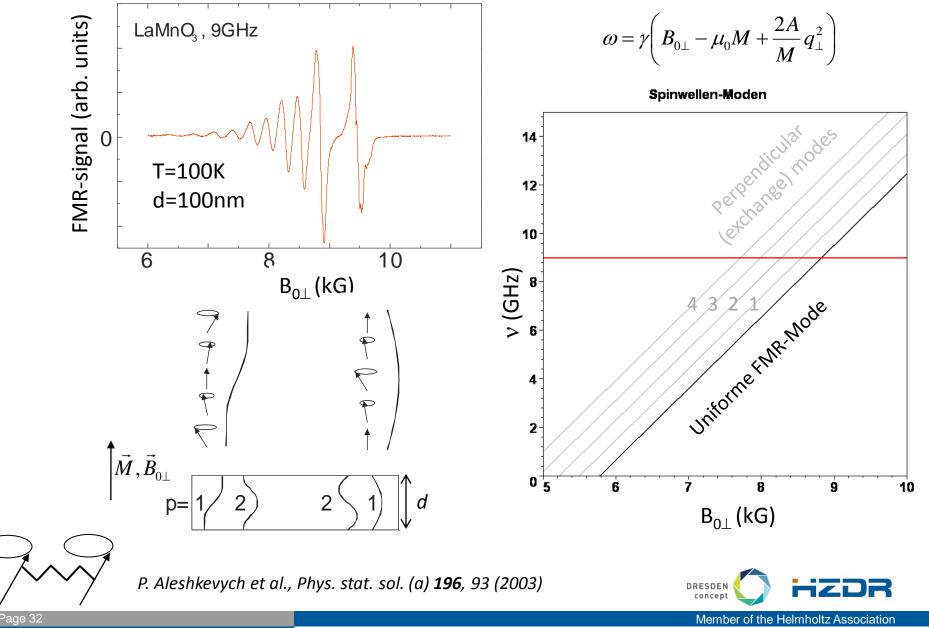




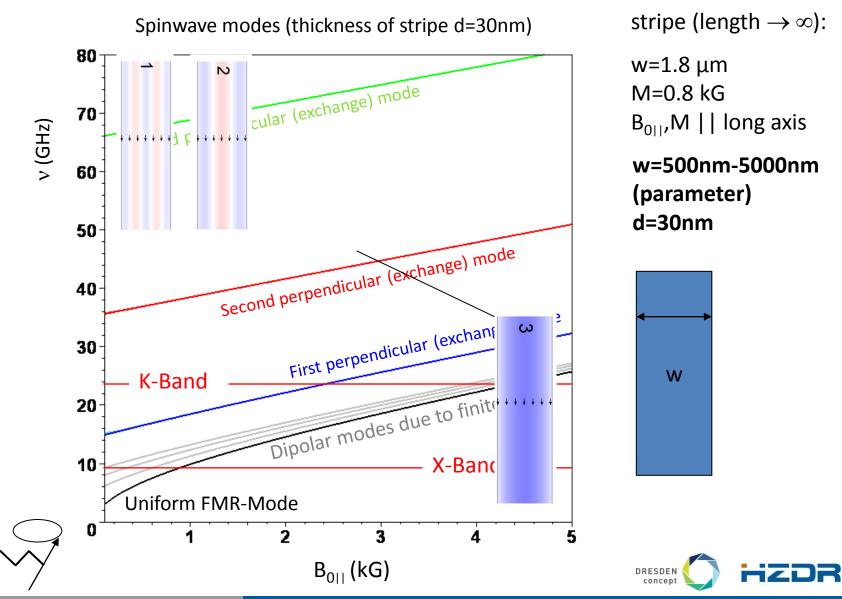


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#### Exchange dominated spinwaves in thin films



#### Dipolar spinwave modes in ferromagnetic stripe



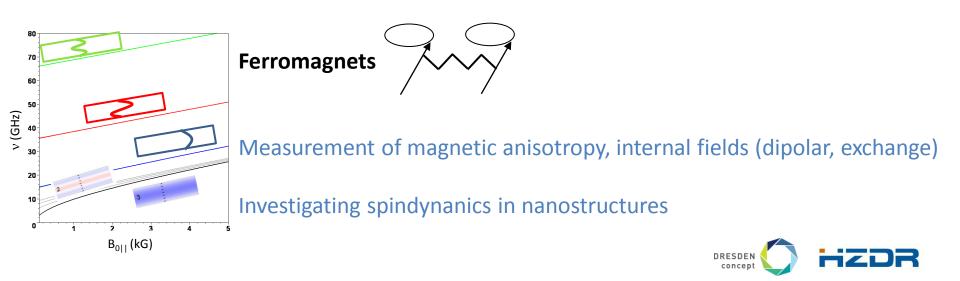
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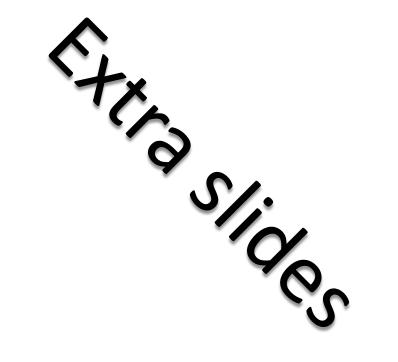
### Summary

Identification of species and environment (crystal symmetry)

Indirect way of investigating lattice sites that are occupied



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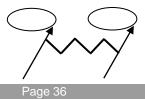
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$$\frac{\mathrm{d}\vec{\mu}}{\mathrm{d}t} = -\gamma \,\vec{\mu} \times \vec{B}_0 + \frac{\eta}{\mu} \left( \vec{\mu} \times \frac{\mathrm{d}\vec{\mu}}{\mathrm{d}t} \right) \qquad \vec{h}_{rf} = \left( h_{rf,x} \,\vec{e}_x + h_{rf,y} \,\vec{e}_y + h_{rf,z} \,\vec{e}_z \right) \cdot e^{i\omega t}$$

$$i\omega\mu_{x} = -(\gamma B_{0} + i\omega\eta)\mu_{y} - \gamma\mu b_{rf,y}$$
  

$$i\omega\mu_{y} = \gamma\mu b_{rf,x} + (\gamma B_{0} + i\omega\eta)\mu_{x}$$
  

$$i\omega\mu_{z} = 0$$





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