MAGNETISM IN MATERIALS

Lecture 10: Experimental Techniques
Specific heat & ESR

Ivica Zivkovic

06.05.2025

EPFL

- specific heat
- ESR

- magnetization
- magnetic susceptibility
- (magnetic) specific heat

$$F = \ldots + MH + \cdots - TS$$

$$C_V = -T\frac{\partial^2 F}{\partial T^2}$$

- magnetization
- magnetic susceptibility
- (magnetic) specific heat

$$F = \ldots + MH + \cdots - TS$$

$$C_V = -T\frac{\partial^2 F}{\partial T^2}$$

constant volume is not feasible in solid state $\rightarrow C_P$

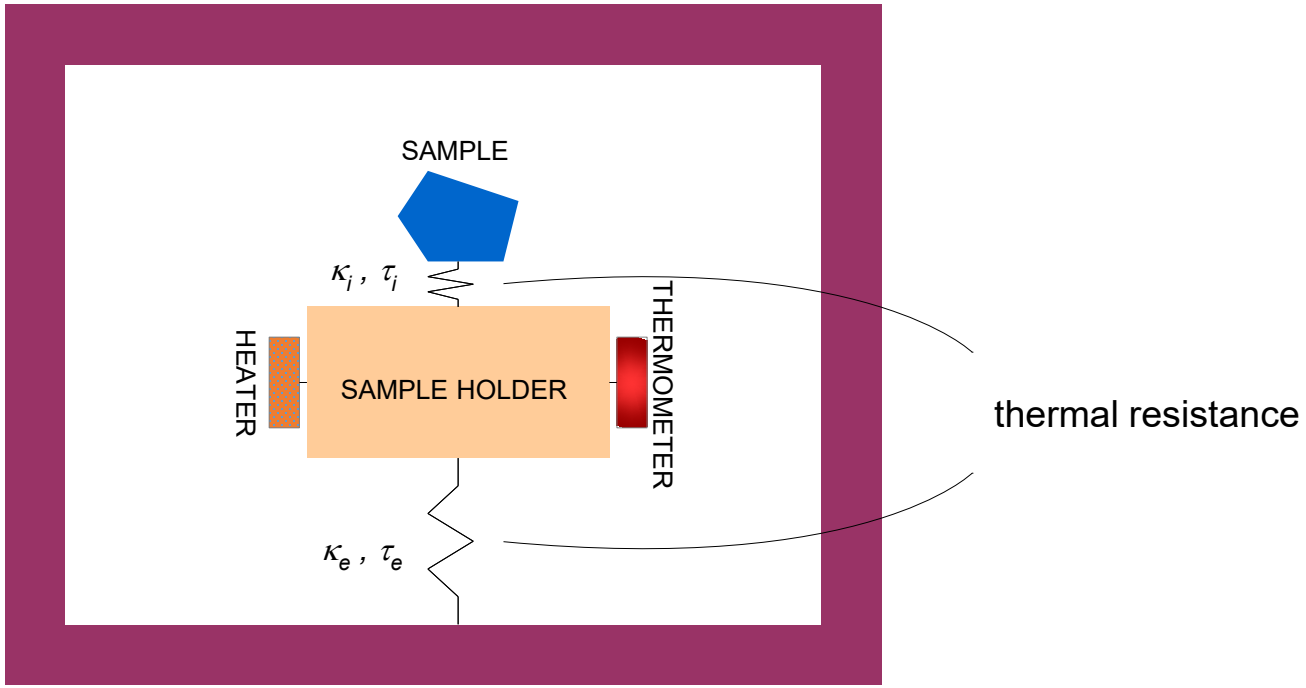
experiment

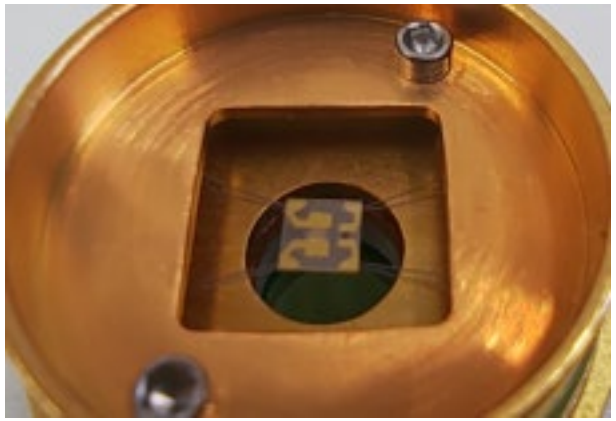
$$C_p \sim \left(\frac{\Delta T}{\Delta Q}\right)^{-1}$$

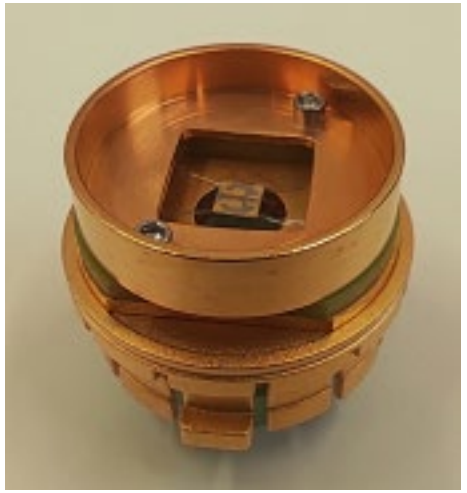
$$C_P - C_V = VT\frac{\alpha^2}{\beta}$$

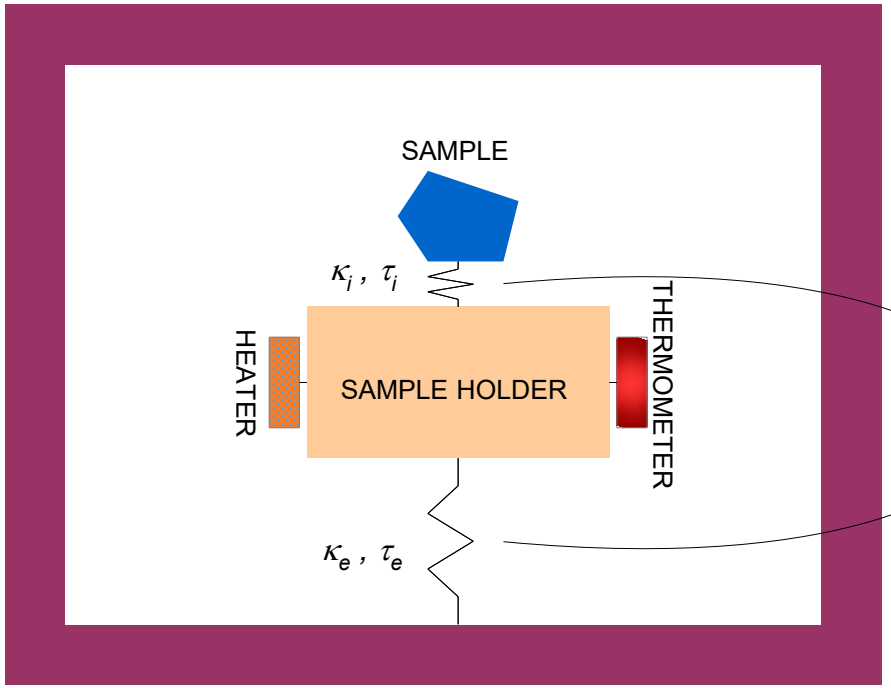
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

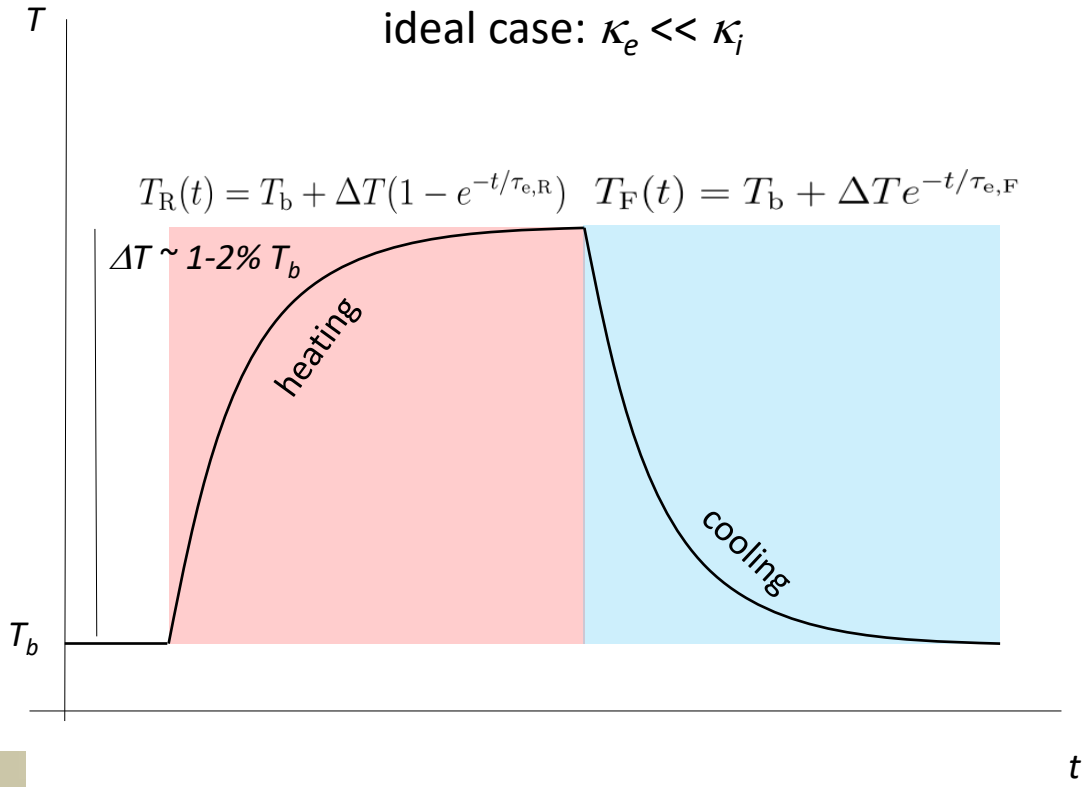

SAMPLE
κ_i , τ_i
HEATER
SAMPLE HOLDER
THERMOMETER
κ_e , τ_e
thermal resistance
THERMAL BATH

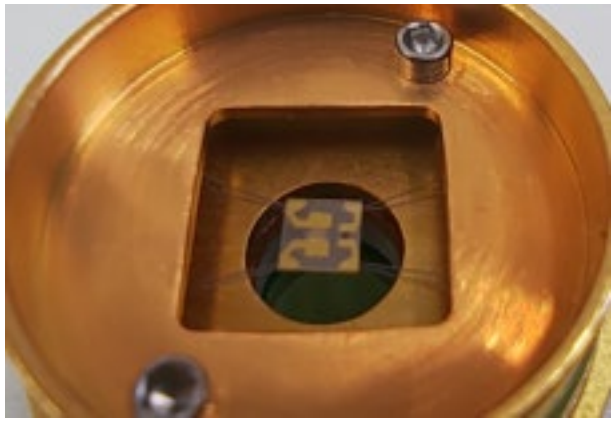


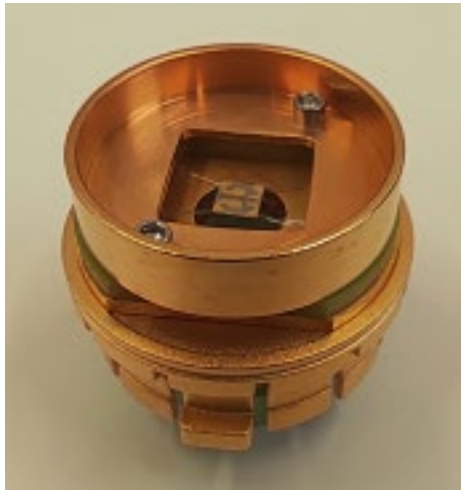


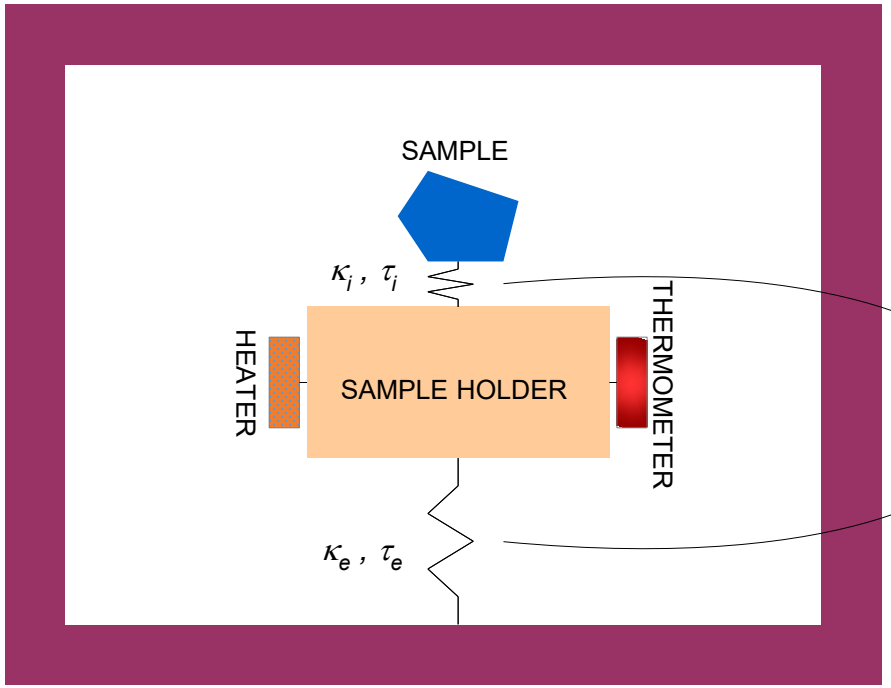


thermal resistance



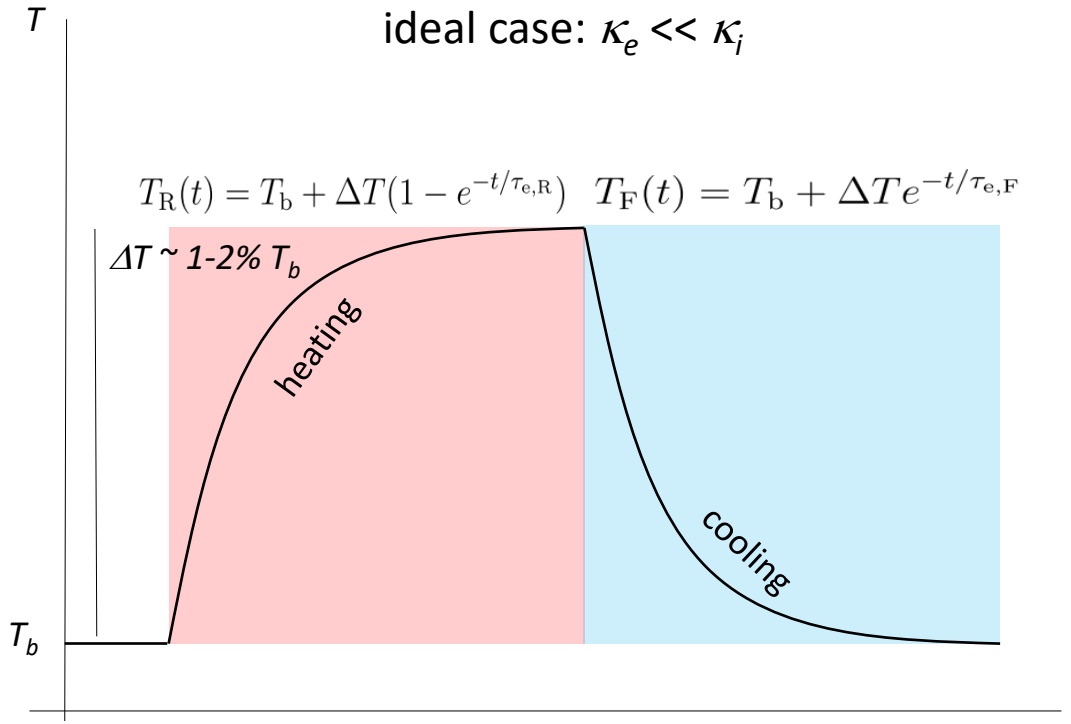


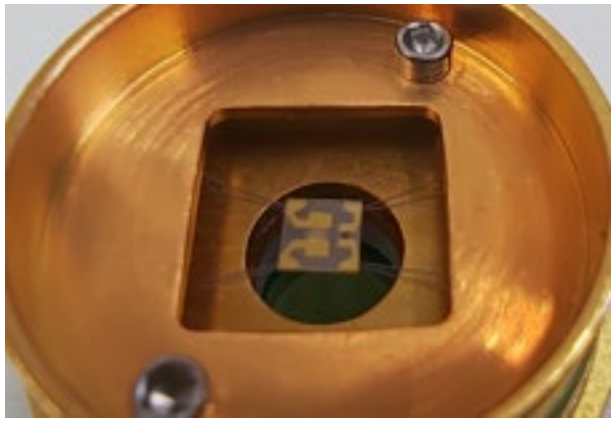


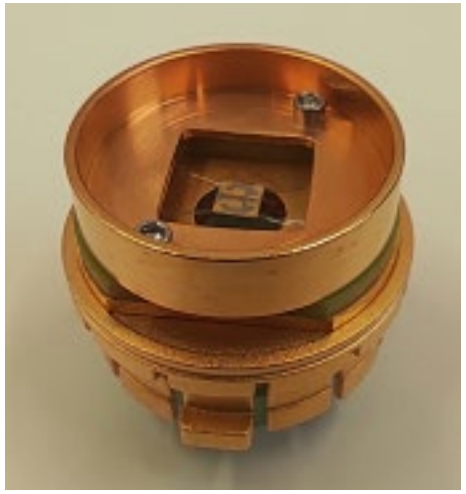


thermal resistance

ideal case: $\kappa_e << \kappa_i$







real life: 2τ-method

$$T_0(t) = T_b + \Delta T(a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2})$$

$$a_1 = \frac{\tau_e - \tau_2}{\tau_1 - \tau_2}, \quad a_2 = \frac{\tau_1 - \tau_e}{\tau_1 - \tau_2}$$

$$\tau_1 = \frac{\tau_e + \tau_i}{2}\left[1 + \sqrt{1 - \frac{4\tau_i\tau_{e,0}}{(\tau_e + \tau_i)^2}}\right]$$

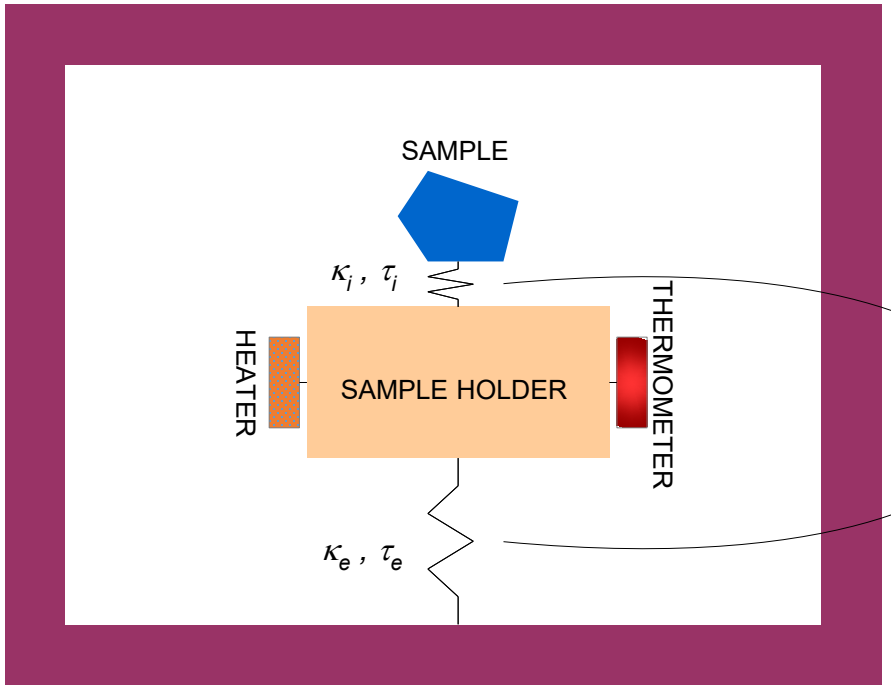
$$\tau_2 = \frac{\tau_e + \tau_i}{2}\left[1 - \sqrt{1 - \frac{4\tau_i\tau_{e,0}}{(\tau_e + \tau_i)^2}}\right]$$

$$\tau_1 = \frac{\tau_e + \tau_i}{2}\left[1 + \sqrt{1 - \frac{4\tau_i\tau_{e,0}}{(\tau_e + \tau_i)^2}}\right]$$

$$\tau_2 = \frac{\tau_e + \tau_i}{2}\left[1 - \sqrt{1 - \frac{4\tau_i\tau_{e,0}}{(\tau_e + \tau_i)^2}}\right]$$

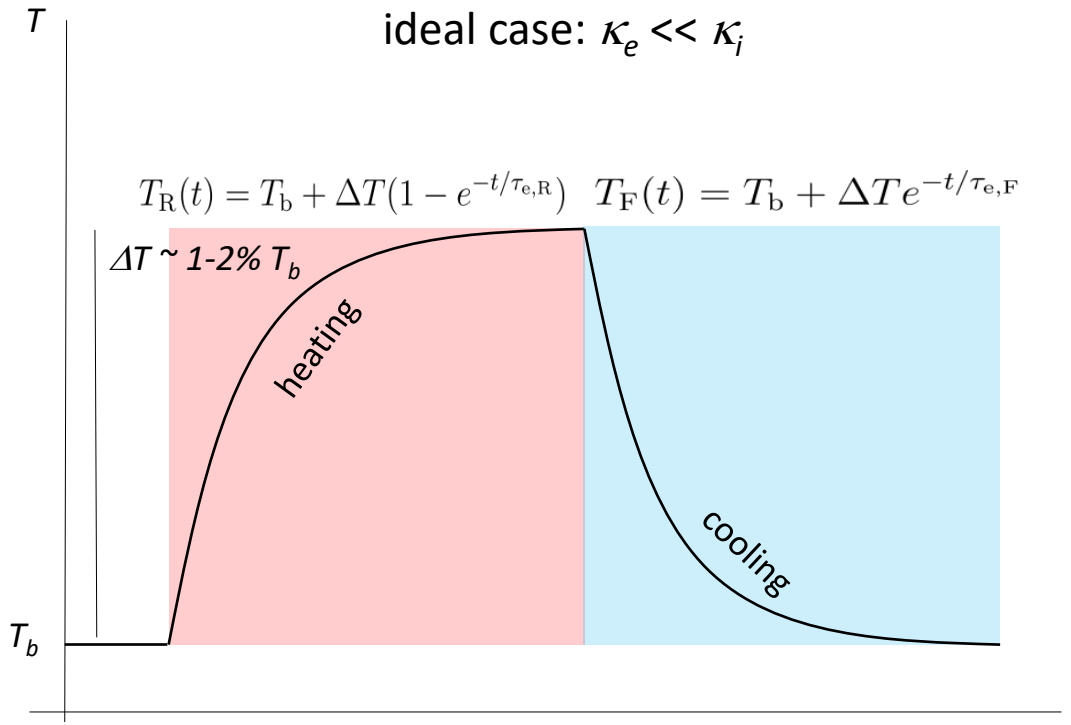
$$K_e = \frac{\Delta P}{\Delta T}$$

$$C_s + C_0 = K_e(a_1\tau_1 + a_2\tau_2)$$

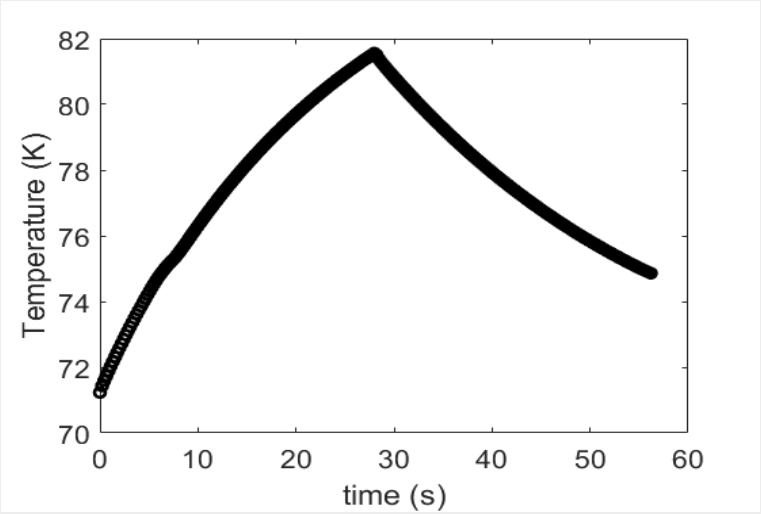


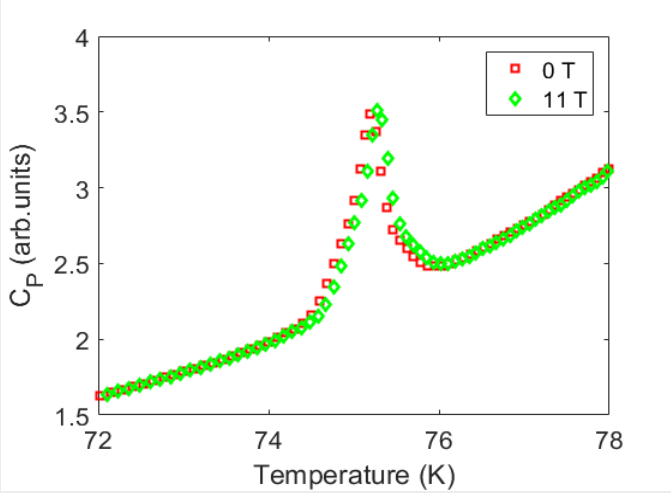
thermal resistance

ideal case: $\kappa_e << \kappa_i$

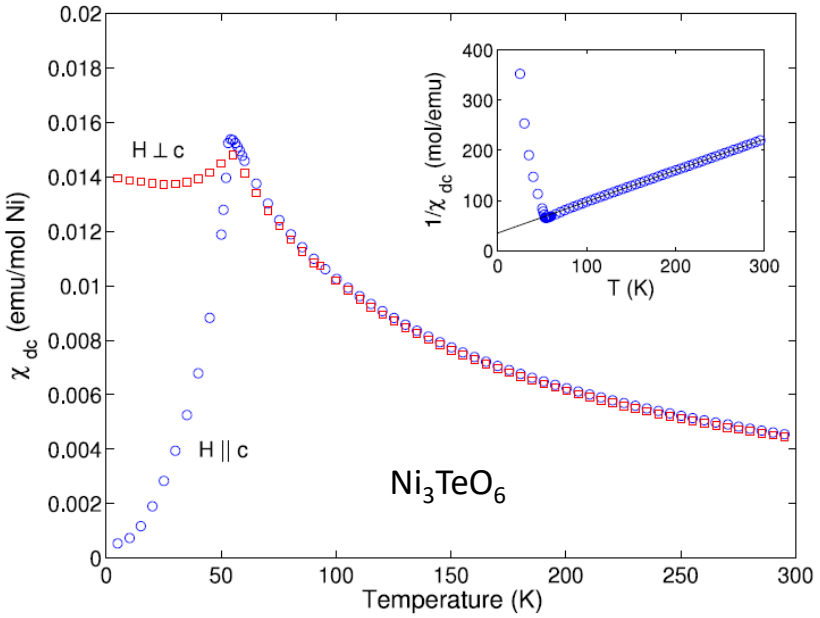


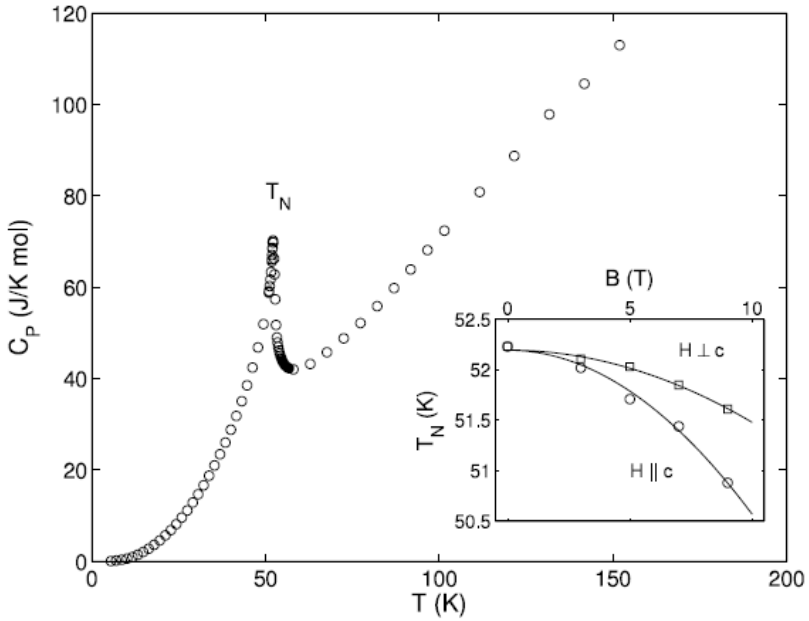
long-shot: 1st order





❖ phase boundaries





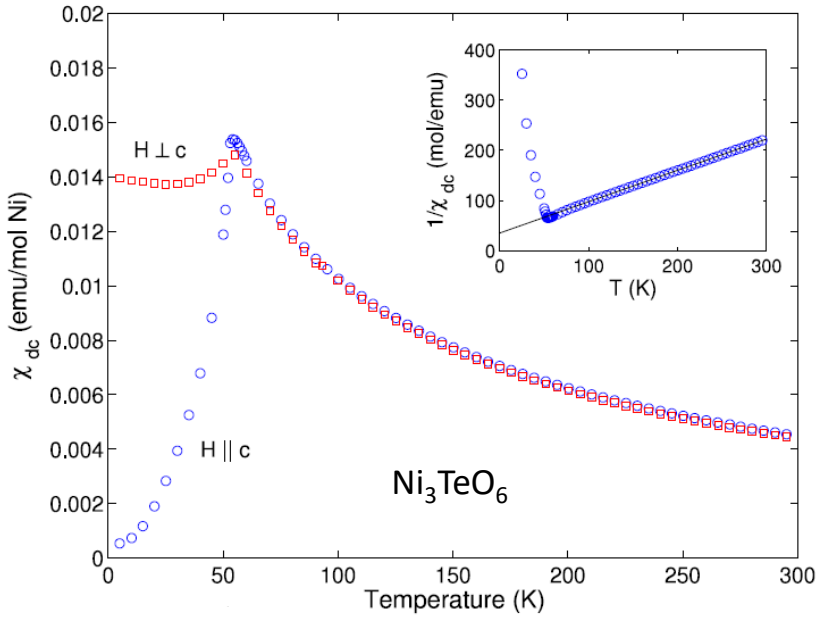
$$F(M) = F_0 + a_0(T - T_C)M^2 + bM^4$$

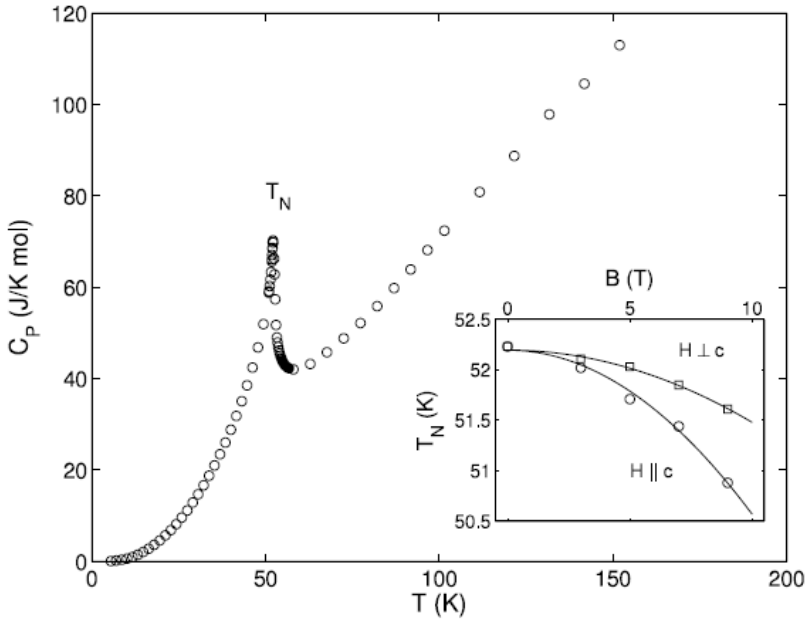
$$\frac{\partial F}{\partial M} = 0 \longrightarrow \begin{cases} M = 0 \\ M = \pm \mathrm{K}\sqrt{T_C - T} \end{cases}$$

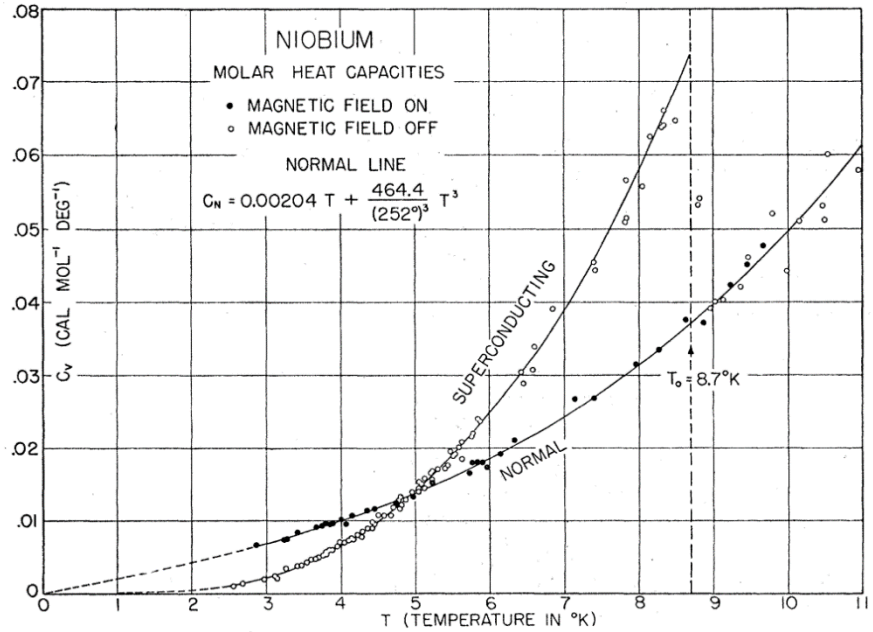
$$\left.\begin{array}{ll} C = C_0 + WT & T < T_c \\ C = C_0 & T > T_c \end{array}\right\} \quad \Delta C|_{T=T_c} = WT_c$$

(2nd order)

❖ phase boundaries







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$$C = C_0 + WT \quad T < T_c$$

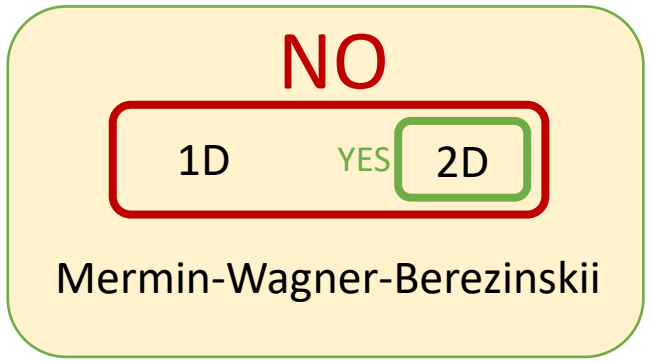
$$C = C_0 \quad T > T_c$$

$$\Delta C|_{T=T_c} = WT_c$$

(2nd order)

(1st order) → latent heat!

- short-range correlations

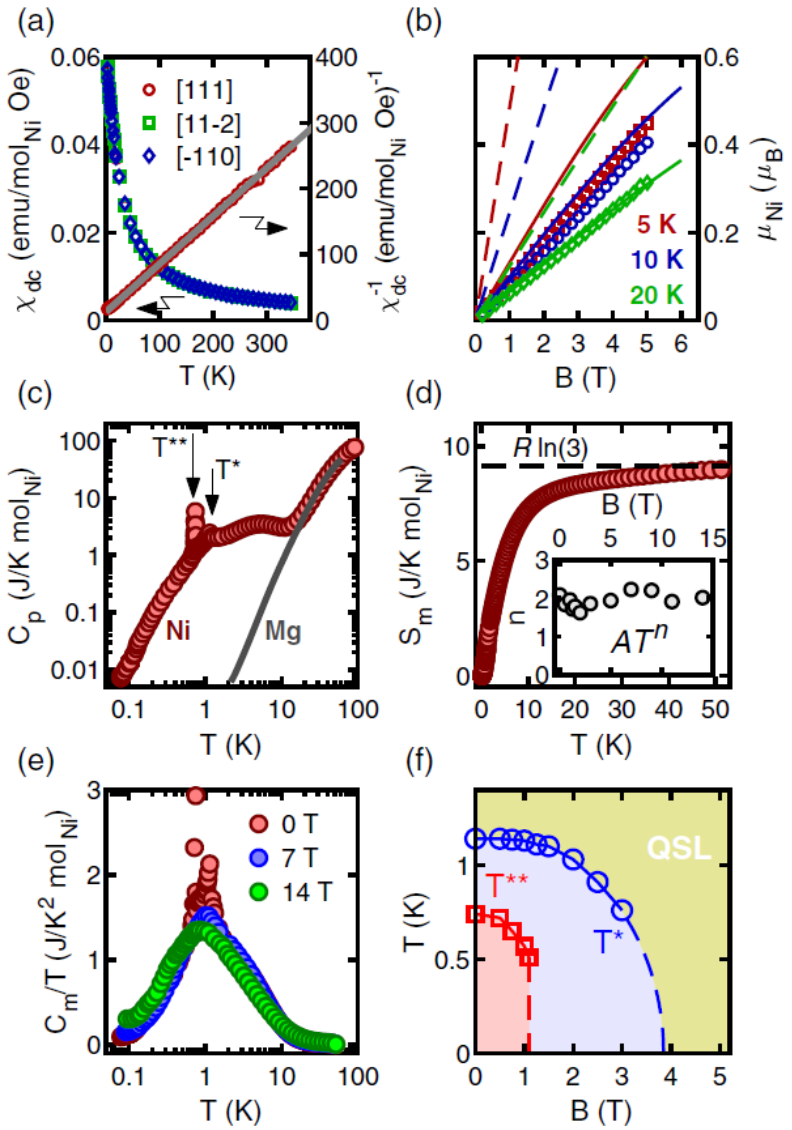


❖ short-range correlations

NO

1D YES 2D

Mermin-Wagner-Berezinskii



Zero-point entropy in 'spin ice'

A. P. Ramirez*, A. Hayashi†, R. J. Cava†, R. Siddharthan‡ & B. S. Shastry‡

** Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974, USA*
† Chemistry Department, Princeton University, Princeton, New Jersey 08540, USA
‡ Department of Physics, Indian Institute of Science, Bangalore 560012, India

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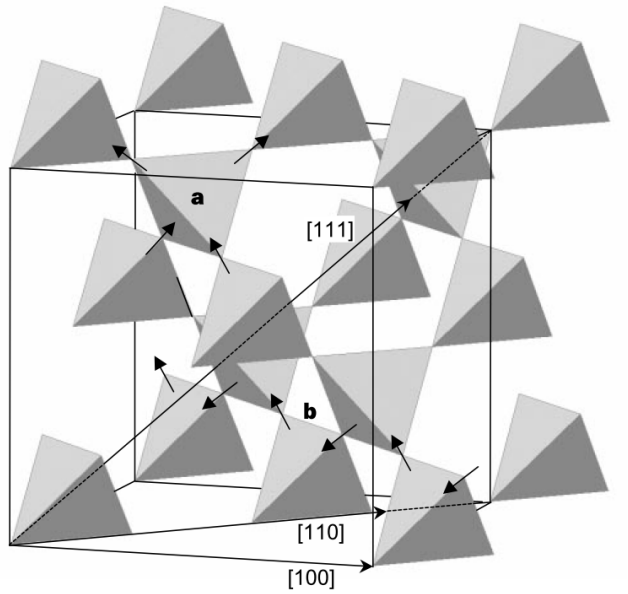
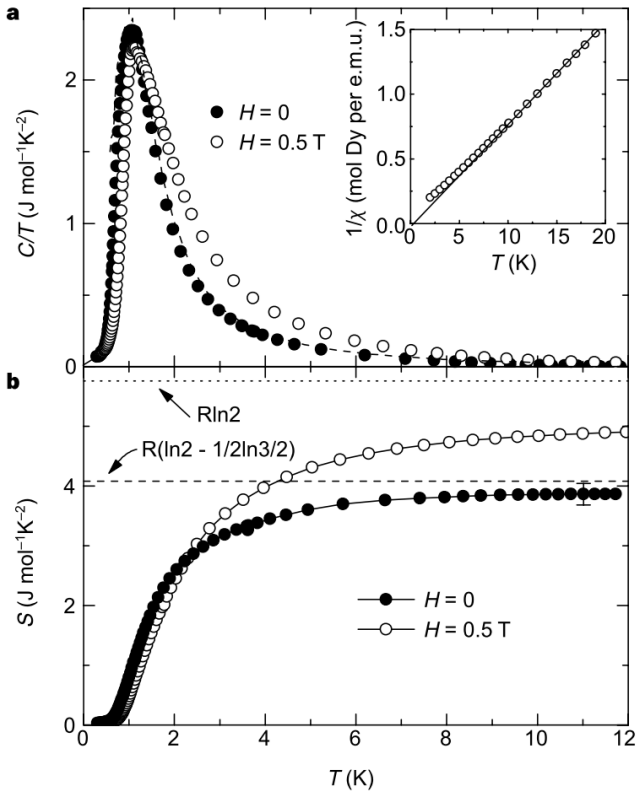


$Dy_2Ti_2O_7$



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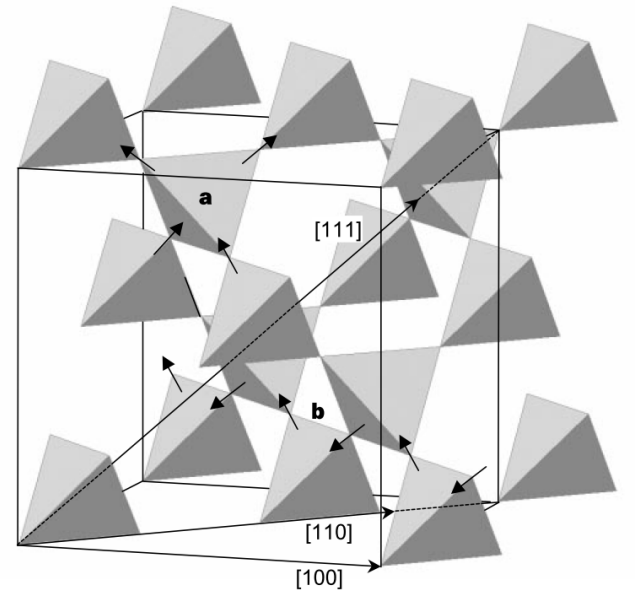

Magnetic Coulomb Phase in the Spin Ice $Ho_2Ti_2O_7$

T. Fennell,[1]* P. P. Deen,[1] A. R. Wildes,[1] K. Schmalzl,[2] D. Prabhakaran,[3] A. T. Boothroyd,[3] R. J. Aldus,[4] D. F. McMorrow,[4] S. T. Bramwell[4]

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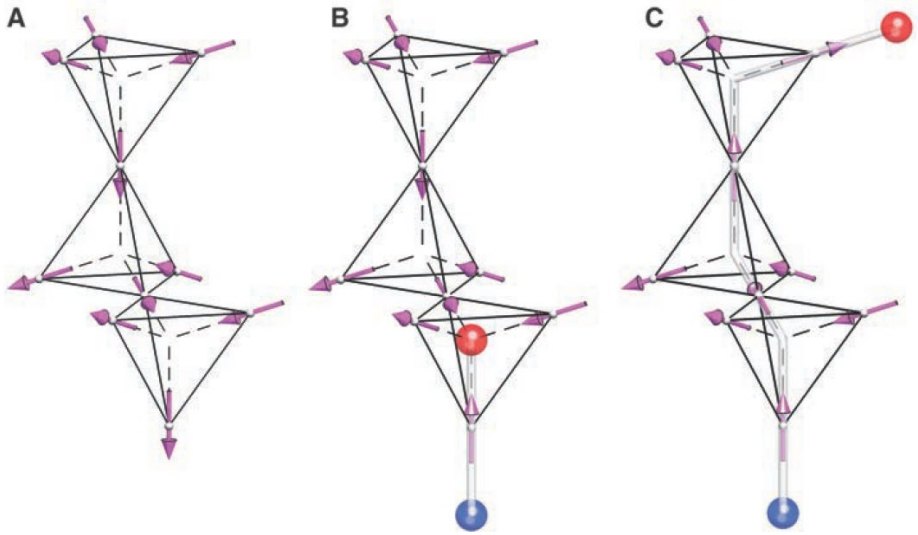

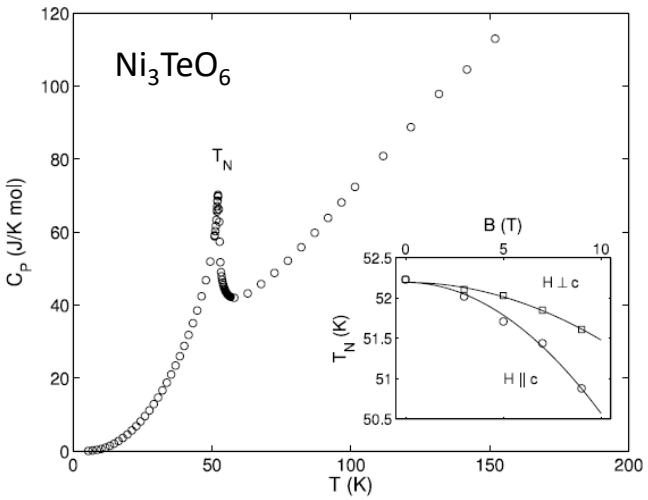

phonon subtraction

$$S = \int \frac{C_m}{T} dT = Rln(2S+1)$$

❖ the ubiquitous contribution is coming from phonons

Debye limit

$$C_V = 9\mathrm{NR}\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x-1)^2} dx$$

$$T \ll \Theta_D \rightarrow\sim \left(\frac{T}{\Theta_D}\right)^3$$

$$T \gg \Theta_D \rightarrow C_V = 3\mathrm{NR}$$

Einstein limit

$$C_V = 3\mathrm{NR}\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}}-1\right)^2}$$

$$T \ll \Theta_E \rightarrow\sim \left(\frac{\Theta_E}{T}\right)^2 e^{-\frac{\Theta_E}{T}}$$

$$T \gg \Theta_E \rightarrow C_V = 3\mathrm{NR}$$

PHYSICAL REVIEW B **83**, 134416 (2011)

Magnetic properties of the heavy-fermion antiferromagnet $CeMg_3$

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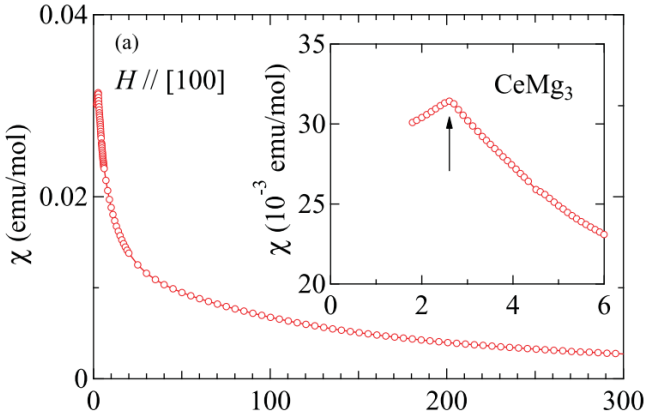
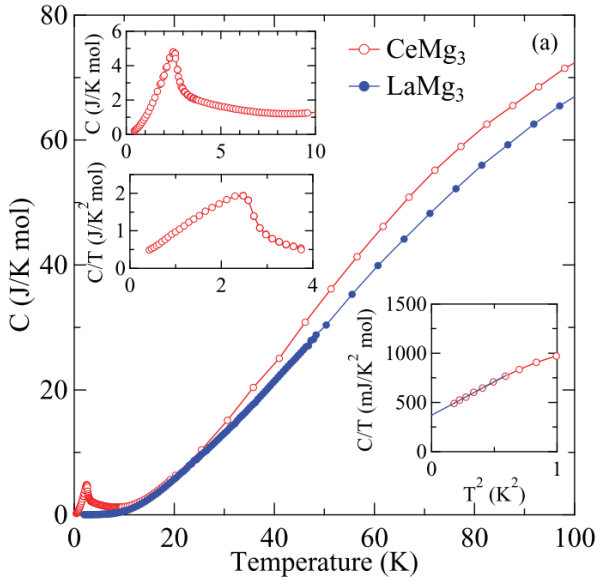
(Received 3 November 2010; revised manuscript received 6 February 2011; published 13 April 2011)

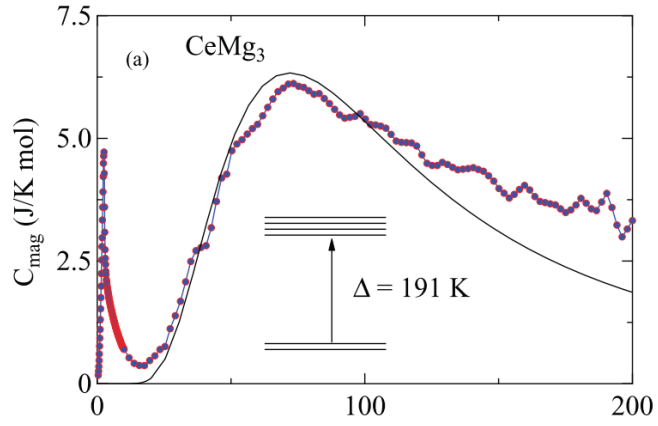
We have grown the single crystals of $CeMg_3$ and its nonmagnetic analog $LaMg_3$, which crystallize in the cubic crystal structure with the space group $Fm\bar{3}m$, and studied their magnetic properties on well-oriented single crystals by measuring the magnetic susceptibility, magnetization, electrical resistivity, and heat capacity. $CeMg_3$ orders antiferromagnetically with a Néel temperature T_N of 2.6 K. The specific heat capacity at low temperature exhibits an enhanced Sommerfeld coefficient of 370 mJ/K^2 mol, indicating the heavy-fermion nature of $CeMg_3$. An estimation of the Kondo temperature T_K was made and it was found that it is of a magnitude similar to that of T_N. The reduced value of the magnetization below the ordering temperature, together with the reduced entropy at the magnetic ordering temperature and the enhanced low-temperature heat capacity, indicates that Kondo effect plays a significant role in this compound. The electrical resistivity measurement suggests that $CeMg_3$ is a Kondo lattice compound. We have performed a crystalline electric field (CEF) analysis on the magnetic susceptibility and the heat capacity data and found that the ground state is a Γ_7 doublet with an overall splitting of 191 K.



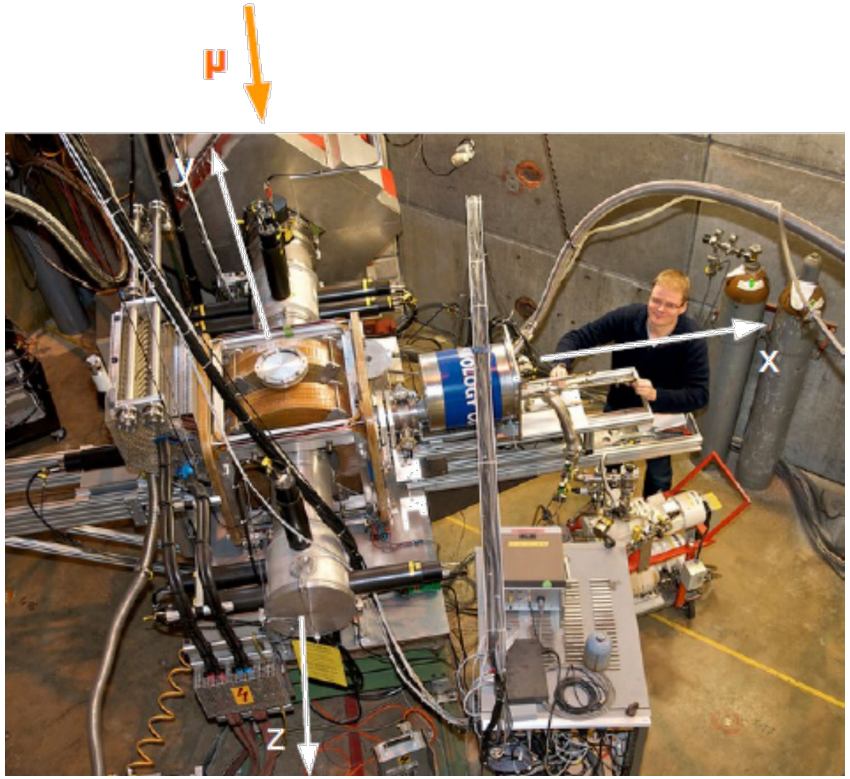


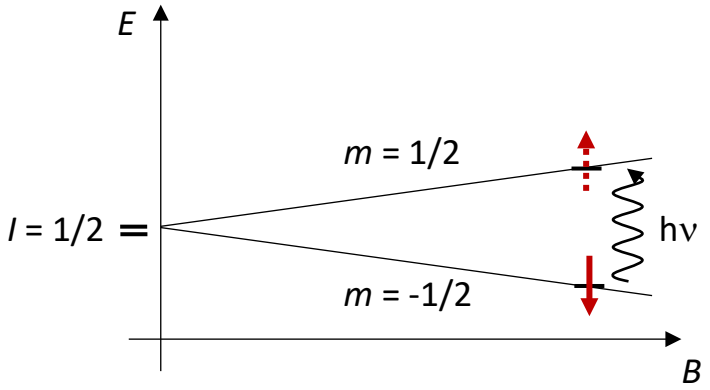
$$C_{tot} = C_{ph} + C_{el} + C_{mag} + C_{sch} + C_{nucl}$$

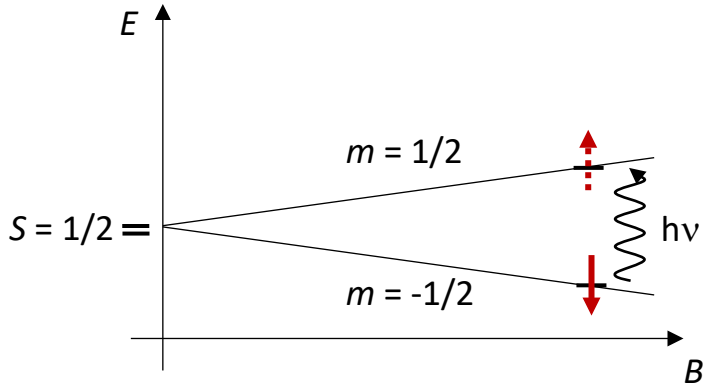
$$C_{Sch}(T) = R\left[\frac{\sum_i g_i e^{-E_i/T}\sum_i g_i E_i^2 e^{-E_i/T} - \left[\sum_i g_i E_i e^{-E_i/T}\right]^2}{T^2\left[\sum_i g_i e^{-E_i/T}\right]^2}\right]$$



- electron spin resonance (ESR/EPR)
- nuclear magnetic resonance (NMR/MRI)
- muon spin resonance (μSR)
- FMR, AFMR, Moessbauer,...

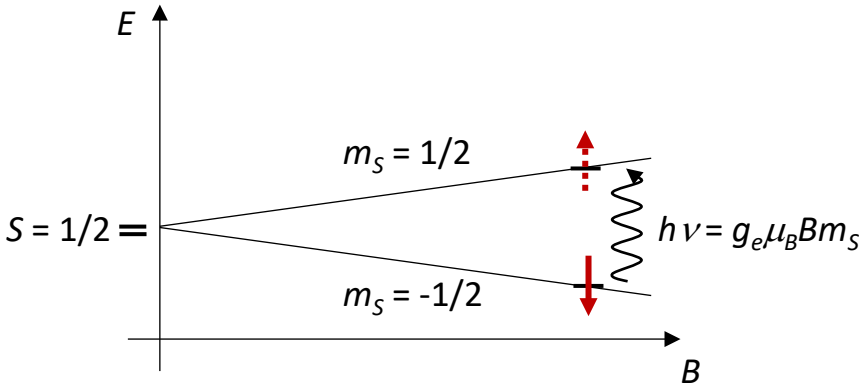


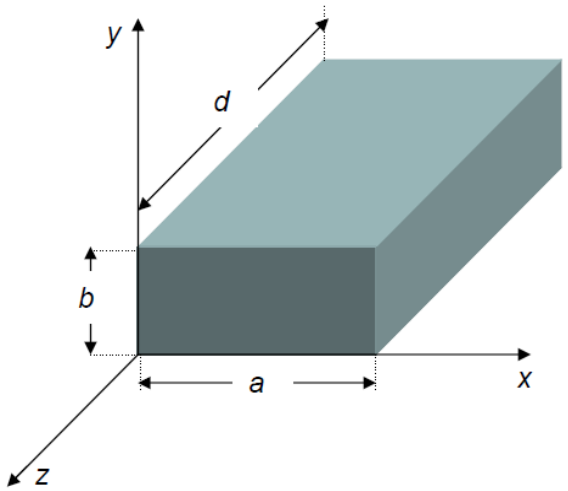


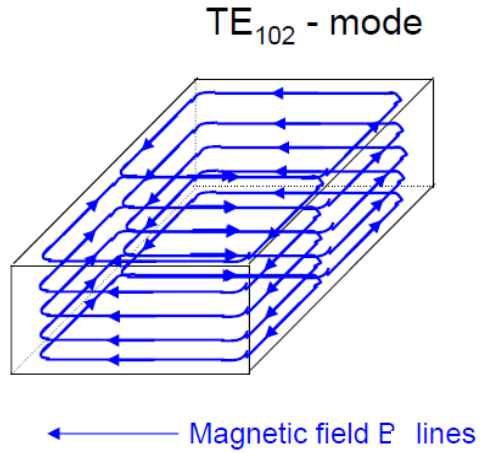


X-band: ~9 GHz (B~0.3 T)
K-band: ~24 GHz
Q-band: ~35 GHz
W-band: ~95 GHz

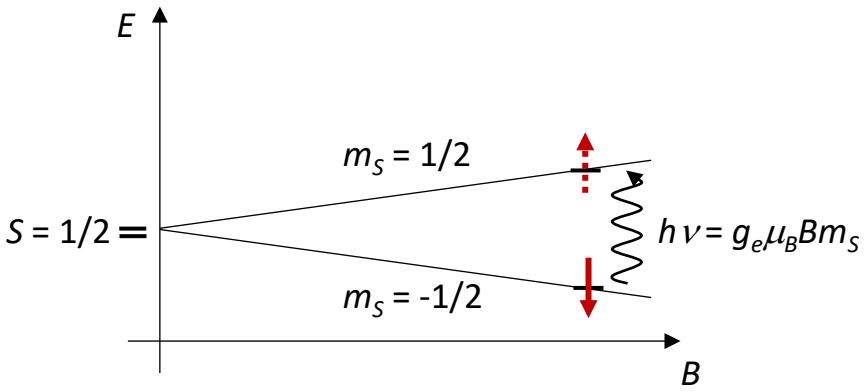
fixed

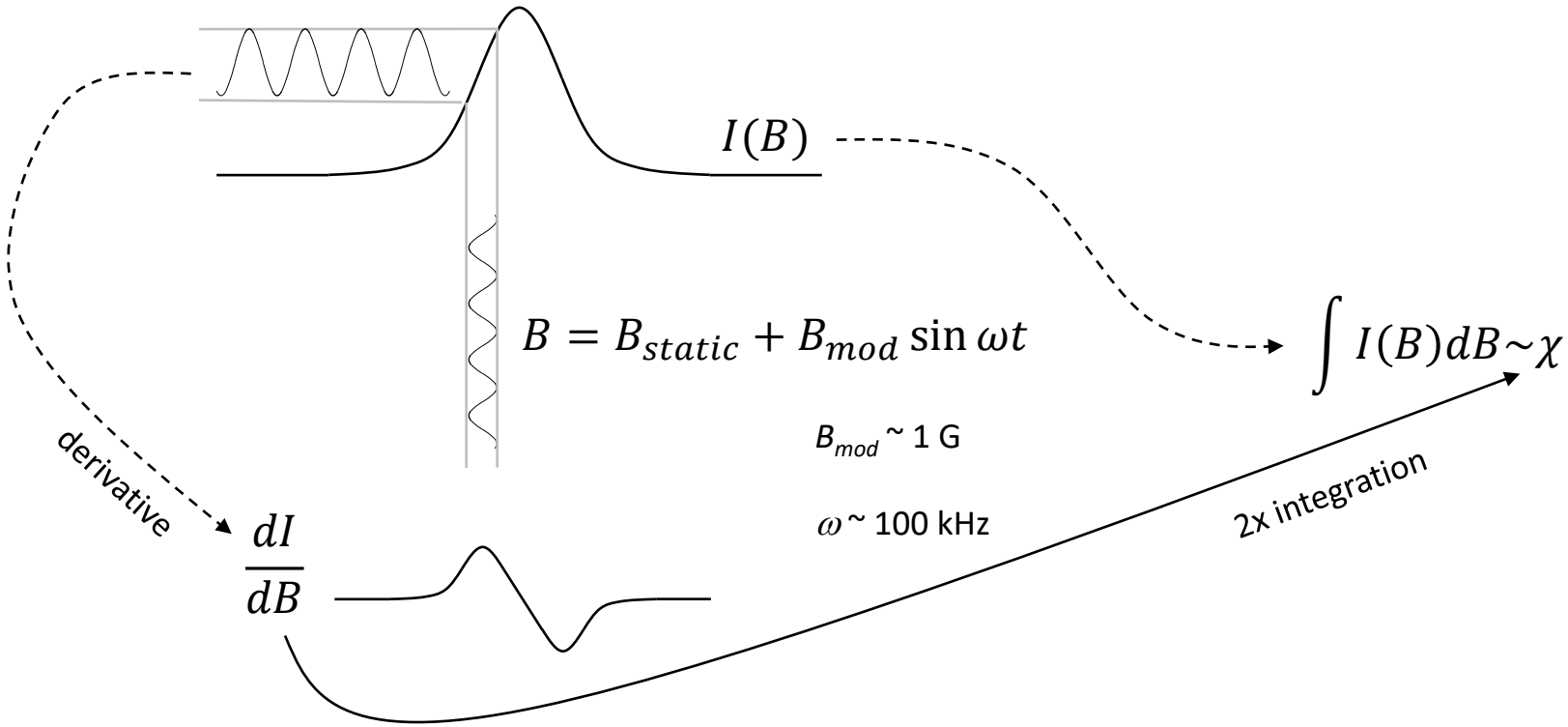


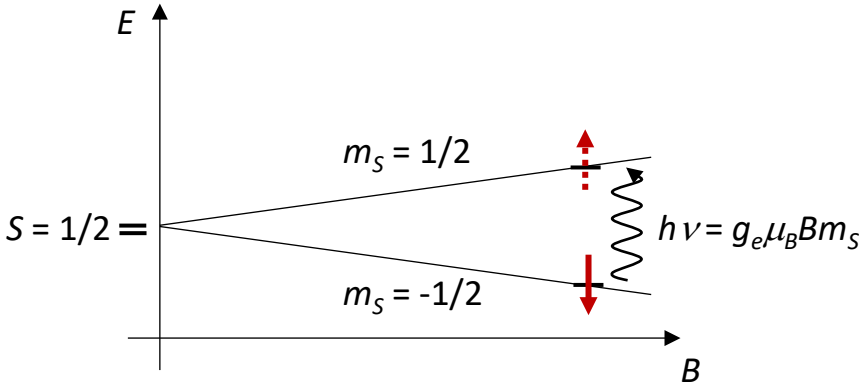


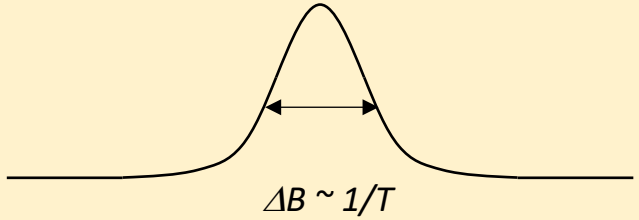


high quality factor *Q*

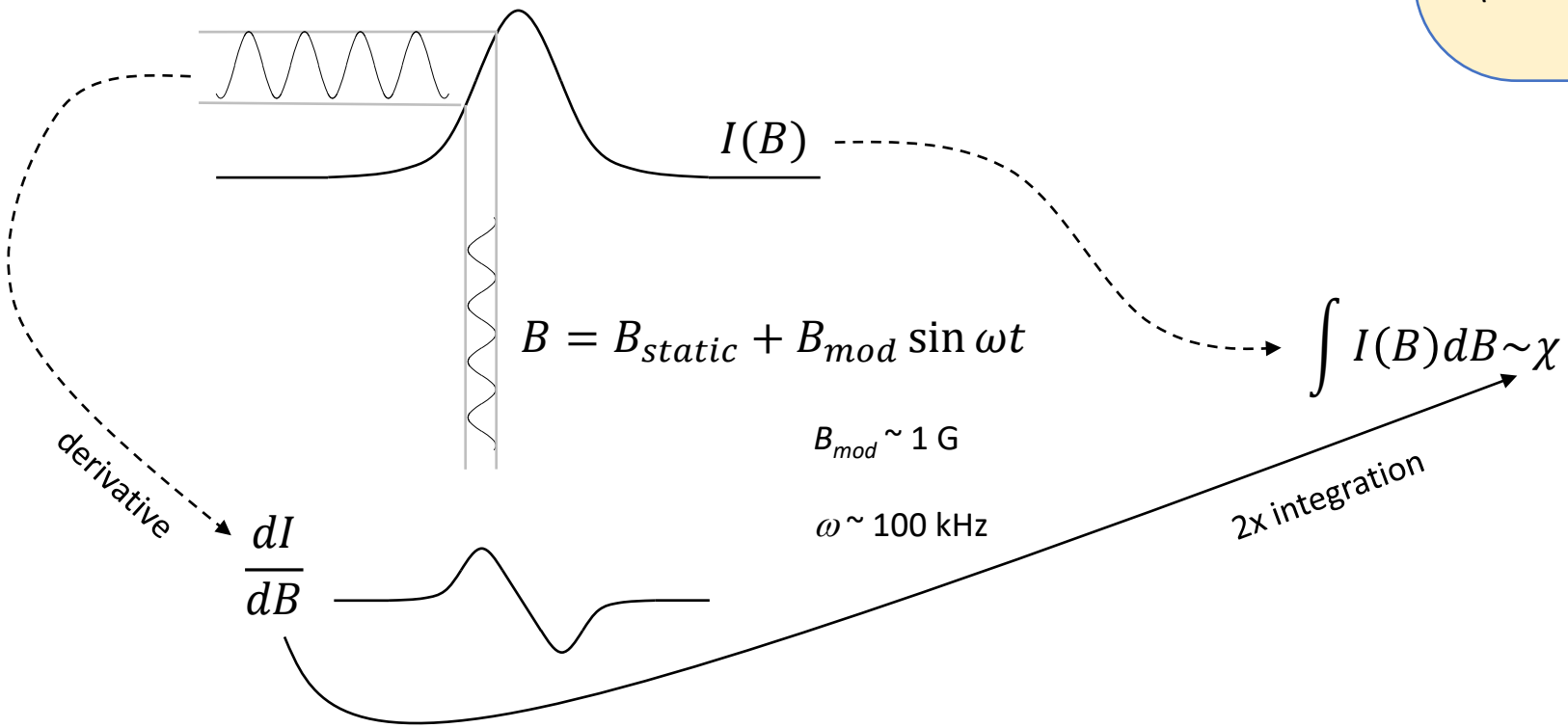

E
m_S = 1/2
S = 1/2
$h\nu = g_e\mu_B B m_S$
m_S = -1/2
B


$I(B)$
$B = B_{static} + B_{mod} \sin \omega t$
B_{mod} ~ 1 G
ω ~ 100 kHz
derivative
$\frac{dI}{dB}$
$\int I(B)dB \sim \chi$
2x integration





T_1 – spin-lattice/longitudinal relaxation (decay of population back to equilibrium)
T_2 – spin-spin/transverse relaxation (decay of coherence between the spins)



$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{zfs} + \mathcal{H}_{hf} + \mathcal{H}_{ee}$$

exchange interaction (narrowing of line-widths)

hyperfine interaction (element identification)

zero-field splitting (anisotropy)

Zeeman splitting (*g*-tensor)

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{zfs} + \mathcal{H}_{hf} + \mathcal{H}_{ee}$$

exchange interaction (narrowing of line-widths)

hyperfine interaction (element identification)

zero-field splitting (anisotropy)

Zeeman splitting (*g*-tensor)

3*d* (*LS* coupling)

$$\mathcal{H}_e + \mathcal{H}_{zfs} = g_e \mu_B \boldsymbol{B}(\boldsymbol{L} + \boldsymbol{S}) + \lambda \boldsymbol{L}\boldsymbol{S} = \mu_B \boldsymbol{B} \bar{\bar{g}} \boldsymbol{S} + \boldsymbol{S} \bar{\bar{D}} \boldsymbol{S}$$

$$g_e = 2.0023$$

$$\bar{\bar{g}} = g_e(\bar{\bar{1}} + 2\lambda \bar{\bar{\Lambda}}) \qquad \bar{\bar{D}} = \lambda^2 \bar{\bar{\Lambda}} \qquad \Lambda_{ij} = \sum_{n \neq 0} \frac{\langle \psi_0 | L_i | \psi_n \rangle \langle \psi_n | L_j | \psi_0 \rangle}{E_0 - E_n}$$

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{zfs} + \mathcal{H}_{hf} + \mathcal{H}_{ee}$$

exchange interaction (narrowing of line-widths)

hyperfine interaction (element identification)

zero-field splitting (anisotropy)

Zeeman splitting (*g*-tensor)

$$\bar{\bar{g}} = \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}$$

diagonalization

$$\begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix}$$

3*d* (*LS* coupling)

$$\mathcal{H}_e + \mathcal{H}_{zfs} = g_e \mu_B \boldsymbol{B}(\boldsymbol{L} + \boldsymbol{S}) + \lambda \boldsymbol{L}\boldsymbol{S} = \mu_B \boldsymbol{B} \bar{\bar{g}} \boldsymbol{S} + \boldsymbol{S} \bar{\bar{D}} \boldsymbol{S}$$

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cubic

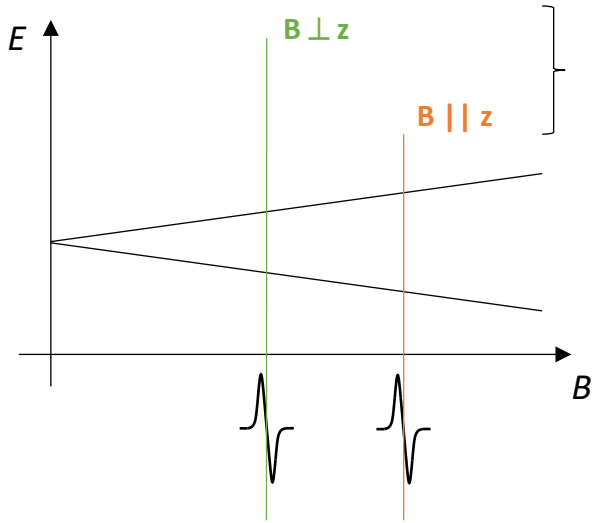
$g_{xx} = g_{yy} = g_{zz}$

trigonal, tetragonal, hexagonal

$g_{xx} = g_{yy} = g_{\perp} \neq g_{zz} = g_{||}$

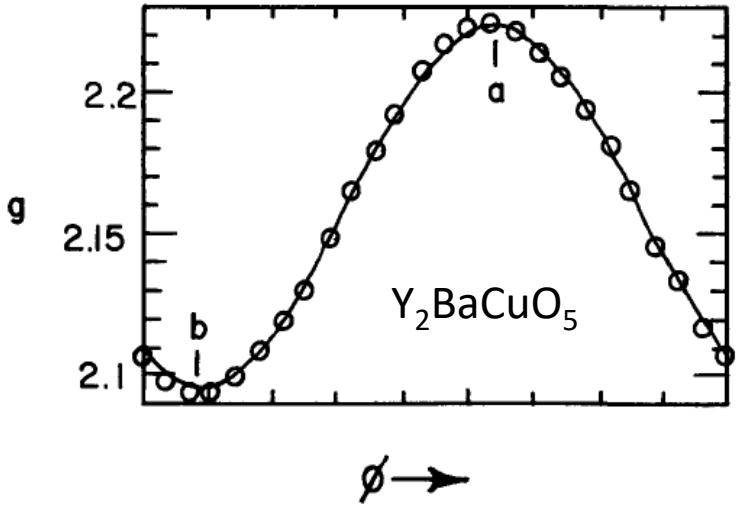
orthorombic

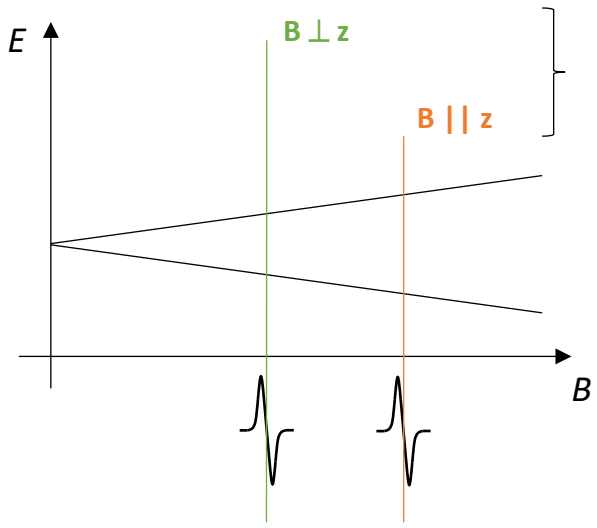
$g_{xx} \neq g_{yy} \neq g_{zz}$



$g_{\perp} > g_{||}$ also possible

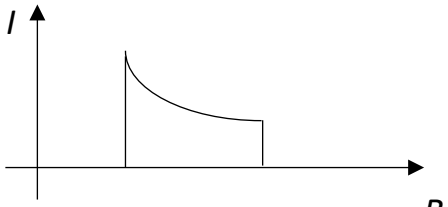
JMaterRes 7, 565 (1992)

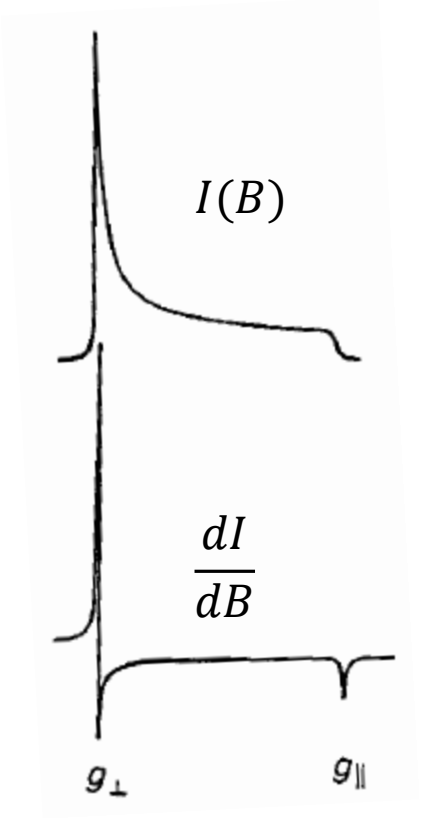




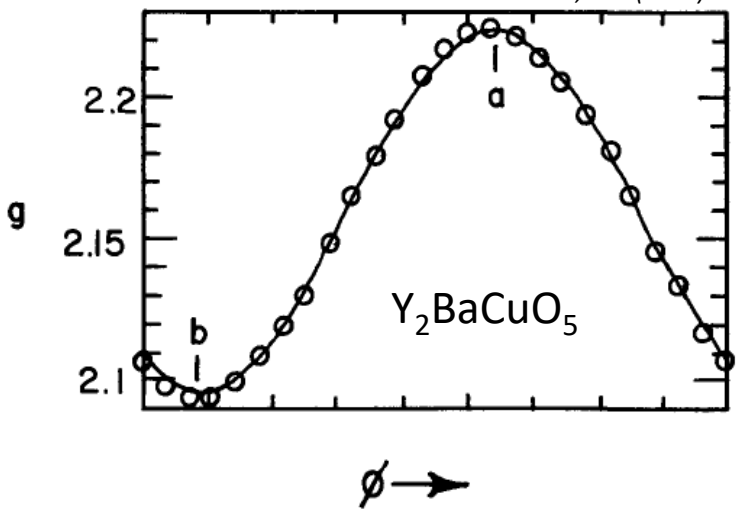
$g_\perp > g_{||}$ also possible

powder





JMaterRes 7, 565 (1992)



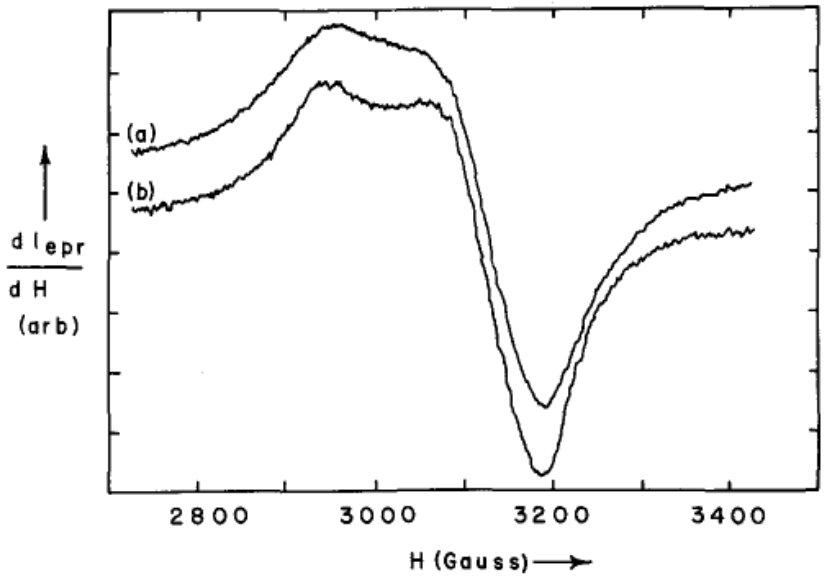


FIG. 2. EPR first-derivative spectra of powder samples of (a) $YBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0.5$) and (b) Y_2BaCuO_5 at room temperature. The microwave frequencies are approximately 9.162 GHz.

$$\mathcal{H}_{zfs} = \boldsymbol{S}\bar{\bar{D}}\boldsymbol{S} = D_x S_x^2 + D_y S_y^2 + D_z S_z^2 = \cdots = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E\left(S_x^2 - S_y^2\right)$$

$$D = \frac{3}{2}D_z \qquad E = \frac{1}{2}\left(D_x - D_y\right)$$

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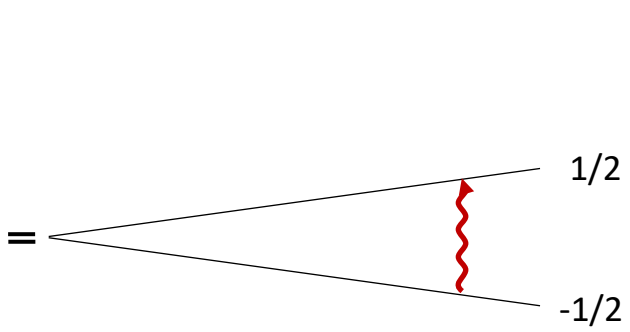
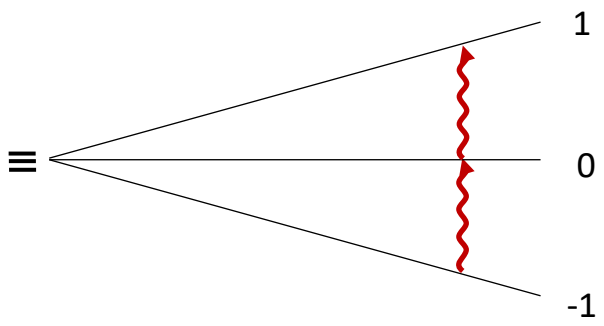
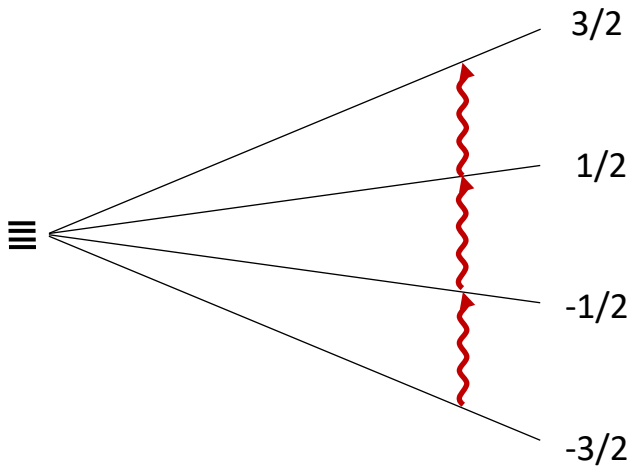
$$D = \frac{3}{2}D_z \qquad E = \frac{1}{2}\left(D_x - D_y\right)$$

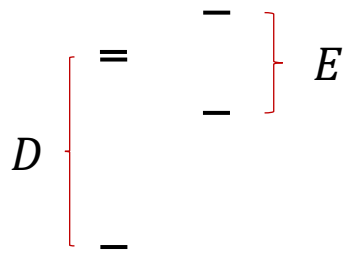






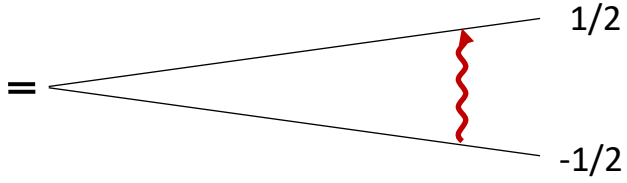
$$\mathcal{H}_{zfs} = \boldsymbol{S}\bar{\bar{D}}\boldsymbol{S} = D_x S_x^2 + D_y S_y^2 + D_z S_z^2 = \cdots = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E\left(S_x^2 - S_y^2\right)$$

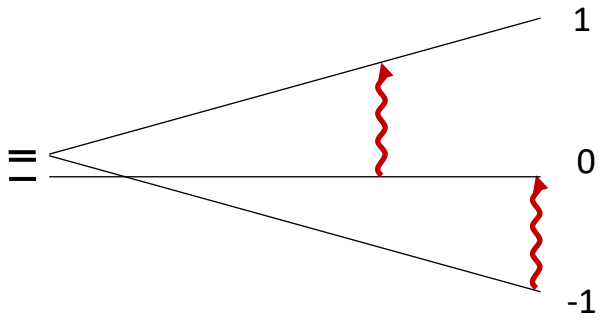
$$D = \frac{3}{2}D_z \qquad E = \frac{1}{2}\left(D_x - D_y\right)$$

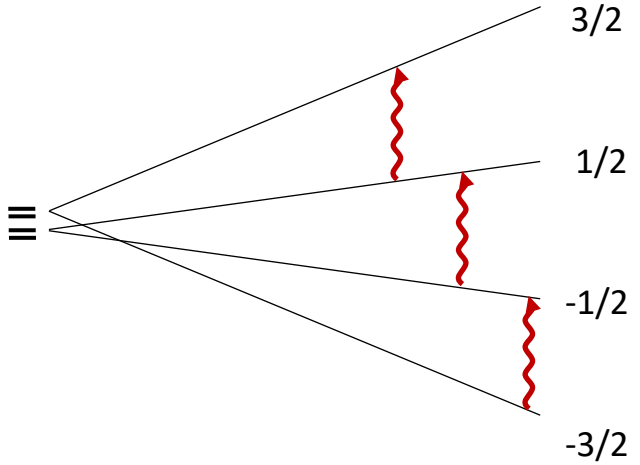


non-degenerate spin-states even for $B = 0$

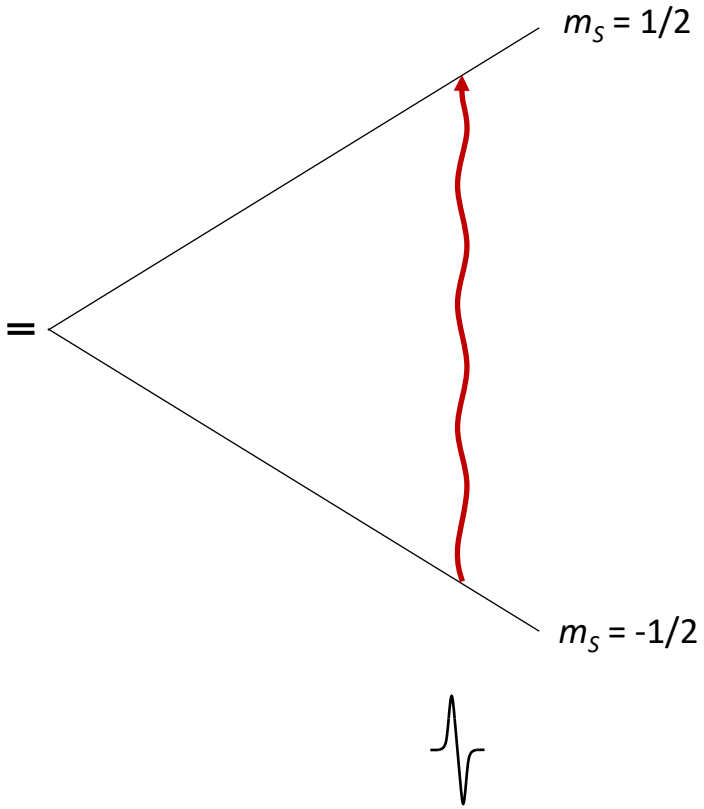
$$\Delta m_s = \pm 1$$



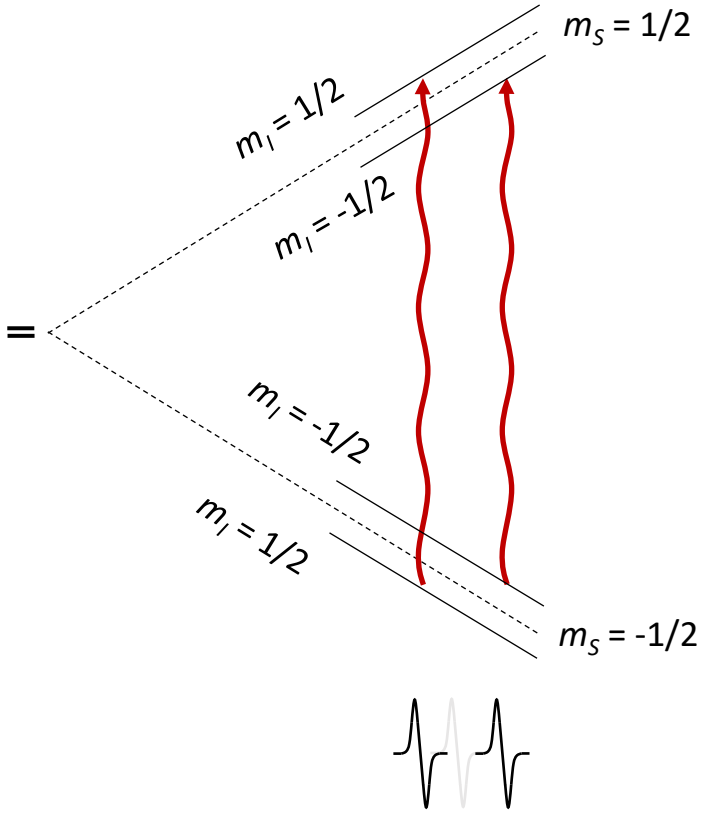


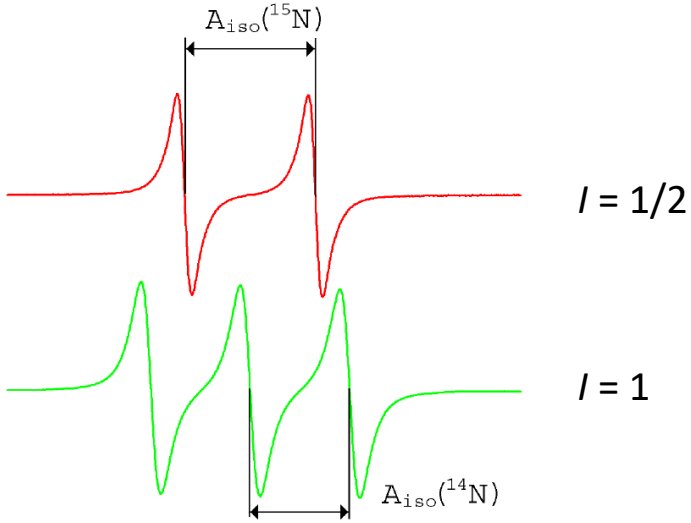


$$\mathcal{H}_{hf} = \boldsymbol{I}\bar{\bar{A}}\boldsymbol{S} \xrightarrow{isotropic} E = g\mu_B B m_S + A m_S m_I$$



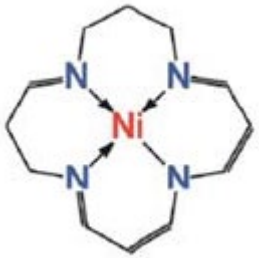
$$\mathcal{H}_{hf} = \boldsymbol{I}\bar{\bar{A}}\boldsymbol{S} \xrightarrow{isotropic} E = g\mu_B B m_S + A m_S m_I$$



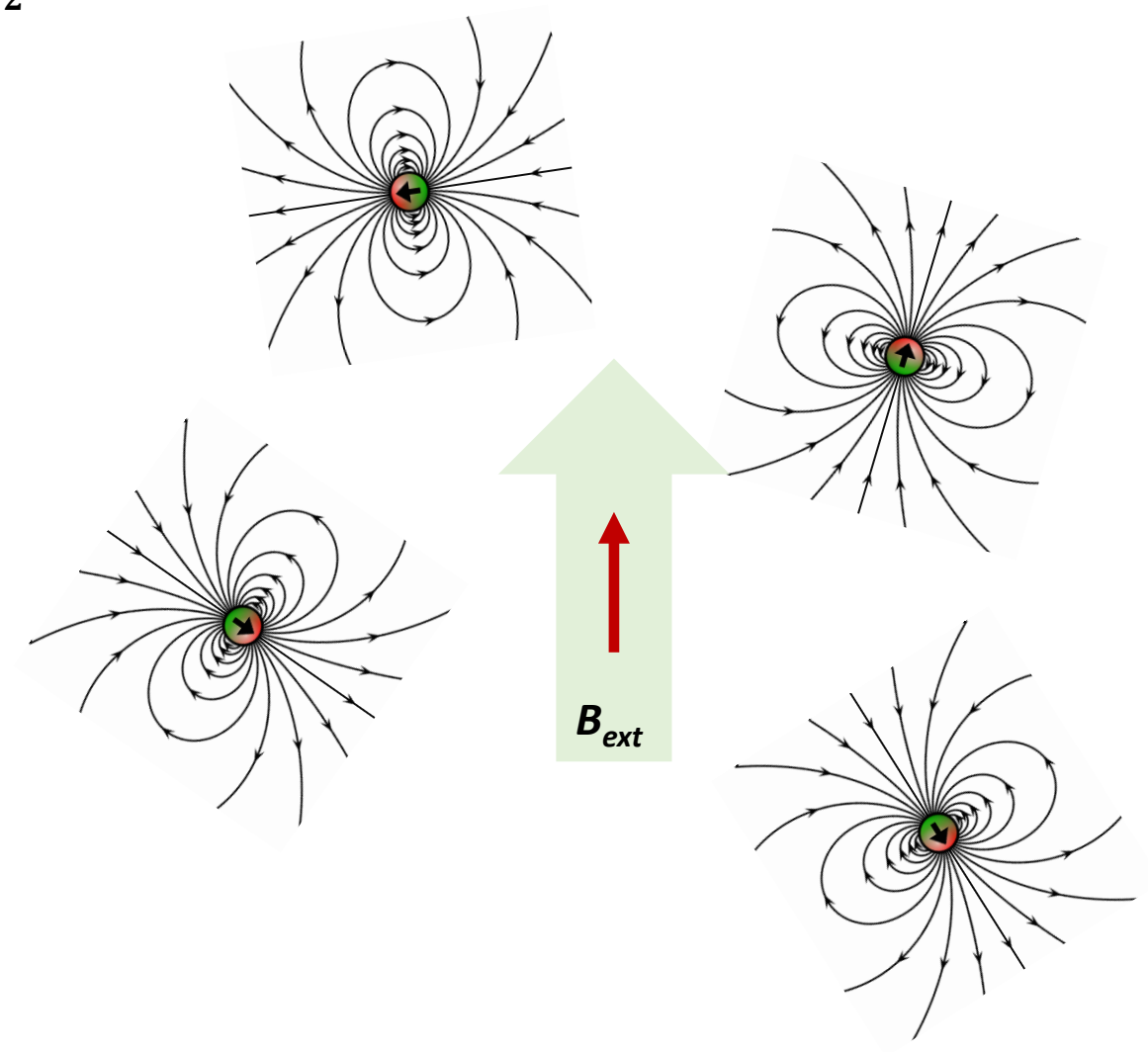


I = 1/2

I = 1



$$\mathcal{H}_{ee} = J\boldsymbol{S_1}\boldsymbol{S_2}$$



$$B_{total} = B_{ext} + \sum B_{dipole}$$

at low *T* spins are less randomly oriented → exchange narrowing

image source: wikimedia.org

- comparison with SQUID

SQUID ~ 10^{-8} emu

NMR ~ 10^{-10} emu

ESR ~ 10^{-15} emu

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