MAGNETOCALORIC AND BAROCALORIC EFFECTS IN METALS

UNIVERSIDADE DO ESTADO DO RIO DE JANEIRO UERJ

CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico

FAPERJ Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro

OUTLINE

- PRELIMINARIES
- THEORY AND CALCULATIONS
- APPLICATIONS
- PROSPECTS

PRELIMINARIES

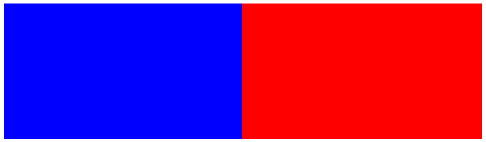
MAGNETOCALORIC EFFECT

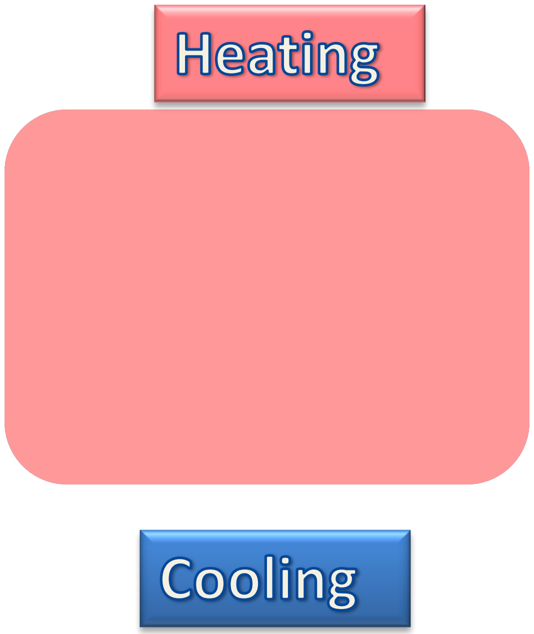
HISTORICAL FACTS

MAGNETIC REFRIGERATION

BAROCALORIC EFFECT

MAGNETOCALORIC EFFECT





HISTORICAL FACTS

Thomson´s work 1878 (Comments)

Thomson W. " Thermoelastic, thermomagnetic and pyroelectric properties of matter" Phil. Mag. Ser 5 5(1878)4.

Weis and Piccard ´s work 1917:Experimental discovery

Weiss, P., Piccard A., " Le phénomène magnétocalorique" J. Phys. 7(1917)103

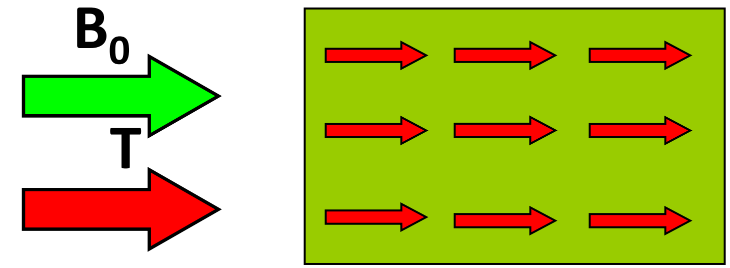
Browns´s work - 1978: Room temperature magnetic refrigerator

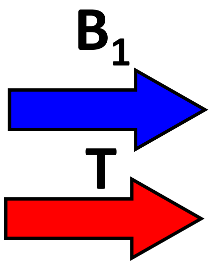
Brown, G. V., " Heat pump near room temperature" J. Appl. Phys . 47(1976)3673.

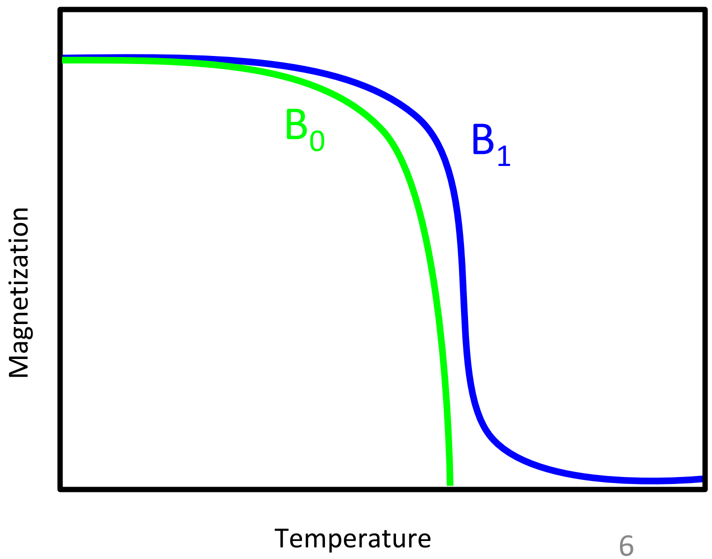
Gschneidner ´s work - 1997: Giant magnetocaloric effect: $Gd_5Si_2Ge_2$

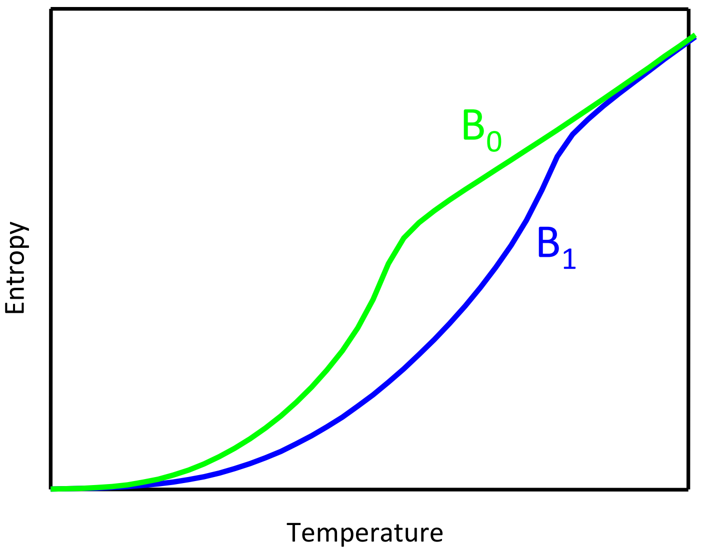
V. K. Pecharsky, K. A. Gschneidner Jr, " Giant magnetocaloric effec in $Gd_5Si_2Ge_2$" Phys. Rev. Let. 78 (1997) 4494

MAGNETOCALORIC EFFECT

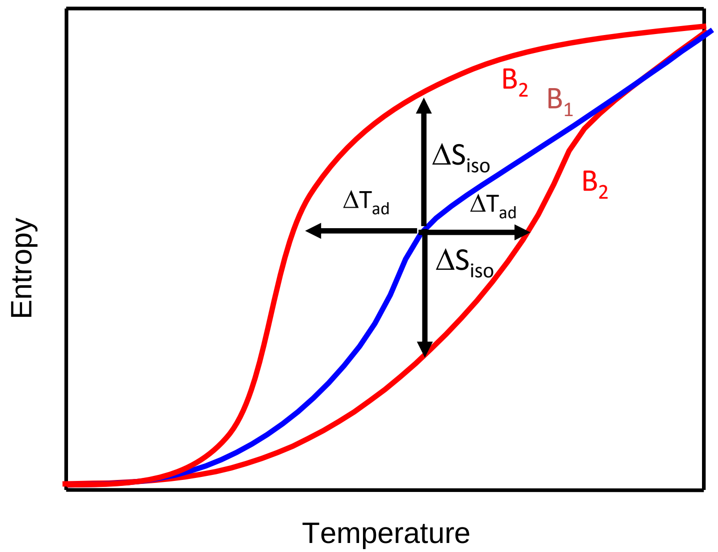




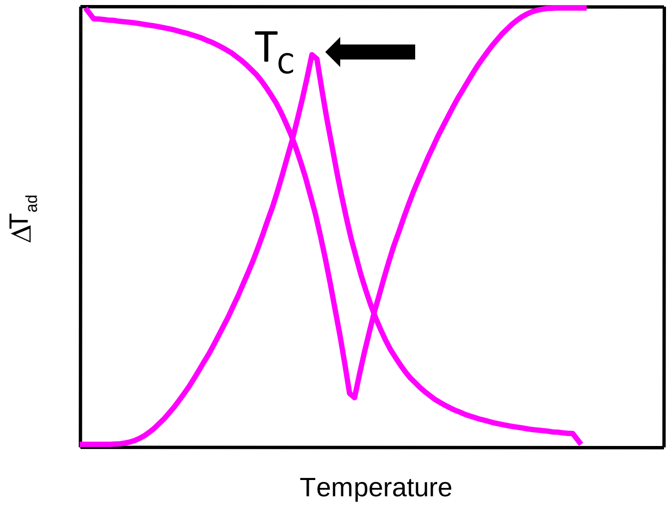


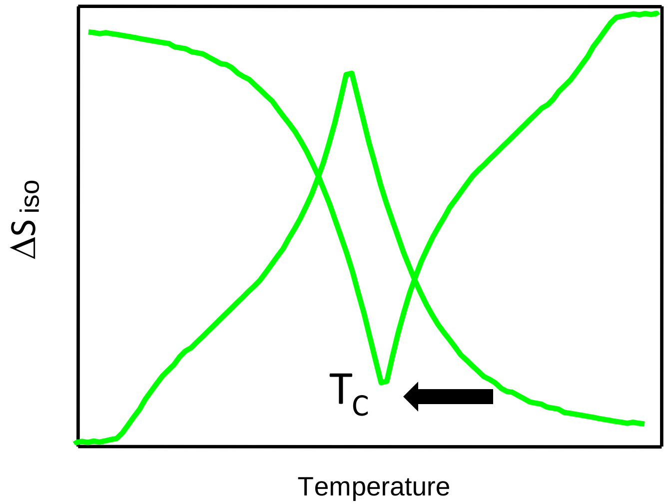


MAGNETOCALORIC QUANTITIES



INVERSE MAGNETOCALORIC EFFECT





How to measure?

EXPERIMENTAL TECHNIQUES

Adiabatic temperature change (ΔT_{ad})

Direct measurements: Thermopar

Indirect measurements: Specific heat

Indirect measurements: Specific heat and magnetization

Isothermal entropy change (ΔS_{iso})

Indirect measurements: Specific heat

Indirect measurements: magnetization

EQUIPMENTS

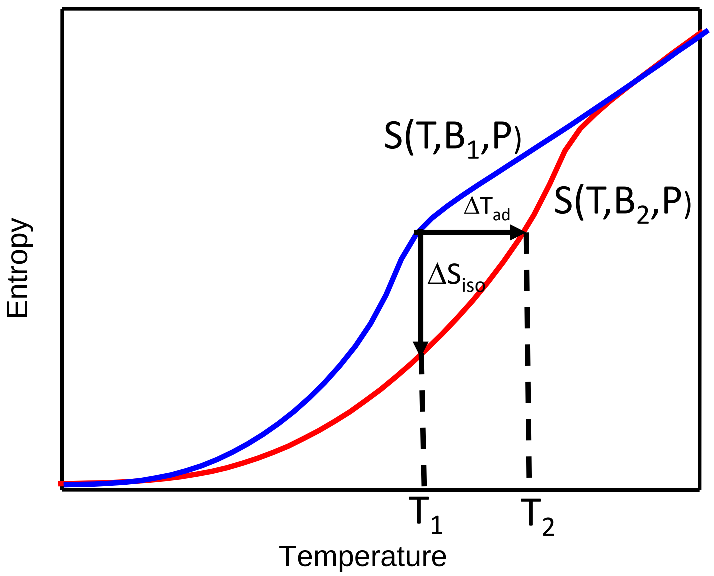
Calorimeter: ΔS_{iso} and ΔT_{ad}

Calorimeter and VSM/Squid: ΔS_{iso} and ΔT_{ad}

Squid/VSM : ΔS_{iso}

How to calculate?

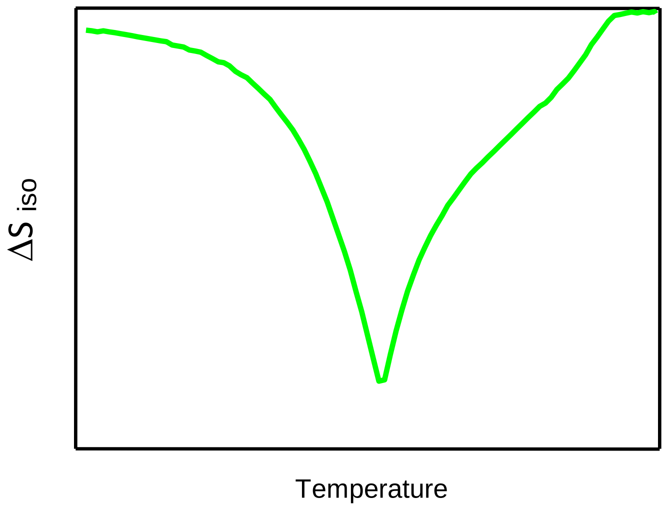
MAGNETOCALORIC EFFECT

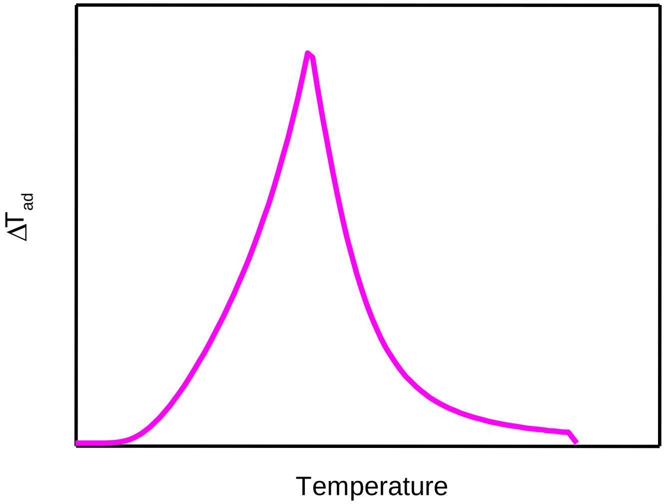


$$\Delta S_{iso}\,(T,\Delta B,P)=S(T,B_2,P)-S(T,B_1,P)$$

$$\Delta T_{ad}\,(T,\Delta B,P)=T_2-T_1$$

$$S(T,B_2,P)=S(T,B_1,P)$$





THERMODYNAMICS OF THE MCE (ΔS_{iso})

ENTROPY CHANGE

$$dS(T,B,P) = \left[\frac{\partial S(T,B,P)}{\partial T} + \frac{\delta S(T_C,B,P)}{\delta T}\right]_{B,P} dT + \left[\frac{\partial S(T,B,P)}{\partial B} + \frac{\delta S(T,B_C,P)}{\delta B}\right]_{T,P} dB$$

$$+ \left[\frac{\partial S(T,B,P)}{\partial P} + \frac{\delta S(T,B,P_C)}{\delta P}\right]_{T,B} dP$$

ISOTHERMAL / ISOBARIC PROCESS

$$\Delta S_{iso}(T,\Delta B,P) = \int_{B_1}^{B_2} \left[\frac{\partial S(T,B,P)}{\partial B} + \frac{\delta S(T,B_C,P)}{\delta B}\right]_{T,P} dB$$

SECOND ORDER TRANSITION

$$\Delta S_{iso}(T,\Delta B,P) = \int_{B_1}^{B_2} \left[\frac{\partial S(T,B,P)}{\partial B}\right]_{T,P} dB$$

THERMODYNAMICS OF THE MCE (ΔT_{ad})

ENTROPY CHANGE

$$dS(T,B,P) = \left[\frac{\partial S(T,B,P)}{\partial T} + \frac{\delta S(T_C,B,P)}{\delta T}\right]_{B,P} dT + \left[\frac{\partial S(T,B,P)}{\partial B} + \frac{\delta S(T,B_C,P)}{\delta B}\right]_{T,P} dB$$

$$+ \left[\frac{\partial S(T,B,P)}{\partial P} + \frac{\delta S(T,B,P_C)}{\delta P}\right]_{T,B} dP$$

$$\Delta T_{ad}(T,\Delta B,P) = -\int_{B_1}^{B_2} \frac{1}{C(T,B,P)} \left[\frac{\partial S(T,B,P)}{\partial B} + \frac{\delta S(T,B_C,P)}{\delta B}\right]_{T,P} dB$$

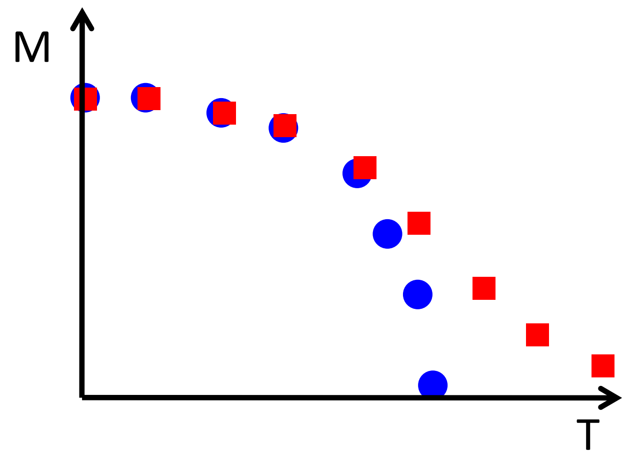
$$\Delta T_{ad}(T,\Delta B,P) = -\int_{B_1}^{B_2} \frac{1}{C(T,B,P)} \left[\frac{\partial S(T,B,P)}{\partial B}\right]_{T,P} dB$$

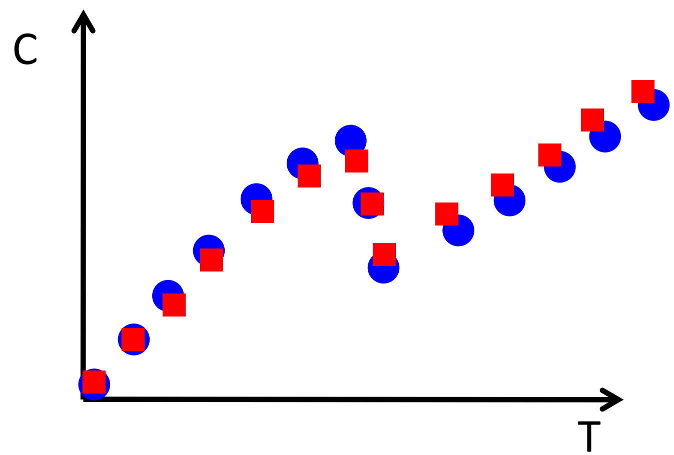
THERMODYNAMICS: MAXWELL RELATION

MCE QUANTITIES

$$\Delta S_{iso}(T, \Delta B, P) = \int_{B_1}^{B_2} \left[\frac{\partial M(T,B,P)}{\partial T}\right]_{B,P} dB$$

$$\Delta T_{ad}(T, \Delta B, P) = -\int_{B_1}^{B_2} \frac{1}{C(T,B,P)} \left[\frac{\partial M(T,B,P)}{\partial T}\right]_{B,P} dB$$





MAXWELL RELATION

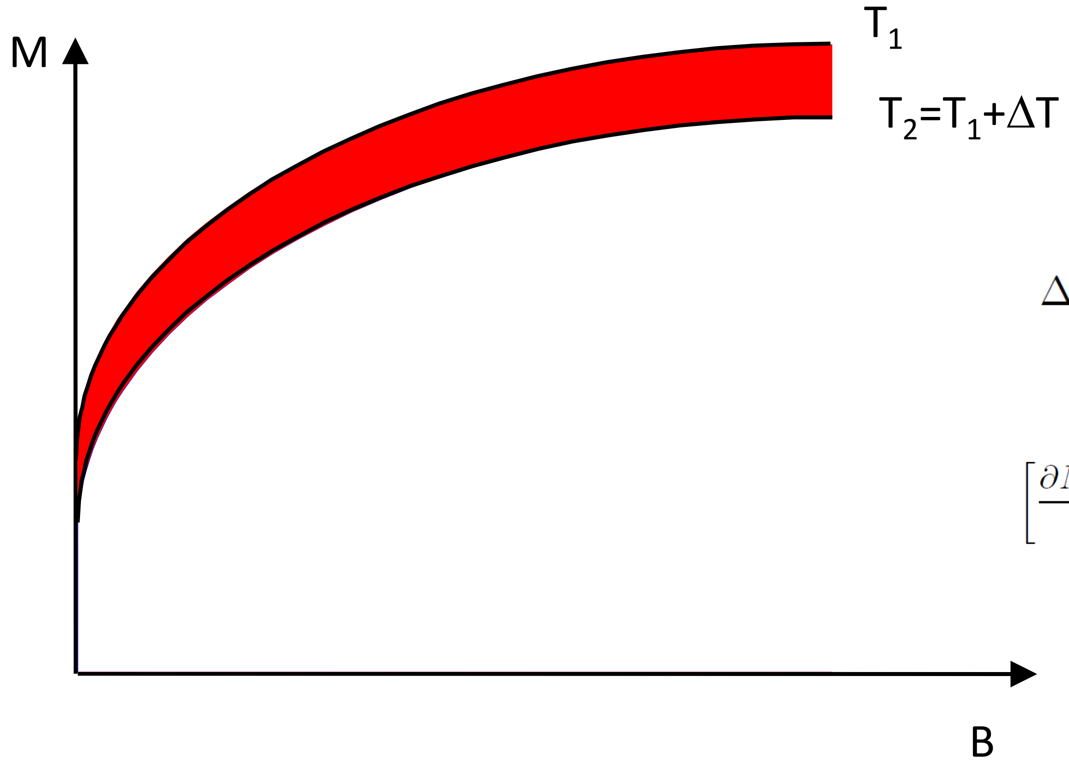
$$\left[\frac{\partial S(T,B,P)}{\partial B}\right]_{T,P} = \left[\frac{\partial M(T,B,P)}{\partial T}\right]_{B,P}$$

FIRST ORDER TRANSITION

SECOND ORDER TRANSITION

THERMODYNAMICS OF THE MCE

MAGNETIZATION CURVE



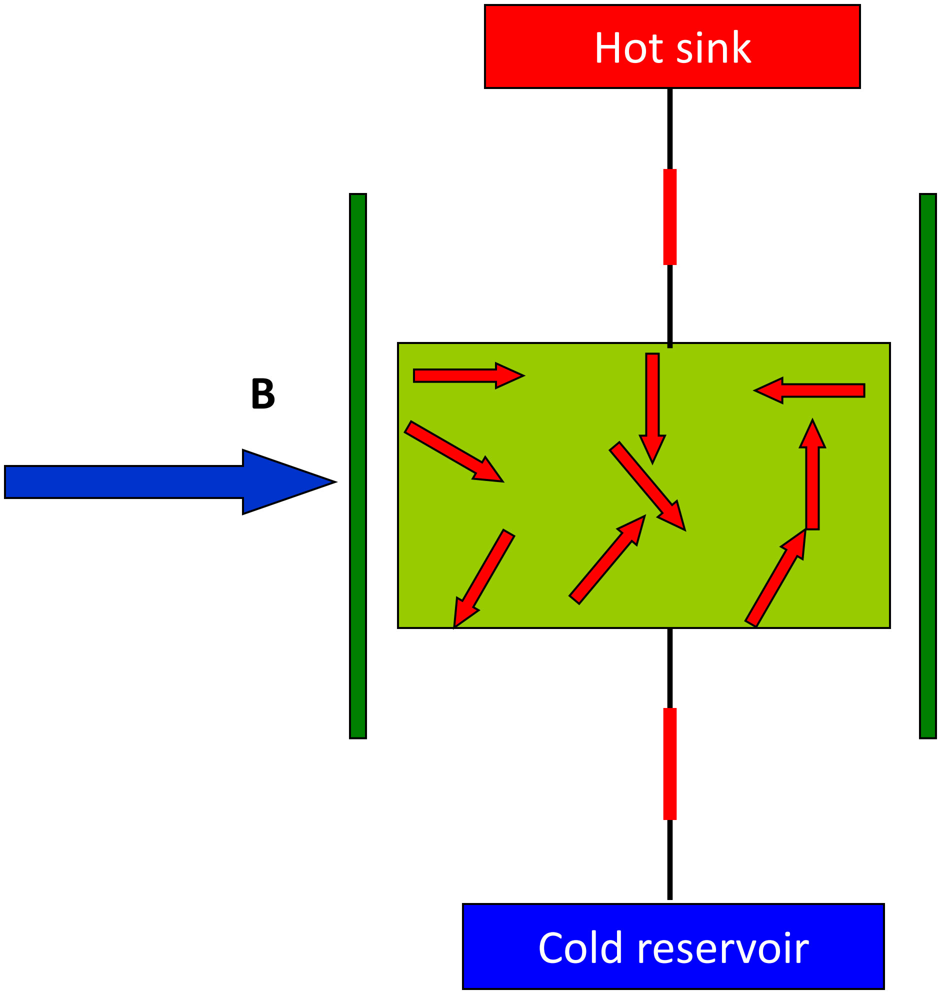
$$\Delta S_{iso}(T,\Delta B,P) = \int_{B_1}^{B_2} \left[\frac{\partial M(T,B,P)}{\partial T}\right]_{B,P} dB$$

$$\left[\frac{\partial M(T,B,P)}{\partial T}\right]_{B,P} = \lim_{\Delta T \longrightarrow 0} \frac{1}{\Delta T} [M(T+\Delta T,B,P)dB - M(T,B,P)dB]$$

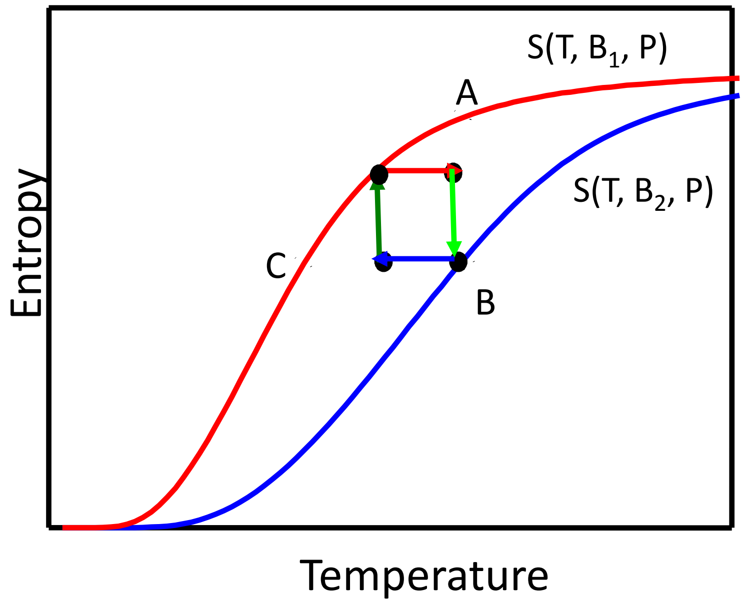
$$\Delta S_{iso}(T,\Delta B,P) = \frac{1}{\Delta T}\left[\int_{B_1}^{B_2} M(T+\Delta T,B,P)dB - \int_{B_1}^{B_2} M(T,B,P)dB\right]$$

MAGNETIC REFRIGERATOR

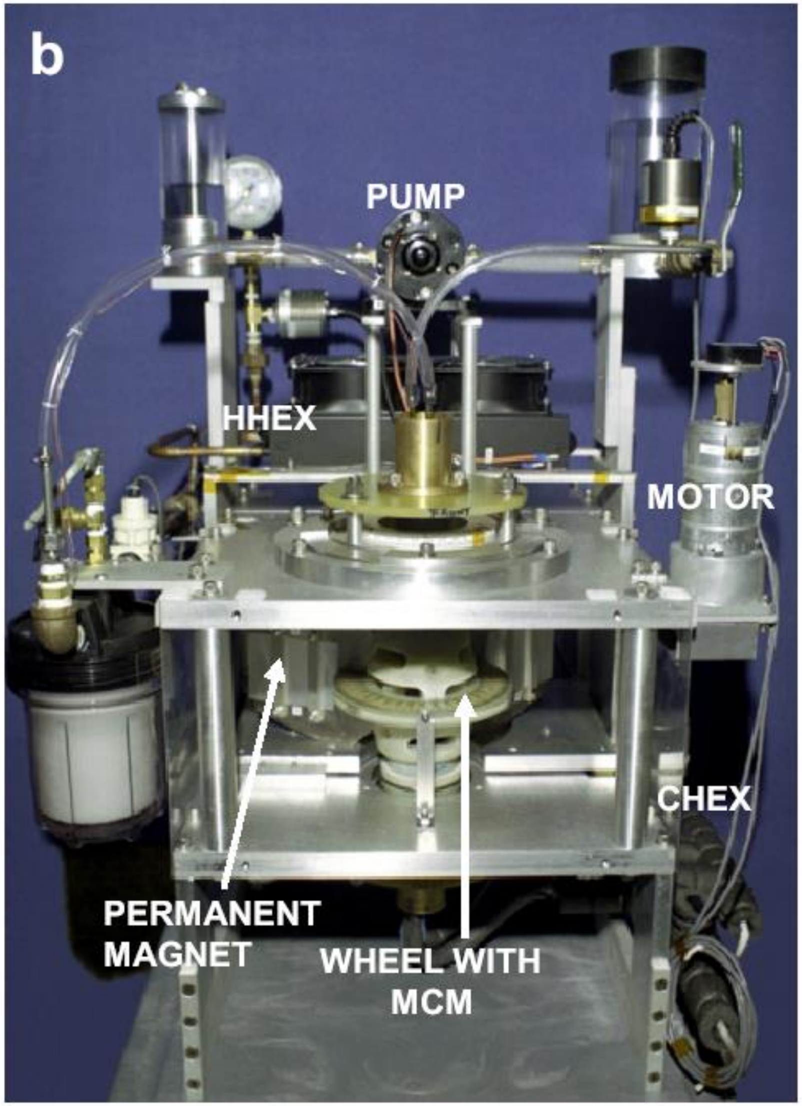
ACADEMIC PROTOTYPE

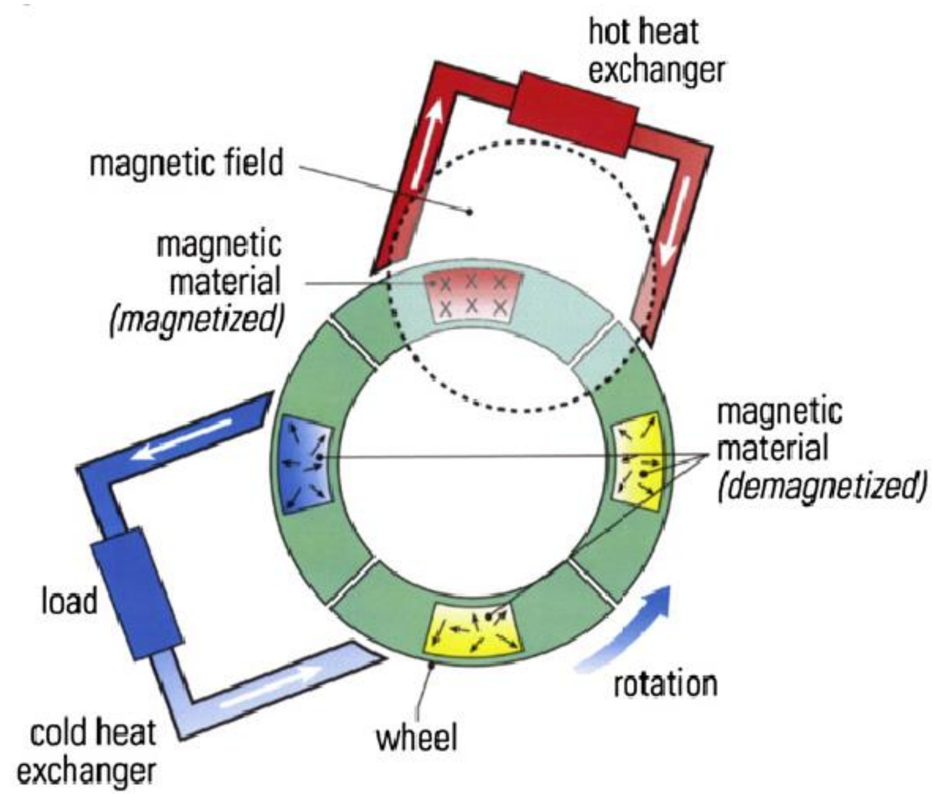


Heating (heat release) n



Carnot cicle

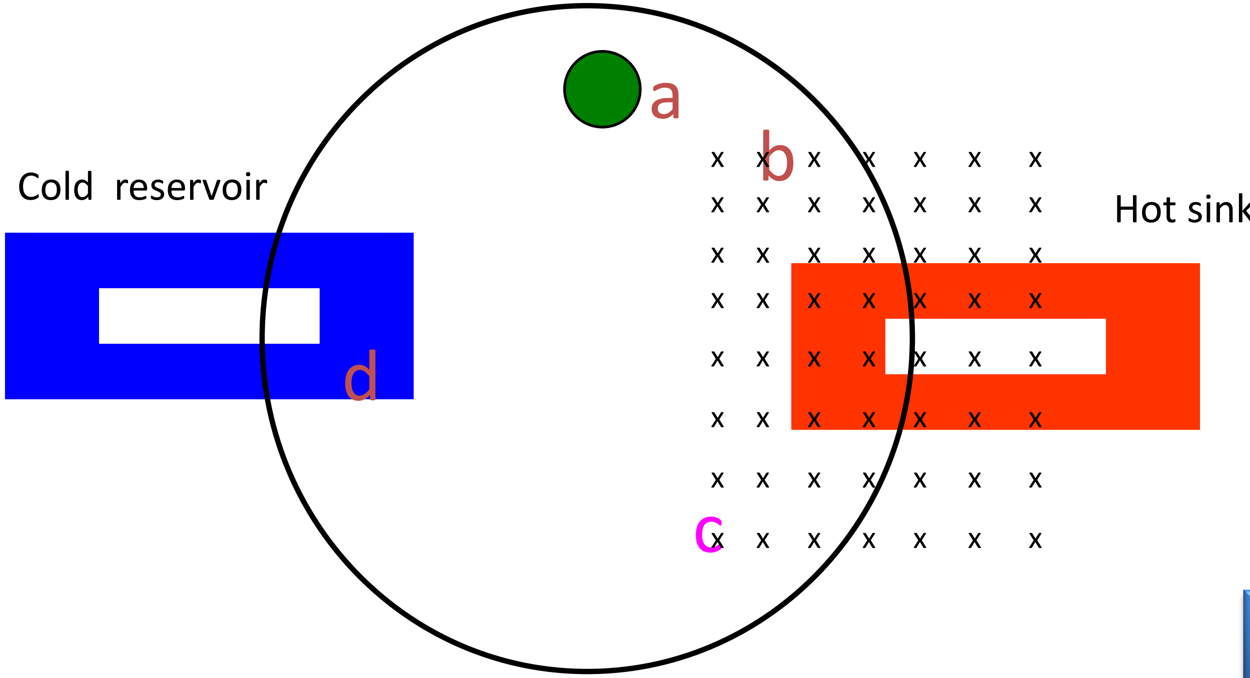


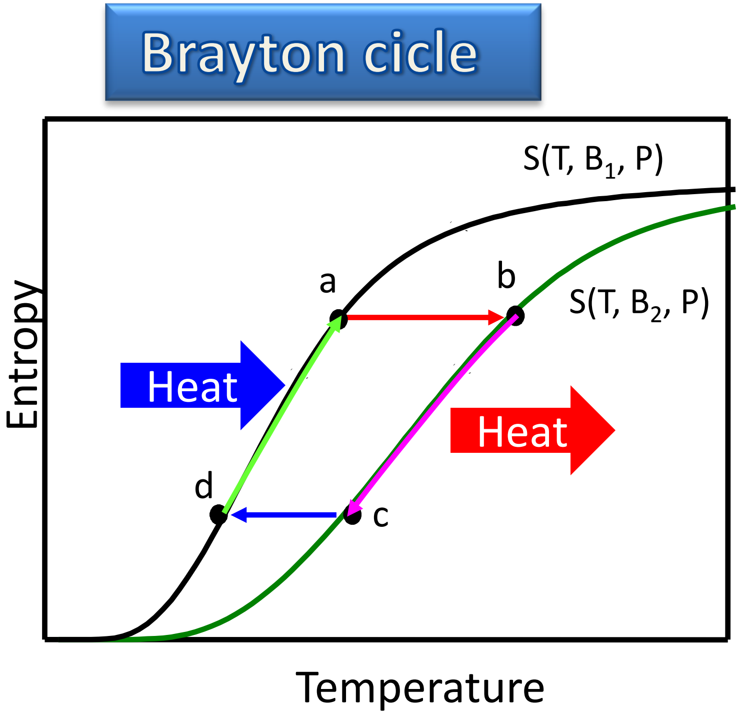


Environmental friendly

Large values of magnetic field

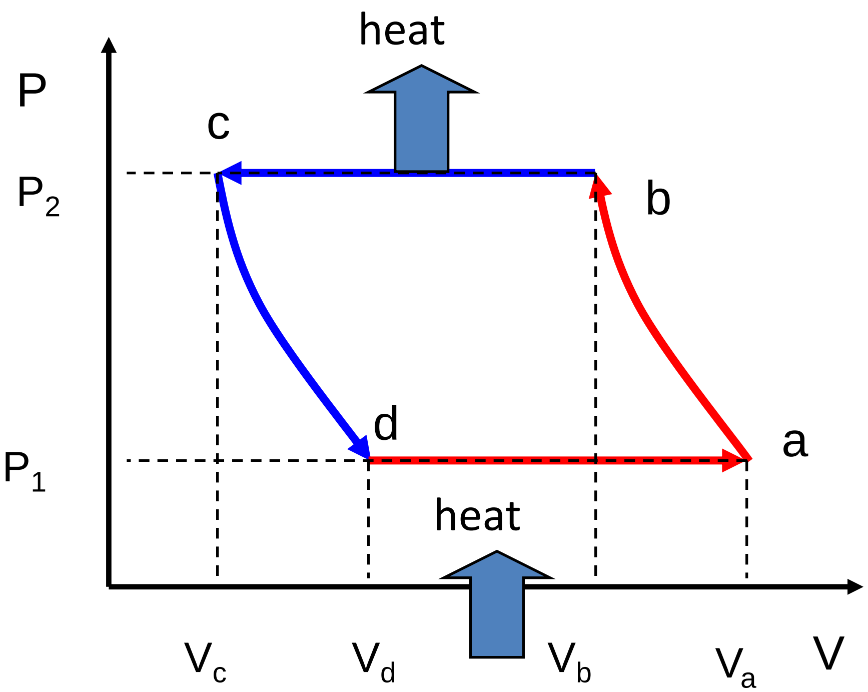
ACADEMIC PROTOTYPE

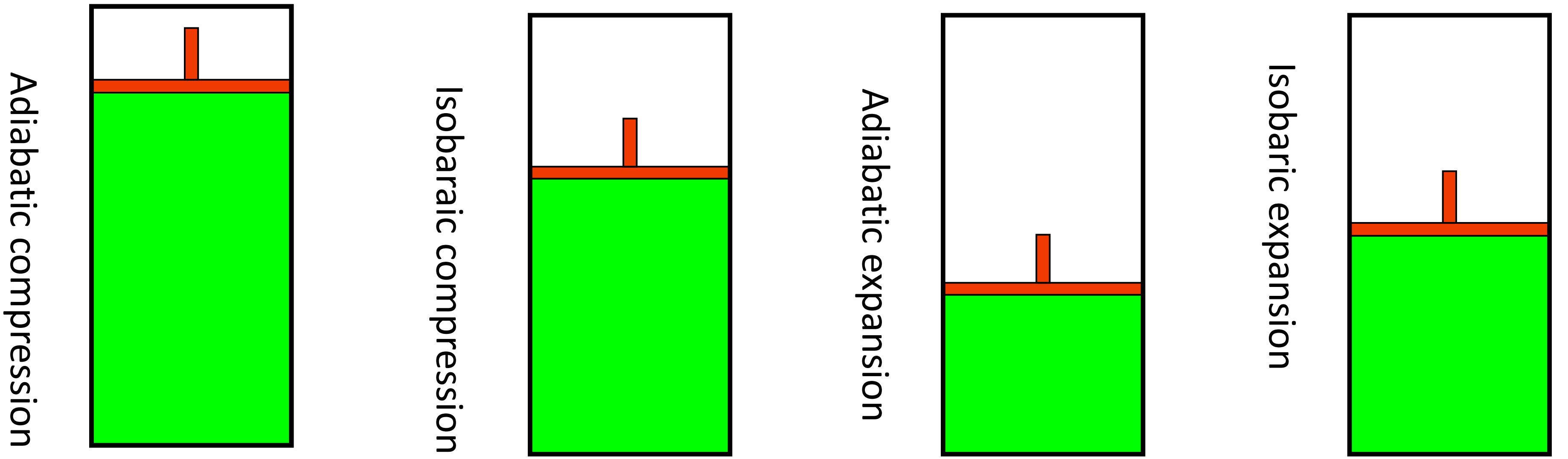




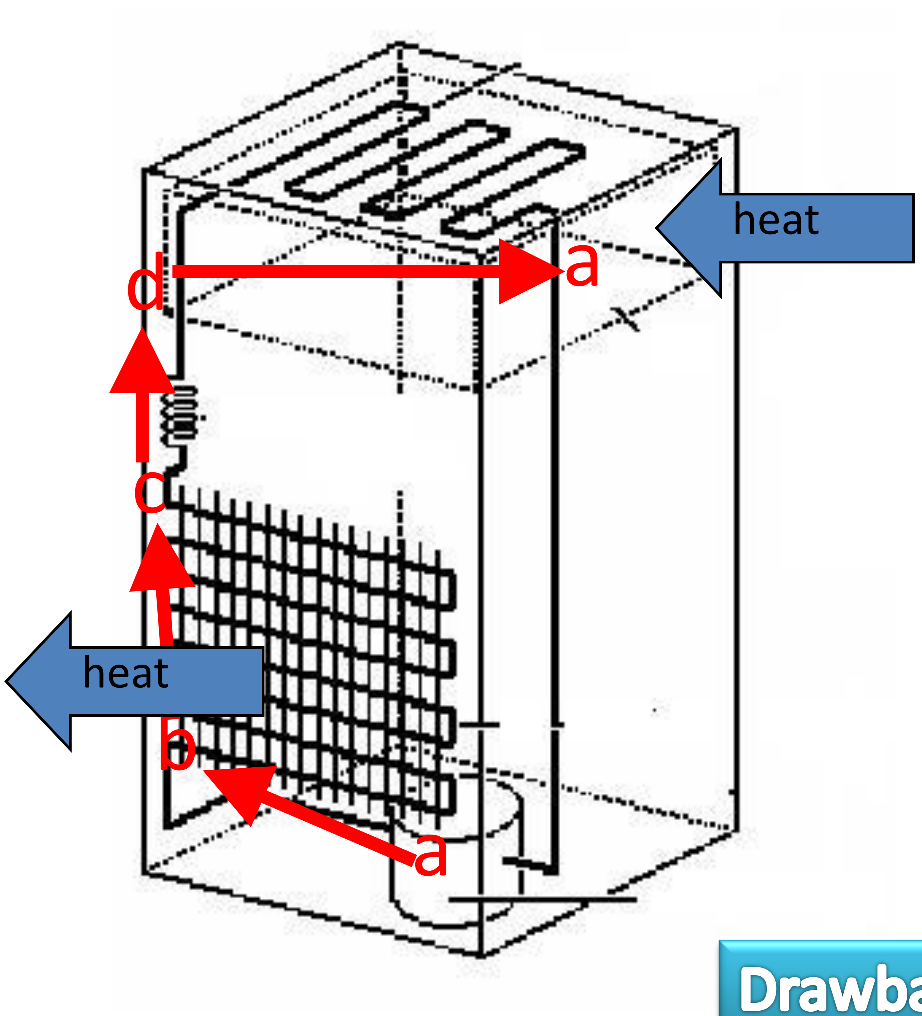
BAROCALORIC EFFECT

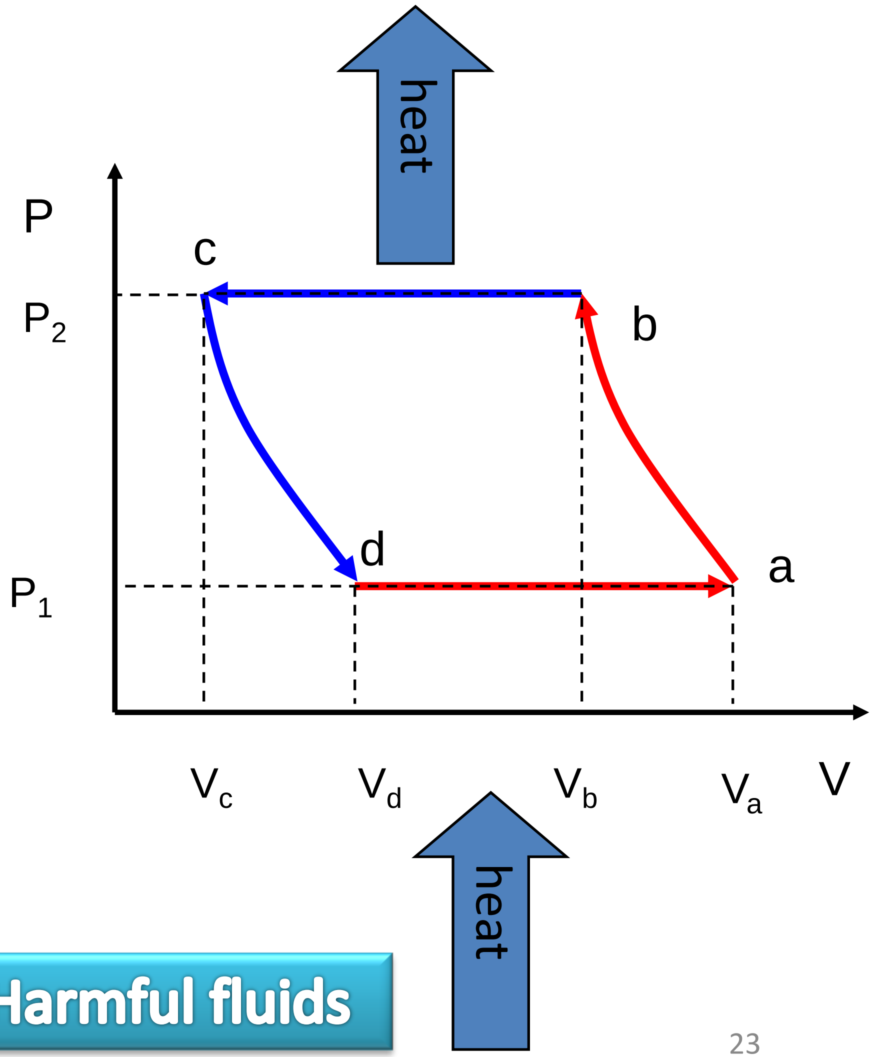
BAROCALORIC EFFECT





CONVENTIONAL REFRIGERATOR

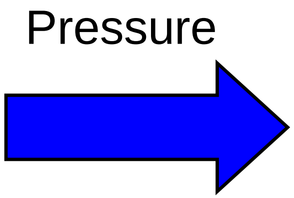


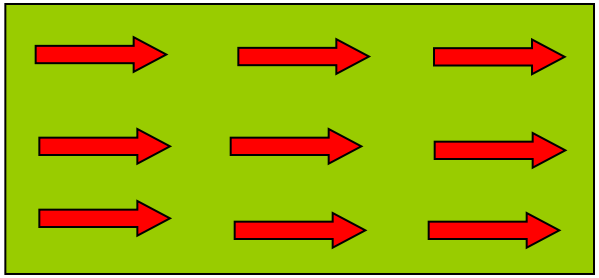


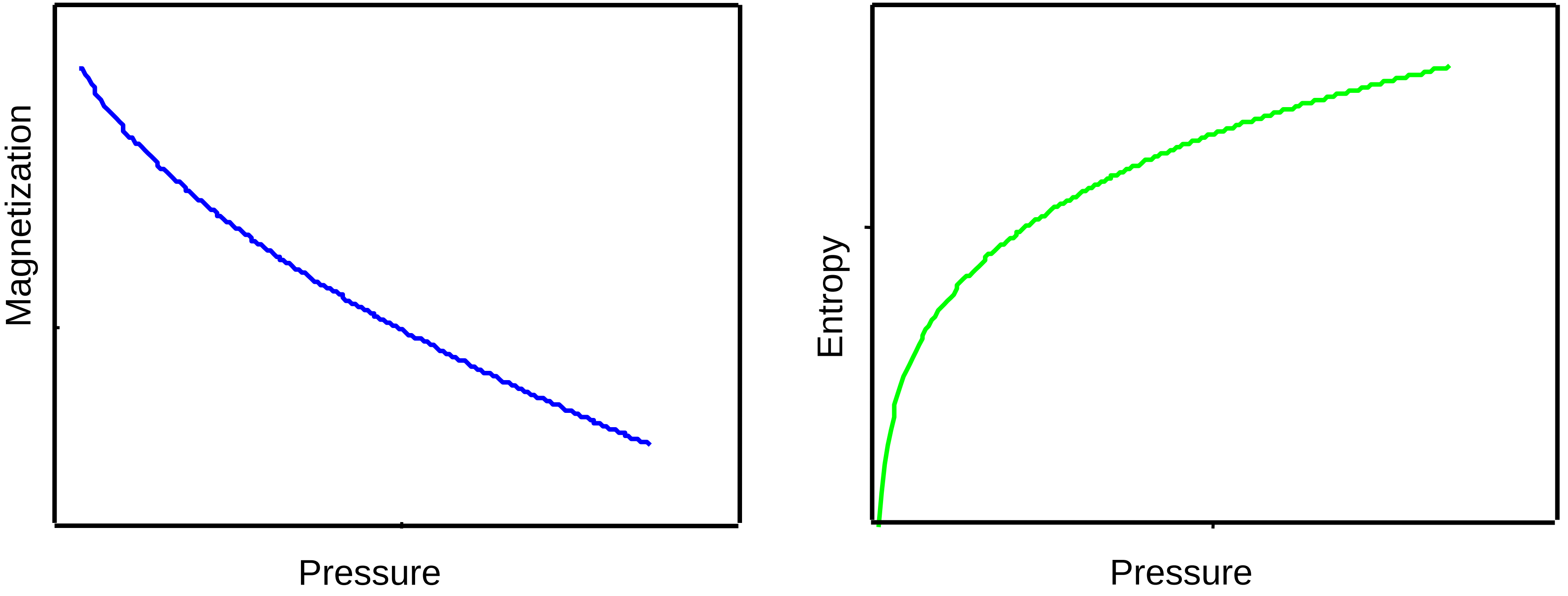
Drawback: Harmful fluids

MAGNETIC BAROCALORIC EFFECT

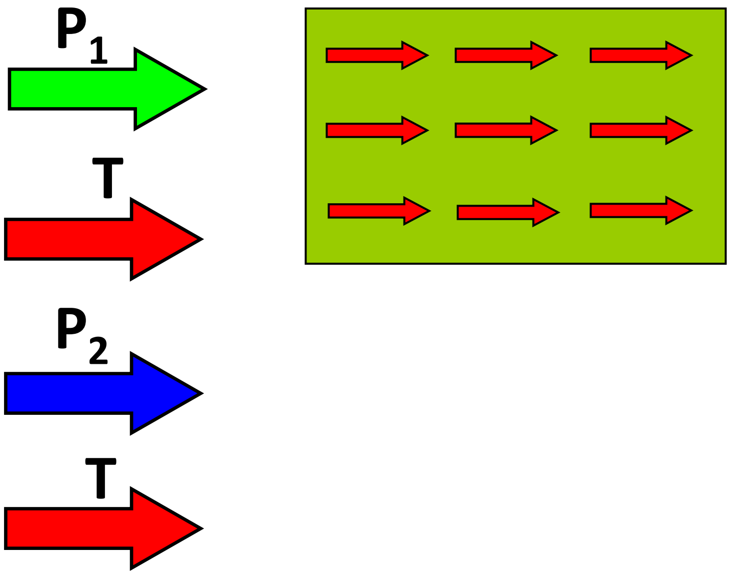
MAGNETIC BAROCALORIC EFFECT







MAGNETIC BAROCALORIC EFFECT

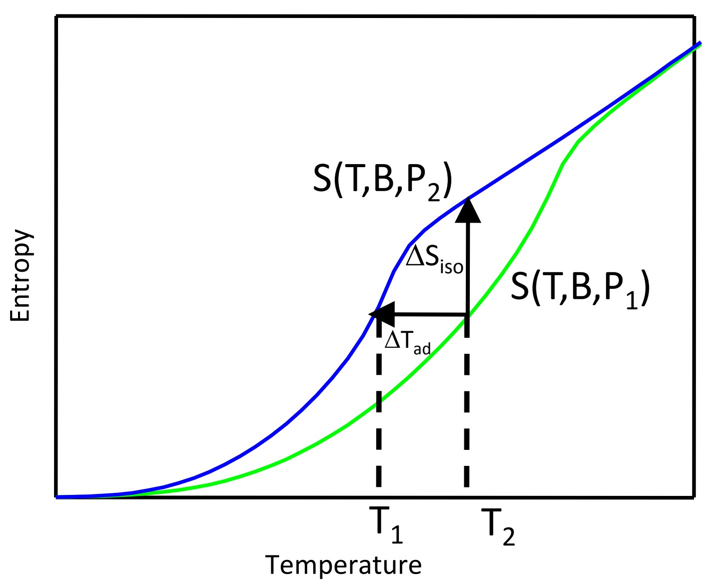


BAROCALORIC QUANTITIES

$$\Delta S_{iso}^{bar}\left(T,B,\Delta P\right) = S(T,B,P_2) - S(T,B,P_1)$$

$$\Delta T_{ad}^{bar}\left(T,B,\Delta P\right) = T_1 - T_2$$

$$S(T,B,P_2) = S(T,B,P_1)$$



THERMODYNAMICS OF THE BCE (ΔS_{iso}^{bar})

ENTROPY CHANGE

$$dS(T,B,P) = \left[\frac{\partial S(T,B,P)}{\partial T} + \frac{\delta S(T_C,B,P)}{\delta T}\right]_{B,P} dT + \left[\frac{\partial S(T,B,P)}{\partial B} + \frac{\delta S(T,B_C,P)}{\delta B}\right]_{T,P} dB$$

$$+ \left[\frac{\partial S(T,B,P)}{\partial P} + \frac{\delta S(T,B,P_C)}{\delta P}\right]_{T,B} dP$$

ISOTHERMAL PROCESS

ISOFIELD PROCESS

$$\Delta S_{iso}^{bar}(T,B,\Delta P) = \int_{P_1}^{P_2} \left[\frac{\partial S(T,B,P)}{\partial P} + \frac{\delta S(T,B_C,P)}{\delta P}\right]_{T,B} dP$$

SECOND ORDER TRANSITION

$$\Delta S_{iso}^{bar}(T,B,\Delta P) = \int_{P_1}^{P_2} \left[\frac{\partial S(T,B,P)}{\partial P}\right]_{T,B} dP$$

THERMODYNAMICS OF THE BCE (ΔT_{ad}^{bar})

ENTROPY CHANGE

$$0 = \left[\frac{\partial S(T,B,P)}{\partial T} + \frac{\delta S(T_C,B,P)}{\delta T}\right]_{B,P} dT + \left[\frac{\partial S(T,B,P)}{\partial B} + \frac{\delta S(T,B_C,P)}{\delta B}\right]_{T,P} dB$$

$$+ \left[\frac{\partial S(T,B,P)}{\partial P} + \frac{\delta S(T,B,P_C)}{\delta P}\right]_{T,B} dP$$

ADIABATIC PROCESS

ISOFIELD PROCESS

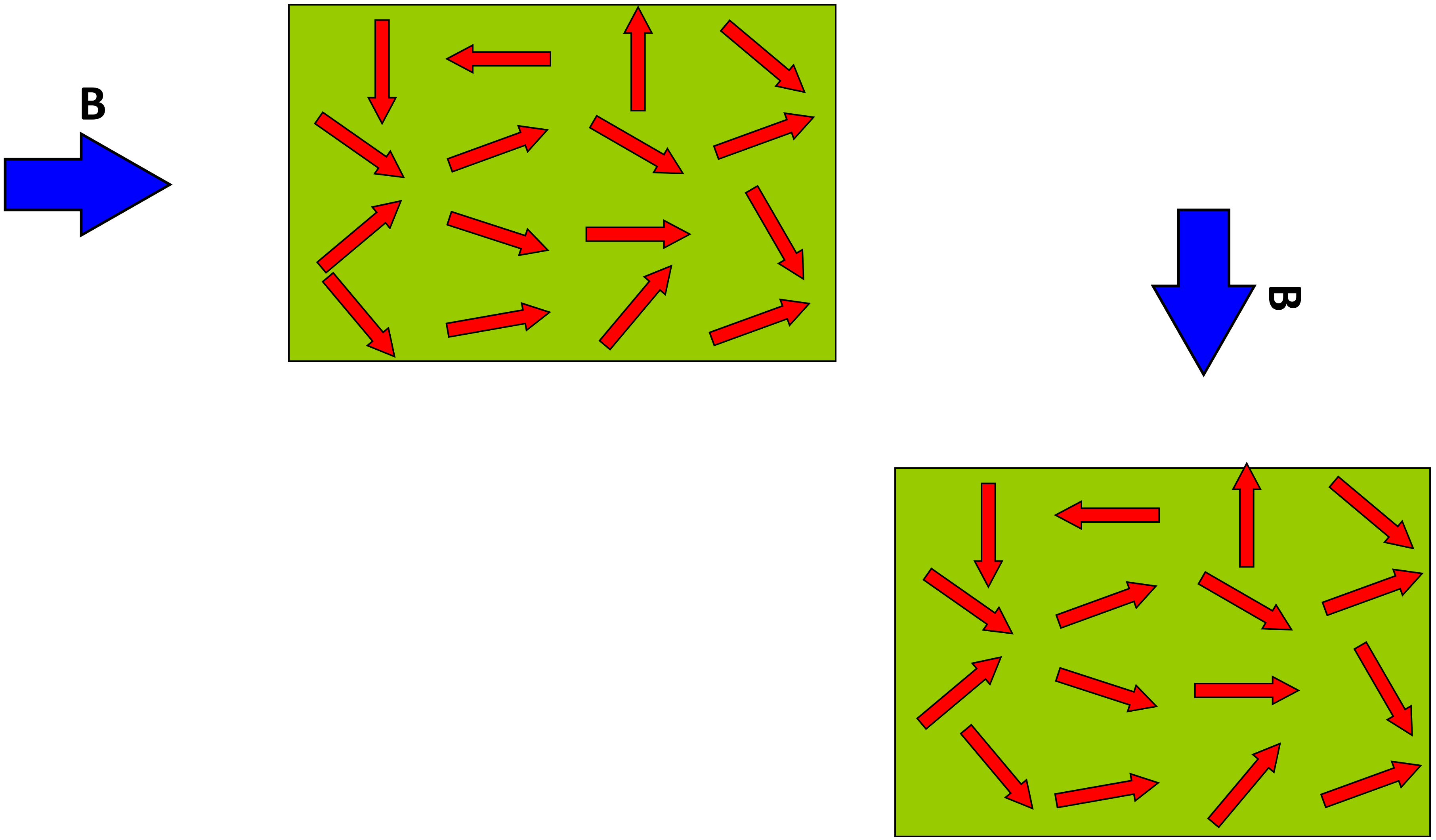
$$\Delta T_{ad}^{bar}(T,B,\Delta P) = -\int_{P_1}^{P_2} \frac{1}{C(T,B,P)} \left[\frac{\partial S(T,B,P)}{\partial P} + \frac{\delta S(T,B,P_C)}{\delta P}\right]_{T,B} dP$$

SECOND ORDER TRANSITION

$$\Delta T_{ad}^{bar}(T,B,\Delta P) = -\int_{P_1}^{P_2} \frac{1}{C(T,B,P)} \left[\frac{\partial S(T,B,P)}{\partial P}\right]_{T,B} dP$$

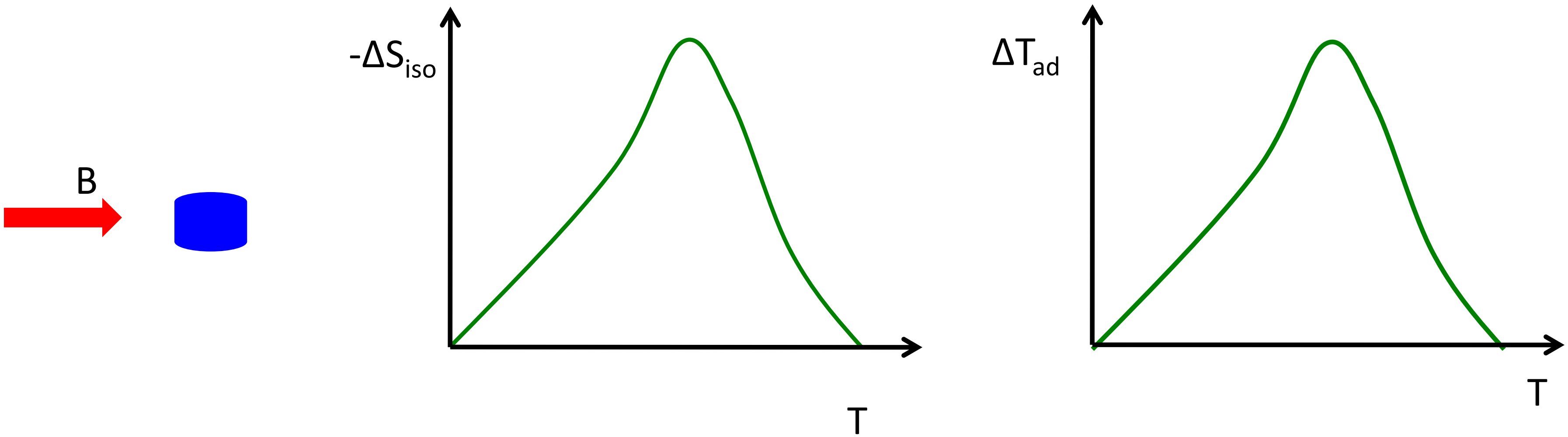
ANISOTROPIC MAGNETOCALORIC EFFECT

ANISOTROPIC MCE



ANISOTROPIC MCE

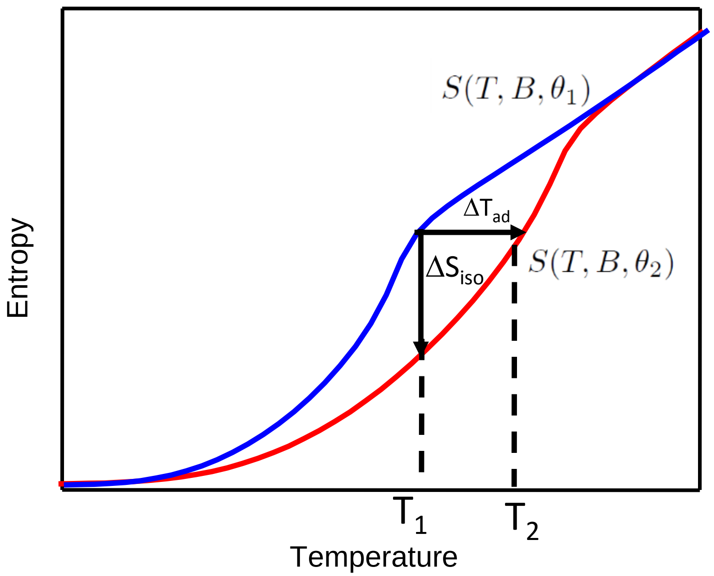
$NdCo_5$ $DyAl_2$



Niktin et al, Phys. Rev. Lett. 105 (2010)137205

von Ranke et al, J. Appl. Phys. 104 (2008)093906

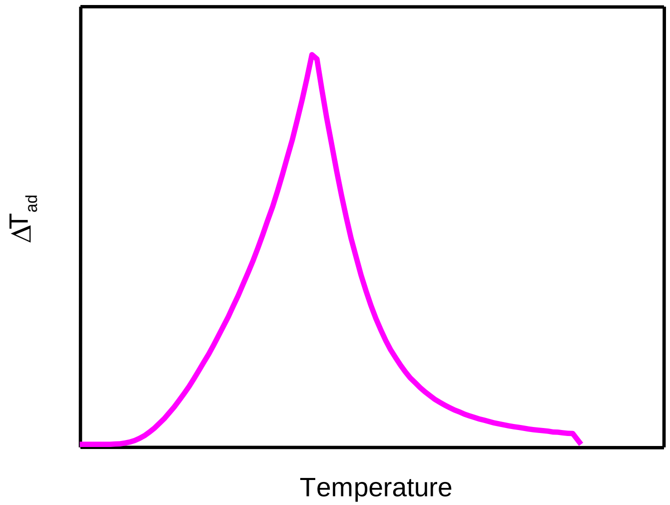
ANISOTROPIC MAGNETOCALORIC EFFECT

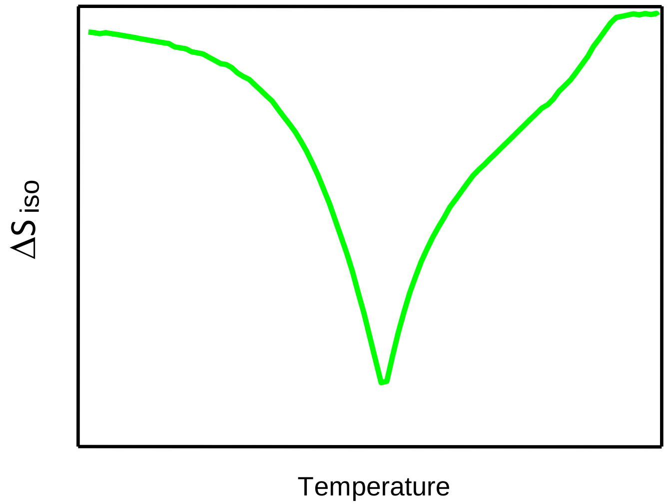


$$\Delta S_{iso}^{ani}(T, B, \Delta\theta) = S(T, B, \theta_2) - S(T, B, \theta_1)$$

$$\Delta T_{ad}^{ani}(T, B, \Delta\theta) = T_2 - T_1$$

$$S(T, B, \theta_2) = S(T, B, \theta_1)$$





THERMODYNAMICS OF THE AMCE (ΔS^{ani}_{iso})

ENTROPY CHANGE

$$dS(T,B,\theta) = \left[\frac{\partial S(T,B,\theta)}{\partial T} + \frac{\delta S(T_C,B,\theta)}{\delta T}\right]_{B,\theta} dT + \left[\frac{\partial S(T,B,\theta)}{\partial B} + \frac{\delta S(T,B_C,\theta)}{\delta B}\right]_{T,\theta} dB$$

$$+ \left[\frac{\partial S(T,B,\theta)}{\partial \theta} + \frac{\delta \theta(T,B,\theta_C)}{\delta \theta}\right]_{T,B} d\theta$$

ISOTHERMAL PROCESS

ISOFIELD PROCESS

$$\Delta S^{ani}_{iso}(T,B,\Delta\theta) = \int_{\theta_1}^{\theta_2} \left[\frac{\partial S(T,B,\theta)}{\partial \theta} + \frac{\delta S(T,B,\theta_C)}{\delta \theta}\right]_{T,B} d\theta$$

SECOND ORDER TRANSITION

$$\Delta S^{ani}_{iso}(T,B,\Delta\theta) = \int_{\theta_1}^{\theta_2} \left[\frac{\partial S(T,B,\theta)}{\partial \theta}\right]_{T,B} d\theta$$

THERMODYNAMICS OF THE AMCE (ΔT_{ad}^{ani})

ENTROPY CHANGE

$$0 = \left[\frac{\partial S(T,B,\theta)}{\partial T} + \frac{\delta S(T_C,B,\theta)}{\delta T}\right]_{B,\theta} dT + \left[\frac{\partial S(T,B,\theta)}{\partial B} + \frac{\delta S(T,B_C,\theta)}{\delta B}\right]_{T,\theta} dB$$

$$+ \left[\frac{\partial S(T,B,\theta)}{\partial \theta} + \frac{\delta \theta(T,B,\theta_C)}{\delta \theta}\right]_{T,B} d\theta$$

ADIABATIC PROCESS

ISOFIELD PROCESS

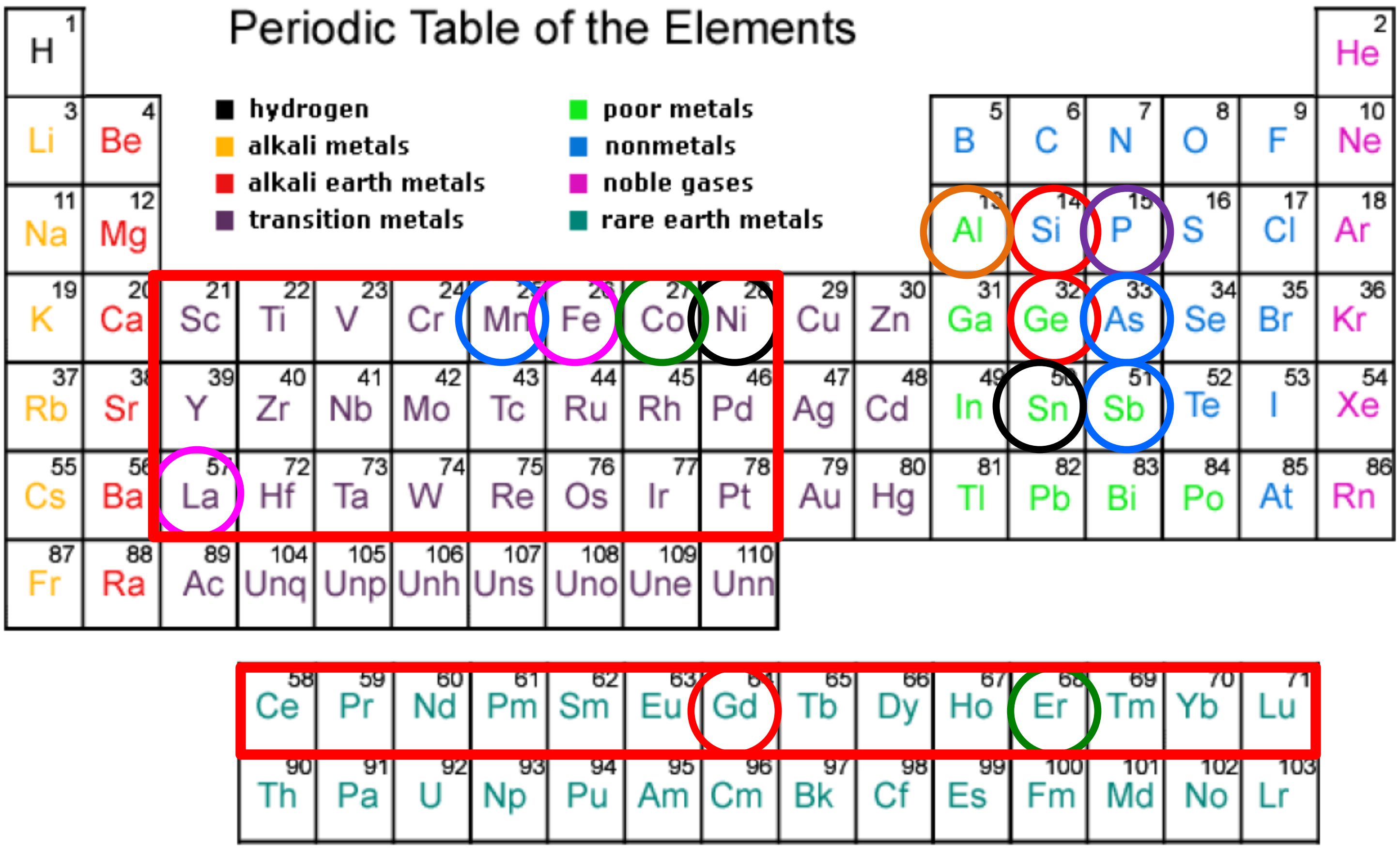
$$\Delta T_{ad}^{ani}(T,B,\Delta\theta) = -\int_{\theta_1}^{\theta_2} \frac{1}{C(T,B,\theta)} \left[\frac{\partial S(T,B,\theta)}{\partial \theta} + \frac{\delta S(T,B,\theta_C)}{\delta \theta}\right]_{T,B} d\theta$$

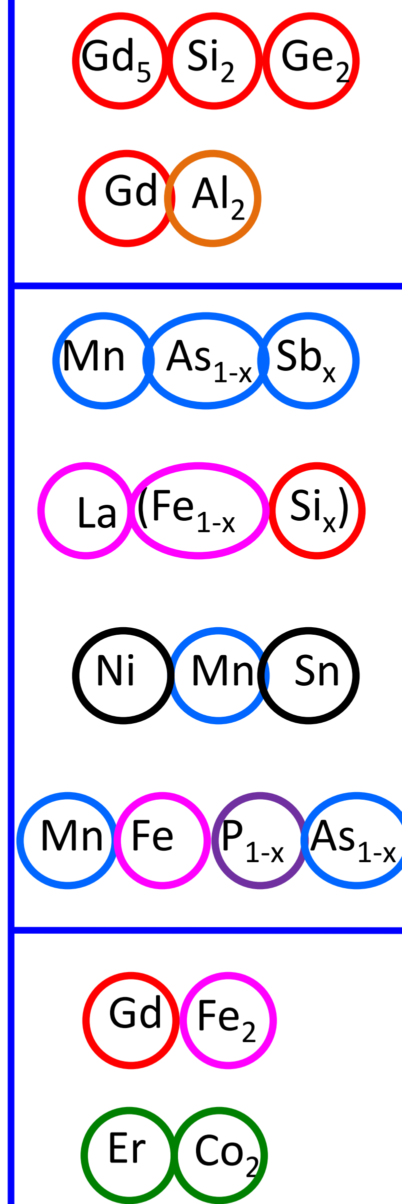
SECOND ORDER TRANSITION

$$\Delta T_{ad}^{ani}(T,B,\Delta\theta) = -\int_{\theta_1}^{\theta_2} \frac{1}{C(T,B,\theta)} \left[\frac{\partial S(T,B,\theta)}{\partial \theta}\right]_{T,B} d\theta$$

MAGNETIC MATERIALS

MAGNETIC MATERIALS





A. M. Tishin and Y. Spickin, The magnetocaloric effect and its application.

Gschneidner et al, Rep. Prog. Phys 68(2005)1479.

THEORY AND CALCULATIONS

GENERAL INTRODUCTION

THERMODYNAMIC VIEW

SYSTEMS OF LOCALIZED MAGNETIC MOMENTS

APROXIMATIONS

CALORIC QUANTITIES

MAGNETISM

Localized

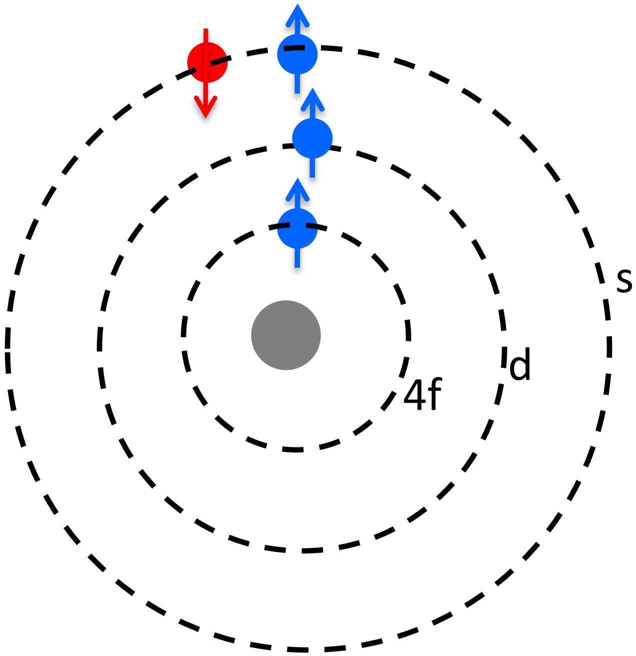
- **4f Spins - Localized levels**
- **Rare earth metals and alloys**

Itinerant

- **3d electrons - Energy band**
- **Transition metals and alloys**

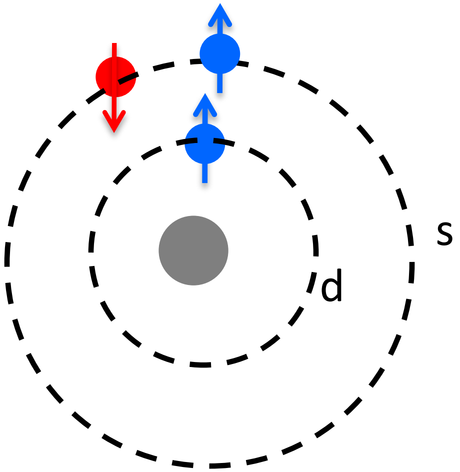
ATOMIC MAGNETISM

Rare earth



$[Xe]4f^n5d^16s^2$

Transition metals



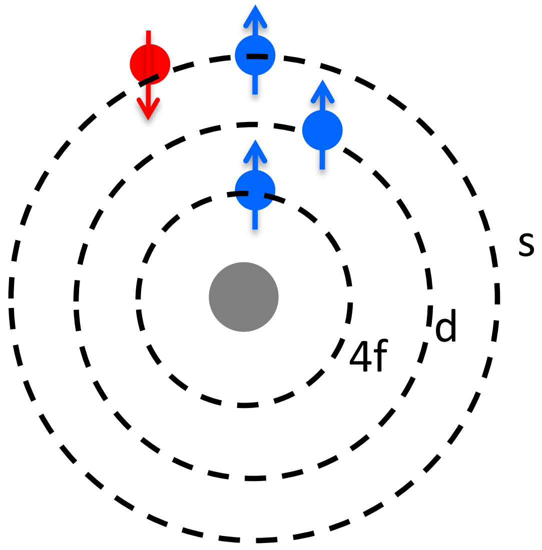
$[Ar]3d^n6s^2$

$[Kr]4d^n6s^2$

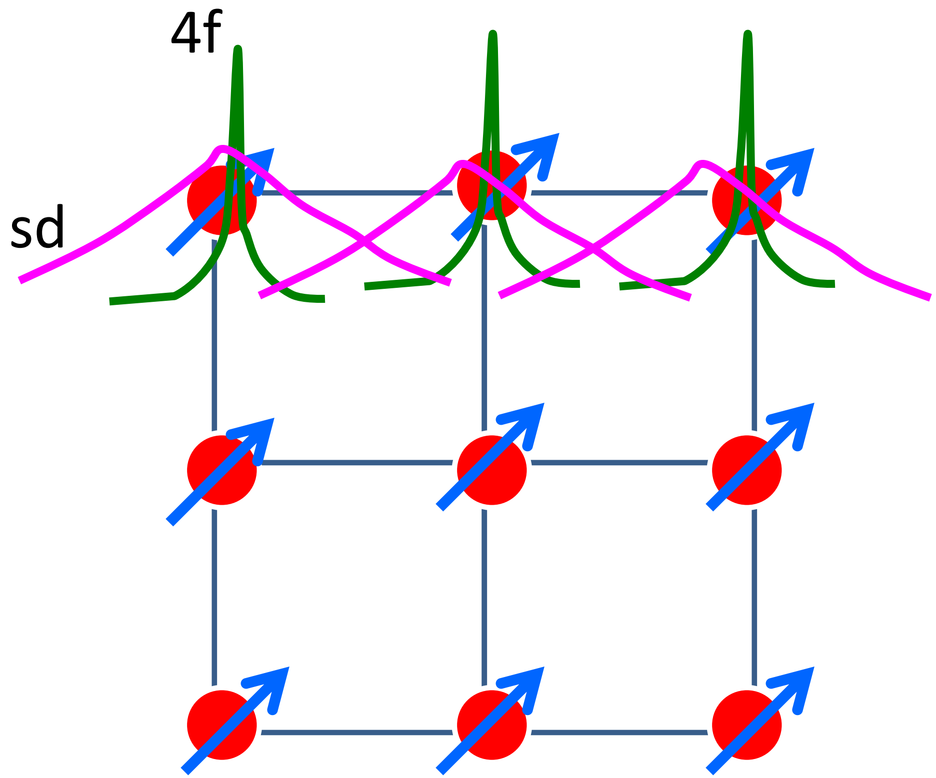
$[Xe]4f^{14}5d^n6s^2$

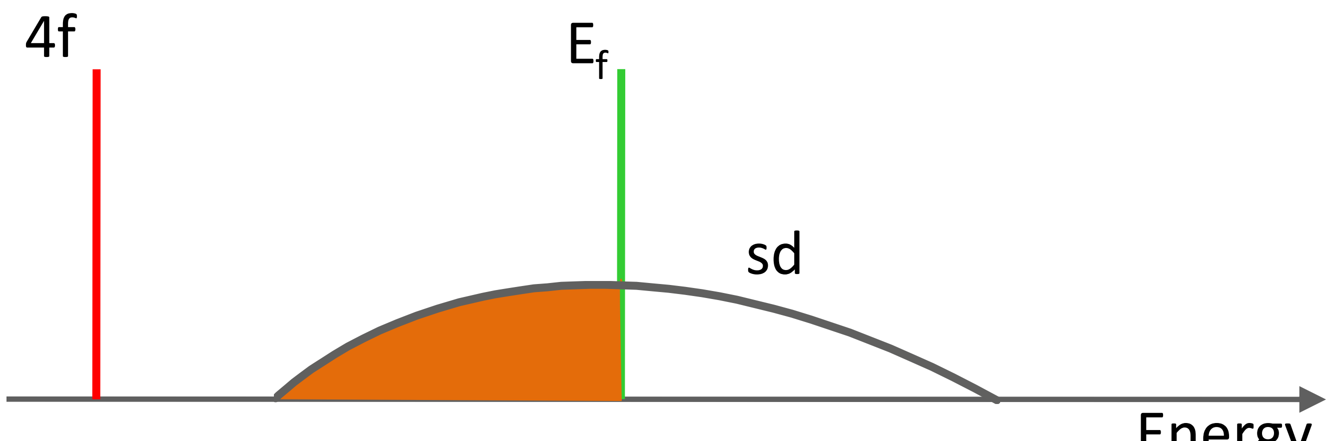
RARE EARTH METALS AND THEIR ALLOYS

RARE EARTH METALS



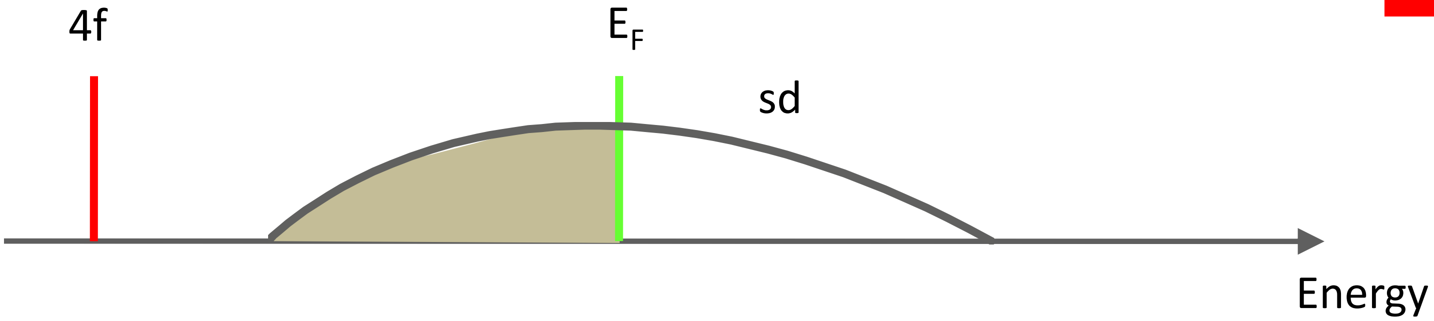
$[Xe]4f^n5d^16s^2$



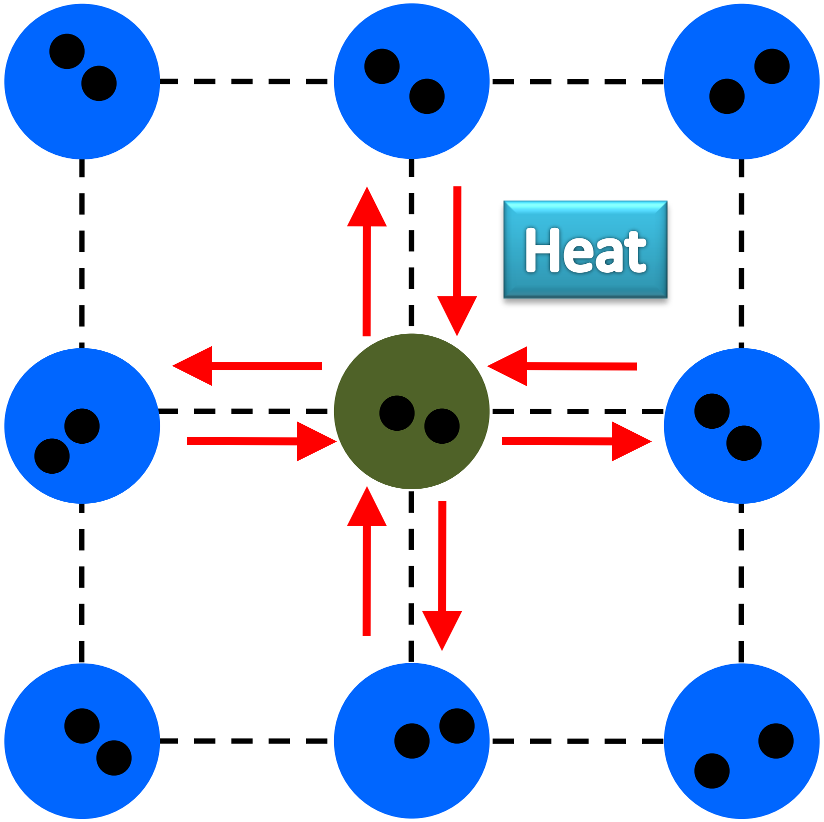


REGIMES

RKKY



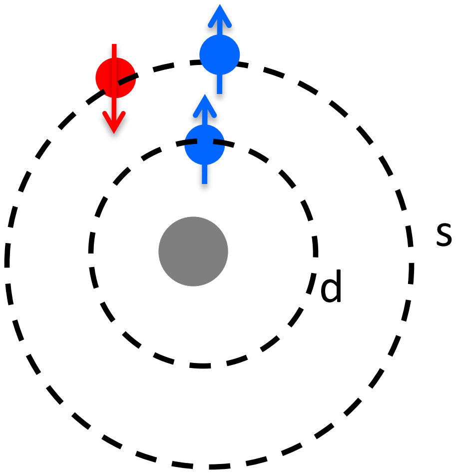
CANONICAL ENSEMBLE

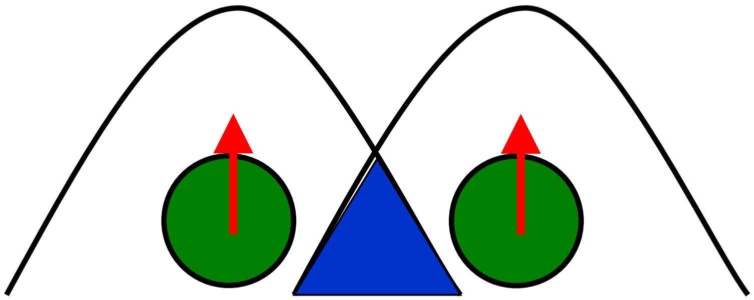


$$Z = \sum_{i=1}^{n} e^{-\beta E_i}$$

TRANSITION METALS AND THEIR ALLOYS

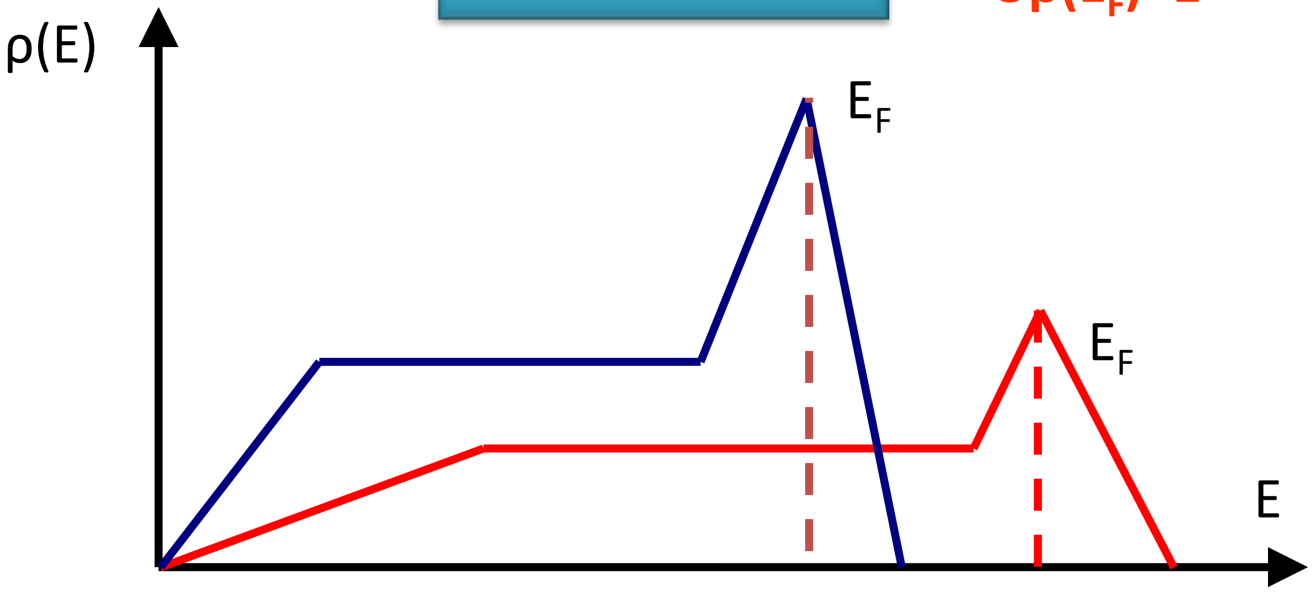
ITINERANT MAGNETISM



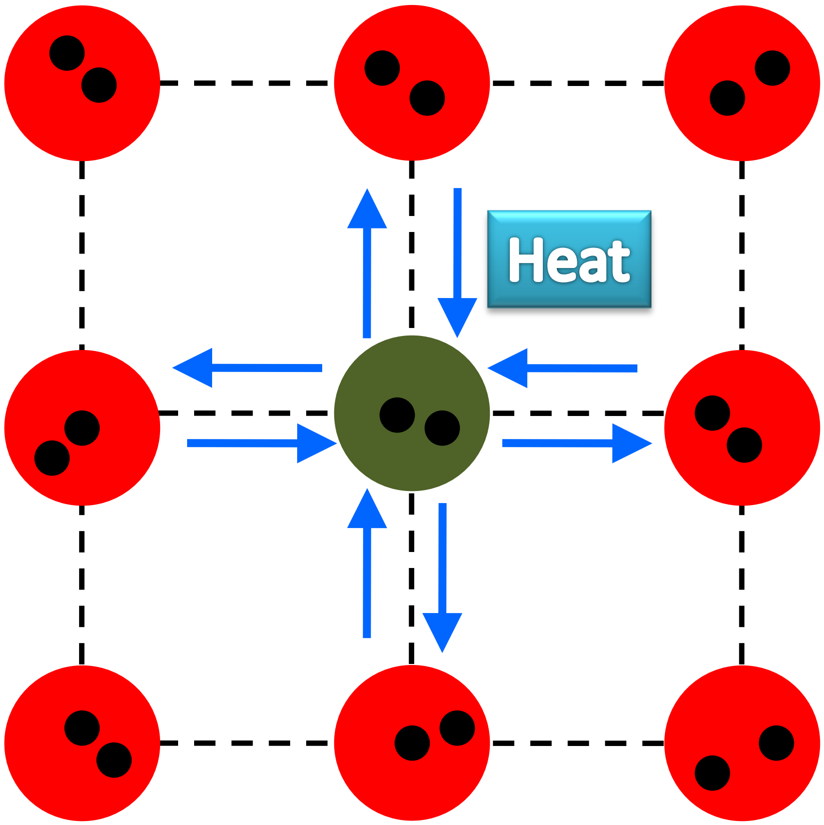


Stoner criterion

$U\rho(E_F)>1$



GRAN-CANONICAL ENSEMBLE



$$Z = \prod_{k\sigma} \{1 + \exp\left[-\beta\left(\varepsilon_{k\sigma} - \mu\right)\right]\}$$

RARE EARTH METALS AND ALLOYS

MICROSCOPIC DESCRIPTION

HAMILTONIAN

Lattice

$$\mathcal{H}_{lat} = \sum_q \hbar\omega_q a_q^+ a_q$$

Non magnetic electrons (spd)

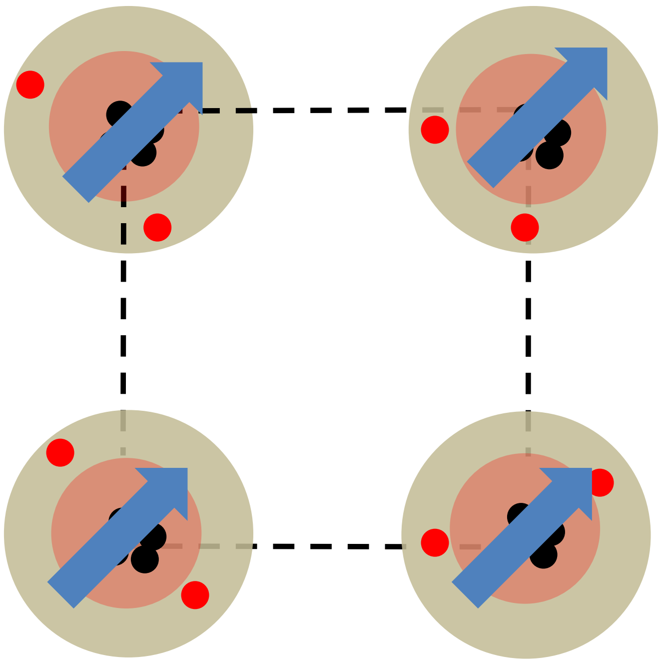
$$\mathcal{H}_{el}^{spd} = \sum_k \varepsilon_k c_k^+ c_k$$

Magnetic electrons (4f)

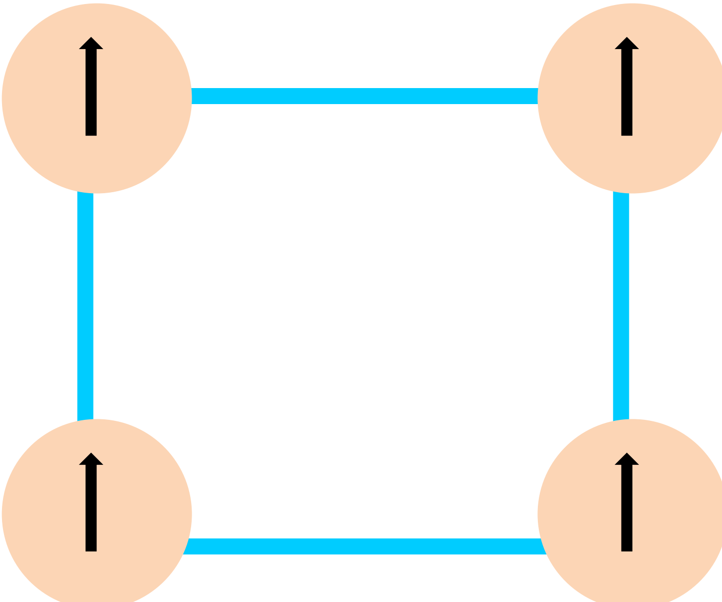
$$\mathcal{H}_{mag}^{4f} = -\sum_{i,j} \mathcal{J}_{ij}(r)\vec{J}_i \cdot \vec{J}_j - \sum_i g\mu_B \vec{B} \cdot \vec{J}_i$$

Total

$$\mathcal{H} = \mathcal{H}_{lat} + \mathcal{H}_{el}^{spd} + \mathcal{H}_{mag}^{4f}$$



MAGNETIC HAMILTONIAN



$$\mathcal{H}_{mag}^{4f} = -\sum_{i,j} \mathcal{J}_{ij}(r) \vec{J}_i \cdot \vec{J}_j - \sum_i g\mu_B \vec{B} \cdot \vec{J}_i$$

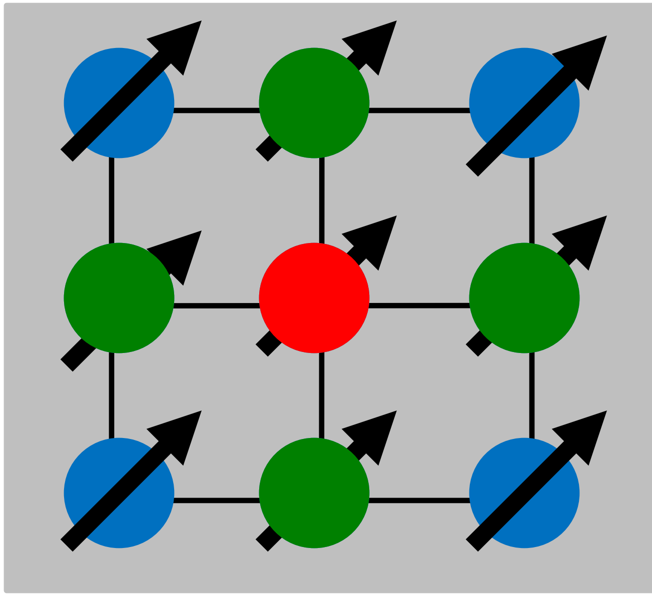
Approximation: Translation invariance

$$\mathcal{H}_{mag}^{4f} = -\sum_{ij} \mathfrak{J}_0 J_i . J_j \quad - \sum_i g\mu_B B J_i$$

MEAN FIELD THEORY

Hamiltonian

$$\mathcal{H}^{4f}_{mag} = -\sum_{i,j} \mathcal{J}_0 \vec{J}_i \cdot \vec{J}_j - \sum_i g\mu_B \vec{B} \cdot \vec{J}_i$$



Mean field

Molecular field

$$\mathcal{H}^{4f}_{mag} = -\mathcal{J}_0 \sum_i \vec{J}_i \cdot \left[\sum_j \left\langle \vec{J}_j \right\rangle \right] - \sum_i g\mu_B \vec{B} \cdot \vec{J}_i$$

Isotropic system

$$\mathcal{H}^{4f}_{mag} = -\sum_i g\mu_B B^{eff} \cdot J^z_i$$

$$B^{eff} = B + \frac{\mathcal{J}_0 \langle J^z \rangle}{g\mu_B}$$

MEAN FIELD THEORY

Equation of motion

$$\mathcal{H}_{mag}^{4f} |\psi\rangle = E |\psi\rangle$$

$$\mathcal{H}_{mag}^{4f} = -\sum_i g\mu_B B^{eff} \cdot J_i^z$$

Mean field

$$-g\mu_B B^{eff} \cdot \left(J_i^z |\psi\rangle\right) = E |\psi\rangle$$

$$\left(J_i^z |\psi\rangle = m |\psi\rangle\right)$$

Energy

$$E_m = -g\mu_B B^{eff} m$$

$$-J \leq m \leq J$$

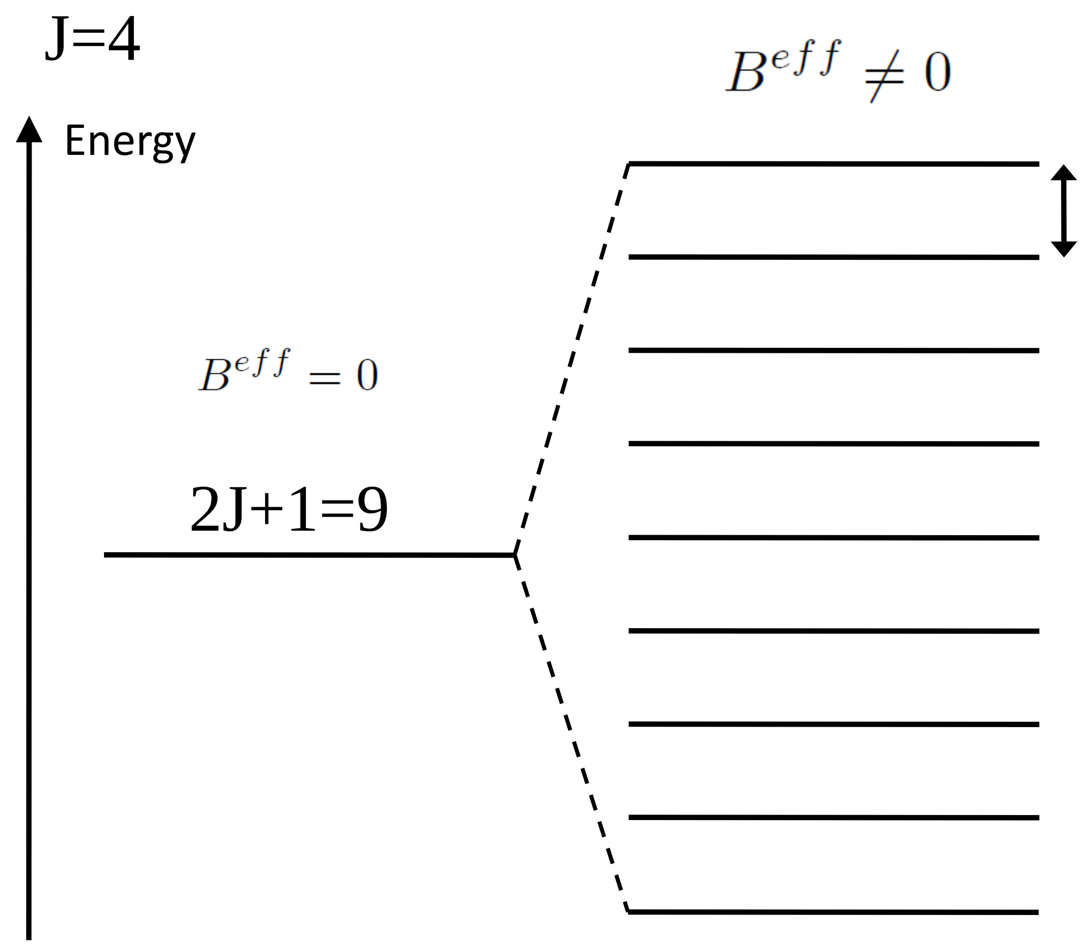
$$B^{eff} = B + \frac{\mathcal{J}_0 \langle J^z \rangle}{g\mu_B}$$

ENERGY LEVELS

$$E_m = -g\mu_B B^{eff} m$$

$$B^{eff} = B + \frac{\mathcal{J}_0 \langle J^z \rangle}{g\mu_B}$$

$$-J \leq m \leq J$$



MAGNETIZATION

Partition function

$$Z_{mag}^{4f}(T,B,P) = \sum_{m=-J}^{m=J} e^{-\beta E_m}$$

Magnetic free energy

$$F_{mag}^{4f}(T,B,P) = -k_B T \ln \left[\sum_{m=-J}^{m=J} e^{-\beta E_m} \right]$$

$$E_m = -g\mu_B B^{eff} m$$

Magnetization

$$M(T,B,P) = -\left[\frac{\partial F_{mag}^{4f}(T,B,P)}{\partial B^{eff}} \right]_{T,P}$$

$$M(T,B,P) = \frac{\sum_{m=-J}^{m=J} \left[\partial E_m / \partial B^{eff} \right] e^{-\beta E_m}}{\sum_{m=-J}^{m=J} e^{-\beta E_m}}$$

$$B^{eff} = B + \frac{\mathcal{J}_0 \langle J^z \rangle}{g\mu_B}$$

Self-consistency

FREE ENERGY AND MAGNETIC ENTROPY

Magnetic free energy

$$F^{4f}_{mag}(T,B,P) = -k_B T \ln\left[\sum_{m=-J}^{m=J} e^{-\beta E_m}\right]$$

Magnetic entropy

$$S^{4f}_{mag}(T,B,P) = -\left[\frac{\partial F^{4f}_{mag}(T,B,P)}{\partial T}\right]_{B,P}$$

$$S^{4f}_{mag}(T,B,P) = N_m \Re\left[\ln \sum_{m=-J}^{m=J} e^{-\beta E_m} + \frac{1}{k_B T}\frac{\sum_{m=-J}^{m=J} E_m e^{-\beta E_m}}{\sum_{m=-J}^{m=J} e^{-\beta E_m}}\right]$$

ALTERNATIVE CALCULATION

PARTITION FUNCTION AND FREE ENERGY

Partition function

$$Z_{mag}^{4f}(T,B,P) = \sum_{m=-J}^{m=J} e^{-\beta E_m}$$

$$E_m = -g\mu_B B^{eff} m$$

Geometric series

$$Z_{mag}^{4f}(T,B,P) = \sum_{m=-J}^{m=J} e^{-\beta E_m} = e^{\beta g\mu_B B^{eff} J} + e^{\beta g\mu_B B^{eff}(J-1)} + ...e^{-\beta g\mu_B B^{eff} J}$$

$$Z_{mag}^{4f}(T,B,P) = \frac{\sinh\left[J+\frac{1}{2}\right]y}{\sinh\left[\frac{y}{2}\right]}$$

$$y = \frac{g\mu_B B^{eff}}{k_B T}$$

Magnetic free energy

$$F_{mag}^{4f}(T,B,P) = -k_B T \ln\left\{\frac{\sinh\left[J+\frac{1}{2}\right]y}{\sinh\left[\frac{y}{2}\right]}\right\}$$

MAGNETIZATION

Magnetic free energy

$$F_{mag}^{4f}(T,B,P) = -k_B T \ln \left\{ \frac{\sinh\left[J+\frac{1}{2}\right] y}{\sinh\left[\frac{y}{2}\right]} \right\}$$

Magnetization

$$M(T,B,P) = -\left[\frac{\partial F_{mag}^{4f}(T,B,P)}{\partial B^{eff}}\right]_{T,P}$$

$$M(T,B,P) = g\mu_B B_J(y)$$

$$B_J(y) = \frac{1}{J}\left\{\left(\frac{2J+1}{2}\right)\coth\left[\left(\frac{2J+1}{2}\right)y\right] - \frac{1}{2}\coth\left(\frac{y}{2}\right)\right\}$$

$$y = \frac{g\mu_B B^{eff}}{k_B T}$$

Brillouin function

Self-consistency

$$B^{eff} = B + \frac{\mathcal{J}_0 \langle J^z \rangle}{g\mu_B}$$

MAGNETIC ENTROPY

Magnetic free energy

$$F_{mag}^{4f}(T,B,P) = -k_B T \ln \left\{ \frac{\sinh\left[J+\frac{1}{2}\right] y}{\sinh\left[\frac{y}{2}\right]} \right\}$$

$$y = \frac{g\mu_B B^{eff}}{k_B T}$$

Magnetic entropy

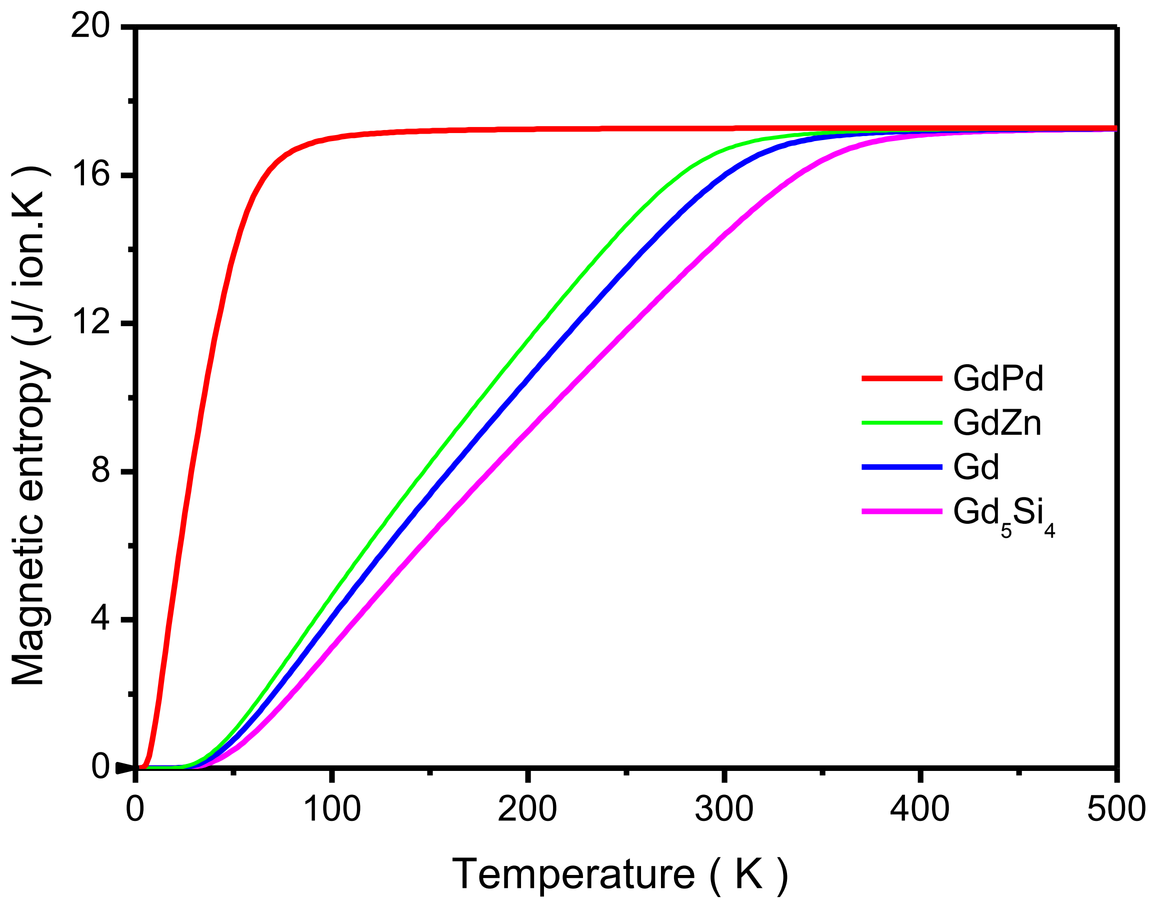
$$S_{mag}^{4f}(T,B,P) = -\left[\frac{\partial F_{mag}^{4f}(T,B,P)}{\partial T}\right]_{B,P}$$

$$S_{mag}^{4f}(T,B,P) = N_m \Re \left\{ \ln\left[\frac{\sinh\left(J+\frac{1}{2}\right) y}{\sinh\left(\frac{y}{2}\right)}\right] - \frac{g\mu_B B^{eff}}{k_B T}\left(J+\frac{1}{2}\right)\coth\left[\left(J+\frac{1}{2}\right)y\right] - \frac{1}{2}\coth\left[\left(\frac{y}{2}\right)\right] \right\}$$

Saturation value

$$S_{mag}^{4f}(T,B,P)\,|_{T\longrightarrow\infty} = N_m \Re \ln\left(2J+1\right)$$

MAGNETIC ENTROPY CURVES



$$S^{4f}_{mag}(T, B, P)\,|_{T\longrightarrow\infty} = N_m \Re \ln\left(2J+1\right)$$

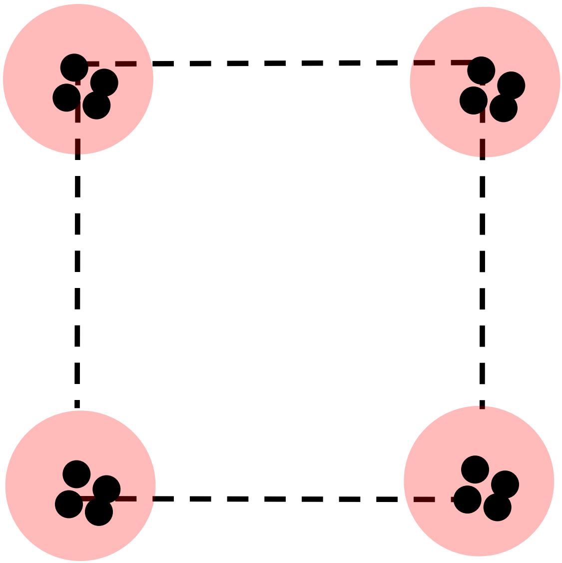
CRYSTAL LATTICE HAMILTONIAN

LATTICE HAMILTONIAN

Lattice Hamiltonian

$$\mathcal{H}_{lat} = \sum_q \hbar\omega_q a_q^+ a_q$$

$$\varepsilon_q = \sum_q (n_q + \frac{1}{2})\hbar\omega_q$$



N. A. de Oliveira and P. J. von Ranke, Phys. Rep. 489 (2010) 89.

LATTICE : CANONICAL ENSEMBLE

Partition function

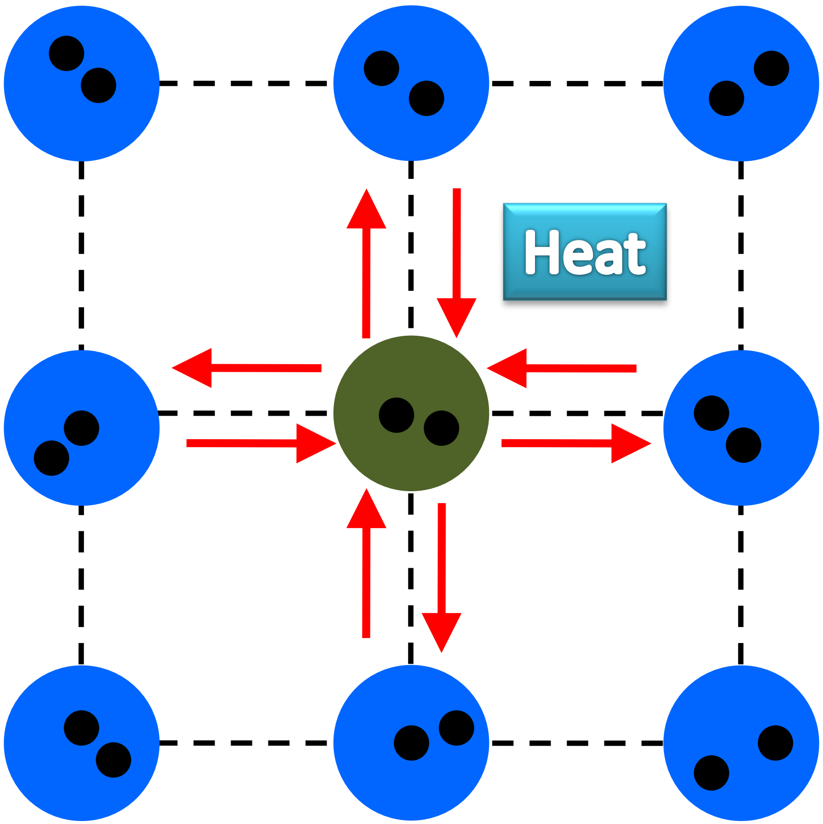
$$Z = \sum_{i=1}^{n} e^{-\beta E_i}$$

$$\varepsilon_q = \sum_q (n_q + \frac{1}{2})\hbar\omega_q$$

$$Z_{lat}(T,B,P) = \sum_{n_q = n_1, n_2 .....} e^{-\beta \sum_q (n_q + \frac{1}{2})\hbar\omega_q}$$

Bosons

$$Z_{lat}(T,B,P) = \prod_q \frac{1}{(1 - e^{-\beta\hbar\omega_q})}$$



Lattice free energy

$$F_{lat}(T,B,P) = 3N_A k_B T \sum_q \ln\left(1 - e^{-\beta\hbar\omega_q}\right)$$

LATTICE ENTROPY

Lattice free energy

$$F_{lat}(T,B,P) = 3N_A k_B T \sum_q \ln\left(1 - e^{-\beta\hbar\omega_q}\right)$$

Density of phonons

$$F_{lat}(T,B,P) = \Re T \int \ln\left(1 - e^{-\beta\hbar\omega}\right) \rho^{ph}(\omega) d\omega$$

Lattice entropy

$$S_{lat}(T,B,P) = -\left[\frac{\partial F_{lat}(T,B,P)}{\partial T}\right]_B$$

$$S_{lat}(T,B,P) = N_i \Re \left[-\int \ln\left(1 - e^{-\beta\hbar\omega}\right) \rho^{ph}(\omega) d\omega + \frac{1}{k_B T}\int \frac{\hbar\omega}{\left(e^{\beta\hbar\omega} - 1\right)} \rho^{ph}(\omega) d\omega\right]$$

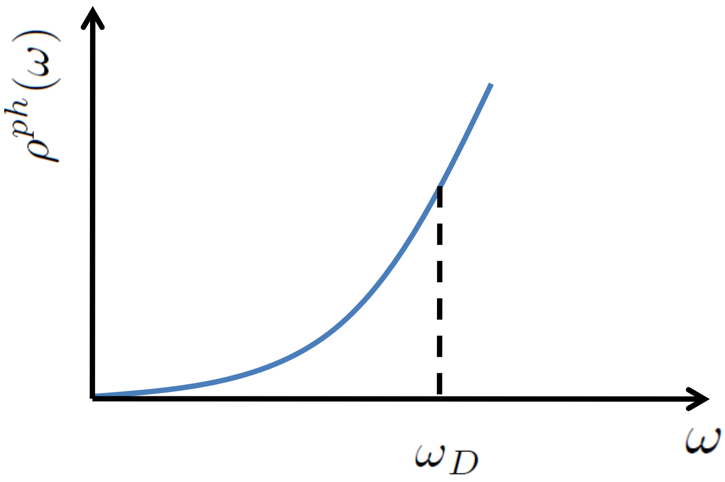
N. A. de Oliveira and P. J. von Ranke, Phys. Rep. 489 (2010) 89.

LATTICE ENTROPY (Debye approximation)

$$S_{lat}(T,B,P) = N_i \Re \left[-\int \ln\left(1 - e^{-\beta\hbar\omega}\right) \rho^{ph}(\omega) d\omega + \frac{1}{k_B T} \int \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \rho^{ph}(\omega) d\omega \right]$$

Debye approximation

$$\begin{cases} \rho^{ph}(\omega) = \left[\dfrac{3V}{2\pi^2 v^3} \right] \omega^2 \\ \omega_D = \left[\dfrac{6\pi^2 v^3 N_A}{V} \right]^{1/3} \end{cases}$$



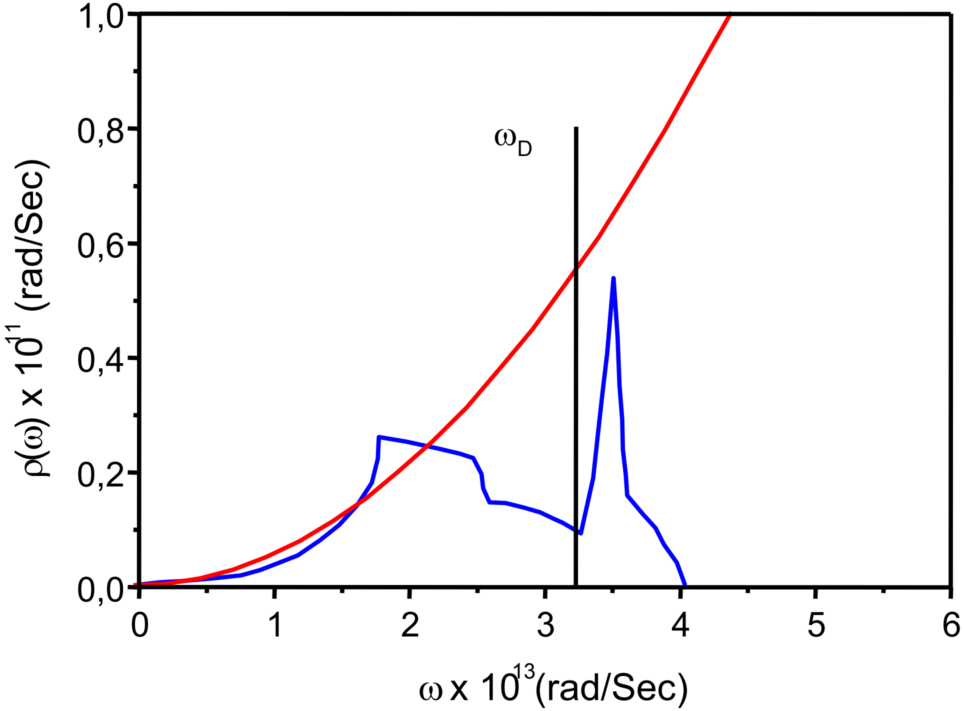
Lattice entropy

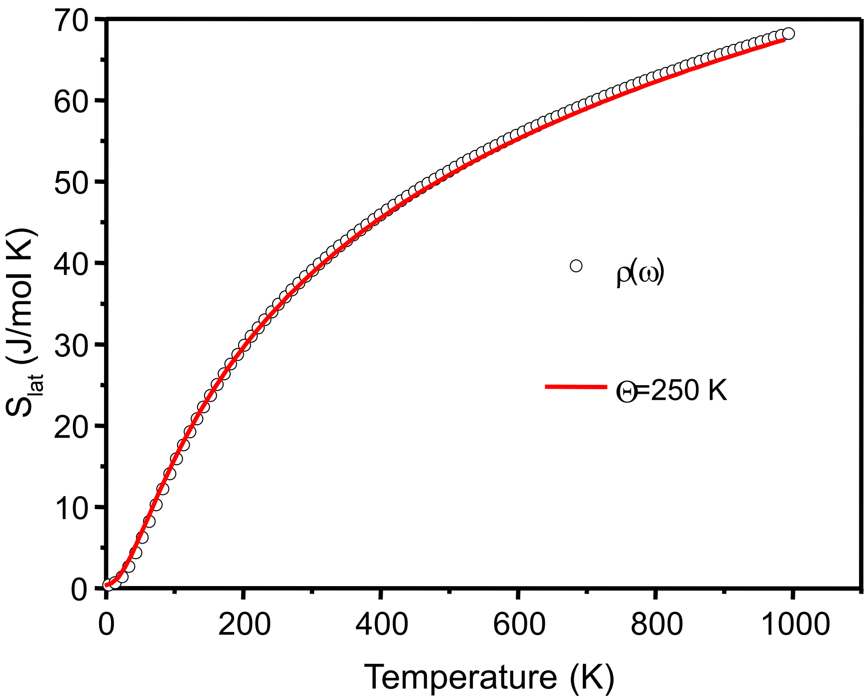
$$S_{lat}(T,B,P) = N_i \left[-3\Re \ln\left(1 - e^{-\frac{\Theta_D}{T}}\right) + 12\Re \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \right]$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$

N. A. de Oliveira and P. J. von Ranke, Phys. Rep. 489 (2010) 89.

LATTICE ENTROPY





$$S_{lat}(T,B,P) = N_i \Re \left[- \int \ln\left(1 - e^{-\beta\hbar\omega}\right) \rho^{ph}(\omega) d\omega + \frac{1}{k_B T} \int \frac{\hbar\omega}{\left(e^{\beta\hbar\omega} - 1\right)} \rho^{ph}(\omega) d\omega \right]$$

$$S_{lat}(T,B,P) = N_i \left[-3\Re \ln\left(1 - e^{-\frac{\Theta_D}{T}}\right) + 12\Re \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \right]$$

NON MAGNETIC CONDUCTION ELECTRONS

Hamiltonian

$$\mathcal{H}_{el}^{spd} = \sum_k \varepsilon_k c_k^+ c_k$$

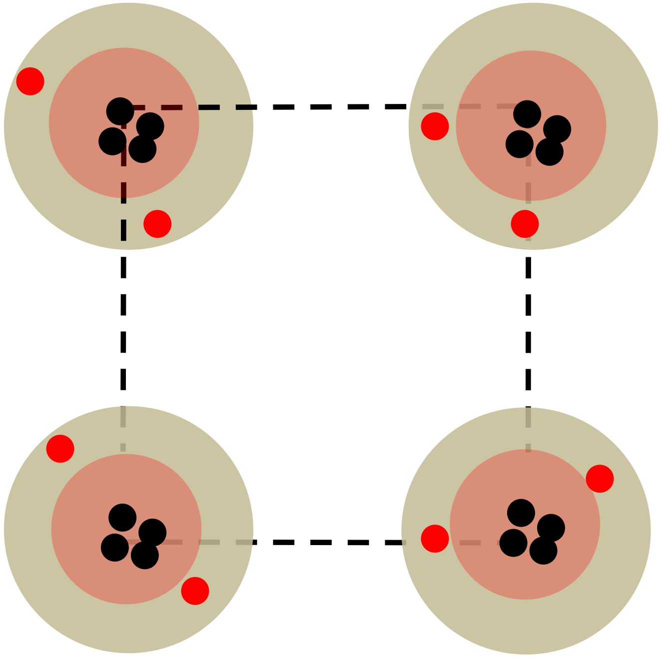
Partition function

$$Z_{el}^{spd}(T,B,P) = \prod_{k\sigma} \left\{1 + \exp\left[-\beta\left(\varepsilon_k^{spd} - \mu\right)\right]\right\}$$

Free energy

$$F_{el}^{spd}(T,B,P) = -\frac{1}{\beta}\sum_{l=1}^{5}\sum_{k\sigma} \ln\left\{1 + \exp\left[-\beta\left(\varepsilon_k^{spd} - \mu\right)\right]\right\}$$

Gran-canonical ensemble



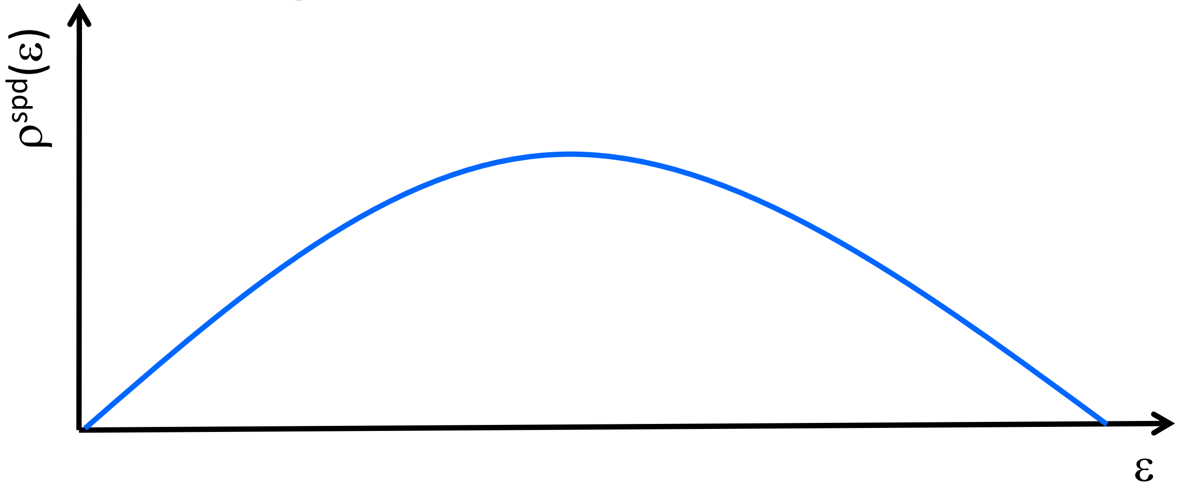
FREE ENERGY

Free energy

$$F_{el}^{spd}(T,B,P) = -\frac{1}{\beta}\sum_{l=1}^{5}\sum_{k\sigma}\ln\left\{1+\exp\left[-\beta\left(\varepsilon_k^{spd}-\mu\right)\right]\right\}$$

Density of phonons

$$F_{el}^{spd}(T,B,P) = -\Re T\sum_{\sigma}\int_{-\infty}^{\infty}\ln\left\{1+\exp\left[-\beta\left(\varepsilon_\sigma-\mu\right)\right]\right\}\rho_\sigma^{spd}(\varepsilon)\,d\varepsilon$$



ELECTRONIC ENTROPY

Free energy

$$F_{el}^{spd}(T,B,P) = -\Re T \sum_{\sigma} \int_{-\infty}^{\infty} \ln\left\{1+\exp\left[-\beta\left(\varepsilon_{\sigma}-\mu\right)\right]\right\} \rho_{\sigma}^{spd}\left(\varepsilon\right)\, d\varepsilon$$

Electronic entropy

$$S_{el}^{spd} = -\left[\frac{\partial F_{el}^{spd}(T,B,P}{\partial T}\right]_B$$

$$S_{el}^{spd}(T,B,P) = N_{el}\Re\left\{\sum_{\sigma}\int_{-\infty}^{\infty} \ln\left\{1+\exp[-\beta(\varepsilon-\mu)]\right\} \rho_{\sigma}^{spd}\left(\varepsilon\right) d\varepsilon + \frac{1}{k_B T}\sum_{\sigma}\int_{-\infty}^{\infty}\left(\varepsilon-\mu\right) f\left(\varepsilon\right) \rho_{\sigma}^{spd}\left(\varepsilon\right) d\varepsilon\right\}$$

Sommerfeld approximation

$$S_{el}^{spd}(T) = \gamma T$$

$$\gamma = \frac{\pi^2 k_B^2 \rho_{\sigma}^{spd}(\varepsilon_f)}{3}$$

MCE QUANTITIES

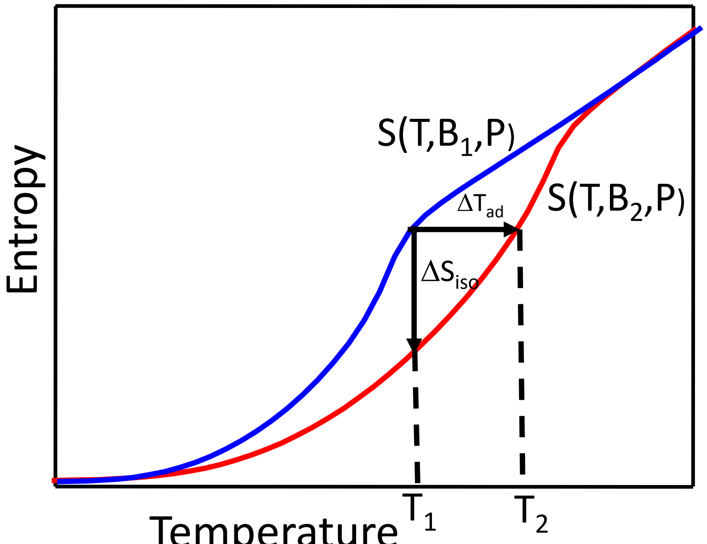
Total entropy

$$S(T,B,P) = S_{mag}^{4f}(T,B,P) + S_{lat}(T,B,P) + S_{el}^{spd}(T,B,P)$$

$$S(T,B,P) = N_m \Re \left[\ln \sum_{m=-J}^{m=J} e^{-\beta E_m} + \frac{1}{k_B T} \frac{\sum_{m=-J}^{m=J} E_m e^{-\beta E_m}}{\sum_{m=-J}^{m=J} e^{-\beta E_m}} \right]$$

$$+ N_i \left[-3\Re \ln\left(1 - e^{-\frac{\Theta_D}{T}}\right) + 12\Re \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \right] + \gamma T$$

Magnetocaloric quantities

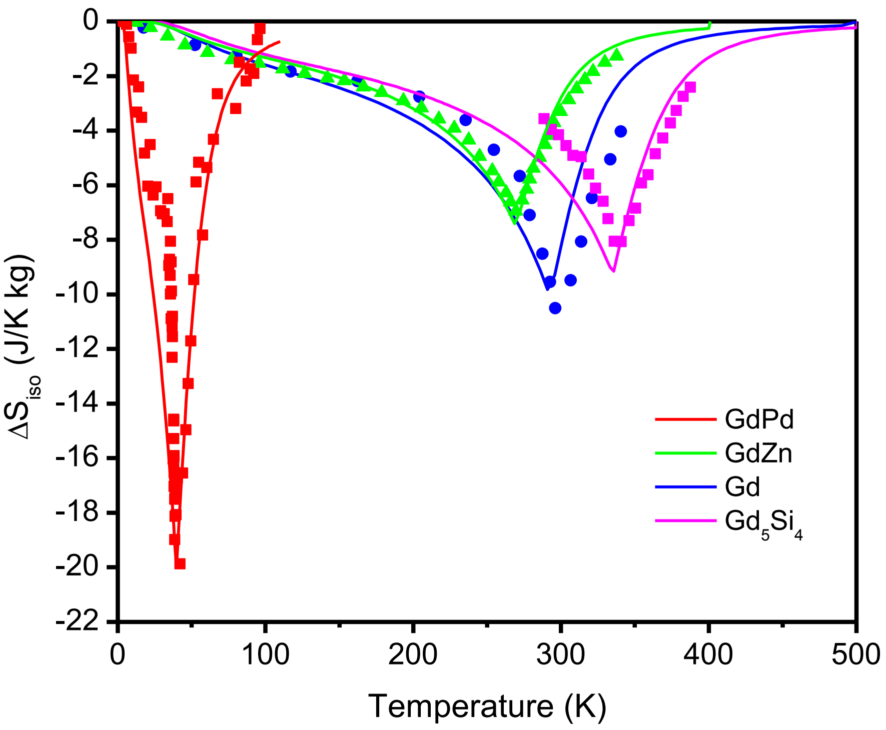


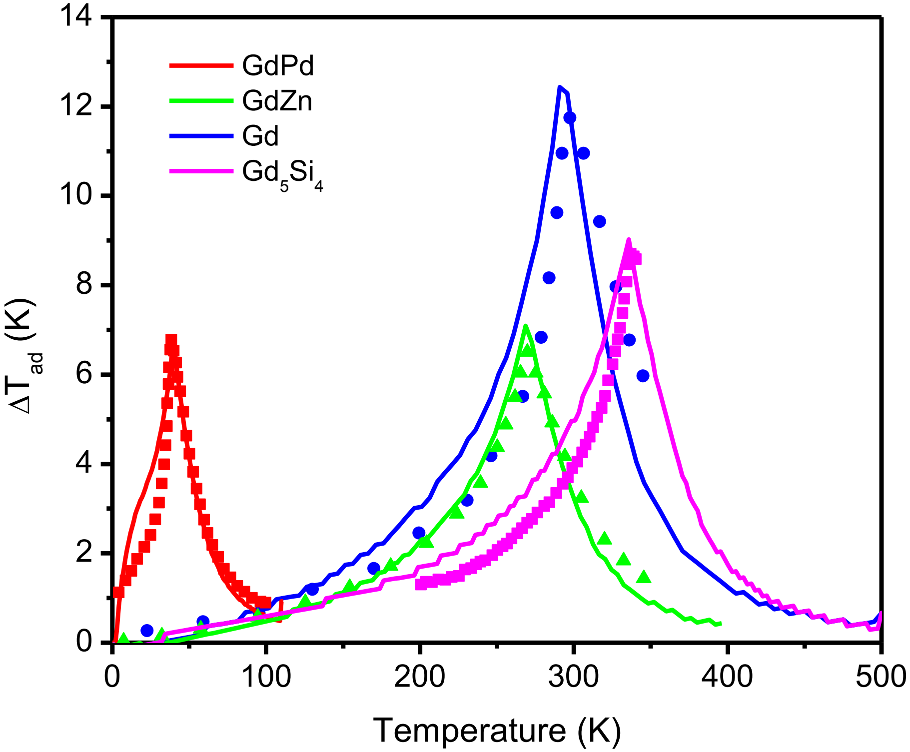
$$\Delta S_{iso}(T,\Delta B,P) = S(T,B_2,P) - S(T,B_1,P)$$

$$\Delta T_{ad}(T,\Delta B,P) = T_2 - T_1$$

$$S(T,B_2,P) = S(T,B_1,P)$$

APPLICATION: Gd COMPOUNDS





ANISOTROPY

HAMILTONIAN

Total

$$\mathcal{H} = \mathcal{H}_{lat} + \mathcal{H}_{el}^{spd} + \mathcal{H}_{mag}^{4f}$$

Lattice

$$\mathcal{H}_{lat} = \sum_q \hbar\omega_q a_q^+ a_q$$

Non magnetic electrons

$$\mathcal{H}_{el}^{spd} = \sum_k \varepsilon_k c_k^+ c_k$$

Magnetic electrons

$$\mathcal{H}_{mag}^{4f} = -\sum_{i,j} \mathcal{J}_{ij}(r)\vec{J}_i \cdot \vec{J}_j - \sum_i g\mu_B \vec{B} \cdot \vec{J}_i - \sum_i D J_{iz}^2$$

MEAN FIELD APPROXIMATION

Hamiltonian

$$\mathcal{H}_{mag}^{4f} = -\sum_{i,j} \mathcal{J}_{ij}(r)\vec{J}_i \cdot \vec{J}_j - \sum_i g\mu_B \vec{B} \cdot \vec{J}_i - \sum_i D J_{iz}^2$$

Mean field approximation

$$\mathcal{H}_{mag}^{4f} = -\mathcal{J}_0 \sum_i \vec{J}_i \cdot \left\langle \vec{J} \right\rangle - \sum_i g\mu_B \vec{B} \cdot \vec{J}_i - \sum_i D J_{iz}^2$$

Magnetic electrons

$$\mathcal{H}_{mag}^{4f} = -\sum_i g\mu_B B_x^{eff} J_{ix} + g\mu_B B_y^{eff} J_{iy} + g\mu_B B_z^{eff} J_{iz}$$

$$B_x^{eff} = B\cos\theta_x + \frac{\mathcal{J}_0 \langle J_x \rangle}{g\mu_B}$$

$$B_y^{eff} = B\cos\theta_y + \frac{\mathcal{J}_0 \langle J_y \rangle}{g\mu_B}$$

$$B_z^{eff} = B\cos\theta_z + \frac{\mathcal{J}_0 \langle J_z \rangle + DJ_z}{g\mu_B}$$

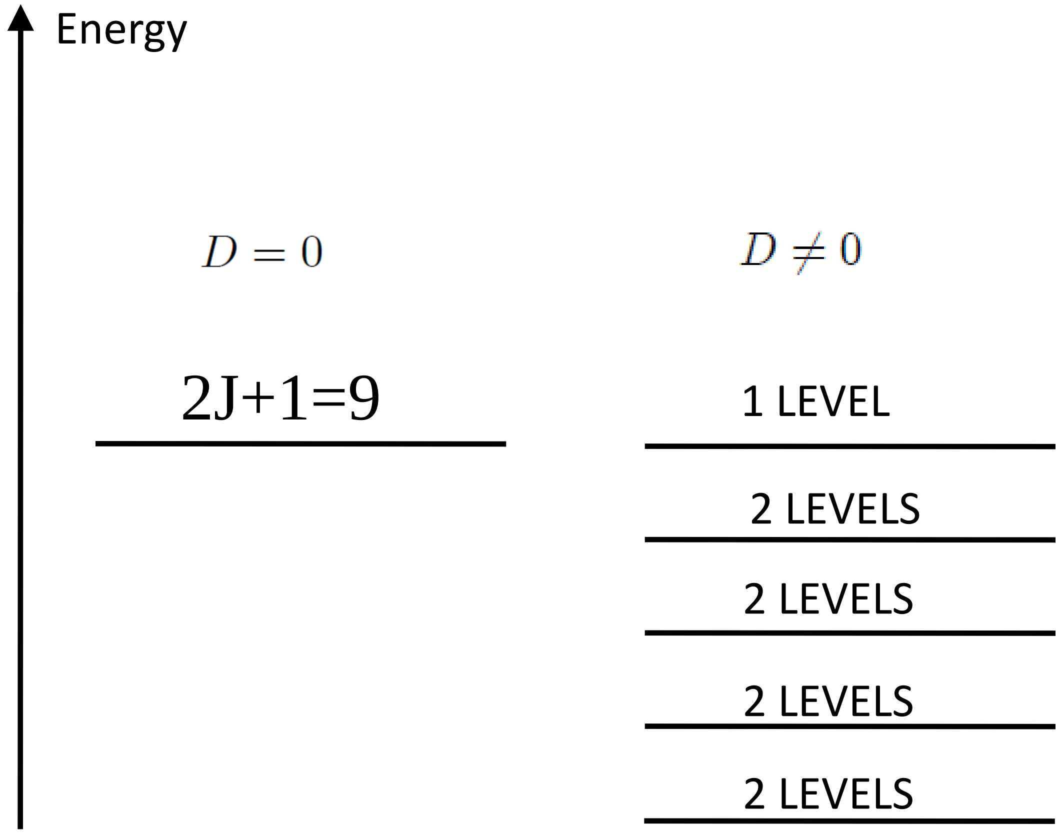
ENERGY LEVELS

$$B_x^{eff} = B\cos\theta_x + \frac{\mathcal{J}_0 \langle J_x \rangle}{g\mu_B}$$

$$B_y^{eff} = B\cos\theta_y + \frac{\mathcal{J}_0 \langle J_y \rangle}{g\mu_B}$$

$$B_z^{eff} = B\cos\theta_z + \frac{\mathcal{J}_0 \langle J_z \rangle + DJ_z}{g\mu_B}$$

J=4



MATRIX HAMILTONIAN

Total

$$\mathcal{H}^{4f}_{mag} = -\sum_i g\mu_B B^{eff}_x J_{ix} + g\mu_B B^{eff}_y J_{iy} + g\mu_B B^{eff}_z J_{iz}$$

Mean field approximation

$$\mathcal{H}^{4f}_{mag} = \begin{bmatrix} \mathcal{H}_{11} & \mathcal{H}_{12} & \cdots & \mathcal{H}_{1(2J+1)} \\ \mathcal{H}_{21} & \mathcal{H}_{22} & \cdots & \mathcal{H}_{2(2J+1)} \\ \vdots & \vdots & \ddots & \vdots \\ \mathcal{H}_{(2J+1)1} & \mathcal{H}_{(2J+1)2} & \cdots & \mathcal{H}_{(2J+1)(2J+1)} \end{bmatrix}$$

$$\mathcal{H}_{ij} = \langle\psi_i| \mathcal{H}^{4f}_{mag} |\psi_j\rangle$$

Energy eigenvalues and eigenvectors

$$E_m \qquad |\psi_m\rangle$$

MAGNETIZATION

Magnetization

$$M(T,B,P) = \hat{\imath} M_x(T,B,P) + \hat{\jmath} M_y(T,B,P) + \hat{k} M_z(T,B,P)$$

Magnetization components

$$M_x(T,B,P) = g\mu_B \langle J_x \rangle$$

$$M_y(T,B,P) = g\mu_B \langle J_y \rangle$$

$$M_z(T,B,P) = g\mu_B \langle J_z \rangle$$

Average values

$$\langle J_x \rangle = \frac{\sum_m \langle \psi_m | J_x | \psi_m \rangle}{\sum_m e^{-\beta E_m}}$$

$$\langle J_y \rangle = \frac{\sum_m \langle \psi_m | J_y | \psi_m \rangle}{\sum_m e^{-\beta E_m}}$$

$$\langle J_z \rangle = \frac{\sum_m \langle \psi_m | J_z | \psi_m \rangle}{\sum_m e^{-\beta E_m}}$$

PARTITION FUNCTION AND FREE ENERGY

Partition function

$$Z_{mag}(T,B,P) = \sum_{m=-J}^{m=J} e^{-\beta E_m}$$

Magnetic free energy

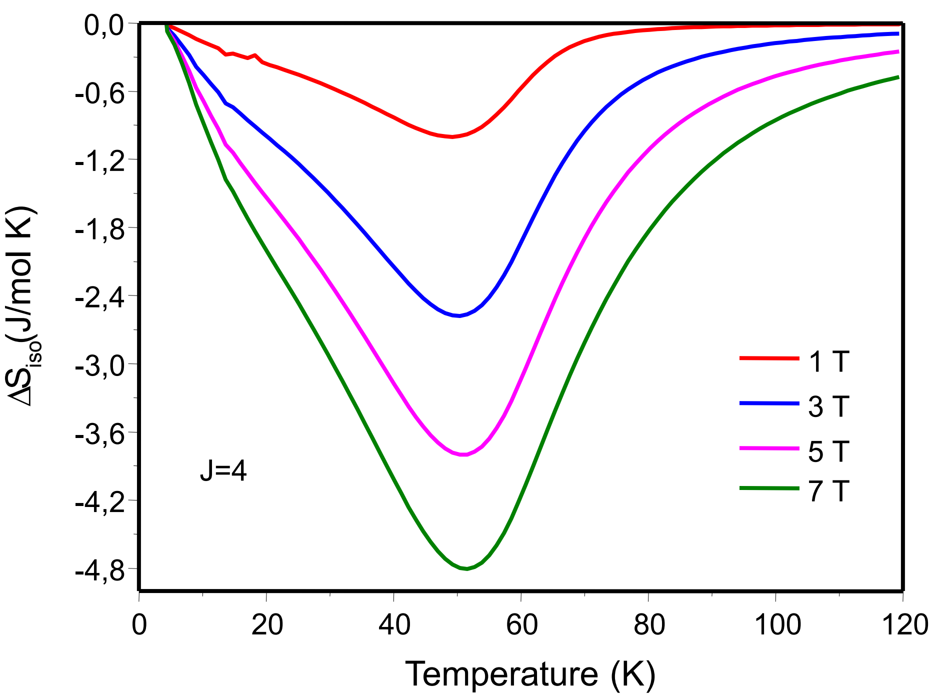
$$F_{mag}^{4f} = -k_B T \ln \sum_m e^{-\beta E_m}$$

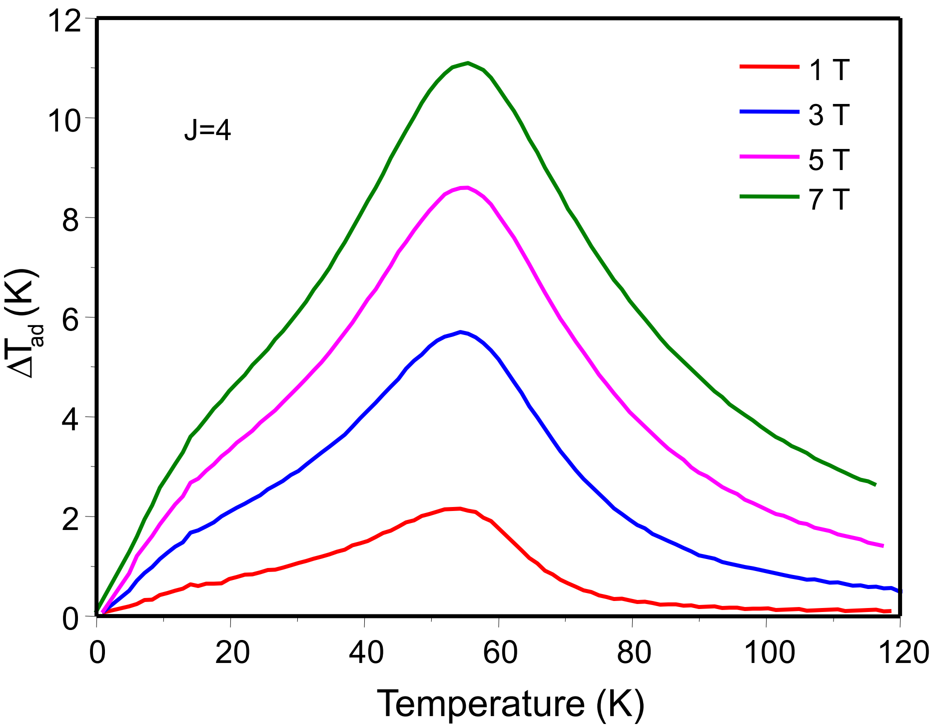
Magnetic entropy

$$S_{mag}(T,B,P) = -\left[\frac{\partial F_{mag}(T,B,P)}{\partial T}\right]_{B,P}$$

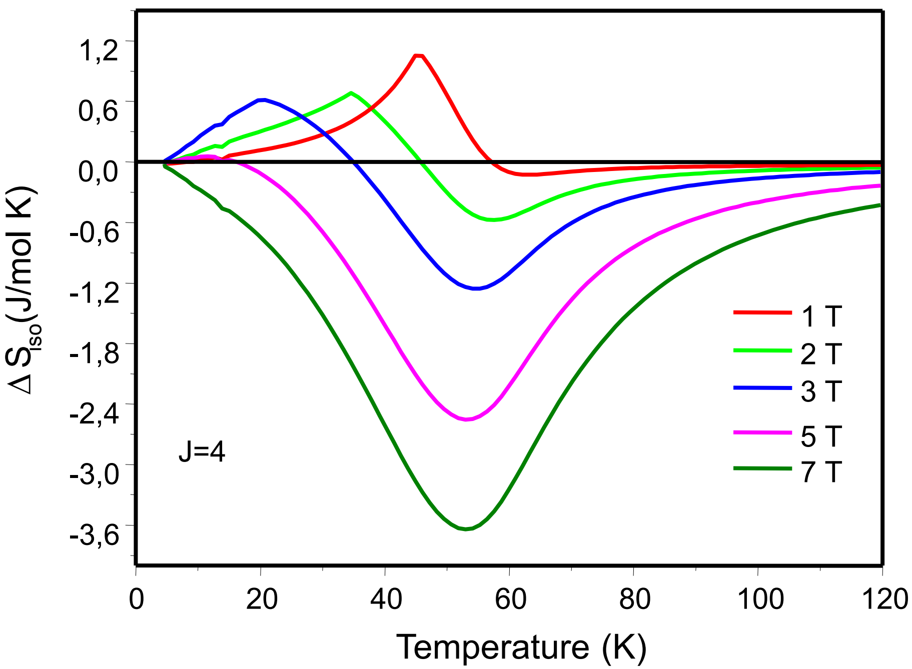
$$S_{mag}(T,B,P) = N_m \Re \left[\ln \sum_{m=-J}^{m=J} e^{-\beta E_m} + \frac{1}{k_B T} \frac{\sum_{m=-J}^{m=J} E_m e^{-\beta E_m}}{\sum_{m=-J}^{m=J} e^{-\beta E_m}} \right]$$

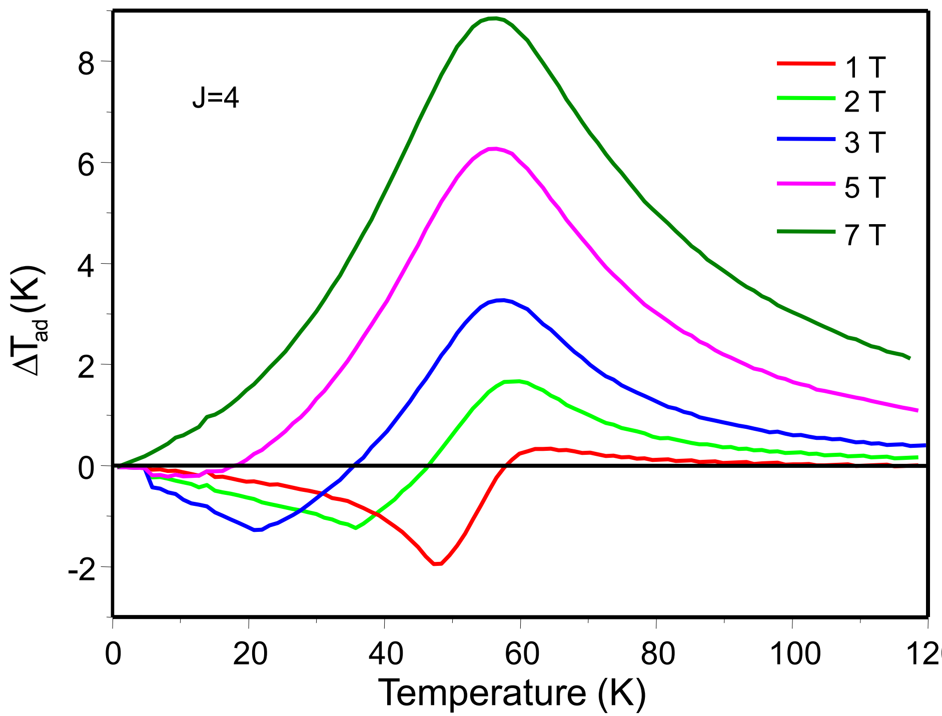
ANISOTROPIC SYSTEM ($B=B_Z$)





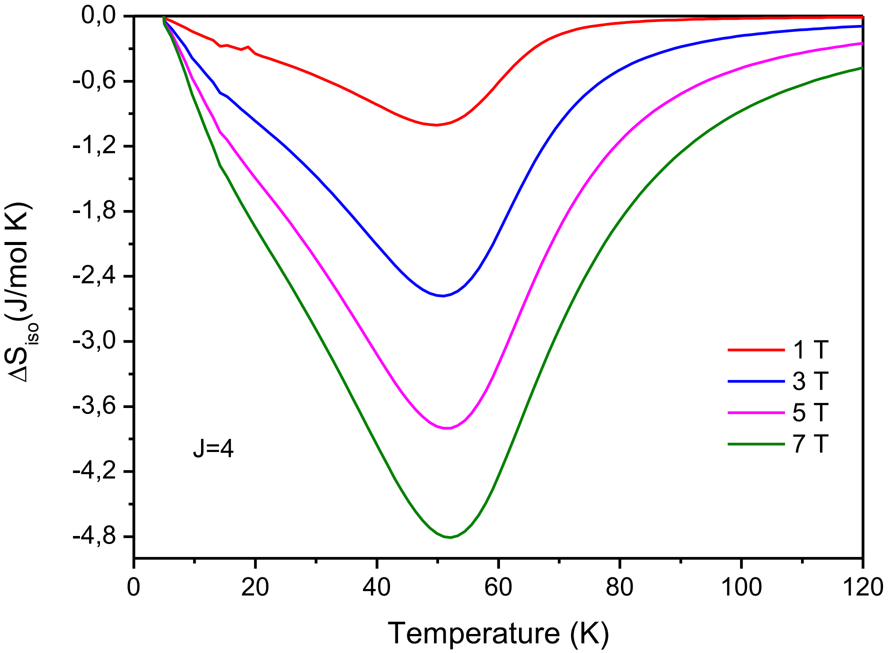
ANISOTROPIC SYSTEM ($B=B_X$)



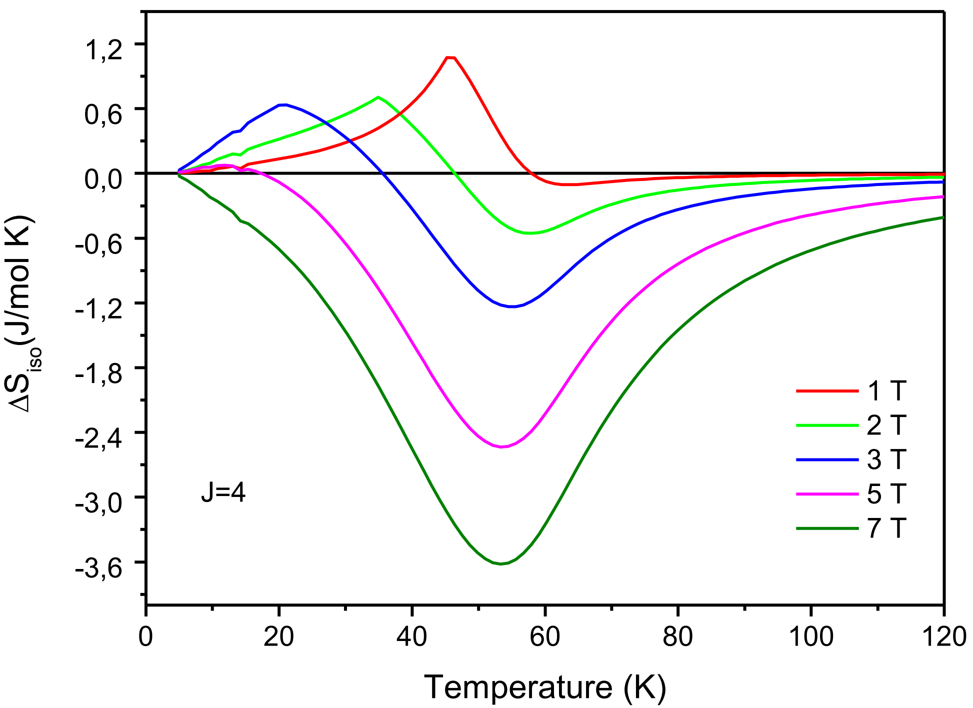


COMPARISON: ΔS_{iso}

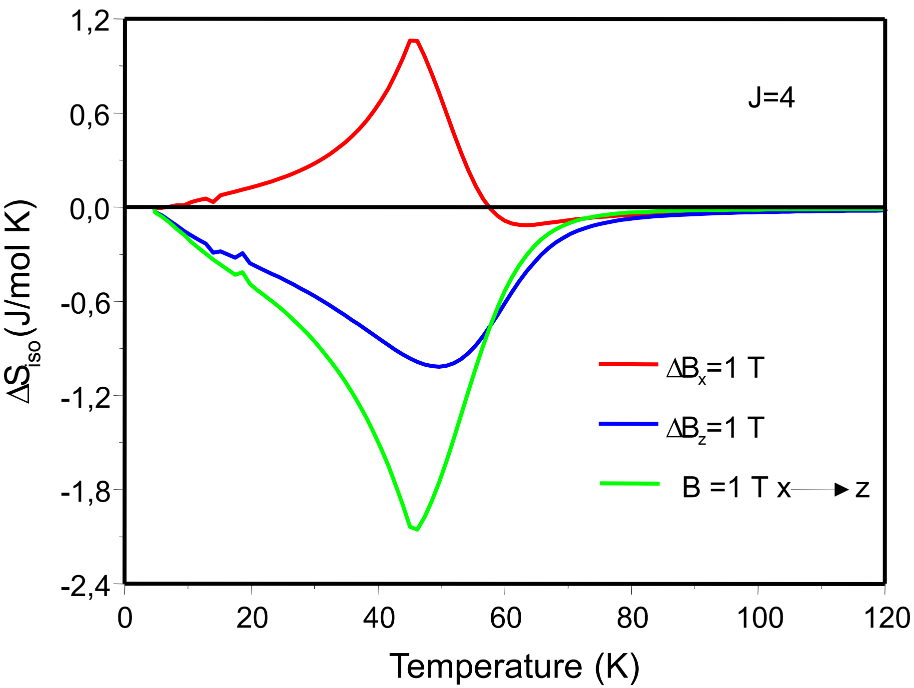
$B=B_Z$

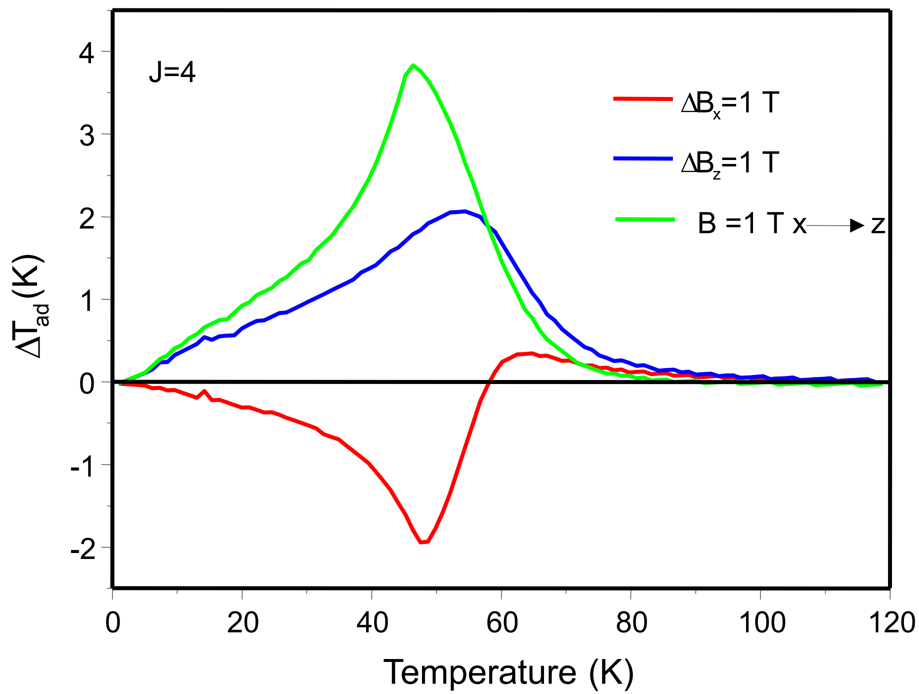


$B=B_X$



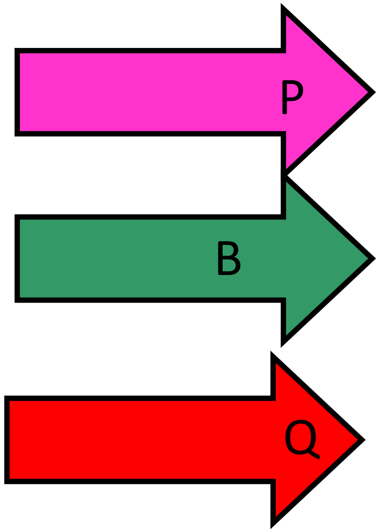
ANISOTROPIC MCE $B_X \rightarrow B_Z$

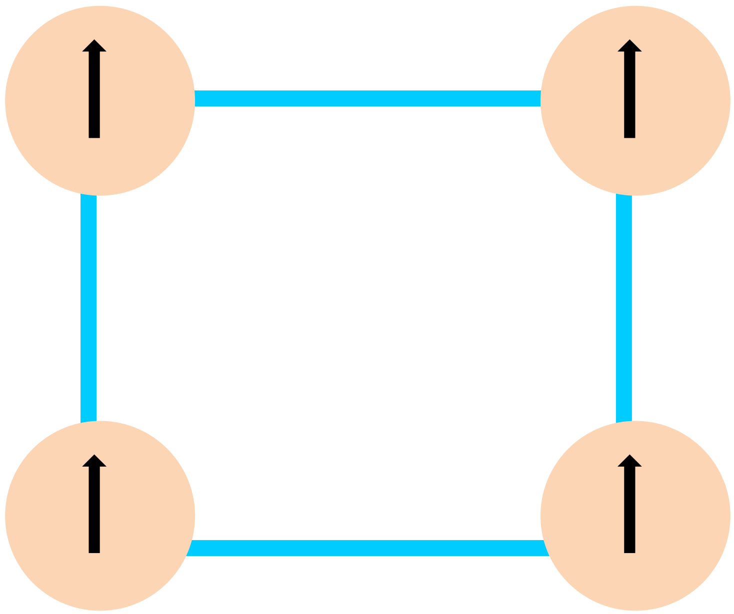




FIRST ORDER MAGNETIC PHASE TRANSITION

MAGNETOELASTIC COUPLING





$$\mathcal{H}^{4f}_{mag} = -\sum_{ij} \mathfrak{J}(r) J_i . J_j \quad - \sum_i g\mu_B B J_i$$

$$\mathcal{J}_{ij}(r) = \mathcal{J}_0(r_0) + \mathcal{J}_1(r_0) J_i J_j$$

$$\mathcal{J}_1 = \left[\frac{d\mathcal{J}(r)}{dr} \right]^2_{r=r_0}$$

$$\mathcal{H}^{4f}_{mag} = -\sum_{ij} \mathfrak{J}_0 J_i . J_j \quad - \sum_{ij} \mathfrak{J}_1 (J_i J_j)^2 \quad - \sum_i g\mu_B B J_i$$

C. Kittel, Phys. Rev. 120 (1960) 335.

MEAN FIELD THEORY

$$\mathcal{H}_{mag}^{4f} = -\sum_{i,j} \mathcal{J}_0 J_i J_j - \sum_{i,j} \mathcal{J}_1 \left(J_i J_j\right)^2 - \sum_i g\mu_B B J_i$$

$$\mathcal{H}_{mag}^{4f} = -\sum_i \left[\mathcal{J}_0 \left\langle J \right\rangle + \mathcal{J}_1 \left\langle J \right\rangle^3 + g\mu_B \vec{B}\right] \cdot J_i$$

$$\mathcal{H}_{mag}^{4f} = -g\mu_B \sum_i B^{eff} J_i$$

$$B^{eff} = B + \frac{\mathcal{J}_0 \left\langle J \right\rangle + \mathcal{J}_1 \left\langle J \right\rangle^3}{g\mu_B}$$

LATTICE ENTROPY (REVISITED)

Debye approximation

$$S_{lat}(T,B,P) = N_i \left[-3\Re \ln\left(1 - e^{-\frac{\Theta_D}{T}}\right) + 12\Re \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \right]$$

$$\Theta_D = \frac{\hbar \omega_D}{k_B}$$

Renormalized Debye frequency

$$\omega_D = \left[\frac{6\pi^2 v^3 N_A}{V}\right]^{1/3}$$

$$\tilde{\omega}_D = \left[\frac{6\pi^2 v^3 N_A}{V_0 + \Delta V}\right]^{1/3}$$

$$\tilde{\omega}_D = \omega_D \left[1 - \frac{1}{3}\frac{\Delta V}{V_0}\right]$$

$$\tilde{\Theta}_D = \frac{\hbar \tilde{\omega}_D}{k_B}$$

$$\tilde{\Theta}_D = \frac{\hbar \omega_D}{k_B}\left[1 - \frac{1}{3}\frac{\Delta V}{V_0}\right]$$

$$\tilde{\Theta}_D = \Theta_D \left[1 - \alpha M^2\right]$$

Renormalized lattice entropy

$$S_{lat}(T,B,P) = N_i \left[-3\Re \ln\left(1 - e^{-\frac{\tilde{\Theta}_D}{T}}\right) + 12\Re \left(\frac{T}{\tilde{\Theta}_D}\right)^3 \int_0^{\tilde{\Theta}_D/T} \frac{x^3}{e^x - 1} dx \right]$$

N. A. de Oliveira and P. J. von Ranke, Phys. Rep. 489 (2010) 89

MCE QUANTITIES

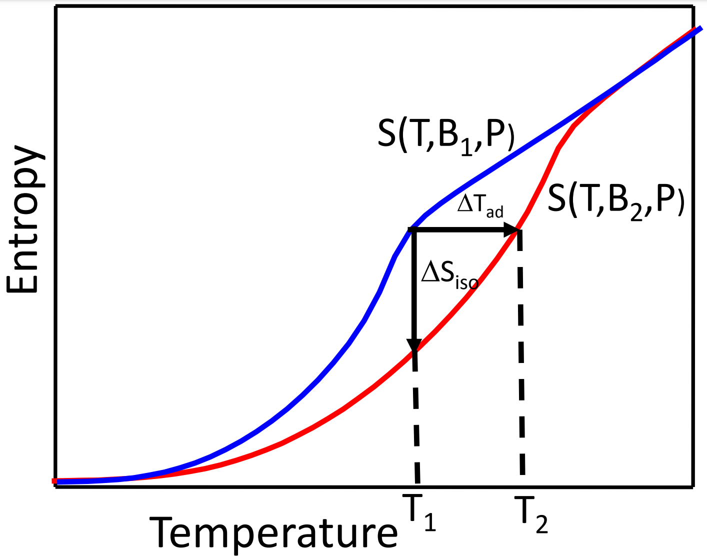
Total entropy

$$S(T,B,P) = S^{4f}_{mag}(T,B,P) + S_{lat}(T,B,P) + S^{spd}_{el}(T,B,P)$$

$$S(T,B,P) = N_m \Re \left[\ln \sum_m e^{-\beta E_m} + \frac{1}{k_B T} \frac{\sum_m E_m e^{-\beta E_m}}{\sum_m e^{-\beta E_m}} \right]$$

$$+ N_i \left[-3\Re ln\left(1 - e^{-\frac{\tilde{\Theta}_D}{T}}\right) + 12\Re \left(\frac{T}{\tilde{\Theta}_D}\right)^3 \int_0^{\frac{\tilde{\Theta}_D}{T}} \frac{x^3}{e^x - 1} dx \right] + \gamma T$$

Magnetocaloric quantities

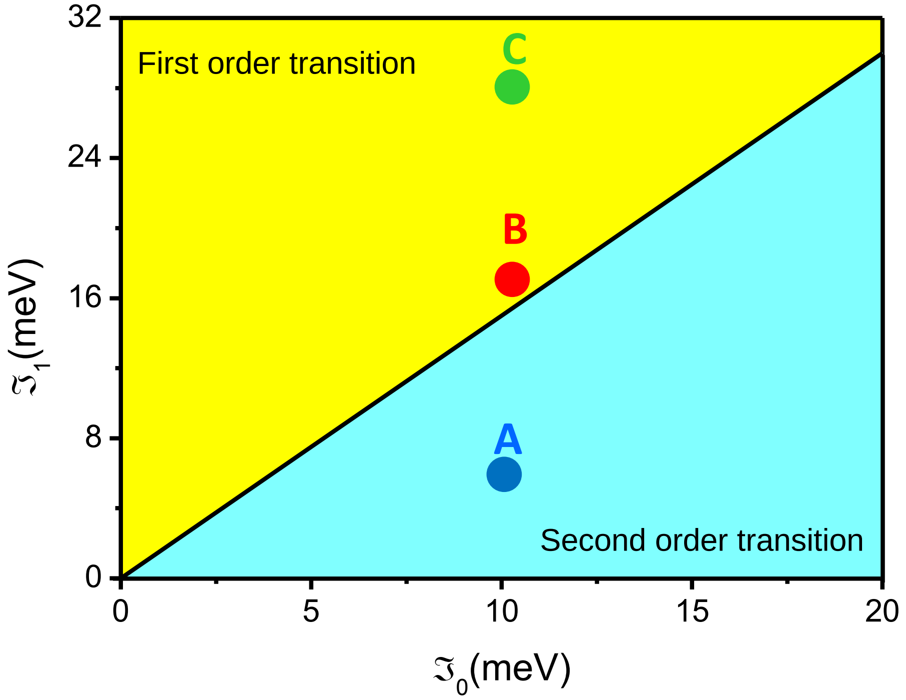


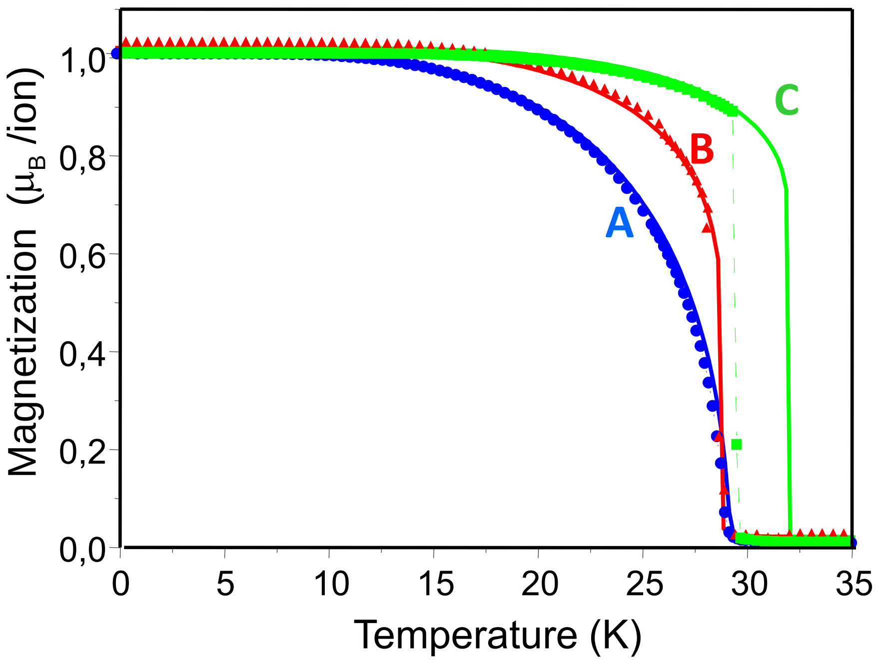
$$\Delta S_{iso}(T,\Delta B,P) = S(T,B_2,P) - S(T,B_1,P)$$

$$\Delta T_{ad}(T,\Delta B,P) = T_2 - T_1$$

$$S(T,B_2,P) = S(T,B_1,P)$$

SYSTEMATIC STUDY (J=1/2)





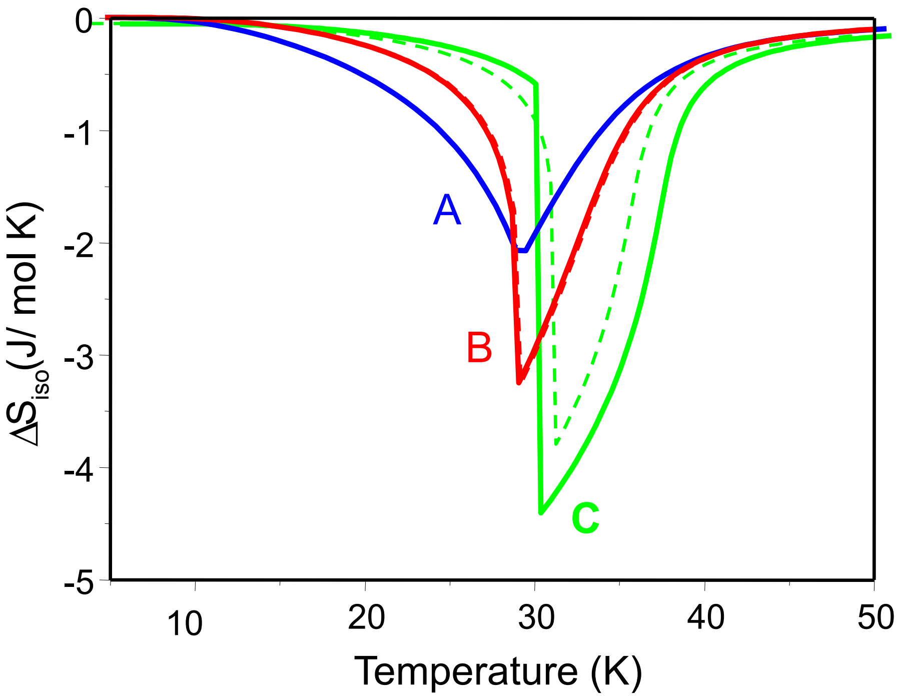
$$\mathcal{H}_{mag}^{4f} = -\sum_{ij} \Im_0 J_i . J_j \quad - \sum_{ij} \Im_1 (J_i J_j)^2 \quad - \sum_i g\mu_B B J_i$$

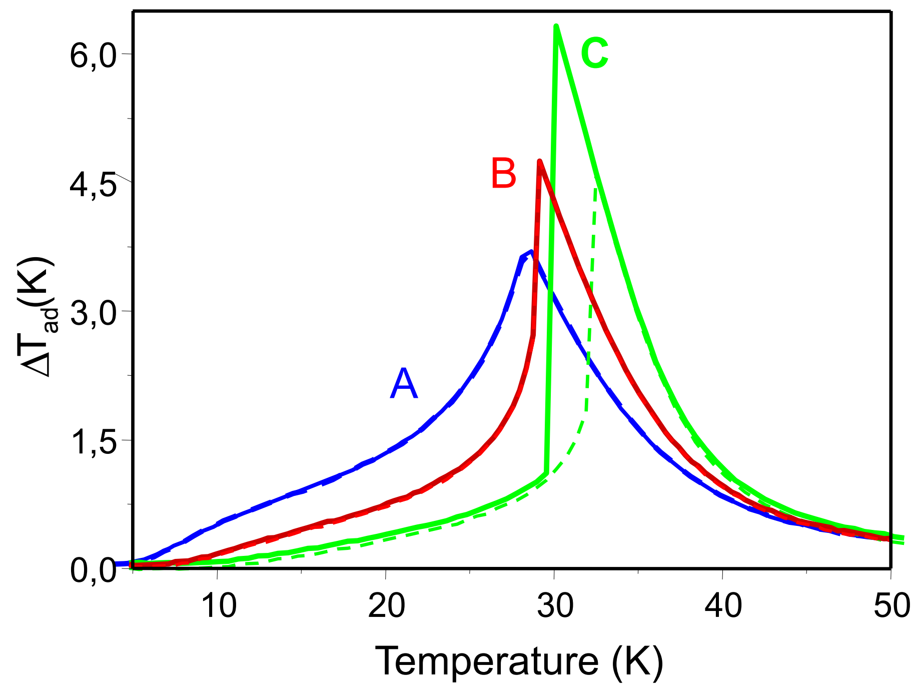
$\mathcal{J}_1 / \mathcal{J}_0$

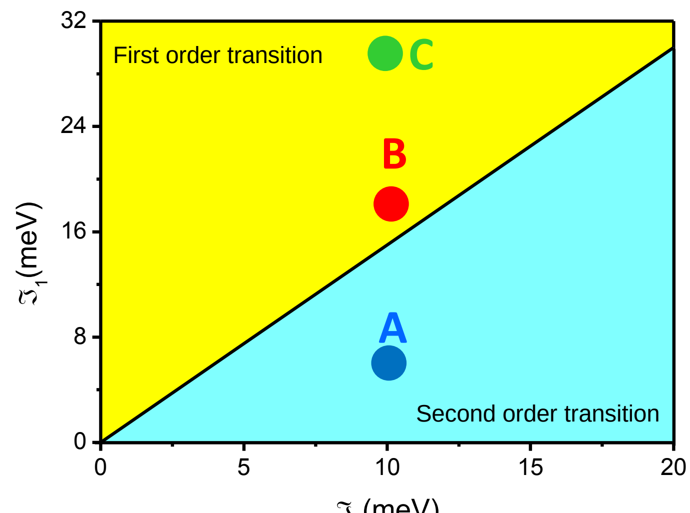
- 2^{nd} order
- 1^{st} order

R. P. Santana et al J. Alloys and Comp. 509(2011)6346

SYSTEMATIC STUDY (J=1/2)

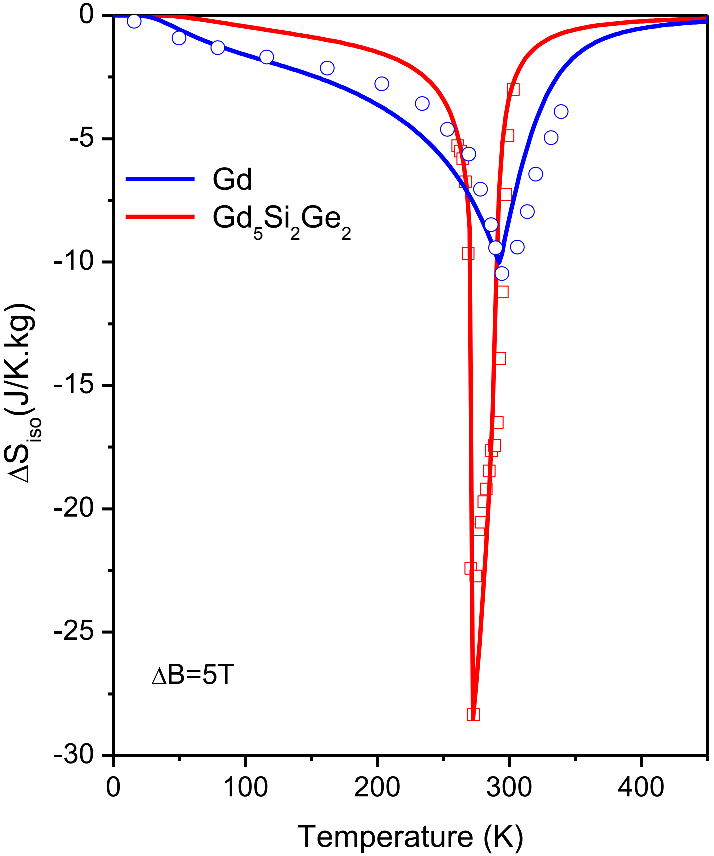


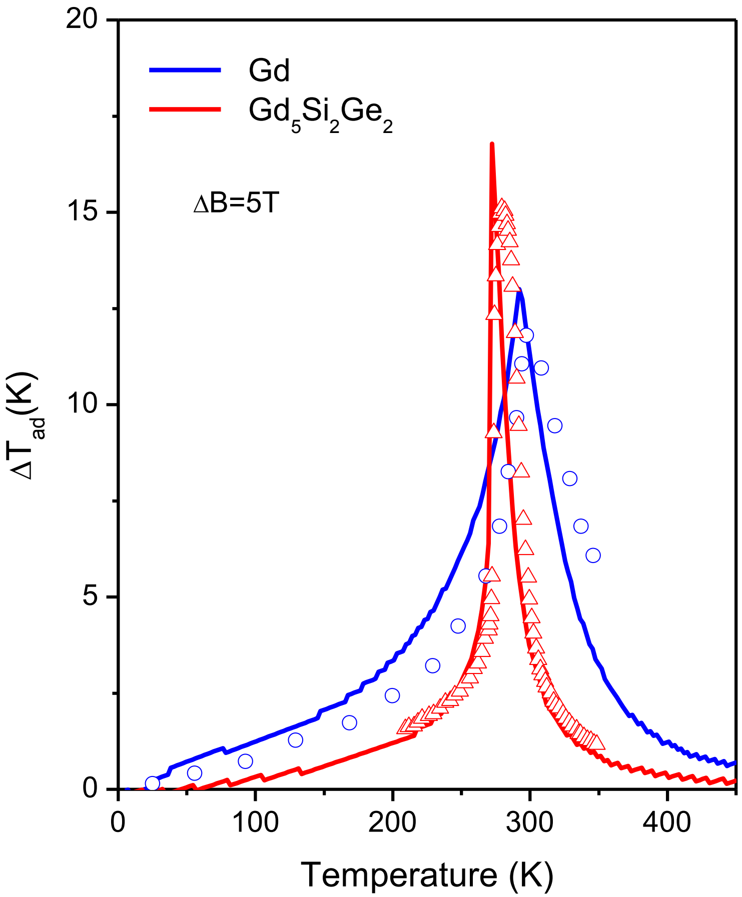




R. P. Santana et al J. Alloys and Comp. 509(2011)6346

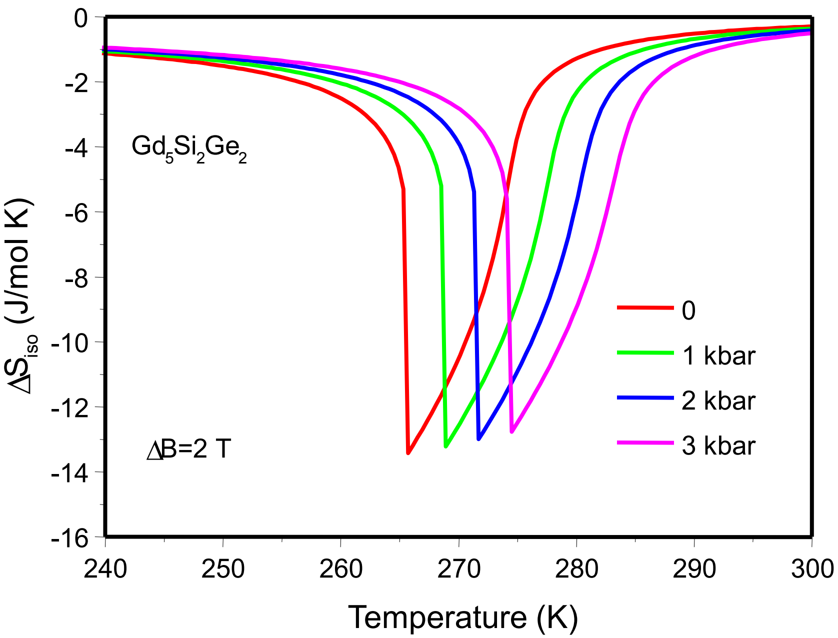
APPLICATION: $Gd_5Si_2Ge_2$

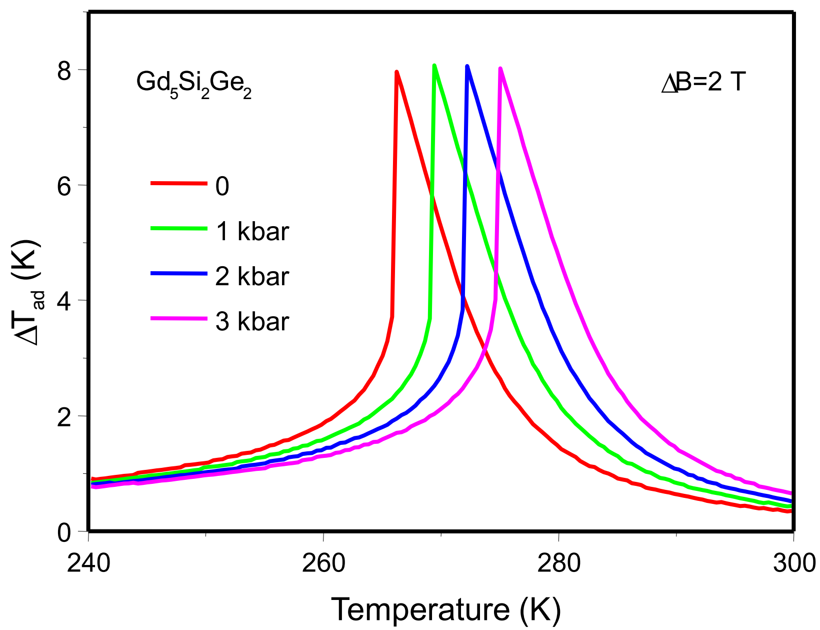




V. K. Pecharsky, K. A. Gschneidner Jr, Phys. Rev. Let. 78 (1997) 4494

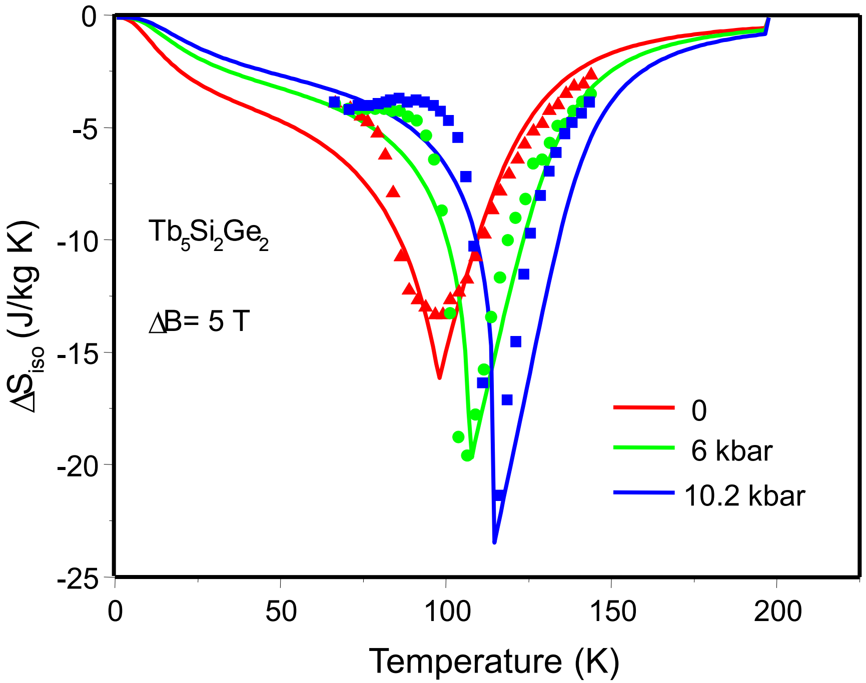
PRESSURE EFFECTS: $Gd_5Si_2Ge_2$

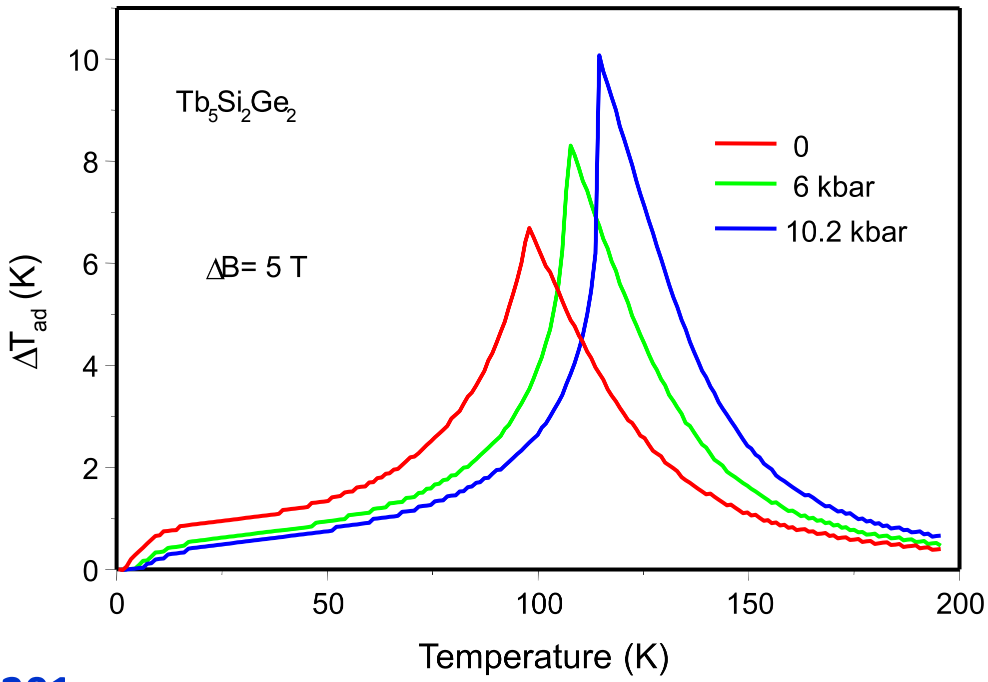




N. A. de Oliveira, Journ. Appl. Phys. 113 (2013) 033910

PRESSURE EFFECTS: $Tb_5Si_2Ge_2$





Morelon et al, Phys. Rev. Let. 93 (2004) 137201

N. A. de Oliveira, Journ. Appl. Phys. 113 (2013) 033910

BCE QUANTITIES

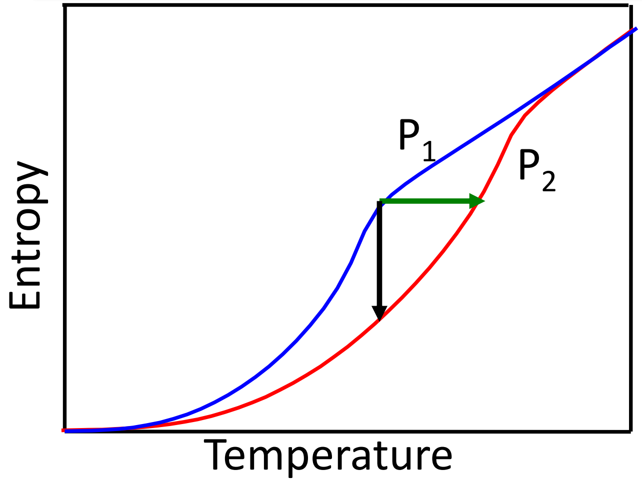
Total entropy

$$S(T,B,P) = S^{4f}_{mag}(T,B,P) + S_{lat}(T,B,P) + S^{spd}_{el}(T,B,P)$$

$$S(T,B,P) = N_m \Re \left[\ln \sum_m e^{-\beta E_m} + \frac{1}{k_B T} \frac{\sum_m E_m e^{-\beta E_m}}{\sum_m e^{-\beta E_m}} \right]$$

$$+ N_i \left[-3\Re ln \left(1 - e^{-\frac{\tilde{\Theta}_D}{T}} \right) + 12\Re \left(\frac{T}{\tilde{\Theta}_D} \right)^3 \int_0^{\frac{\tilde{\Theta}_D}{T}} \frac{x^3}{e^x - 1} dx \right] + \gamma T$$

Barocaloric quantities

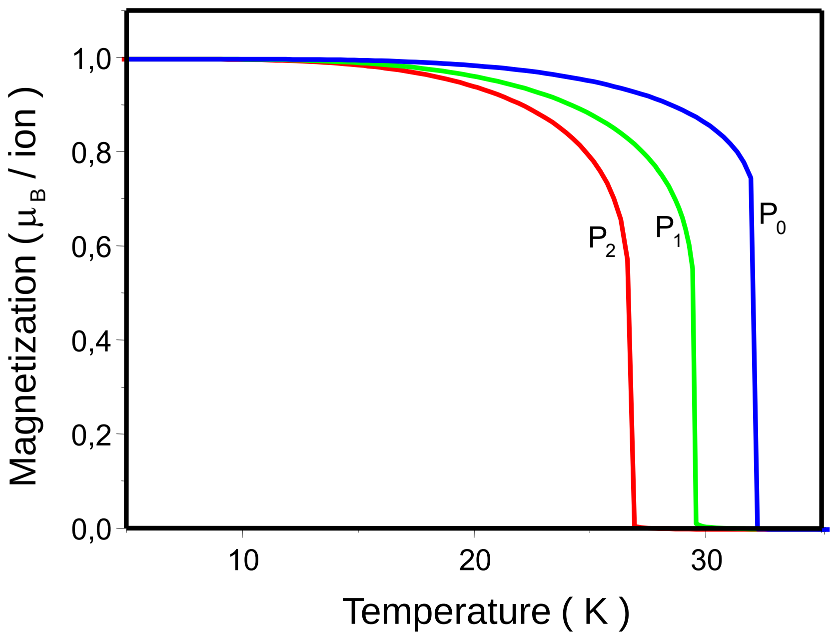


$$\Delta S^{bar}_{iso}(T,B,\Delta P) = S(T,B,P_2) - S(T,B,P_1)$$

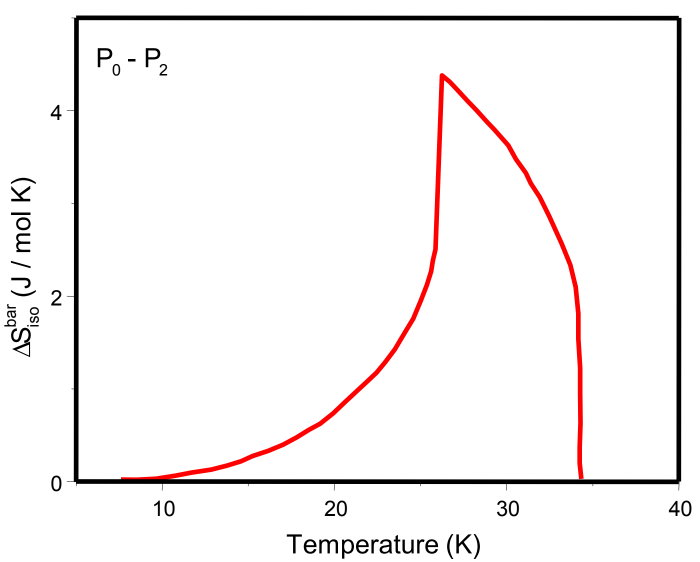
$$\Delta T^{bar}_{ad}(T,B,\Delta P) = T_1 - T_2$$

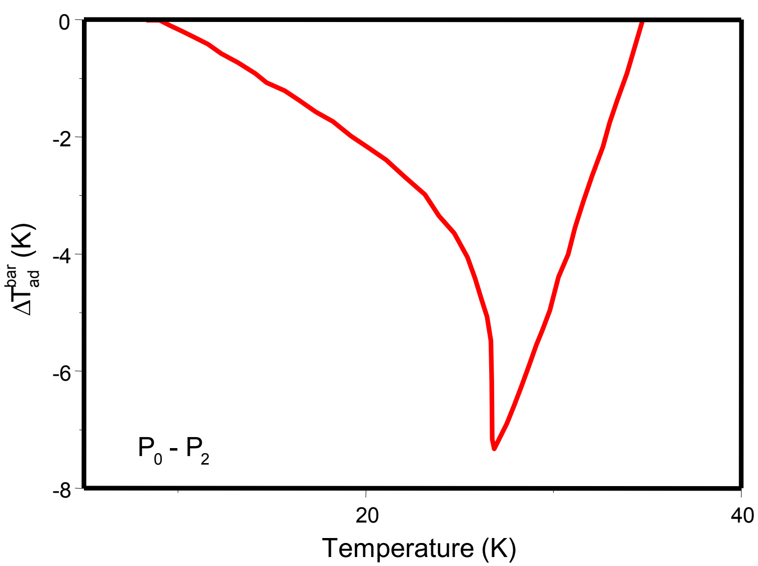
$$S(T,B,P_2) = S(T,B,P_1)$$

Systematic analysis: Scenario 1



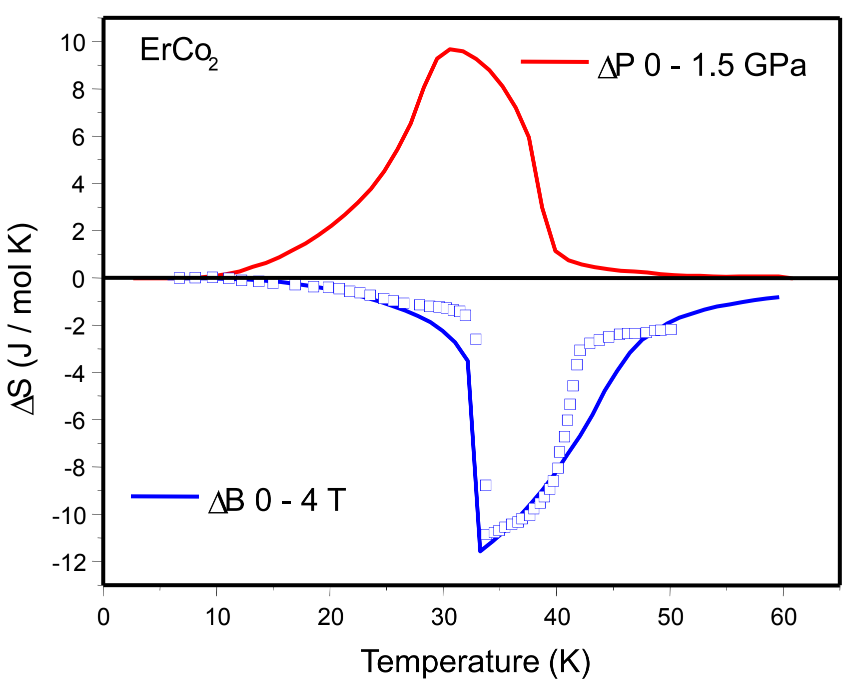
INVERSE BAROCALORIC EFFECT

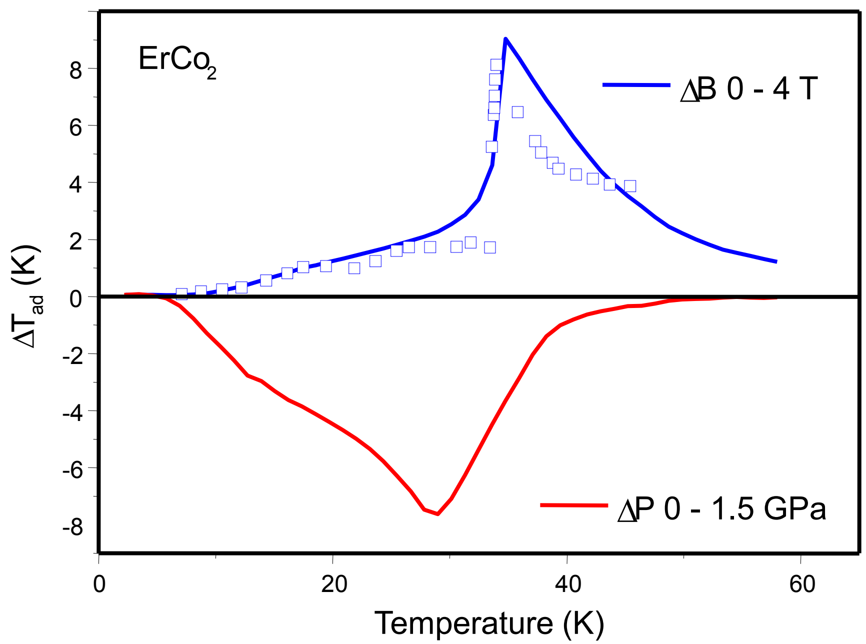




BCE - $ErCo_2$

INVERSE BAROCALORIC EFFECT



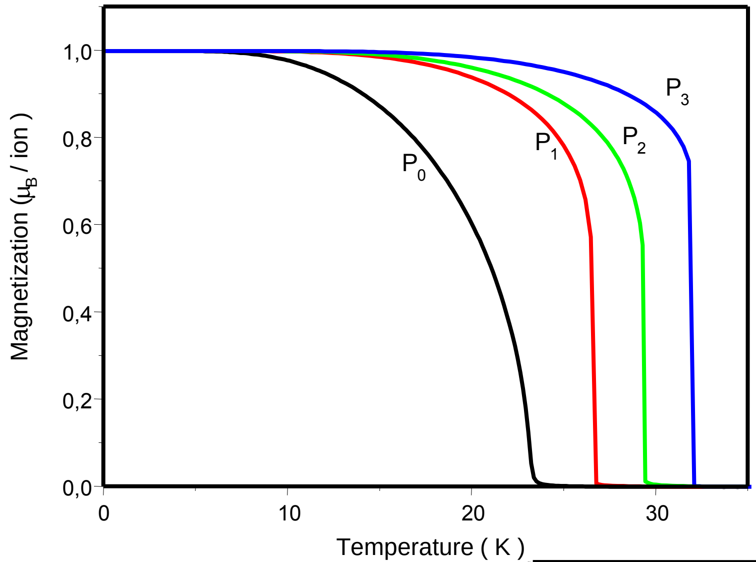


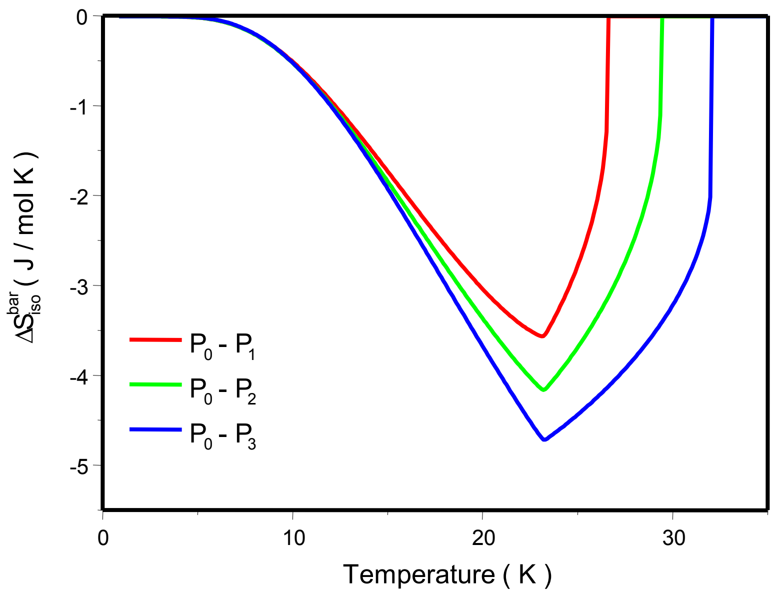
NORMAL MAGNETOCALORIC EFFECT

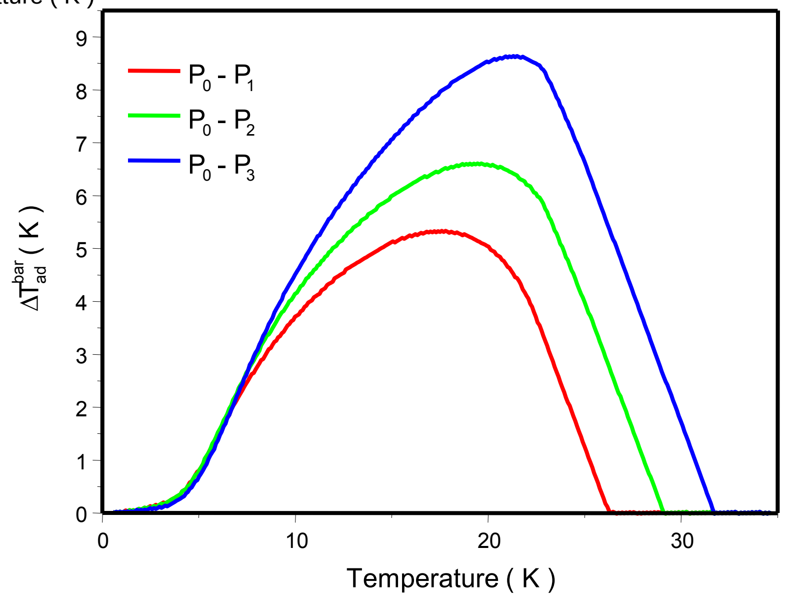
Wada et al, Cryogenics 39 (1999) 915

N. A. de Oliveira, Journ. Appl. Phys. 70 (2007) 052501

Systematic analysis: Scenario 2



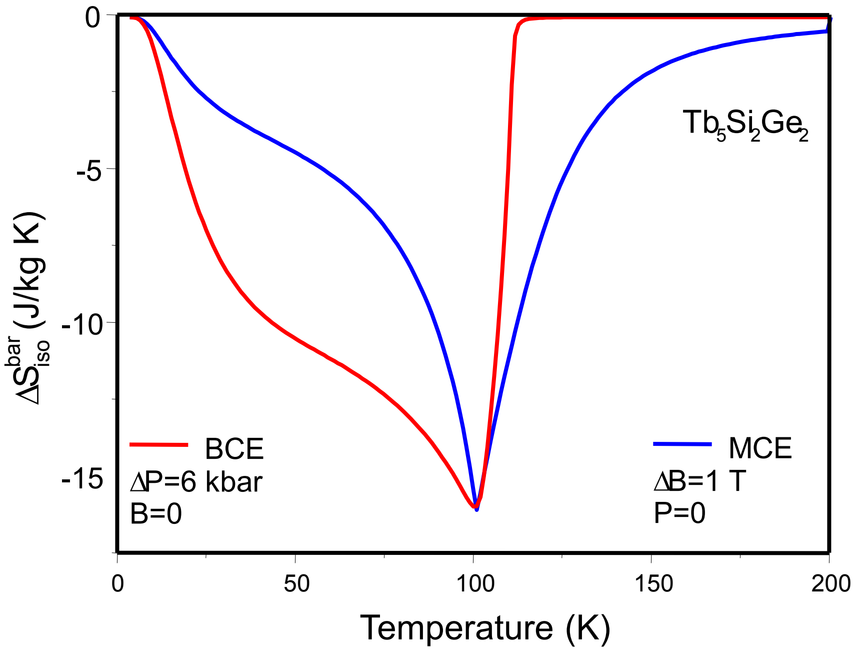


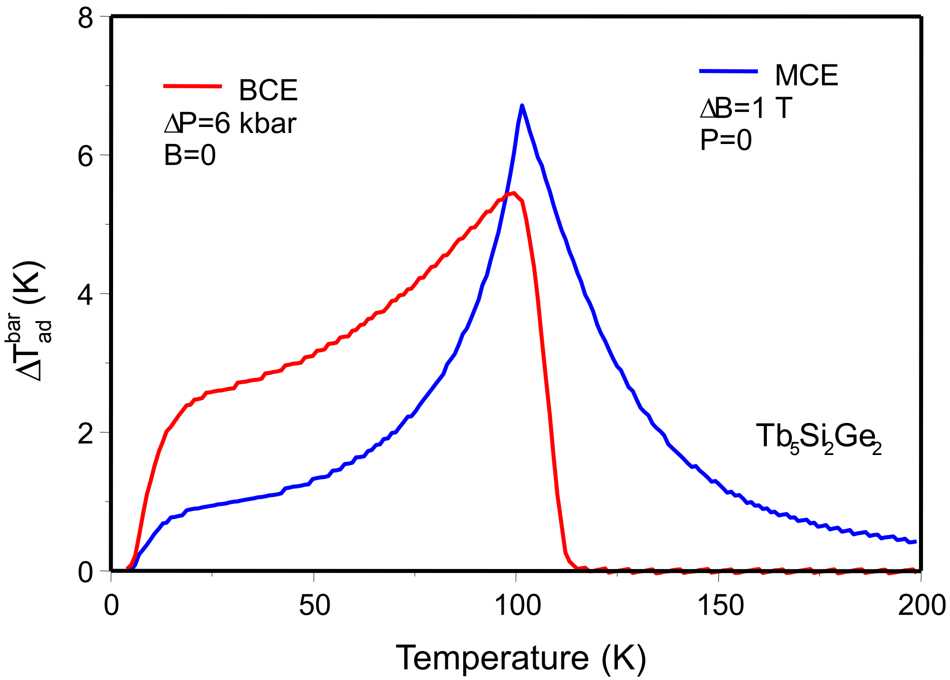


NORMAL BAROCALORIC EFFECT

BCE - $Tb_5Si_2Ge_2$

NORMAL BAROCALORIC EFFECT

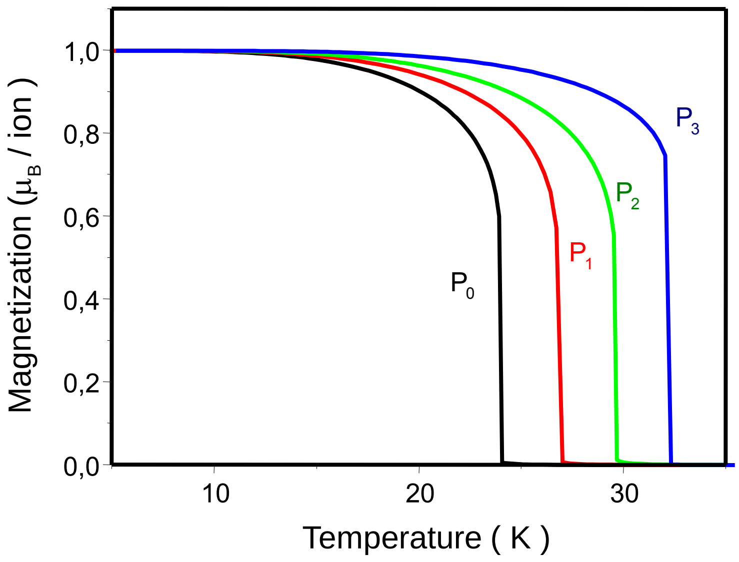


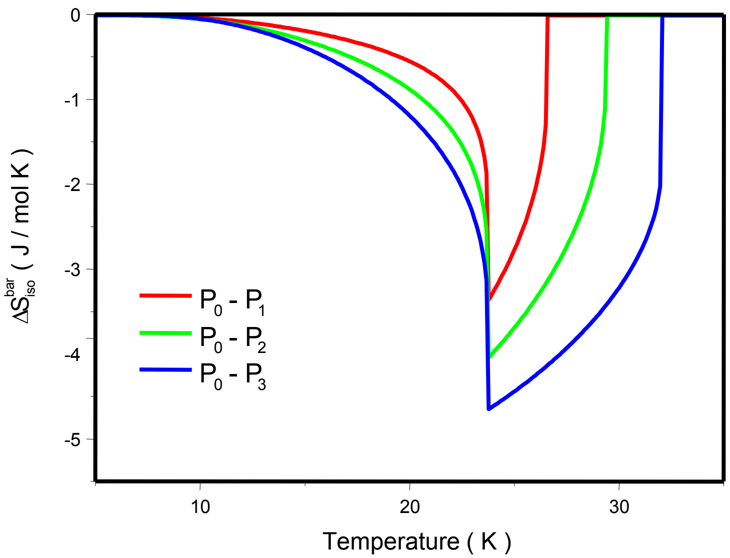


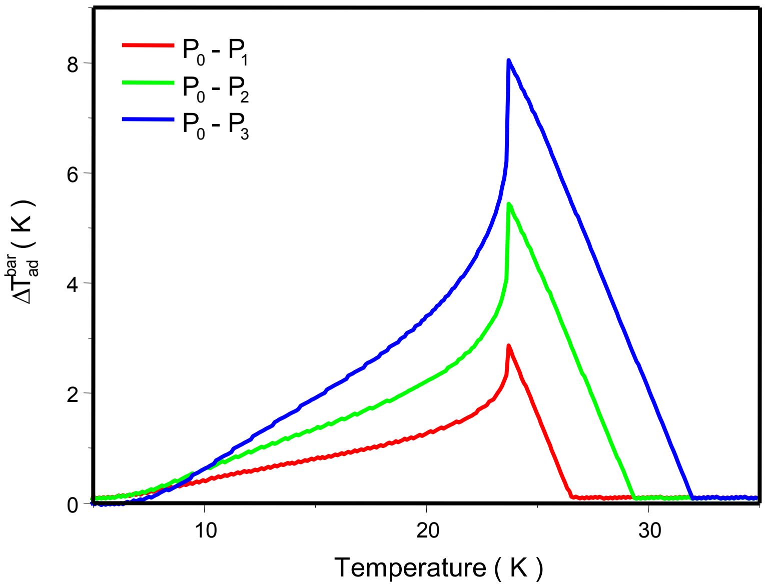
NORMAL MAGNETOCALORIC EFFECT

N. A. de Oliveira, Journ. Appl. Phys. 113 (2013) 033910

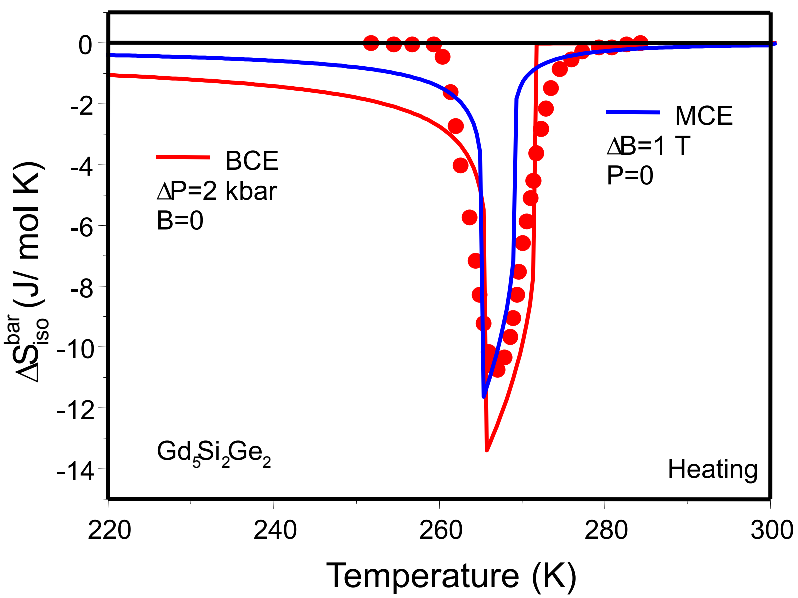
Systematic analysis: Scenario 3

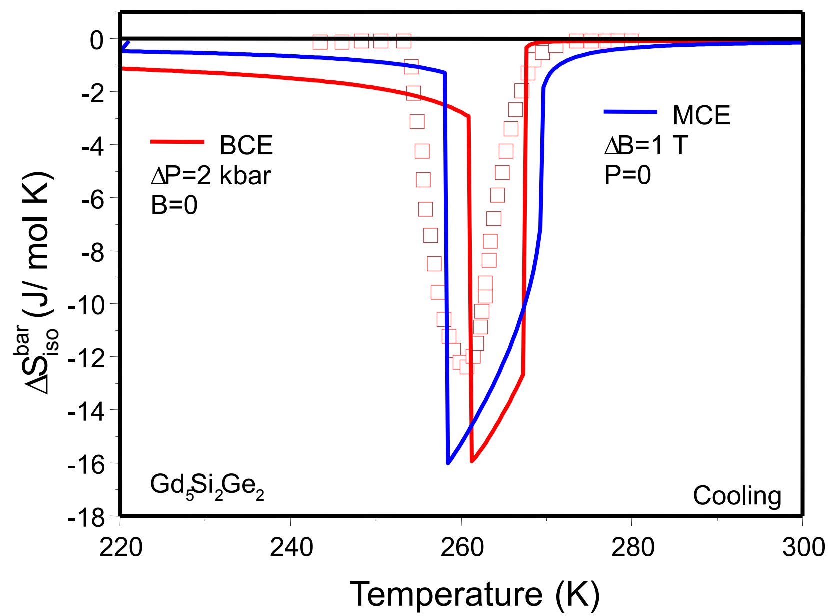


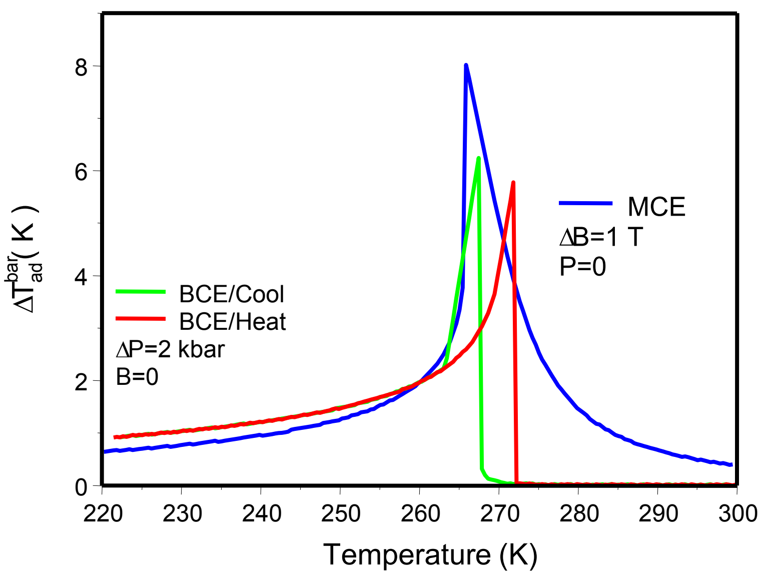




APPLICATION: $Gd_5Si_2Ge_2$

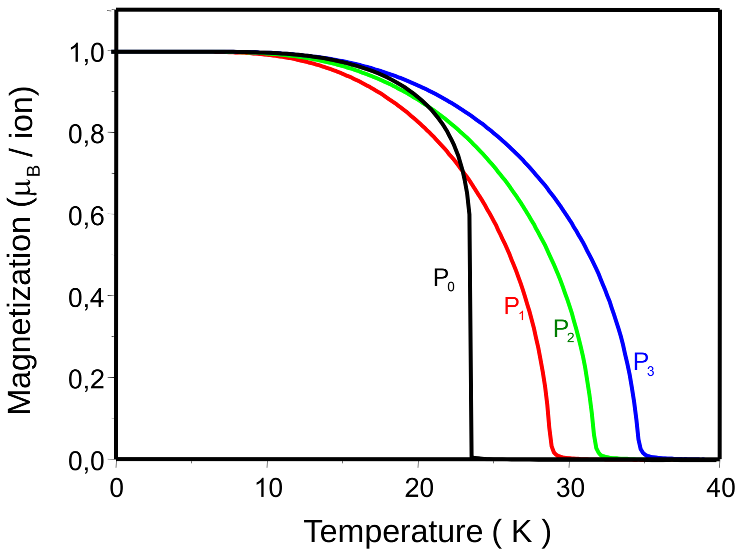


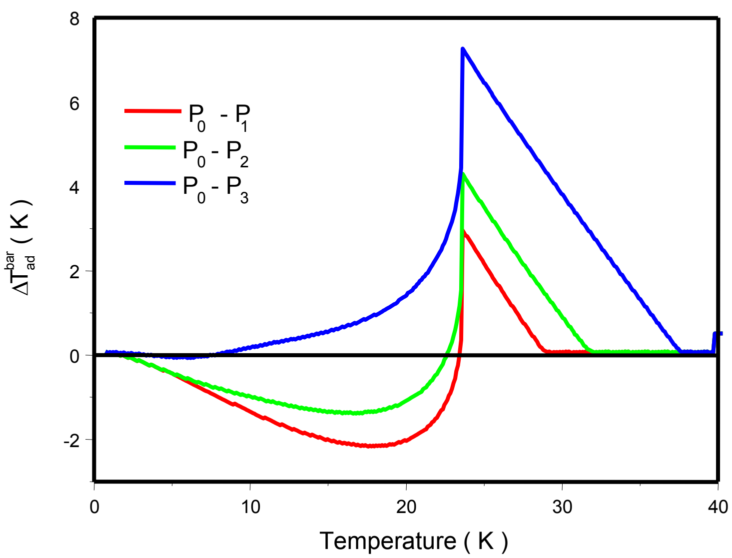


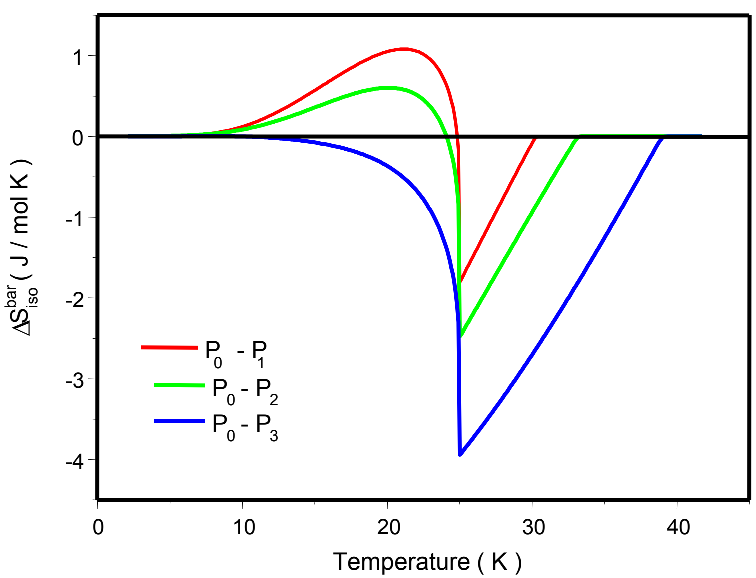


Yuce et al., Appl. Phys. Lett. 101 (2012) 071906.

Systematic analysis: Scenario 4







PROSPECTS (Experimental)

Measurements

- ΔT_{ad}
- Pressure effects
- Anisotropic MCE
- BCE/ECE

Materials

- Heusler alloys
- Manganites
- Multiferroics
- Molecular magnets

PROSPECTS (THEORY)

Localized systems

- Electron-phonon coupling
- Monte Carlo simulations
- Disordered effects
- First order transition
- Anisotropy

Itinerant systems

- Electron-phonon coupling
- Multi-band calculations
- Antiferomagnetic systems
- Beyond mean field
- Field theory
- QMC

ACKNOWLEDGEMENTS

UNIVERSIDADE DO ESTADO DO RIO DE JANEIRO
UERJ

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CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

FIRST ORDER MAGNETIC PHASE TRANSITION

AlTERNATIVE CALCULATION

ALTERNATIVE CALCULATION

Gibbs eneegy

$$G = F_{mag} + E_{mag}$$

$$E_{mag} = \int M \cdot dB^{eff}$$

Effective field

$$B^{eff} = B + \frac{\mathcal{J}_0 \langle J \rangle + \mathcal{J}_1 \langle J \rangle^3}{g\mu_B}$$

$$M(T, B, P) = g\mu_B \langle J \rangle$$

$$B^{eff} = B + \overbrace{\left[\frac{\mathcal{J}_0}{g^2\mu_B^2}\right]}^{\lambda_0} M + \overbrace{\left[\frac{\mathcal{J}_1}{g^4\mu_B^4}\right]}^{\lambda_1} M^3$$

$$B^{eff} = B_0 + \lambda_0 M + \lambda_1 M^3$$

$$dB^{eff} = \left(\lambda_0 + 3\lambda_1 M^2\right) dM$$

Magnetic energy

$$E_{mag} = \frac{\lambda_0 M^2}{2} + \frac{3\lambda_1 M^4}{4} + F_0$$

$$G = F_{mag} + \frac{\lambda_0 M^2}{2} + \frac{3\lambda_1 M^4}{4} + F_0$$

ALTERNATIVE CALCULATION

Energy

$$G = F_{mag} + \frac{\lambda_0 M^2}{2} + \frac{3\lambda_1 M^4}{4} + F_0$$

Derivative

$$B^{eff} = B_0 + \lambda_0 M + \lambda_1 M^3$$

$$\left(\frac{\partial G}{\partial M}\right)_T = \left(\frac{\partial F_{mag}}{\partial B^{eff}}\right)_T \underbrace{\left(\frac{\partial B^{eff}}{\partial M}\right)_T}_{\lambda_0 + 3\lambda_1 M^2} + \lambda_0 M + 3\lambda_1 M^3$$

Algebra

$$\underbrace{\left(\frac{\partial G}{\partial M}\right)_T}_{0} = \left(\frac{\partial B^{eff}}{\partial M}\right)_T \underbrace{\left[\left(\frac{\partial F_{mag}}{\partial B^{eff}}\right)_T + M\right]}_{0}$$

$$M = -\left(\frac{\partial F_{mag}}{\partial B^{eff}}\right)_T$$

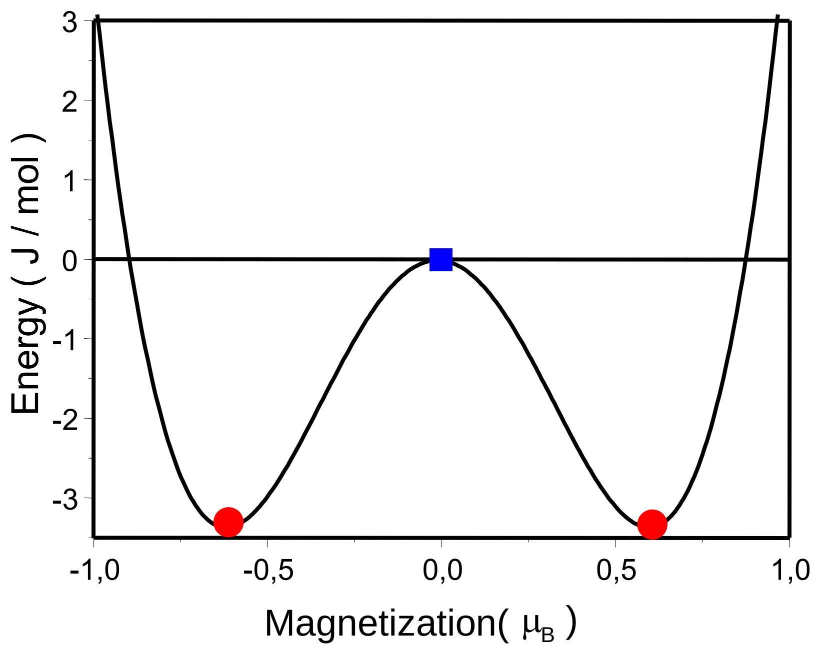
ALTERNATIVE CALCULATION

Free energy

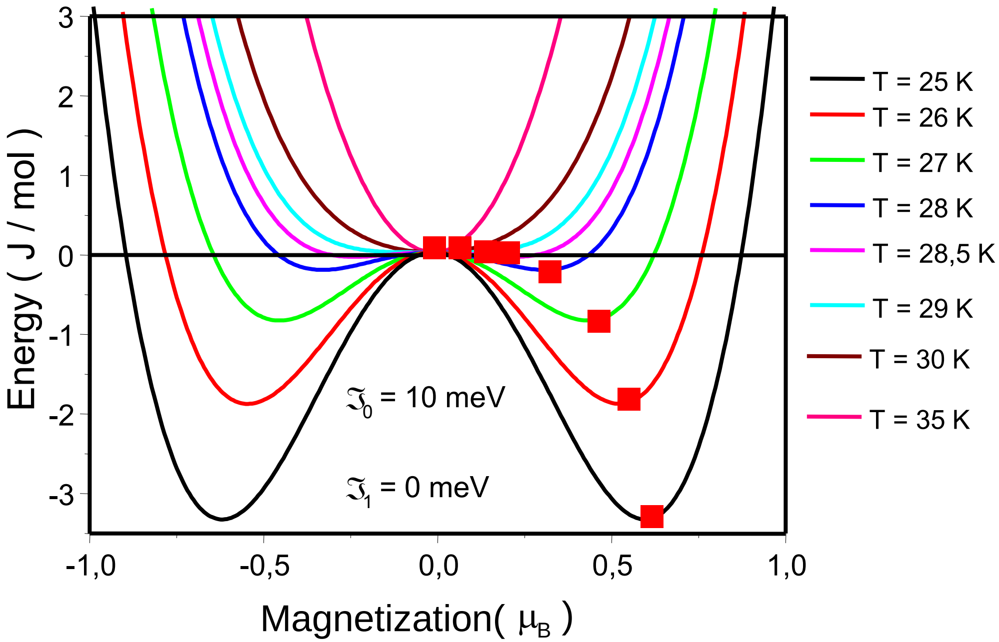
$$G = F_{mag} + \frac{\lambda_0 M^2}{2} + \frac{3\lambda_1 M^4}{4} + F_0$$

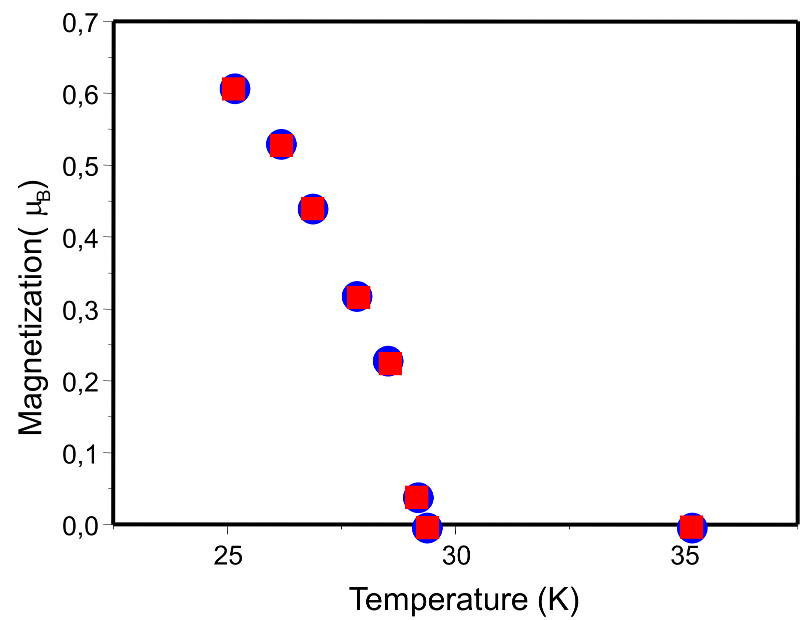
$$\frac{\partial G}{\partial M} = 0$$

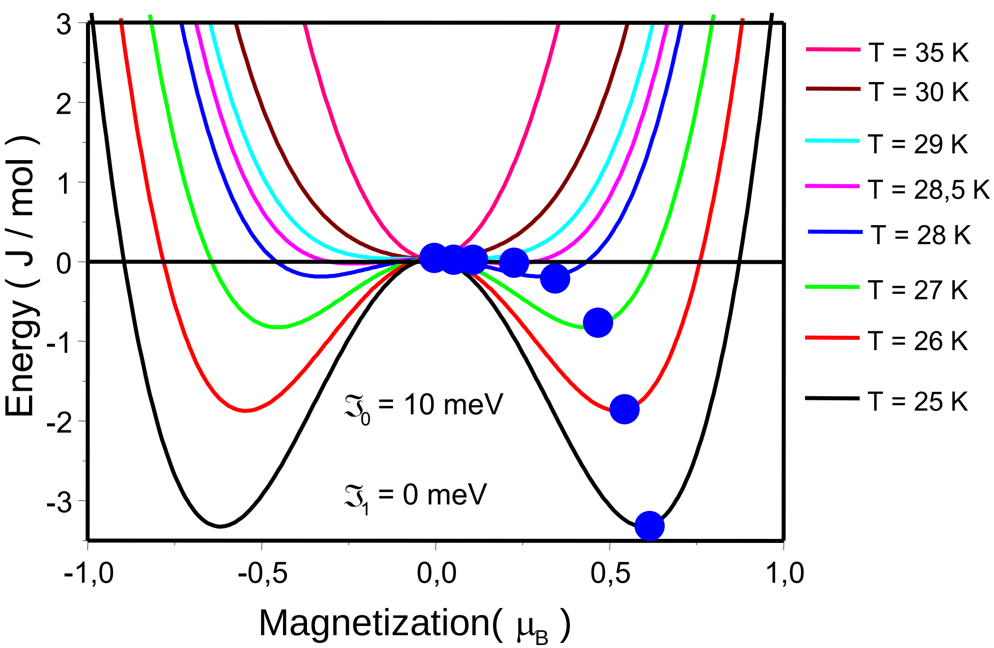
$$M = -\left(\frac{\partial F_{mag}}{\partial B^{eff}}\right)_T$$

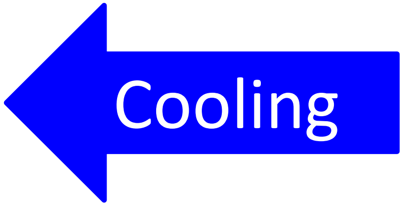


SECOND ORDER TRANSITION









FIRST ORDER TRANSITION