Magnetismo e efeitos calóricos em sólidos: aspectos básicos

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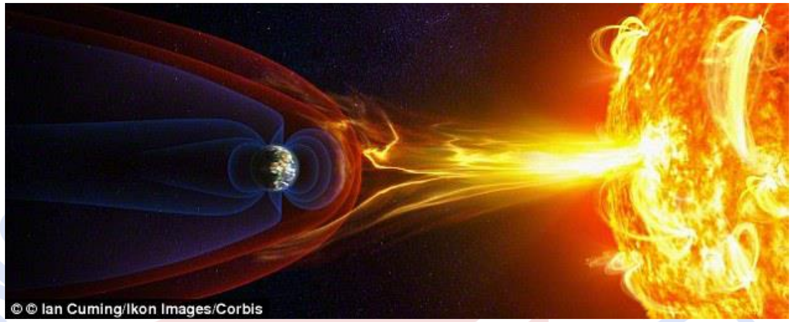
Introdução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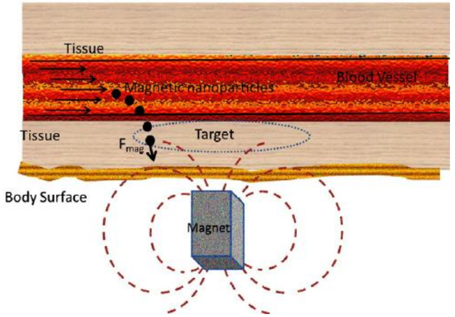
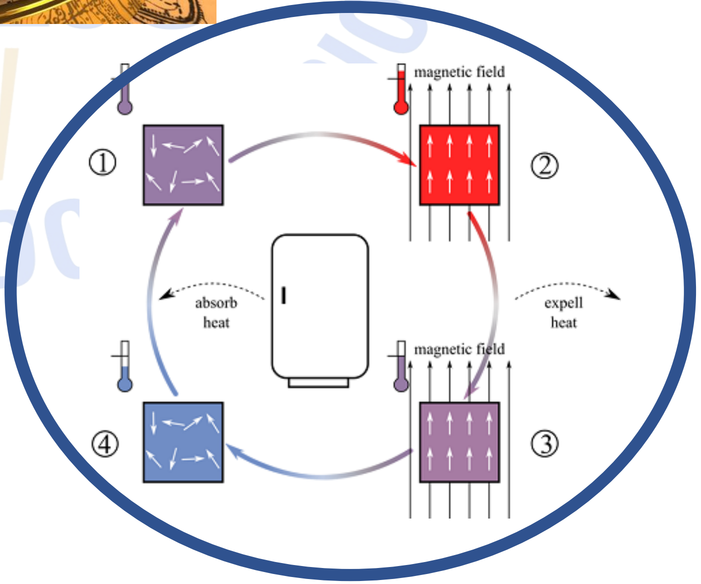
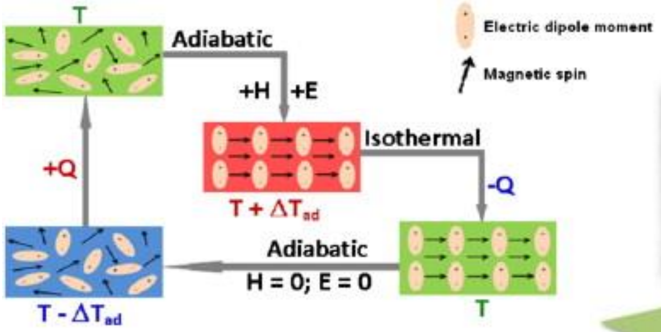
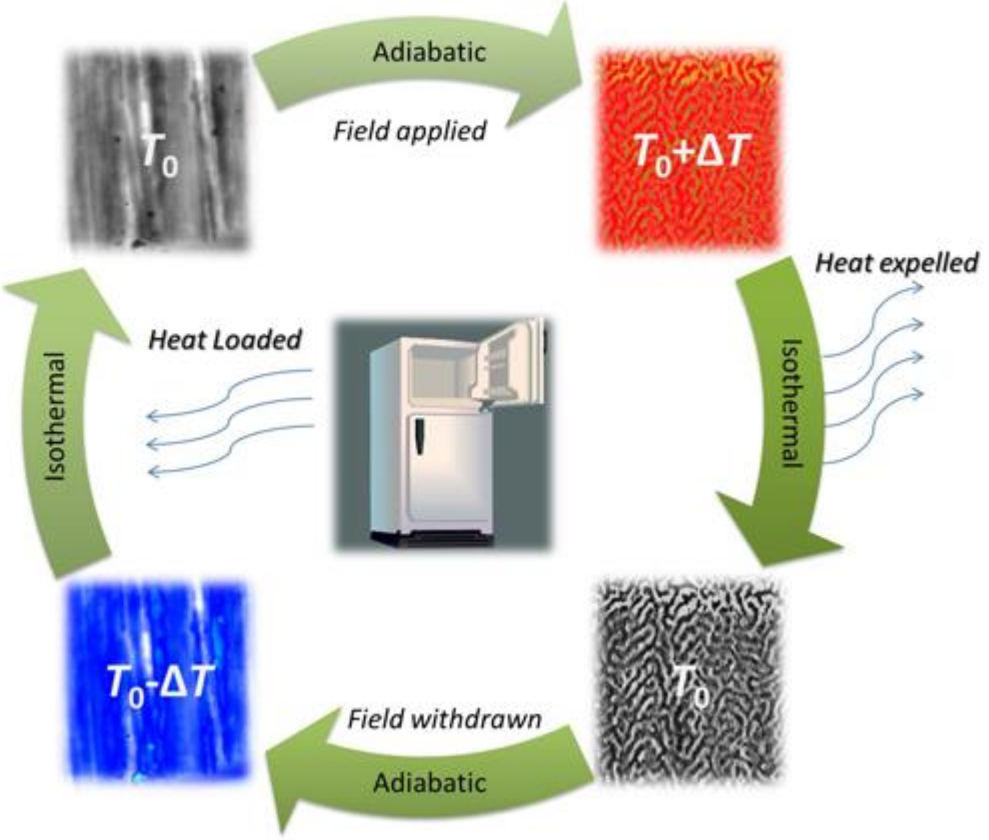

Tissue
Blood Vessel
Magnetic nanoparticles
Tissue
Target
F_{mag}
Body Surface
Magnet


magnetic field
①
②
absorb heat
expell heat
magnetic field
④
③

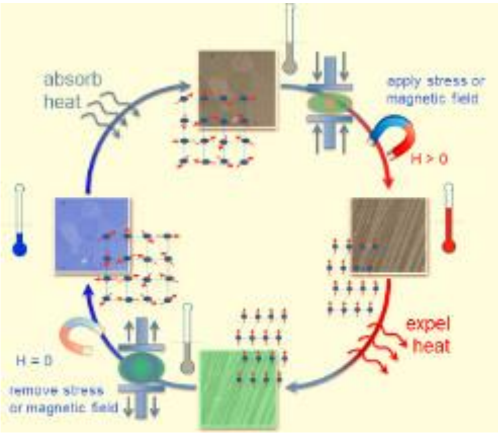
Introdução



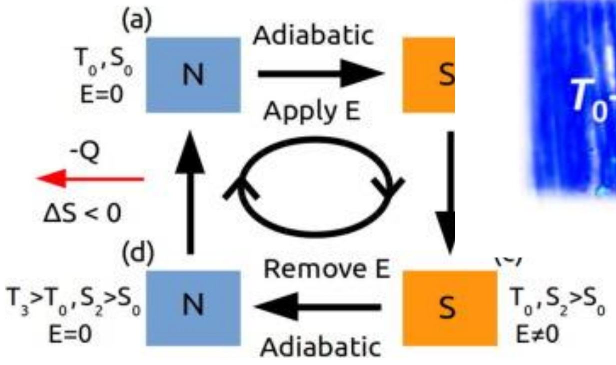
T
Adiabatic
+H +E
Electric dipole moment
Magnetic spin
Isothermal
+Q
-Q
T + ΔT_ad
Adiabatic
H = 0; E = 0
T - ΔT_ad
T



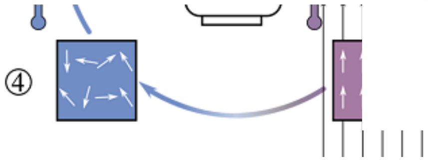
Adiabatic
Field applied
T0
T0+ΔT
Heat expelled
Isothermal
Heat Loaded
Isothermal
T0-ΔT
T0
Field withdrawn
Adiabatic



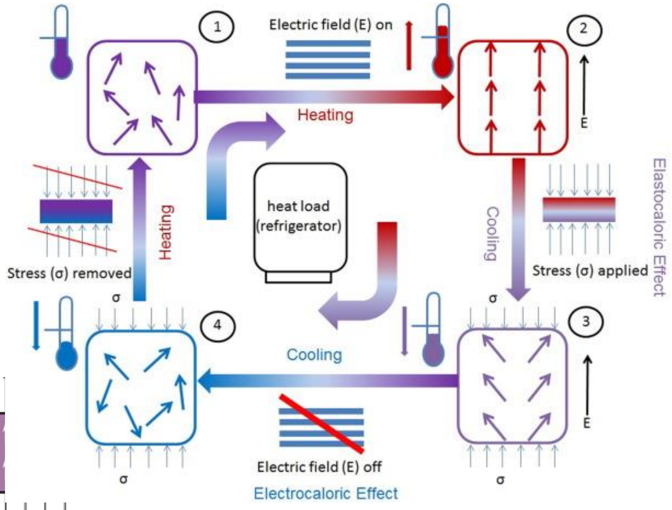
absorb heat
apply stress or magnetic field
H > 0
expel heat
H = 0
remove stress or magnetic field



(a)
T0, S0
E=0
N
Adiabatic
Apply E
S
-Q
ΔS < 0
(d)
T3>T0, S2>S0
E=0
N
Remove E
Adiabatic
S
T0, S2>S0
E≠0



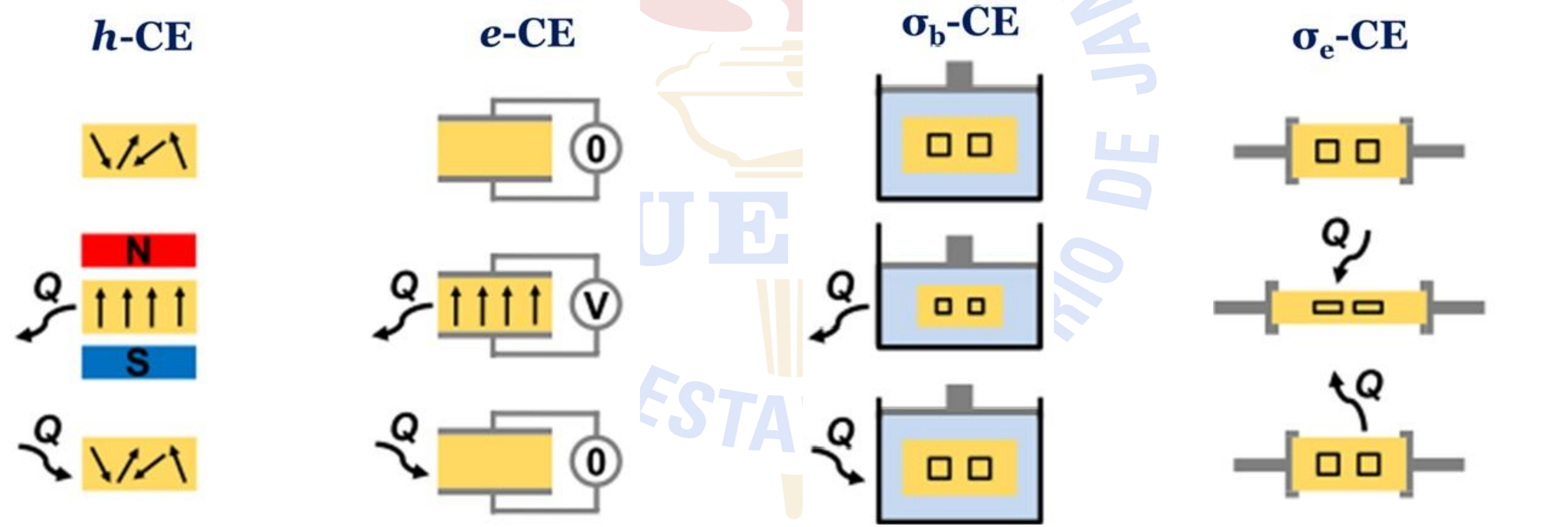
④



1
Electric field (E) on
2
Heating
Heating
heat load (refrigerator)
Cooling
Stress (σ) removed
Stress (σ) applied
Elastocaloric Effect
4
3
Cooling
Electric field (E) off
Electrocaloric Effect

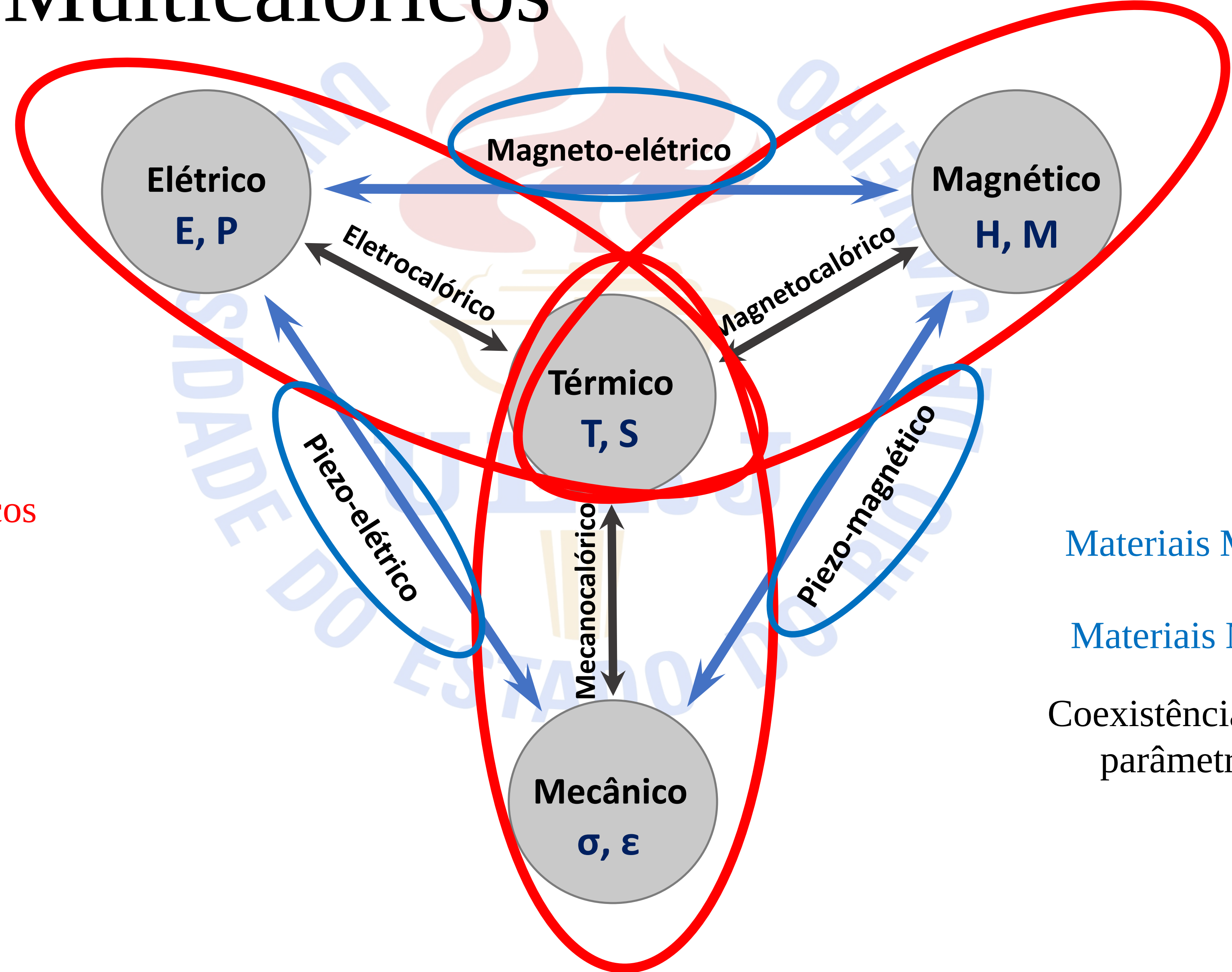
Efeitos "*i*"-calóricos

magnetocalórico *eletrocalórico* *mecanocalórico*



"*i*" – variáveis termodinâmicas intensivas

Efeitos Multicalóricos

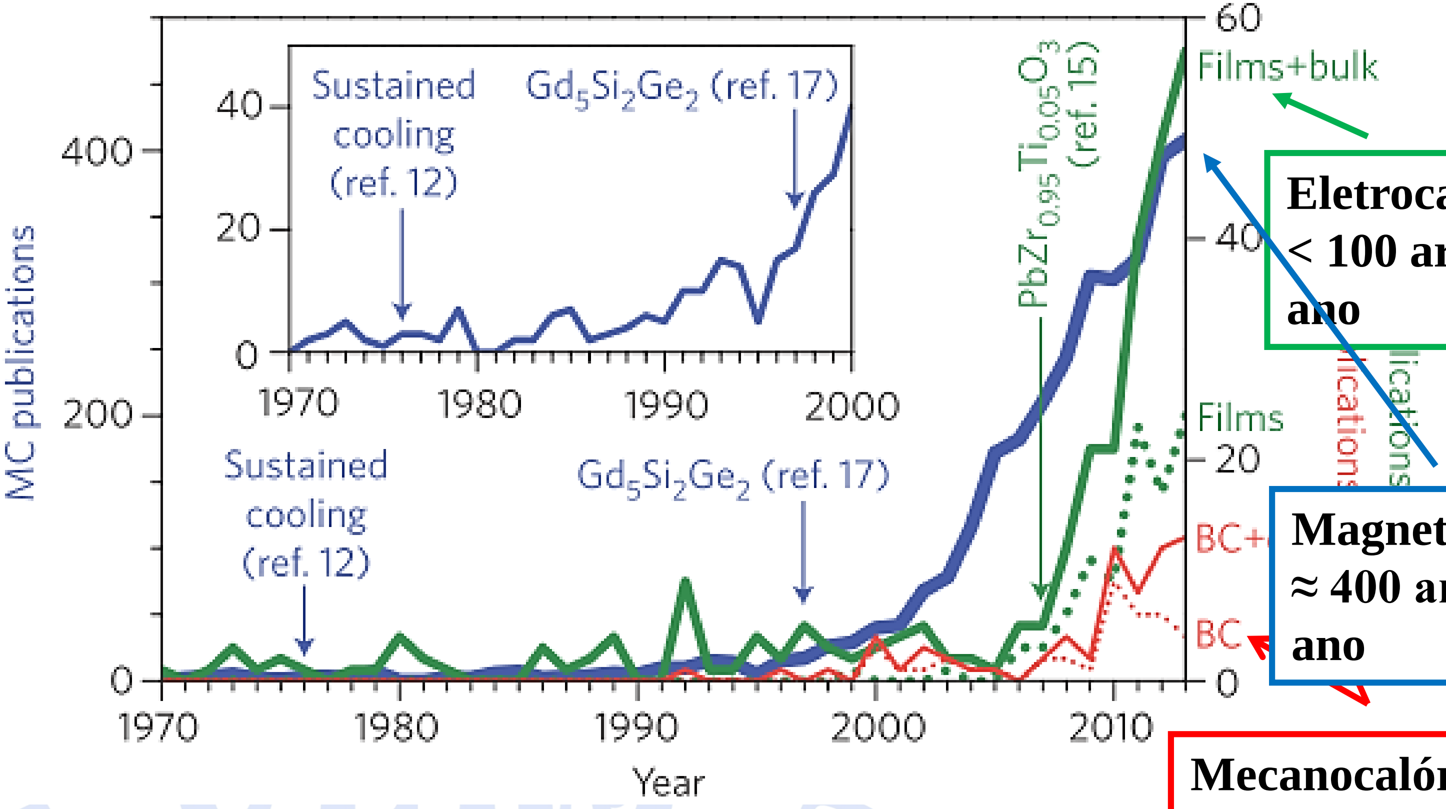


Materiais *"i"*-calóricos

Materiais Multicalóricos
ou
Materiais Multiferróicos

Coexistência de ao menos 2 parâmetros de ordem

Publicações



Eletrocalórico
< 100 artigos por ano

Magnetocalórico
≈ 400 artigos por ano

Mecanocalórico
< 20 artigos por ano

VOLUME 78, NUMBER 23 PHYSICAL REVIEW LETTERS 9 JUNE 1997

Giant Magnetocaloric Effect in $Gd_5(Si_2Ge_2)$

V. K. Pecharsky and K. A. Gschneidner, Jr.
Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-3020
(Received 22 November 1996)

An extremely large magnetic entropy change has been discovered in $Gd_5(Si_2Ge_2)$ when subjected to a change in the magnetic field. It exceeds the *reversible* (with respect to an alternating magnetic field) magnetocaloric effect in any known magnetic material by at least a factor of 2, and it is due to a first order [ferromagnetic (I) ↔ ferromagnetic (II)] phase transition at 276 K and its unique magnetic field dependence. [S0031-9007(97)03321-8]

Giant Electrocaloric Effect in Thin-Film $PbZr_{0.95}Ti_{0.05}O_3$

A. S. Mischenko,[1*] Q. Zhang,[2] J. F. Scott,[3] R. W. Whatmore,[2] N. D. Mathur[1]

An applied electric field can reversibly change the temperature of an electrocaloric material under adiabatic conditions, and the effect is strongest near phase transitions. We demonstrate a giant electrocaloric effect (0.48 kelvin per volt) in 350-nanometer $PbZr_{0.95}Ti_{0.05}O_3$ films near the ferroelectric Curie temperature of 222°C. A large electrocaloric effect may find application in electrical refrigeration.

Entropia

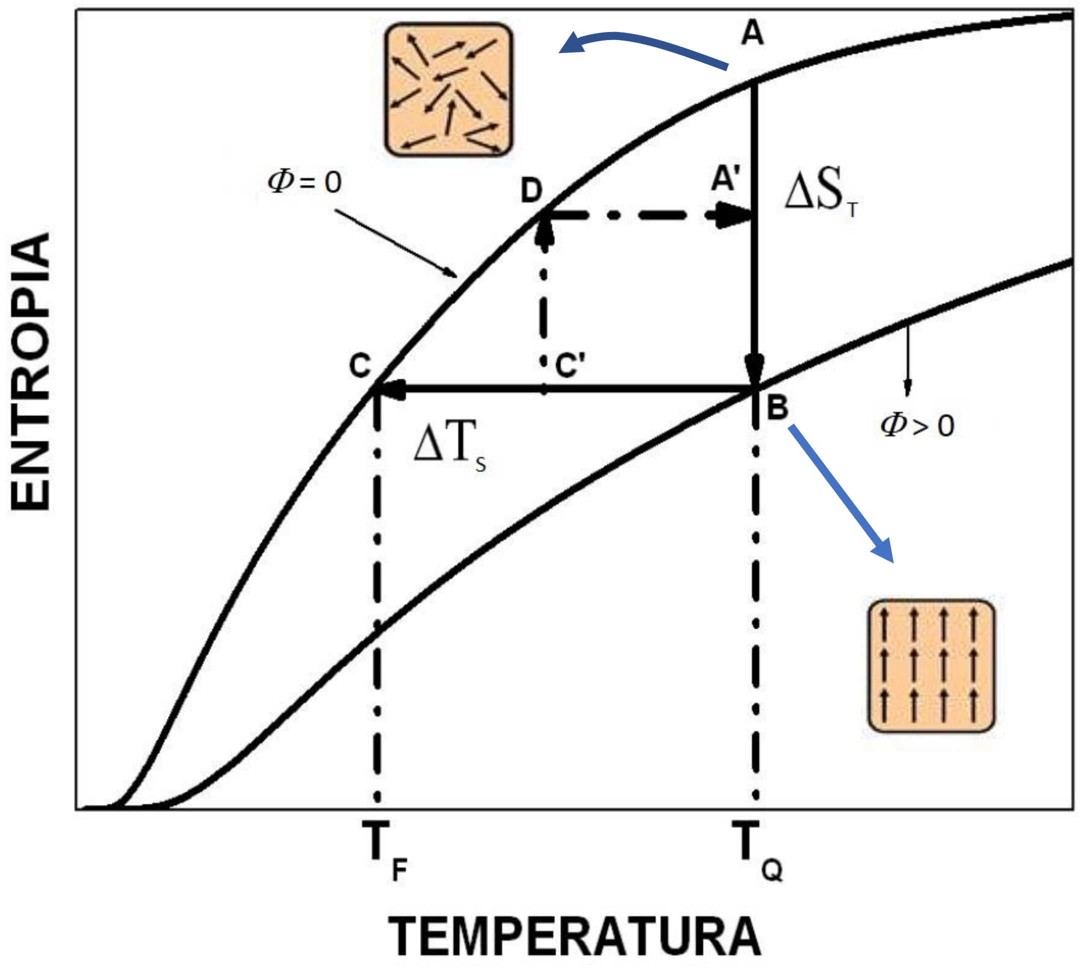
"Φ" – Campo magnético, elétrico ou ~~pressão~~ tensão.

ΔS_T –Variação isotérmica da entropia.

ΔT_S –Variação adiabática da entropia.

Relembrando:
Segunda lei da termodinâmica:

$$dS \geq \frac{\delta Q}{T}$$



Termodinâmica

Para o efeito magnetocalórico:

$$S = S(T,H)$$

Processo isotérmico

$$dS = \left(\frac{\partial S}{\partial T}\right)_H \underbrace{dT}_{=0} + \underbrace{\left(\frac{\partial S}{\partial H}\right)_T}_{\left(\frac{\partial M}{\partial T}\right)_T} dH$$

Relação de Maxwell

Retornando...

$$dS = \left(\frac{\partial M}{\partial T}\right)_T \mathrm{dH}$$

Integrando...

$$\boxed{\Delta S_T = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_T dH}$$

Relembrando:

$$dU = dQ - dW \quad \text{(1ª Lei)}$$

$$dQ = TdS \quad \text{(2ª Lei)}$$

O trabalho magnético:

$$dW = MdH$$

$$dU = TdS - MdH$$

A energia livre de Helmholtz:

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dF = -SdT - MdH$$

Como, $F = F(T,H)$:

$$dF = \left(\frac{\partial F}{\partial T}\right)_H dT + \left(\frac{\partial F}{\partial H}\right)_T dH$$

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_H} \qquad \boxed{M = -\left(\frac{\partial F}{\partial H}\right)_T}$$

Relação de Maxwell $\boxed{\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H}$

Termodinâmica

Relações de Maxwell para o efeito magnetocalórico:

$$dS = \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH$$

$$dQ = \cancel{T}\underbrace{\left(\frac{\partial S}{\partial T}\right)_H}_{\frac{C_p}{T}} dT + \cancel{T}\underbrace{\left(\frac{\partial S}{\partial H}\right)_T}_{\left(\frac{\partial M}{\partial T}\right)_H} dH$$

$= 0$

Processo adiabático

$$\boxed{\Delta T_S = -\int_{H_1}^{H_2} \frac{T}{C_p(T,H)}\left(\frac{\partial M}{\partial T}\right)_H \mathrm{dH}}$$

$$\boxed{\Delta S_T = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_T dH}$$

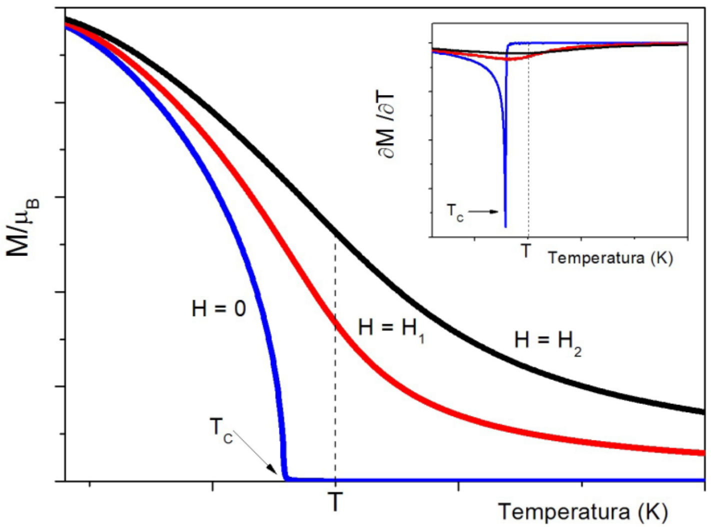
$$dT = -\frac{T}{C_p}\left(\frac{\partial M}{\partial T}\right)_H \mathrm{dH}$$

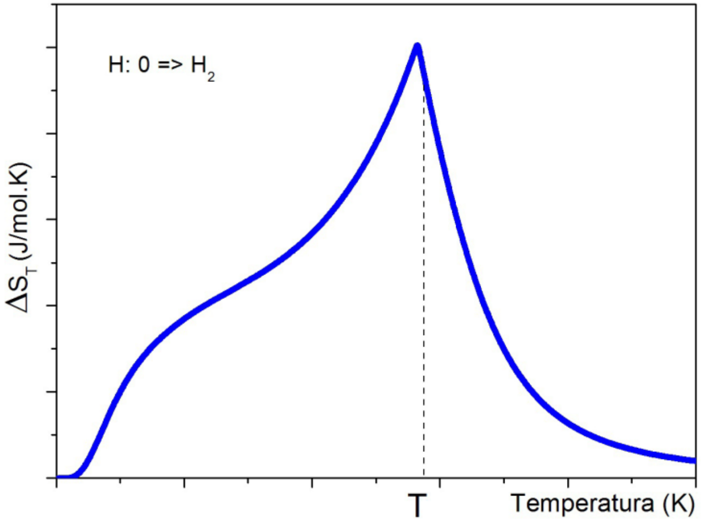
Integrando...

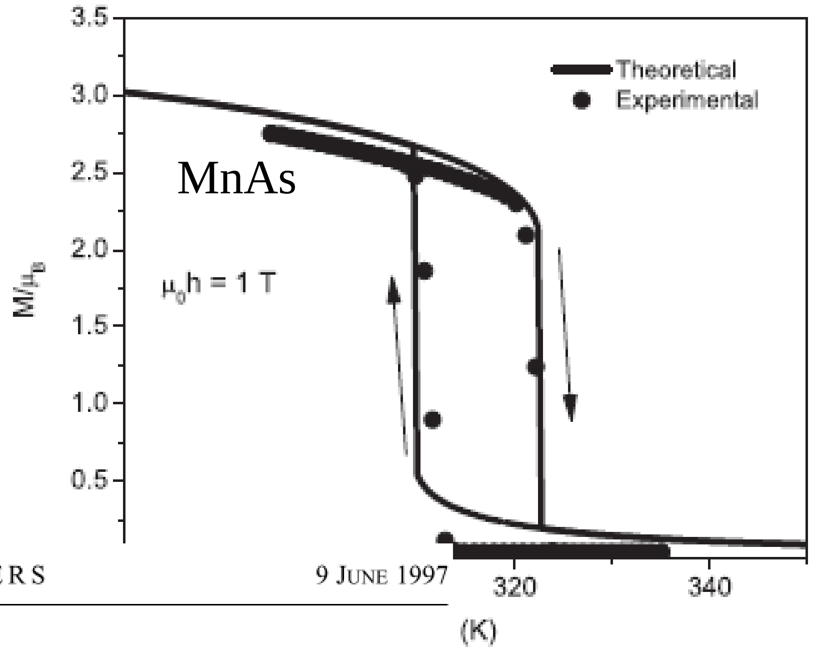
Relações de Maxwell

Segunda Ordem

Primeira Ordem







ΔT_{ad}

ΔS_T

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$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_H}$$

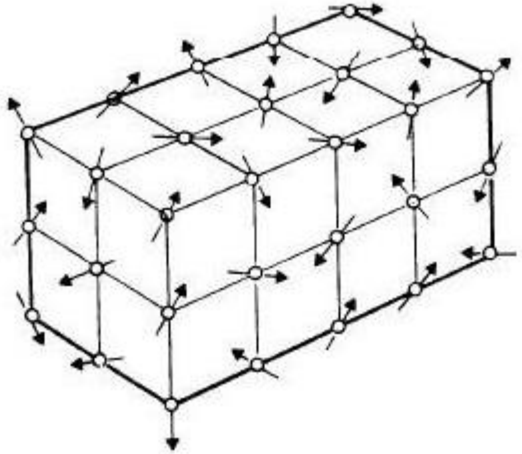
$$\boxed{M = -\left(\frac{\partial F}{\partial H}\right.}$$

$$\boxed{C_p = T\left(\frac{\partial S}{\partial T}\right)_H}$$

$$dS \geq \frac{\delta Q}{T}$$

Hamiltoniano

$$H = -\sum_{i,j} \widetilde{J_{ij}} \overrightarrow{J_i}.\overrightarrow{J_j} - \sum_i g\mu_B \vec{B}.\overrightarrow{J_i}$$



$$\Delta\vec{J} = \vec{J} - \langle\vec{J}\rangle$$

Aproximações:

- Somatório realizado somente nos primeiros vizinhos.

- Equivalência dos íons na rede.

- Campo médio.

$$H = -\sum_{i,j} \widetilde{J_{ij}} \left(\Delta\overrightarrow{J_i} + \langle\overrightarrow{J_i}\rangle\right).\left(\Delta\overrightarrow{J_j} + \langle\overrightarrow{J_j}\rangle\right) - \sum_i g\mu_B \vec{B}.\overrightarrow{J_i}$$

$$H = -\sum_i Z\tilde{J}\left(\underbrace{\Delta\vec{J}.\Delta\vec{J}}_{\approx 0} + 2\langle\vec{J}\rangle.\overrightarrow{J_i} \underbrace{- \langle\vec{J}\rangle^2}_{+\tilde{J}\langle\vec{J}\rangle^2}\right) - \sum_i g\mu_B \vec{B}.\overrightarrow{J_i}$$

$$\boxed{H = -\sum_i g\mu_B \overrightarrow{B_{ef}}.\overrightarrow{J_i}}$$

$$\overrightarrow{B_{ef}} = \vec{B} + \lambda\vec{M} \qquad \vec{M} = Ng\mu_B\langle\vec{J}\rangle \qquad \lambda = \frac{2Z\tilde{J}}{Ng^2{\mu_B}^2}$$

Forma Matricial

Hamiltoniano por íon:

$$H = -g\mu_B \overrightarrow{B_{ef}} . \vec{J}$$

Operadores de momento angular:

$$J_z|m\rangle = m|m\rangle$$

$$m = -J, -J+1, \ldots, J-1, J$$

Exemplo Gd^{3+}:

	$\|-7/2\rangle$	$\|-5/2\rangle$	$\|-3/2\rangle$	$\|-1/2\rangle$	$\|1/2\rangle$	$\|3/2\rangle$	$\|5/2\rangle$	$\|7/2\rangle$
$\langle -7/2\|$	$-7/2$	0	0	0	0	0	0	0
$\langle -5/2\|$	0	$-5/2$	0	0	0	0	0	0
$\langle -3/2\|$	0	0	$-3/2$	0	0	0	0	0
$\langle -1/2\|$	0	0	0	$-1/2$	0	0	0	0
$\langle 1/2\|$	0	0	0	0	$1/2$	0	0	0
$\langle 3/2\|$	0	0	0	0	0	$3/2$	0	0
$\langle 5/2\|$	0	0	0	0	0	0	$5/2$	0
$\langle 7/2\|$	0	0	0	0	0	0	0	$7/2$

$(2J+1) \times (2J+1)$

Grandezas termodinâmicas

Passo a passo para determinar as grandezas de interesse:

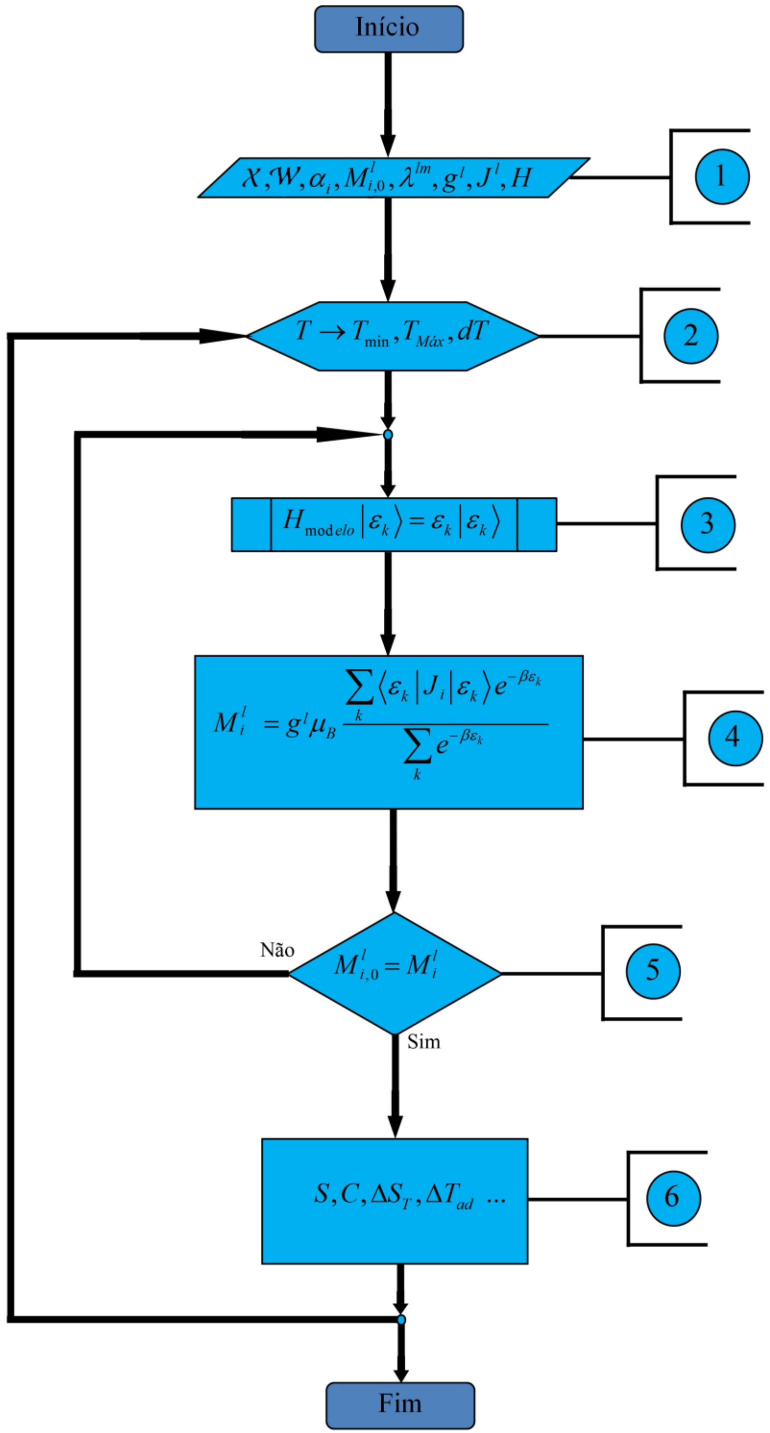
- Determinar o hamiltoniano modelo.

- Determinar os autovalores e autovetores.

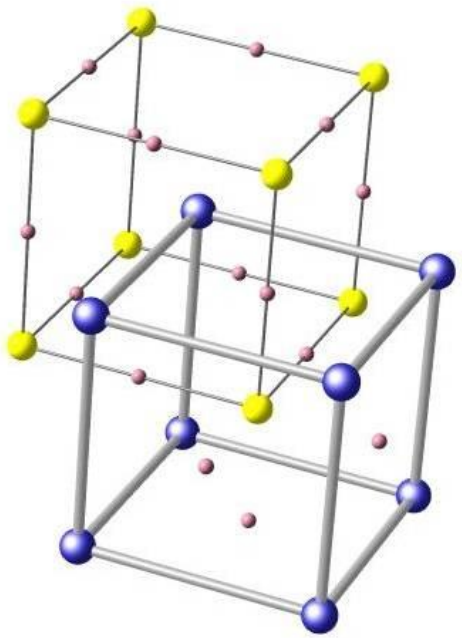
- Determinar a magnetização e as demais grandezas de inter

$$\left.\begin{aligned} M &= NgJ\mu_B B_J(x) \\ x &= \frac{g\mu_B J(B+\lambda M)}{k_B T} \end{aligned}\right\} \quad M = M(T, B, M) \longrightarrow \text{Método autocons}$$

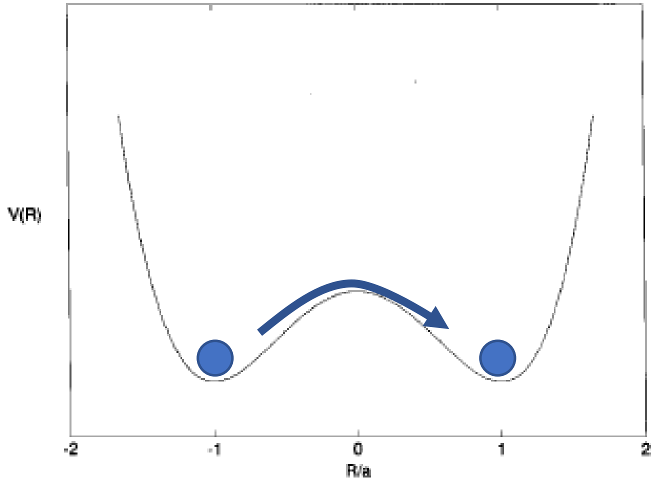
Chute inicial para magnetizaç



Modelos “tipo-Ising”



BaTiO$_3$



Modelo “TIM”:

$$H^e = -\sum_k \Omega \sigma_k^x - \sum_{k,l} J_{kl} \sigma_k^z \sigma_l^z - 2E \sum_k \mu \sigma_k^z$$

Matrizes de Pauli

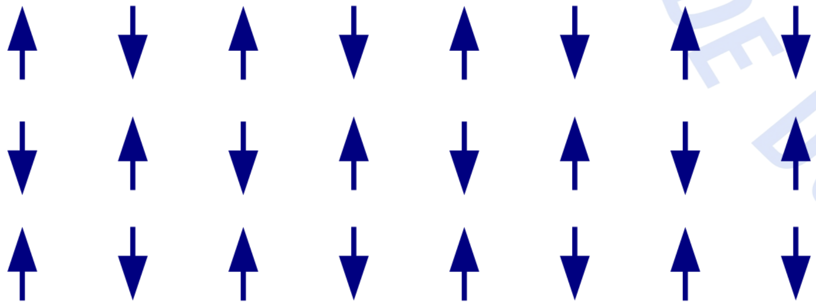
Descreve os ferroelétricos!

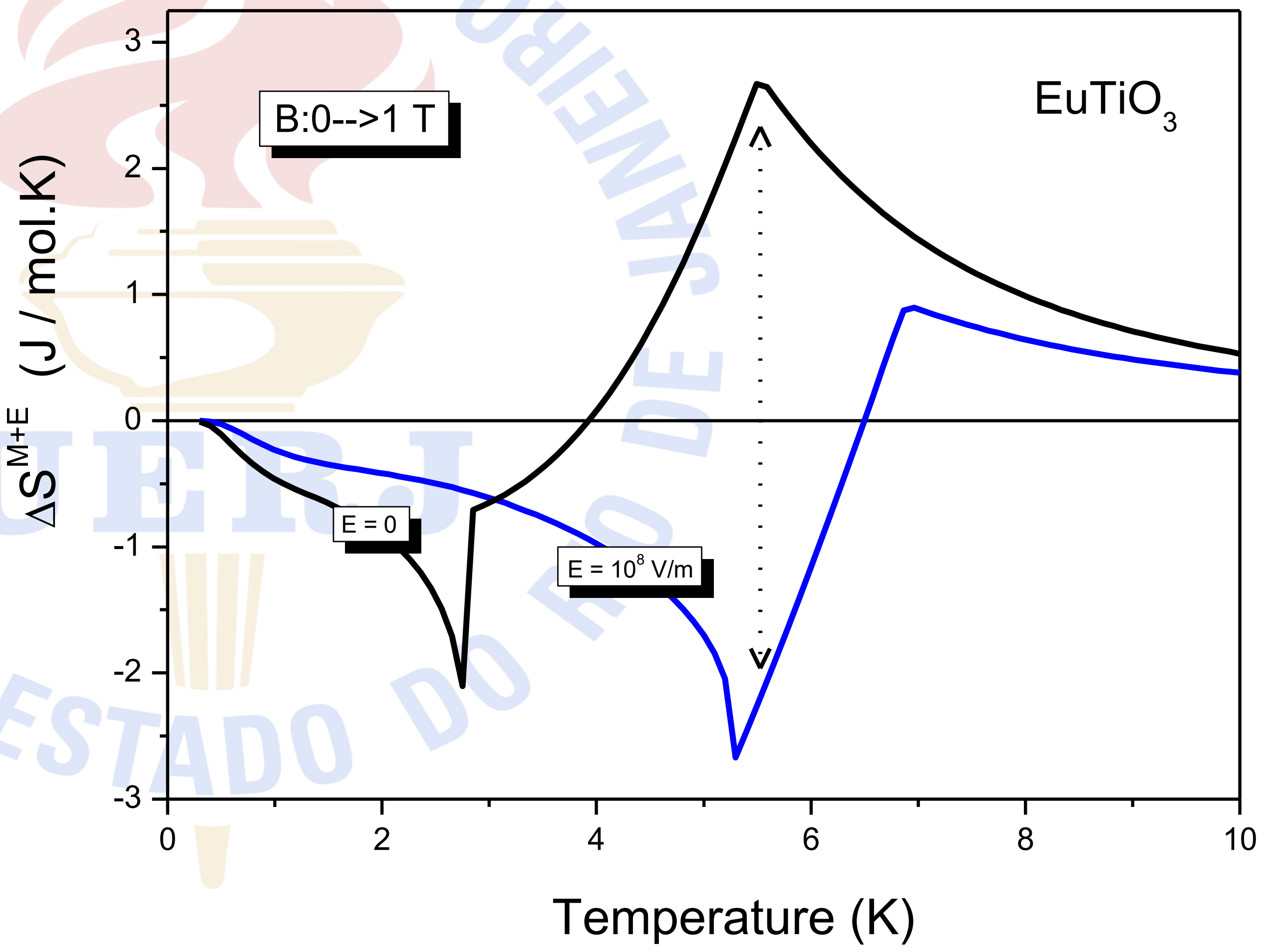
Multiferróico – $EuTiO_3$

Antiferromagnético

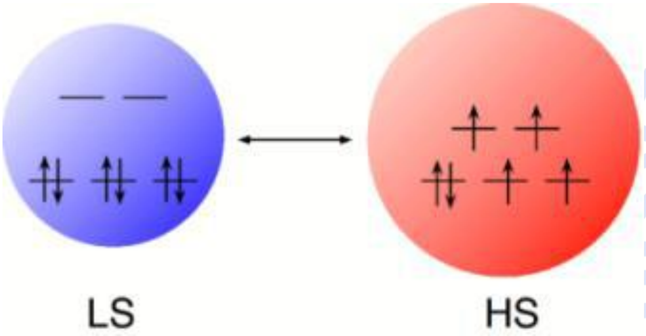
Paraelétrico

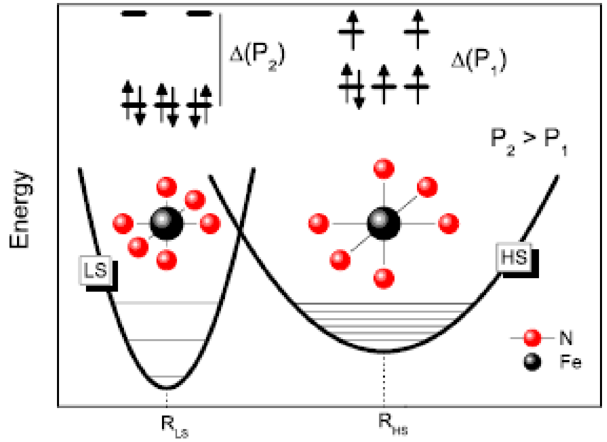
Acoplamento magnetoelétrico





Cristais orgânicos





Operador fictício de Spin

$$H = -h\sum_{i}\sigma_i - \sum_{i,j}\widetilde{J_{ij}}\sigma_i\sigma_j + \frac{1}{2}KV_{LS}\omega^2$$

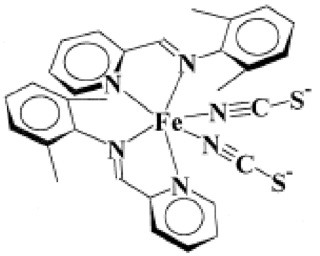
$$h = -\left(\Delta + \delta V_{LS} - \frac{K_B T}{2}ln\left({}^{g_{HS}}/_{g_{LS}}\right)\right)$$

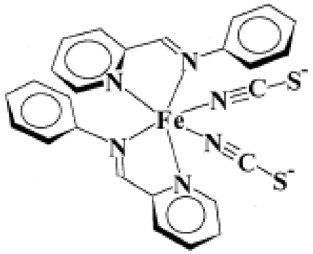
$$\Delta S_{mag}^{Max} = Rln(2S+1)$$

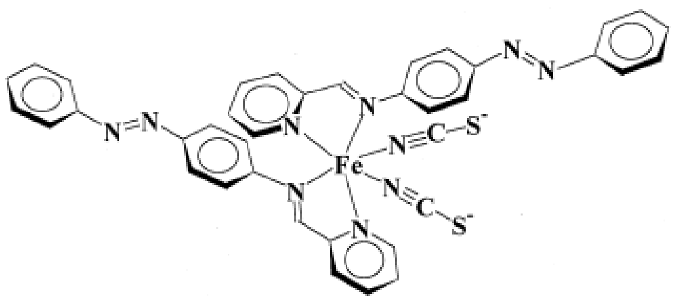
$$\Delta S_{mag}^{Max} \approx 13.38\frac{J}{mol.K}$$

Enthalpy changes $\Delta H = H_{HS} - H_{LS}$ are typically 10 to 20 kJ mol^{-1}, and entropy changes $\Delta S = S_{HS} - S_{LS}$ are on the order of 50 to 80 J mol^{-1} K^{-1} [22]. The thermally induced ST is

König, E. *Struct. Bonding* **1991**, *76*, 51.







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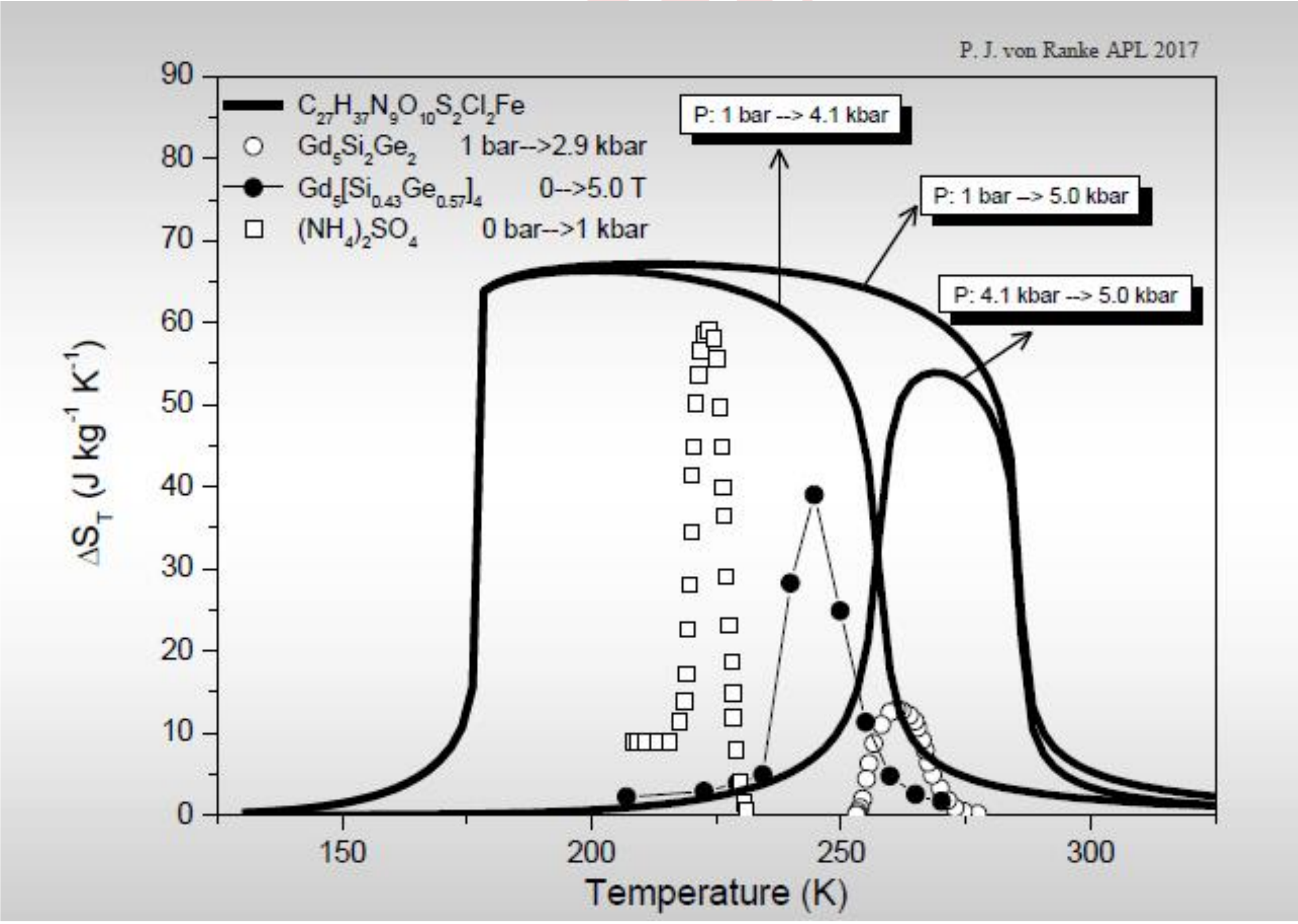

Obrigado!!!

Interessados? nos procurem!

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