Kvantno tuneliranje magnetizacije: magnetske nanočestice i jednomolekulski magneti

Damir Pajić
FO@PMF
Seminar iz fizike čvrstog stanja
Poslijediplomski studij
08.04.2003.

"Koji prirodni zakon čini
da ovaj kamen privlači
željezo k sebi.
Grci su ga nazvali po mjestu
gdje je nađen ...
I taj kamen još uvijek
začuđuje ljude."

Lukrecije, 99.-55. pr.Kr.

Fizika magnetizma

* Međudjelovanje na atomskoj razini
  - ◇ Heisenberg, Ising, Fermijeve tekućine, Hubbard
  - ◇ osnovno stanje, pobuđenja
  - ◇ lokalna gustoća spina, saturacija, toplinski kapacitet
* Magnetska svojstva mezoskopskih magneta (100$\AA$ ...)
  - ◇ irelevantna atomska razina
  - ◇ slaba međudjelovanja: anizotropija, magnetski dipoli, defekti, nečistoće, ...
* Makroskopski magneti

Mikromagnetizam

Jednadžba gibanja:

$$\frac{\partial \vec{M}}{\partial t} = -\gamma \vec{M} \times \frac{\delta E}{\delta \vec{M}}$$

* Opis i do dimenzija nekoliko konstanti rešetke
  - ravnotežna konfiguracija
  - gibanje domenskih zidova
  - feromagnetska rezonancija
  - spinski valovi

Makroskopski magnetski moment

Jako međudjelovanje izmjene

* ukupni magnetski moment 1000 atoma ponaša se kao jedinstvena veličina

$$M_i M_j - M_j M_i = 2i\mu_B \epsilon_{ijk} M_k$$

* makroskopskim mjerenjem moguće je odrediti $\vec{M}$

Kvantno tuneliranje

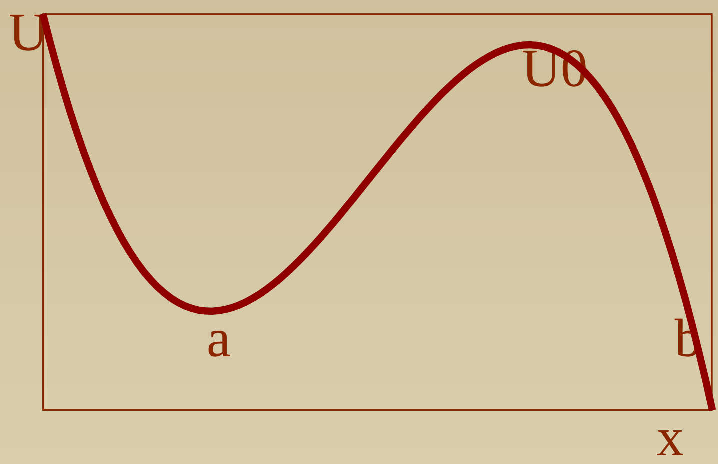
Tuneliranje makroskopskog $\vec{M}$ između klasičnih stabilnih konfiguracija

* Razlozi pažnje
  - kvantna mehanika na makroskopskoj razini?
  - magnetski instanton
* Prepreka ?
  - $e^{-I_{ef}/\hbar}$
  - magnetizacija može postati "laki" objekt za tuneliranje

Makroskopsko kvantno tuneliranje (MQT):

Caldeira & Leggett, PRL 46 (1981) 211

Tuneliranje



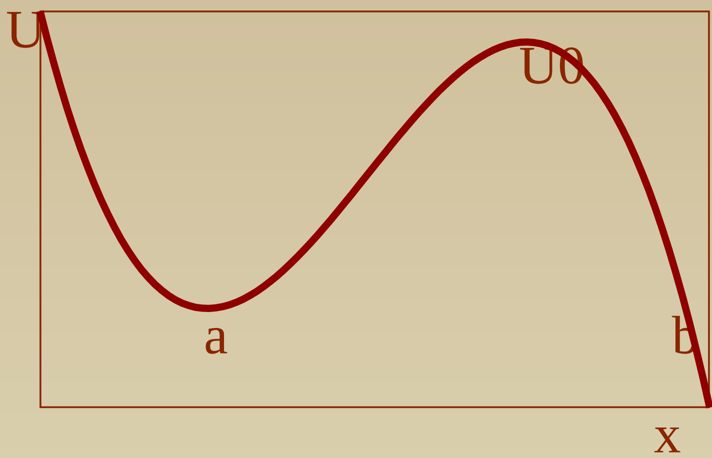
WKB: $\Gamma = Ae^{-B}$

$A \approx \omega_a$

$B = 2|\int_a^b p dx|/\hbar$

$k_B T \ll \hbar\omega_0$

Tuneliranje

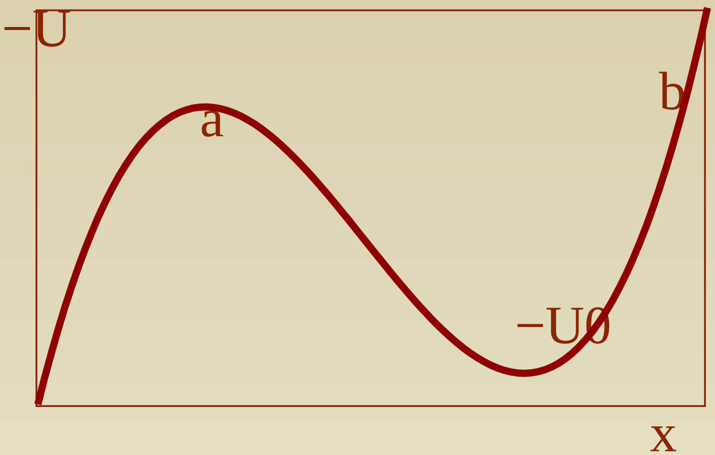


WKB: $\Gamma = Ae^{-B}$

$A \approx \omega_a$

$B = 2|\int_a^b pdx|/\hbar$

$k_B T \ll \hbar\omega_0$



$\tau = it$

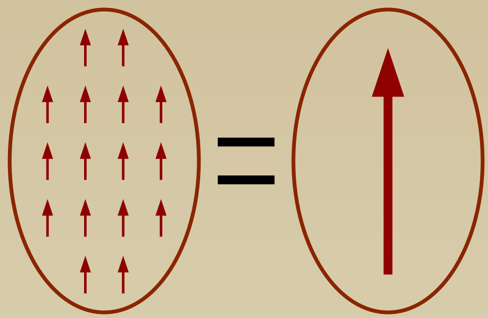
$\ddot{x}_\tau = \frac{\partial U}{\partial x}$

Monodomenske čestice

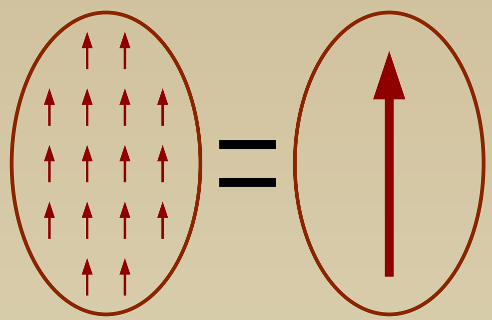
* Heisenbergovo međudjelovanje
  - $\epsilon_{ex} \simeq 1eV \cdot matr.el.prekl.v.f.$
  - vjerojatnost okretanja $e^{-\epsilon_{ex}/T}$

Monodomenske čestice

* Heisenbergovo međudjelovanje
  - $\epsilon_{ex} \simeq 1eV \cdot matr.el.prekl.v.f.$
  - vjerojatnost okretanja $e^{-\epsilon_{ex}/T}$

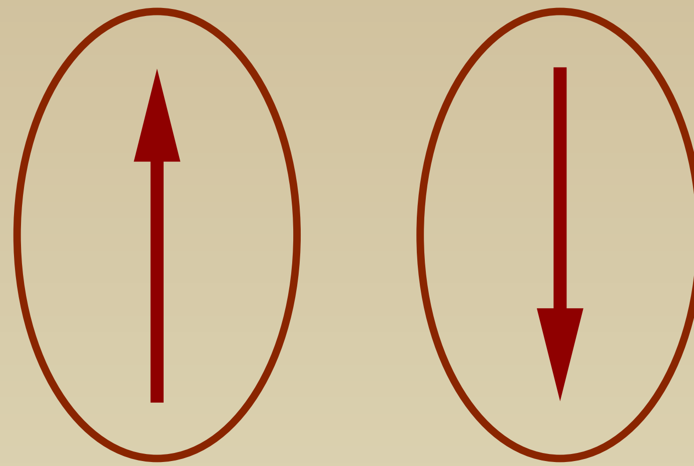


Monodomenske čestice



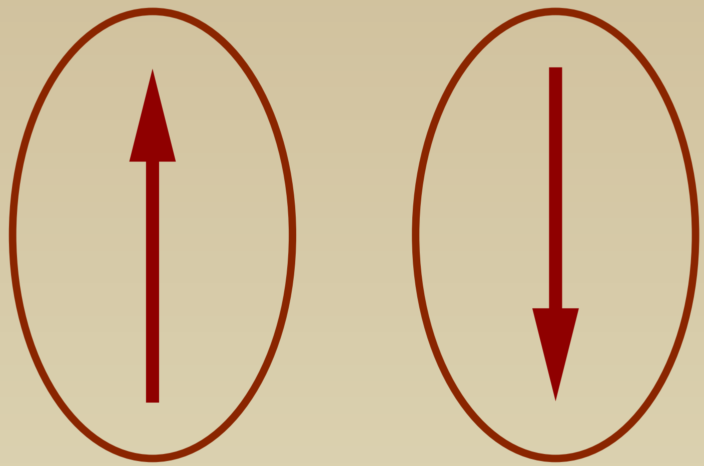
* Heisenbergovo međudjelovanje
  - $\epsilon_{ex} \simeq 1eV \cdot matr.el.prekl.v.f.$
  - vjerojatnost okretanja $e^{-\epsilon_{ex}/T}$
* Anizotropija
  - okretanje $\vec{M}$
  - simetrija i osi
  - $\epsilon_{an} \approx (v/c)^2 \cdot \epsilon_{ex}$
* Potvrđeno eksperimentima

Promjena smjera $\vec{M}$



- $e^{-\frac{U}{T}}$
  - $T > T_B$ ... superparamagnet
  - $T < T_B$ ... blokiranje spina

Promjena smjera $\vec{M}$



* $e^{-\frac{U}{T}}$
  - ◇ $T > T_B$ ... superparamagnet
  - ◇ $T < T_B$ ... blokiranje spina

* Tuneliranje

Rješavanje problema

$$\frac{\partial \vec{M}}{\partial t} = -\gamma \vec{M} \times \frac{\delta E}{\delta \vec{M}}$$

$$(M, \theta, \phi)\colon \vec{M} \to (M \sin\theta \sin\phi, M \sin\theta \cos\phi, M \cos\theta)$$

$$\frac{d\phi}{dt} = -\frac{\gamma}{M \sin\theta}\frac{\partial E}{\partial \theta}, \frac{d\theta}{dt} = -\frac{\gamma}{M \sin\theta}\frac{\partial E}{\partial \phi}$$

$$\mathcal{L} = p\dot{x} - E(x,p) = \frac{M}{\gamma}\dot{\phi}\cos\theta - E(\theta,\phi) + \frac{df(\theta,\phi)}{dt}$$

$$\dot{x} = \frac{\partial E}{\partial p}, \dot{p} = -\frac{\partial E}{\partial x}, f = \frac{M}{\gamma}\phi$$

$$I = \int dt \mathcal{L} = \int \mathrm{dt}(\frac{M}{\gamma}\dot{\phi}(\cos\theta - 1) - E(\theta,\phi))$$

Izračunavanje eksponenta tuneliranja ...

Modeliranje energije $E(\theta, \phi)$

* Jednoosna anizotropija u Z smjeru u transverzalnom magnetskom polju u X smjeru
  - ◇ $E = V(K \sin^2\theta - HM_0 \sin\theta \cos\phi)$

* X-Y ravnina lakog magnetiziranja i X os lakog magnetiziranja i primijenjeno magnetsko polje u -X smjeru
  - ◇ $E = k_\perp M_z^2 - k_\parallel M_x^2 + M_x H =$
    $= V(K_\perp \cos^2\theta - K_\parallel \sin^2\theta \cos^2\phi + M_0 H \sin\theta \cos\phi)$

Računamo: $\phi(\tau)$, $\theta(\tau)$, Γ, T_C, ...

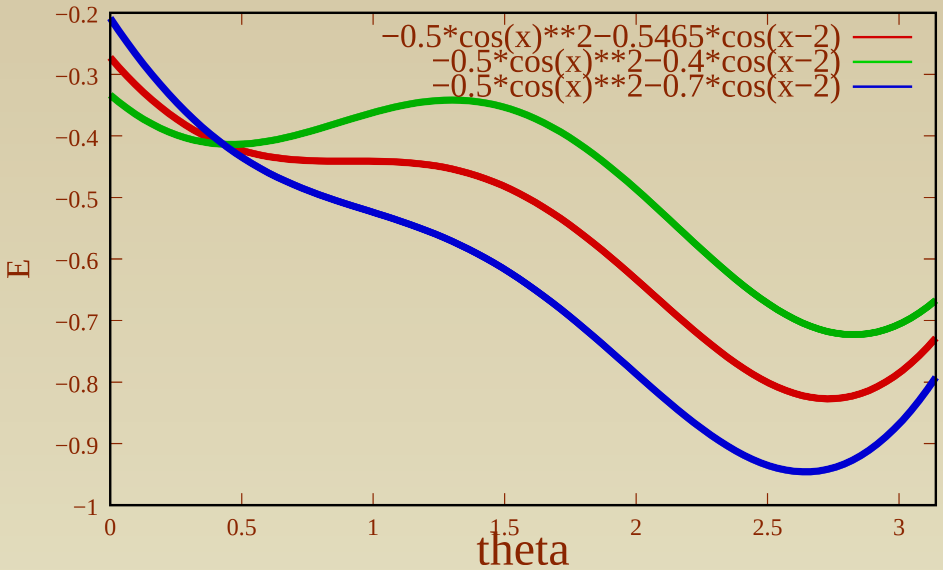
Chudnovsky & Gunther, PRL <u>60</u> (1988) 661

Jednoosna anizotropija i polje

$$E = -kM_z^2 - M_x H_x - M_z H_z =$$

$$= -H_a M(\tfrac{1}{2}\cos^2\theta + h_z \cos\theta + h_x \sin\theta\cos\theta)$$

$$H_a = 2kM, h_{x,z} = H_{x,z}/H_a$$



$$E_\theta = -(\tfrac{1}{2}\cos^2\theta - h\cos(\theta - \theta_H))$$

$$h_c = (\sin^{2/3}\theta_H + |\cos^{2/3}\theta_H|)^{-3/2}$$

Rješavanje problema

* Promatramo: $h = h_c(1 - \epsilon)$

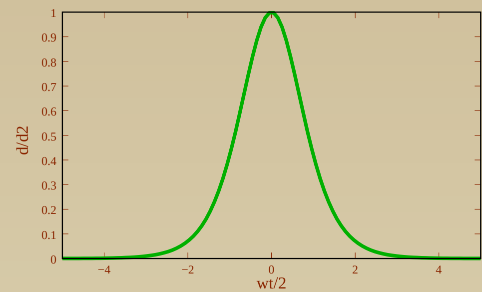
* Uvodimo: $\delta = \theta - \theta_0$

* Djelovanje: $I = -\hbar S \int \mathrm{d}\bar{\tau} \bar{\mathcal{L}}_E$

* Euler-Lagrange jednadžbe (ekstremalne trajektorije)
  - ◇ Instanton: rotacija $\vec{M}$ ispod barijere (*spori* instanton)

* Integracija po putanjama: $\int \mathcal{D}\{\phi(\tau)\} \int \mathcal{D}\{\cos\theta(\tau)\} e^{-\frac{I}{\hbar}}$

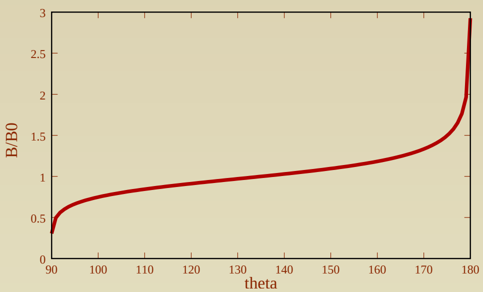
Rješenje problema



Ekstremalna putanja:

* $\delta(\tau) = \dfrac{\delta_2}{\mathrm{ch}^2(\omega_0 \tau/2)}$

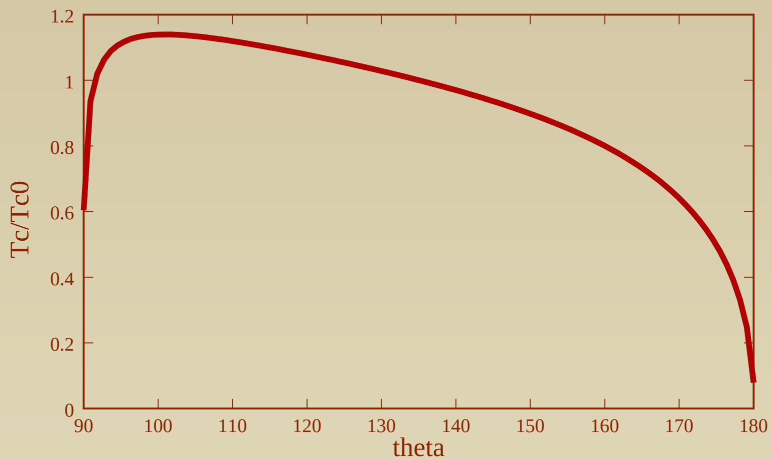
* Konstanta: $\omega_0 = (6\epsilon)^{1/4} \dfrac{|\mathrm{ctg}\theta_H|^{1/6}}{1+|\mathrm{ctg}\theta_H|^{2/3}} \omega_a$



* Eksponent tuneliranja:
  $B = \dfrac{16\sqrt[4]{6}}{5} S \epsilon^{5/4} |\mathrm{ctg}\theta_H|^{1/6}$

"Kvantna" temperatura

* Prijelaz: $B \approx \frac{U}{T}$



* $T_c = \frac{5}{36}\hbar\omega_0$

Eksperimentalna perspektiva

* Slobodni parametri: θ_H, $\epsilon = 1 - H/H_c$, T

* $T_c \propto H_a$, $T_c \propto \epsilon^{1/4}$

* $H_a = 1T$, $\epsilon = 10^{-3}$, $T_c(135°) \approx 30mK$

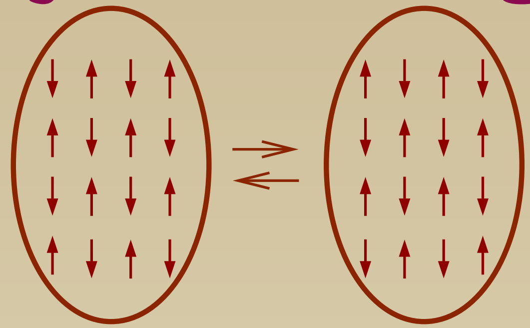
* $\Gamma \propto 10^{11}s^{-1} \cdot e^{-B}$

  ◇ $B < 25 - 30 \Rightarrow$ tuneliranje prebrzo i teško primjetljivo
  ◇ $B > 30 - 35 \Rightarrow$ metastabilno stanje traje znatno dulje od eksperimenta
  ◇ $B \simeq 30$: mjerljivo MQT

* $\epsilon \simeq 10^{-3} \Rightarrow S \simeq 3 \cdot 10^4$

Drugi: $K_\parallel, K_\perp \simeq 10^6 - 10^8 erg/cm^3$, $S \simeq 10^2 - 10^5$, $T_c \simeq 1K$

Tuneliranje Néelovog vektora

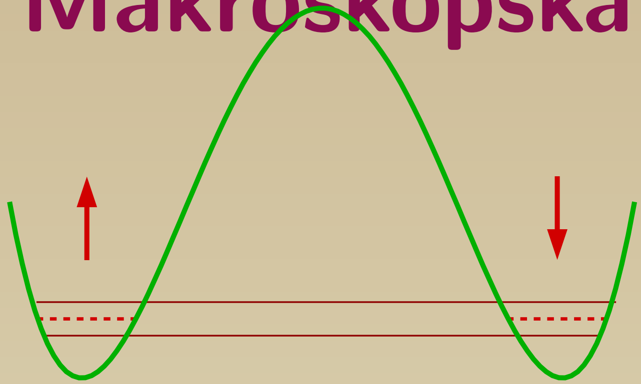


* Veća anizotropija i izraženije tuneliranje nego kod FM
* Detekcija nekompenziranih spinova
* $\Gamma \approx |\cos(s\pi)|\omega_0 e^{-\frac{2V}{\hbar\gamma}\sqrt{2\chi_\perp K_\parallel + m^2 \frac{K_\parallel}{K_\perp}}}$

$$\omega_0 = 2\gamma\sqrt{\frac{K_\parallel K_\perp}{m^2 + 2\chi_\perp K_\perp}}$$

* $T_c \simeq \mu_B \sqrt{H_\parallel H_{ex}}$, (nekoliko K)
* Tuneliranje $10^3 - 10^4$ magnetskih atoma

Makroskopska kvantna koherencija (MQC)



$$\Delta = \hbar\Gamma$$
$$|0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$$
$$|1\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle)$$
$$\langle\vec{M}(t)\cdot\vec{M}(0)\rangle = M_0^2\cos(\Gamma t)$$

* Rezonantna apsorpcija pri AC polju od $\omega = \Gamma$
* Međudjelovanje $\vec{M}$ i okoline uništava koherentne oscilacije
* Što veća makroskopnost, to lomljivija koherentnost ($\Gamma \simeq 1s^{-1}$, međudjelovanje $10^{-15}eV$)
* Antiferomagnet - dobar kandidat za MQC (100 atoma, nisko polje i temperatura)
* Nekoherentno tuneliranje nije tako osjetljivo na međudjelovanje s okolinom

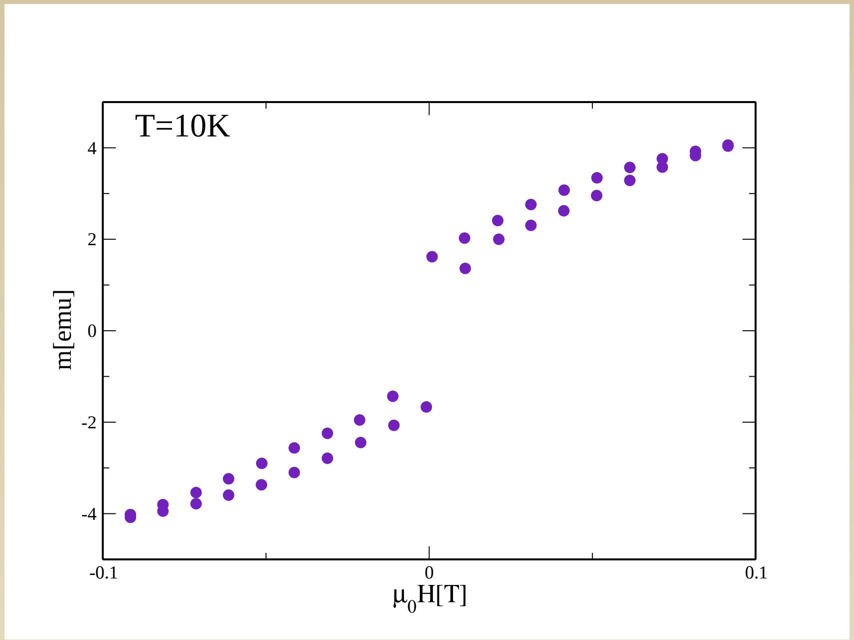
Eksperimentalne činjenice i tuneliranje

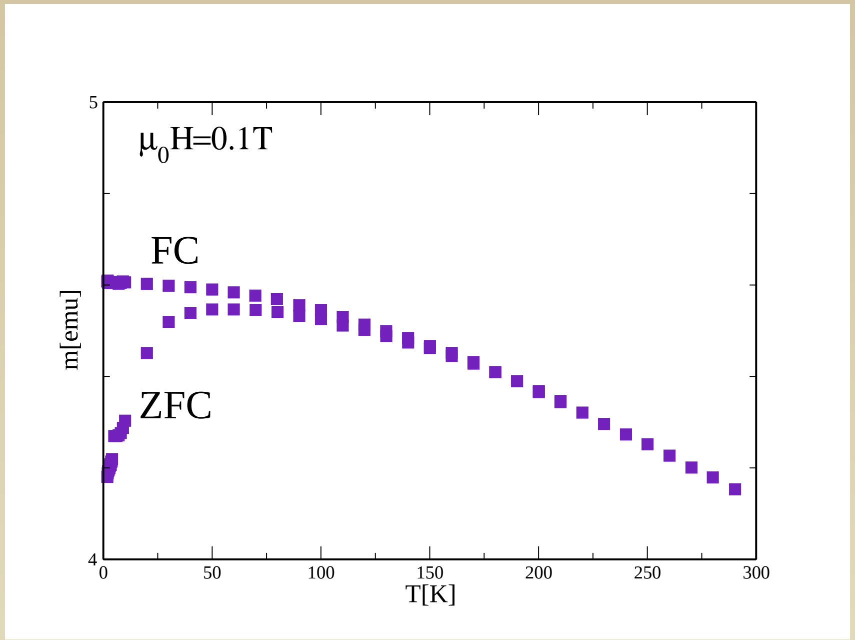
- Nanomagneti
  - jednodomenske magnetske nanočestice
  - jednomolekulski magneti
- Magnetska svojstva
  - magnetska histereza
  - m(T)
  - relaksacija m(t)

Magnetska histereza i FC-ZFC razdvajanje

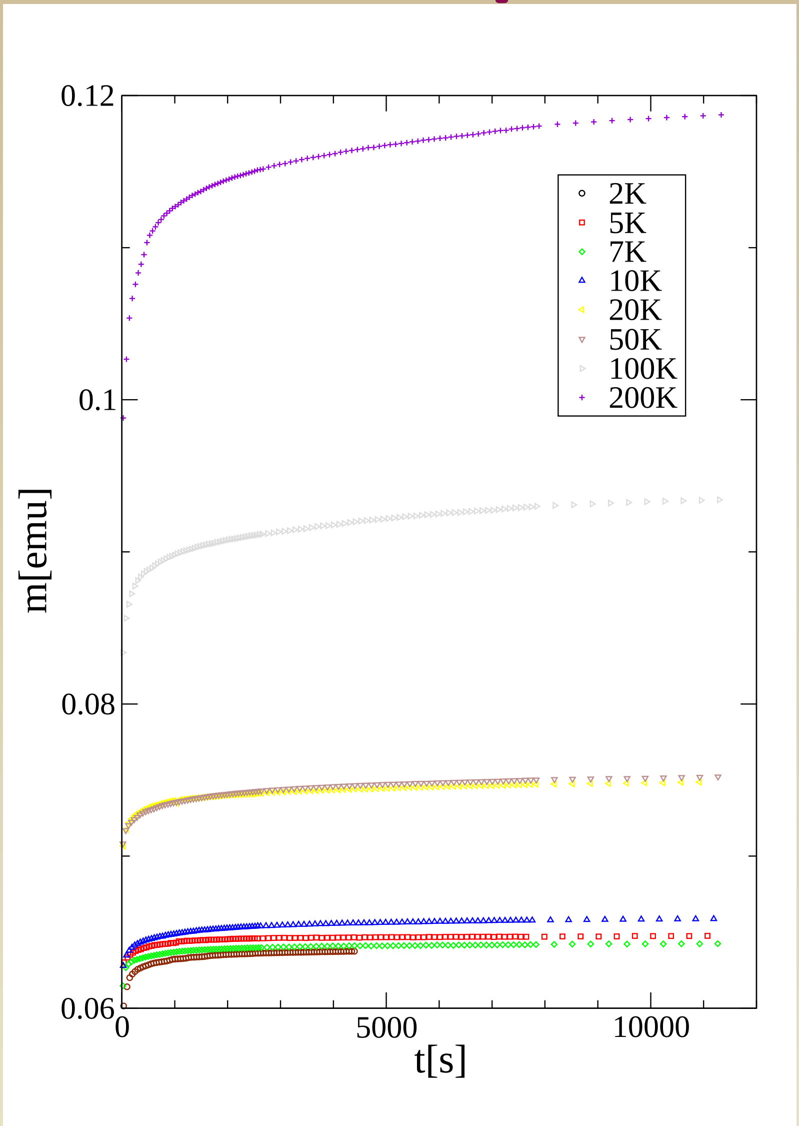
Fe_3O_4 - 8nm

m ne stigne pratiti H

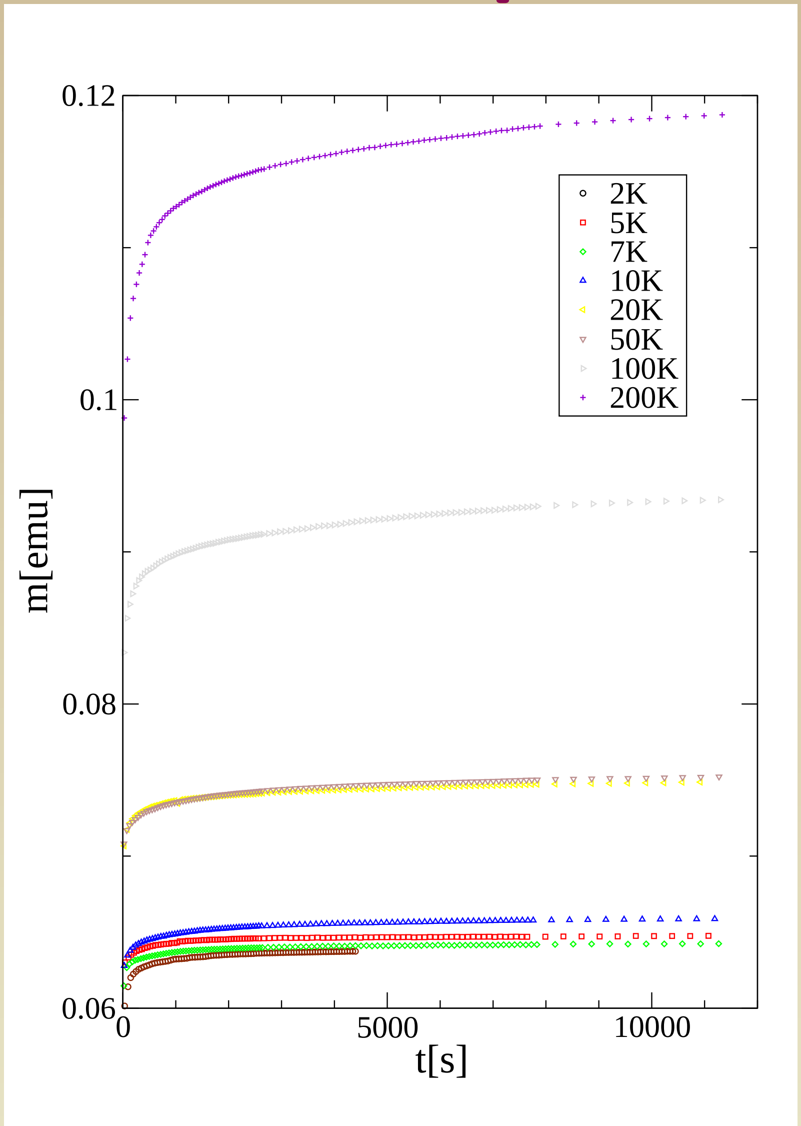


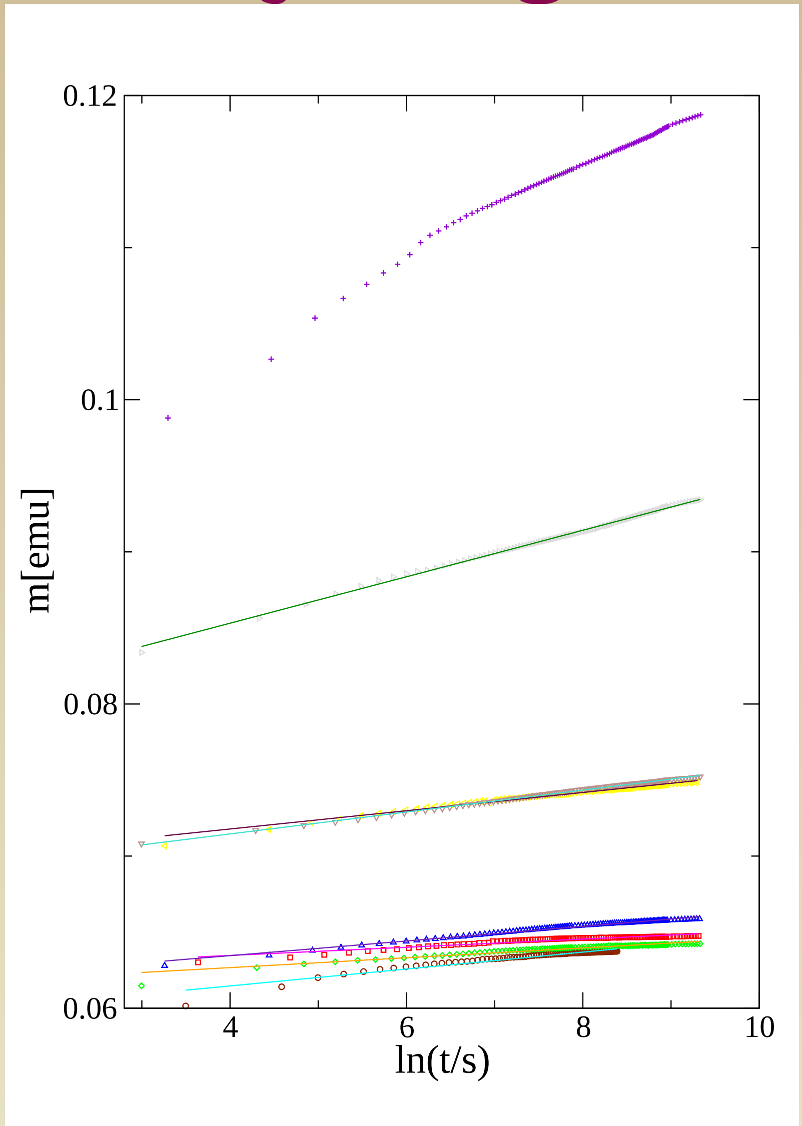


Uzrok: spora relaksacija magnetizacije



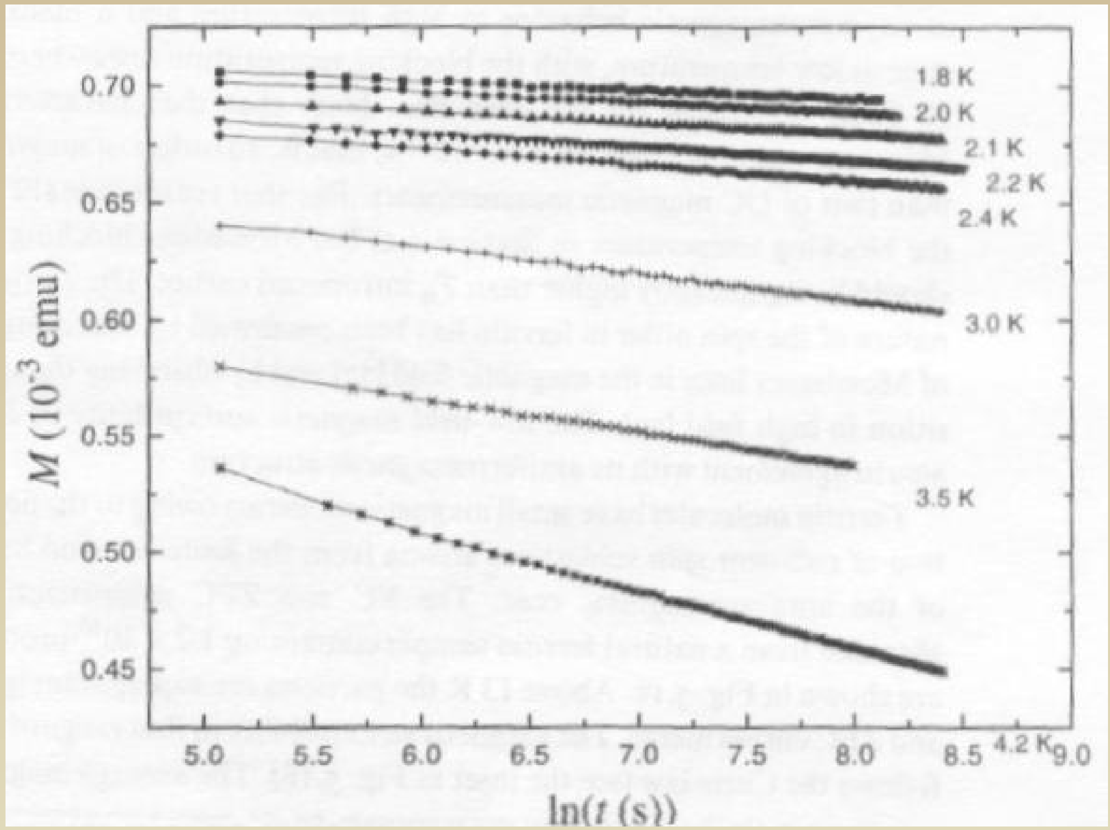
Uzrok: spora relaksacija magnetizacije





Ferritin

$\alpha - \mathrm{Fe_3O_4}$ (hematite)
iz konjske slezene
3-7.5nm
4500 Fe^{3+} iona
15 nekompenziranih
AFM



Tejada & Zhang, J.Phys.:Condens.Matter 6 (1994) 263

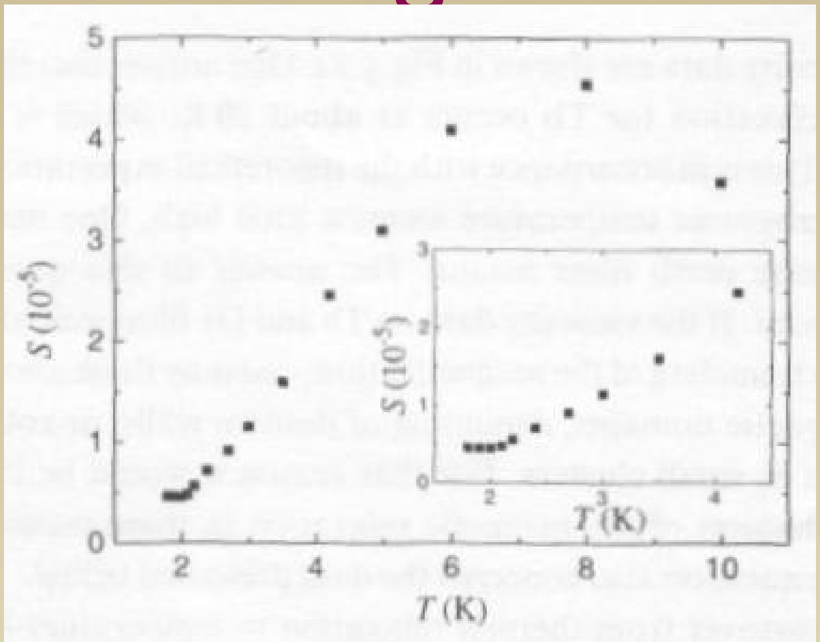
$ln(t)$ relaksacija

* Univerzalnost: sustav u kritičnom stanju
  * i kod monodomenskih čestica

* Raspad metastabilnih stanja: jedini opis sporih relaksacija

* Model: nailazak na sve veće barijere
  * $U = U_0(1 - \frac{M}{M_c})$, $\frac{\mathrm{d}M}{\mathrm{d}t} \propto e^{-\frac{U_0}{T}(1-\frac{M}{M_c})}$
  * $M(t) = M(t_0)(1 - \frac{T}{U_0}\ln\frac{t}{t_0})$
  * magnetska viskoznost: $S = -\frac{1}{M(t_0)}\frac{\partial M}{\partial \ln(t)}$

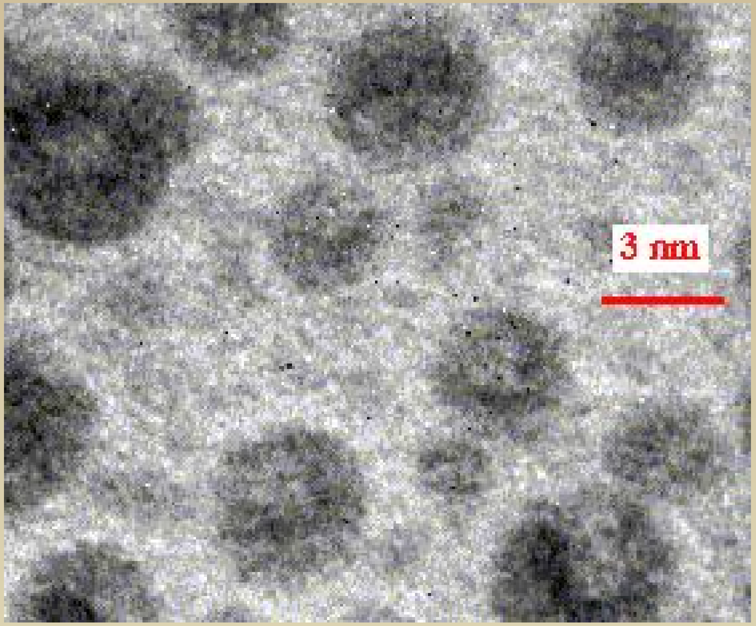
Magnetska viskoznost



Tejada & Zhang, J.Phys.:Condens.Matter 6 (1994) 263

- $S \propto \frac{T}{U_0}$ prestaje vrijediti
- S postaje konstanta ispod određene temperature
- Tuneliranje

Problemi s nanočesticama

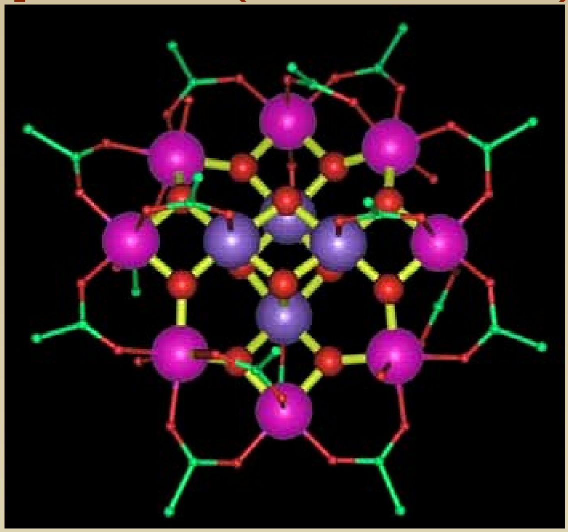


www.lps.u-psud.fr

- Raspodjela po veličinama
  - $U = KV$
  - $\tau = \tau_0 e^{\frac{KV}{kT}}$
- Raspodjela po oblicima
- Kako uočiti tuneliranje?
- Izvedba aparature ($T_c(180^\circ)$?)

Jednomolekulski magnet

$[\mathrm{Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}}]\cdot 2\mathrm{CH_3COOH}\cdot 4\mathrm{H_2O}$

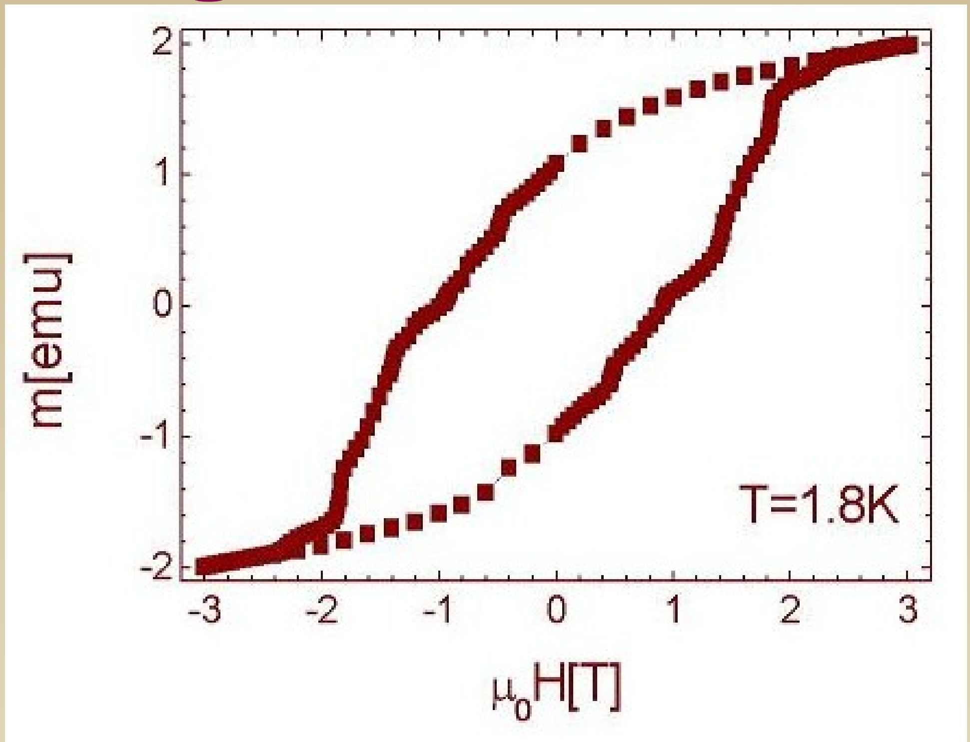


sinteza: T.Lis, Acta Crystallogr. B 36 (1980) 2042

bistabilnost: Sessoli, Gatteschi, Caneschi, Novak, Nature 365 (1993) 141

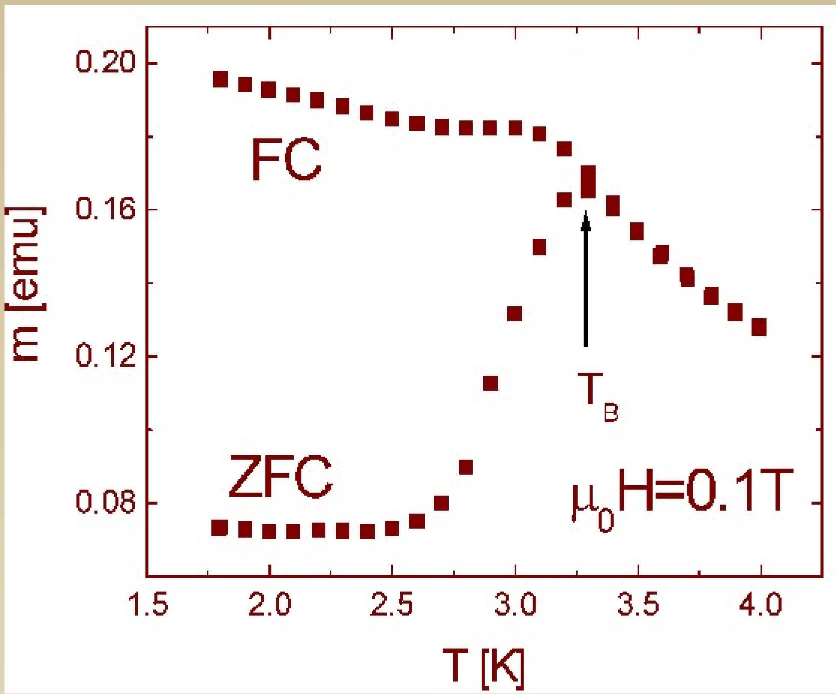
* Tetragonska rešetka ($a = 17,32\mathring{A}, c = 12,39\mathring{A}$)
* Spin molekule: $8\cdot 2 - 4\cdot\frac{3}{2} = 10$ (i do 50K; jako međudjelovanje izmjene)
* Visoka magnetska anizotropija

Magnetska histereza

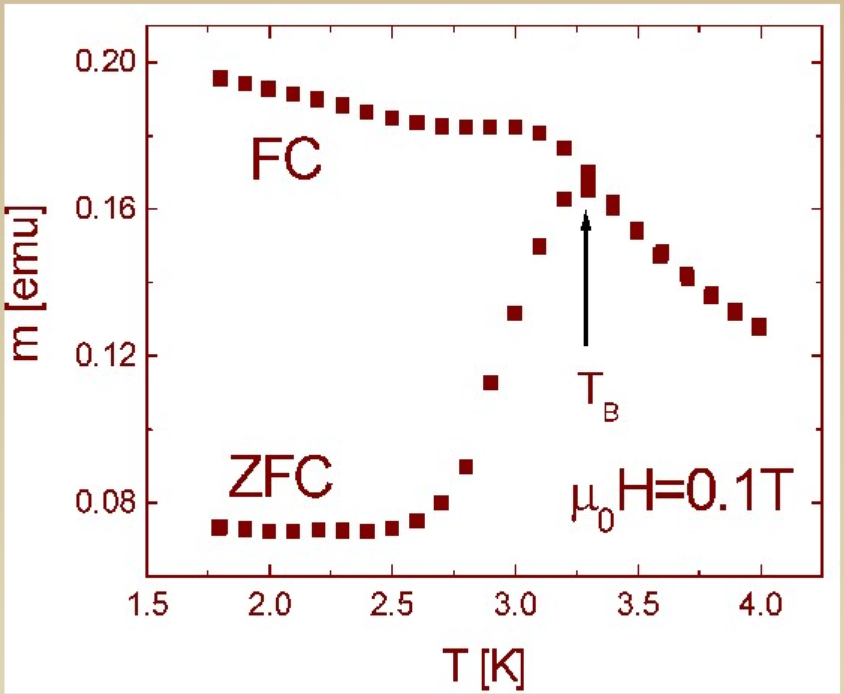


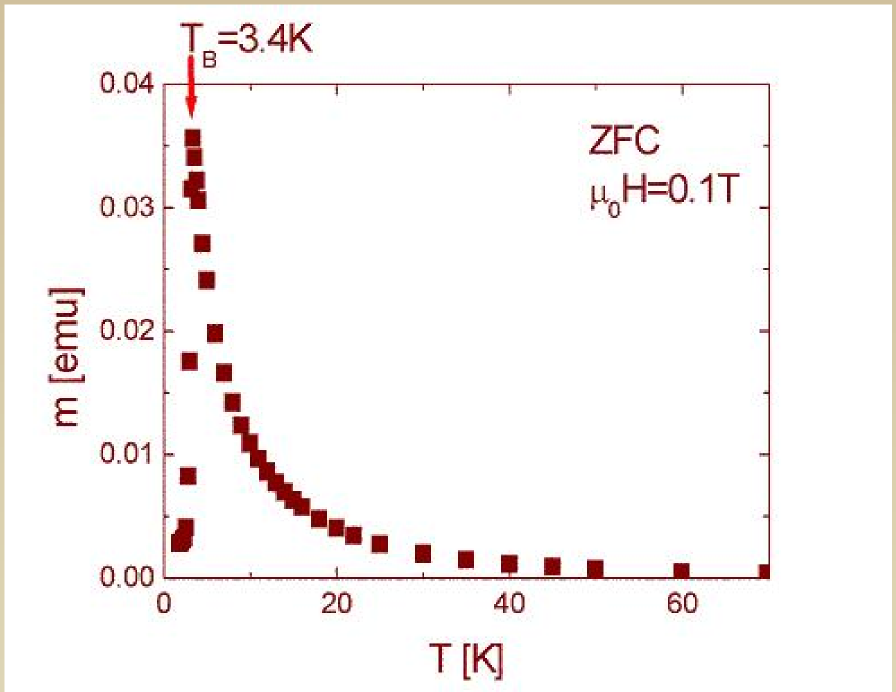
* ispod 3K blokiran spin
* iznad 3K superparamagnet

”FC i ZFC krivulje”



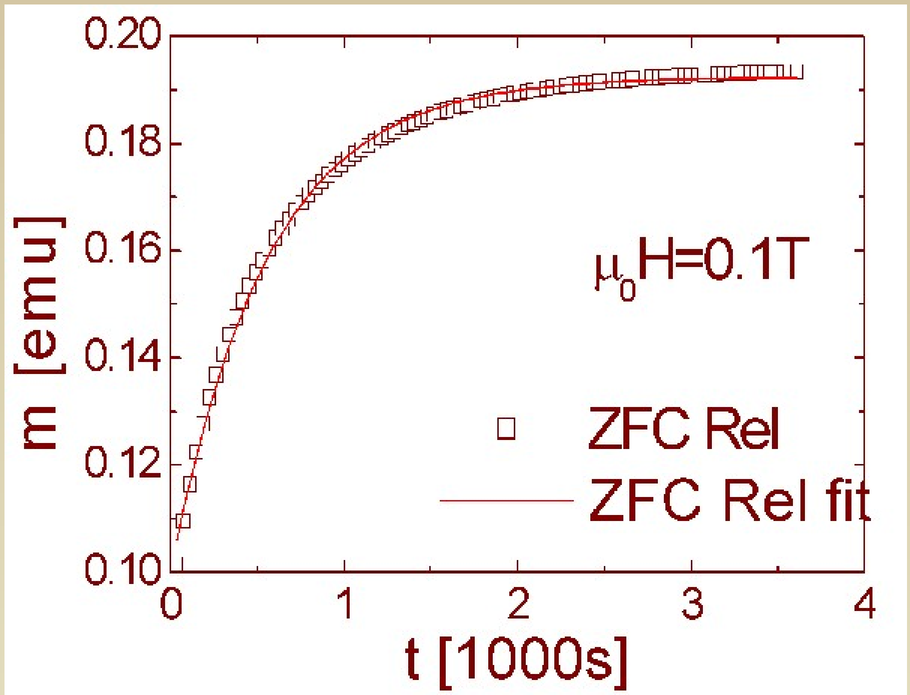
"FC i ZFC krivulje"





Relaksacija magnetizacije

* Ansambl
* $S_z \to S_z \pm 1$



$M = M_0(1 - e^{-t/\tau})$

Arrheniusova aktivacija:

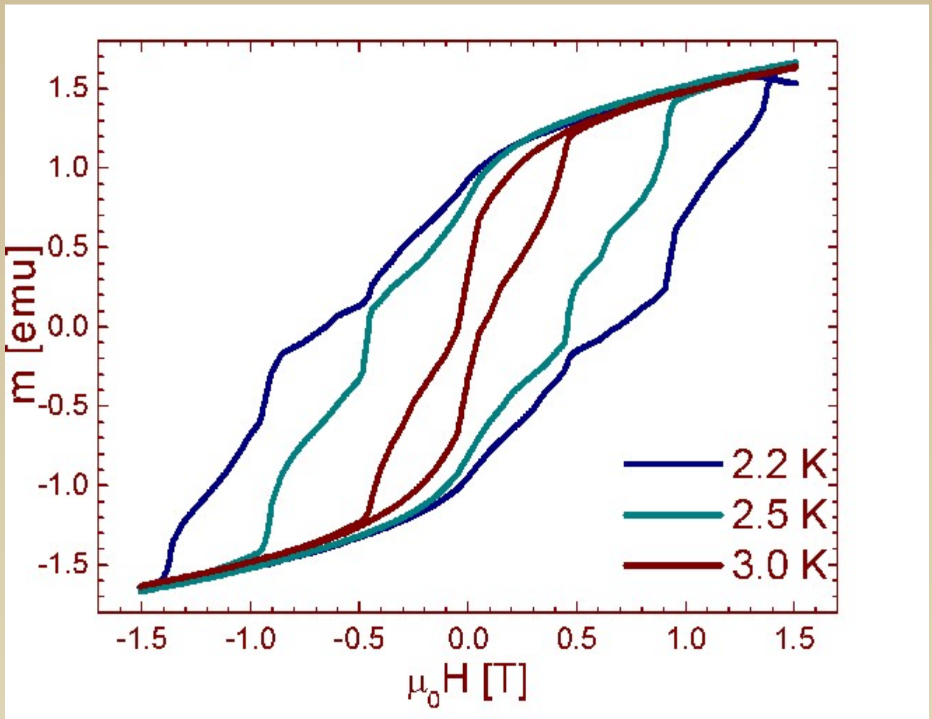
$\tau = \tau_0 e^{\frac{S^2 D}{kT}}$

$\tau_0 = 2,1 \cdot 10^{-7} s$

$D/k = 0,61K$

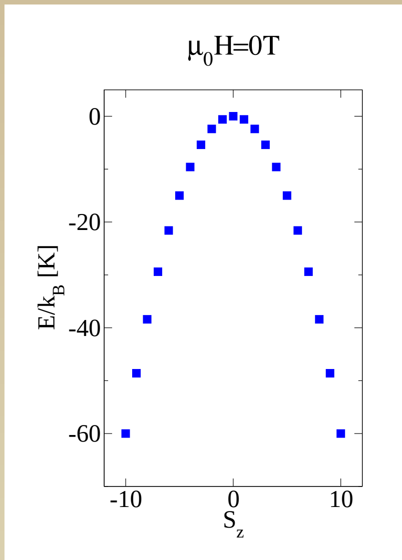
T	20K	10K	7K	5K	4K	3,5K	3K	2K	1K
τ	4,4 μs	0,093ms	1,23ms	0,042s	0,88s	7,8s	140s	43d	2Tg

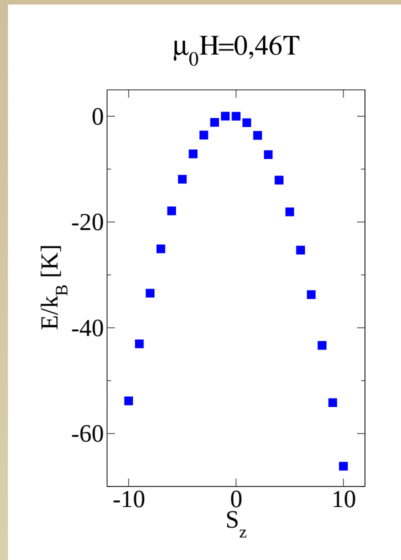
Kvantna histereza

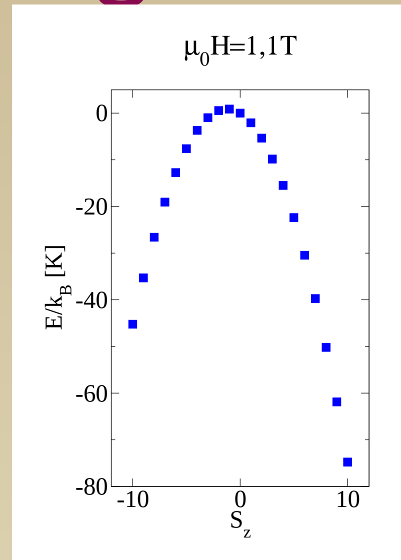


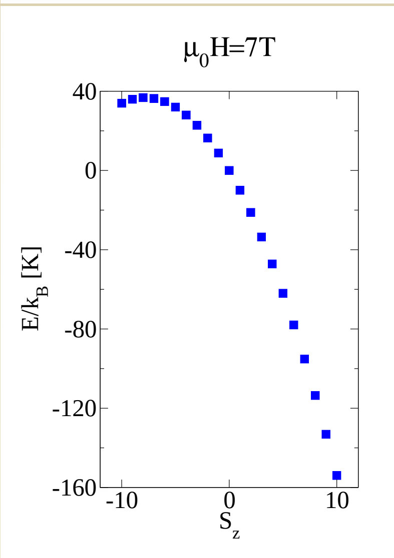
- ∗ Relaksacija brža pri nekim poljima
- ∗ Rezonantno tuneliranje?
- ∗ Friedman, Sarachik, Tejada, Ziolo: PRL **76** (1996) 3830

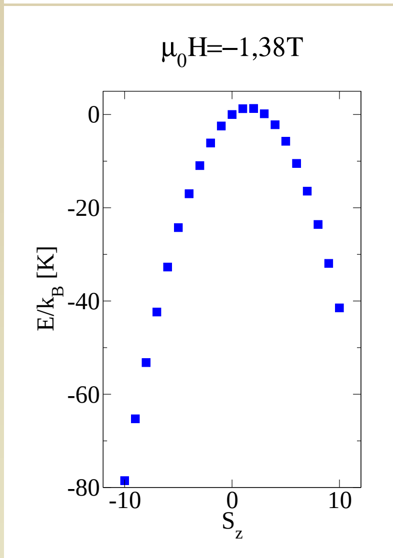
Proces magnetiziranja

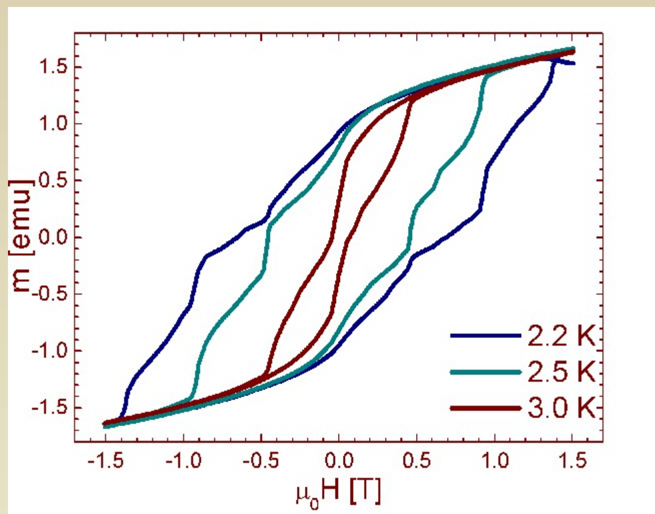












Hamiltonijan

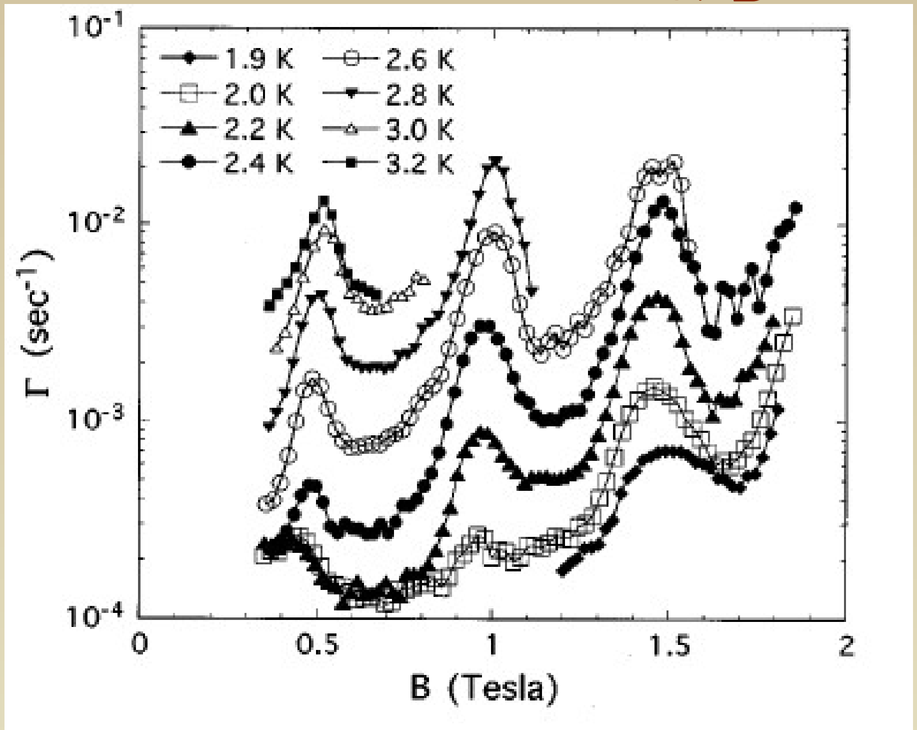
* $\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z$

Hamiltonijan

- $\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z - g\mu_B H_x S_x - C((S^+)^4 + (S^-)^4)$
- $D/k = 0,61K$, $C/k = 0.03mK$
- Svojstvene energije: $E = -DS_z^2 - g\mu_B H_z S_z$
- Nedijagonalno međudjelovanje
  - dipolna polja (100G)
  - nuklearna polja (500G): nasumična (usrednjenje 100-200G)
  - anizotropija
  - spin-fonon

Rezonantno tuneliranje

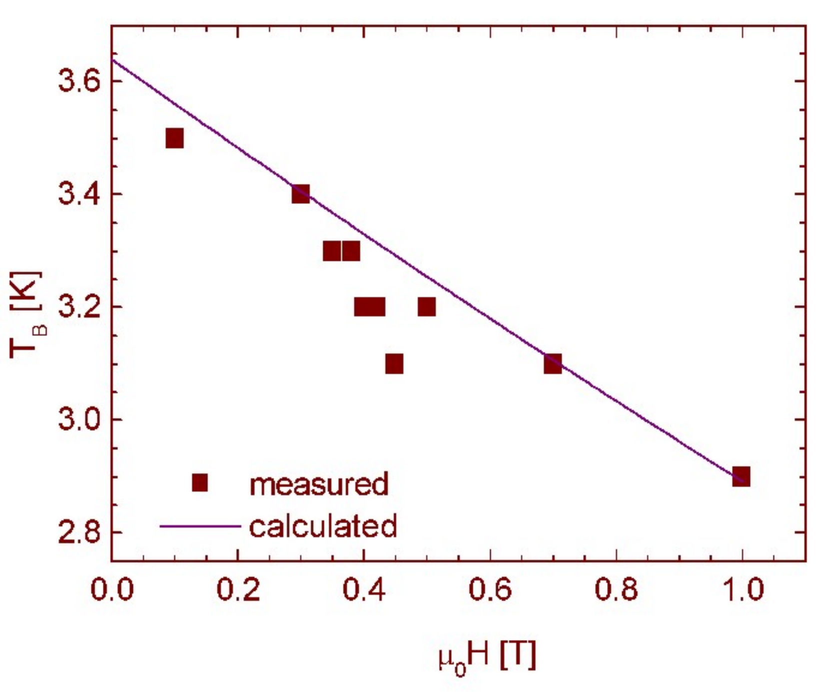
$$E_R = E_L \Rightarrow H_z = \frac{D}{g\mu_B} \cdot n$$



Hernández et al, PRB <u>55</u> (1997) 5858

Rezonantno tuneliranje

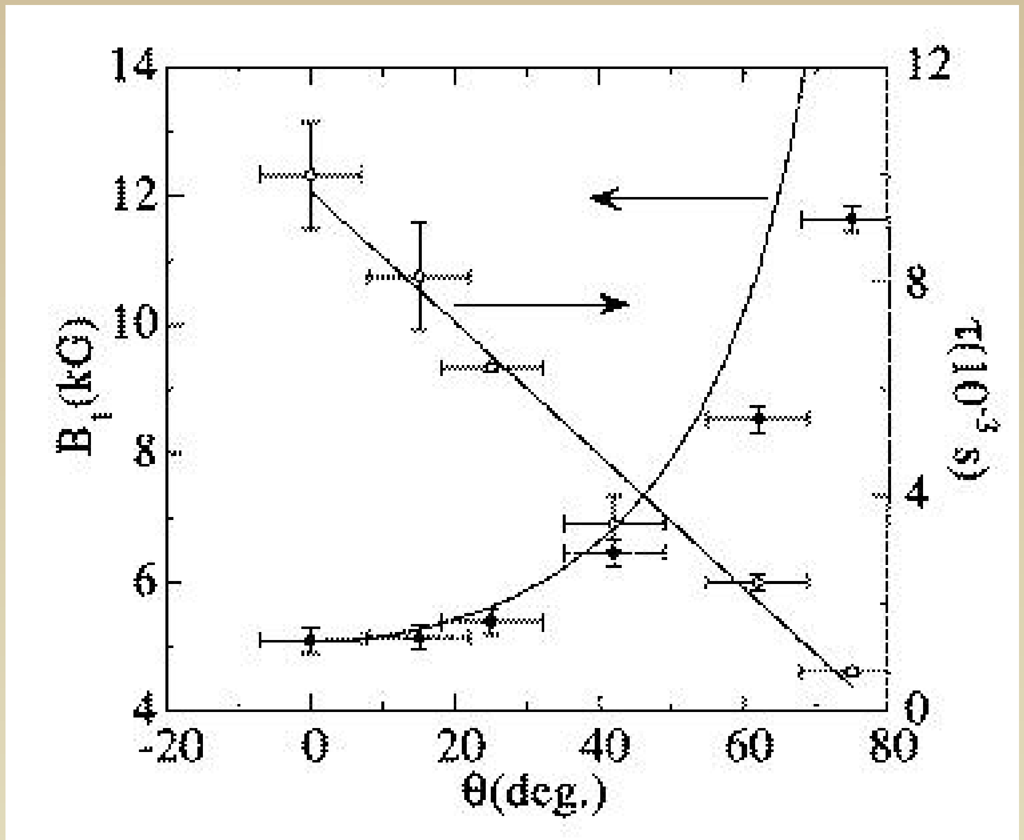
monotono i nemonotono



* H_z mijenja barijeru

* H_z ostvaruje rezonanciju

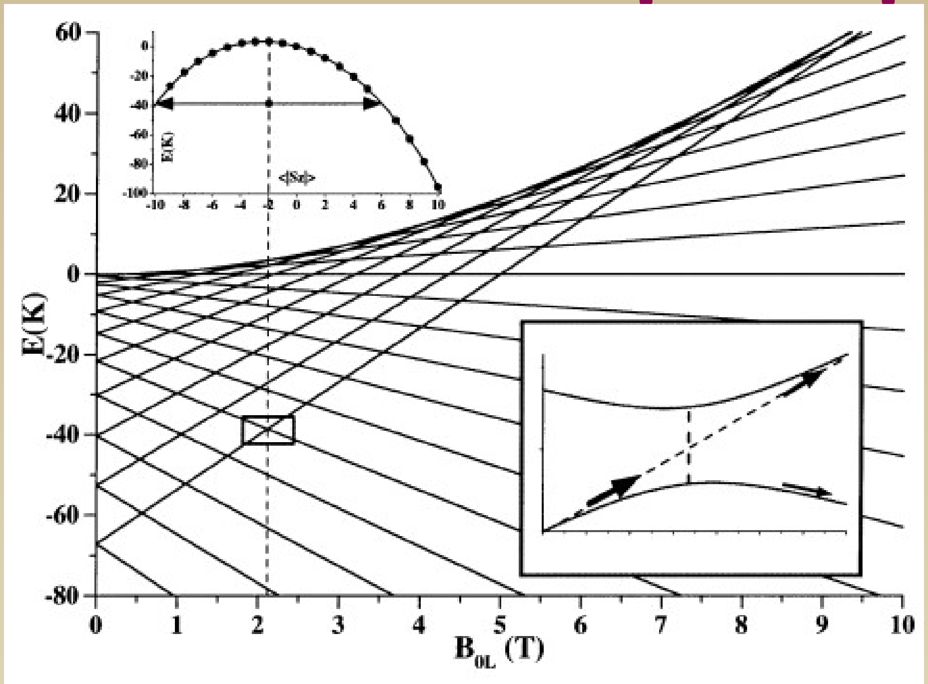
Rezonantno tuneliranje



Hernández, Zhang, Luis, Bartolomé, Tejada, Ziolo, Europhys.Lett. 35 (1996) 301

$$H_0 \frac{1}{\cos\theta}$$

Landau-Zener pristup



* Tuneliranje S_z iz m u $n - m$

* $P_{m,n} = 1 - e^{-\frac{\pi \Delta^2}{2g\mu_B(2m-n)\frac{\mathrm{d}H}{\mathrm{d}t}}}$

Mehanizam prijelaza

- Transverzalno polje utječe na tuneliranje

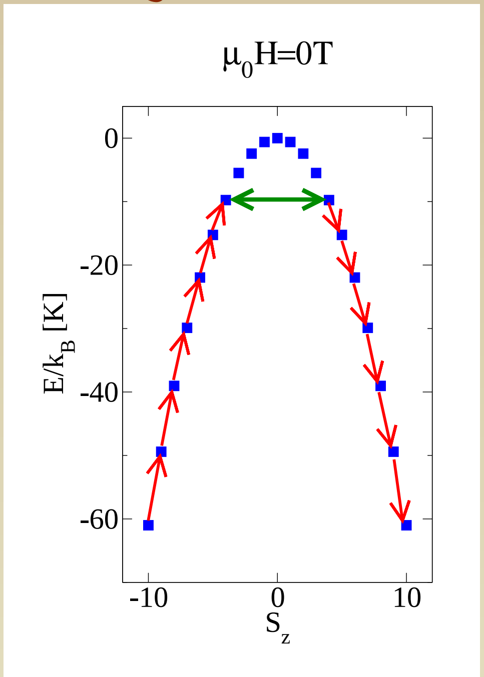
- $\Delta\epsilon_{mm'} = \frac{2D}{[(m'-m-1)!]^2} \cdot \sqrt{\frac{(S+m')!(S-m)!}{(S-m')!(S+m)!}} \cdot (\frac{H_x}{2D})^{m'-m}$
  - Garanin i Chudnovsky: PRB 56 (1997) 11102
  - $\Delta\epsilon_{mm'} = 2V_{m,m+1}\frac{1}{\epsilon_{m+1}-\epsilon_m}V_{m+1,m+2}\frac{1}{\epsilon_{m+2}-\epsilon_{m+1}} \dots V_{m'-1,m'}$
  - $V_{m,m+1} = \langle m|H_x S_x|m+1\rangle = \frac{1}{2}H_x\sqrt{S(S+1)-m(m+1)}$

$-m, m'$	10	9	8	7	6	5	4	3	2	1
Γ	2,1E-45	1,1E-37	1,7E-30	1,2E-23	3,7E-17	4,7E-11	2,3E-5	3,5E0	1,1E5	3,2E8

Termički potpomognuto tuneliranje

Arrhenius + rezonancija

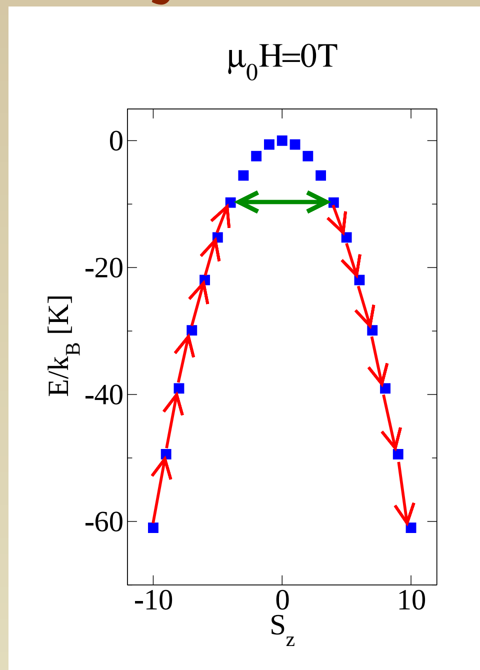
naseljenost + brzina tuneliranja

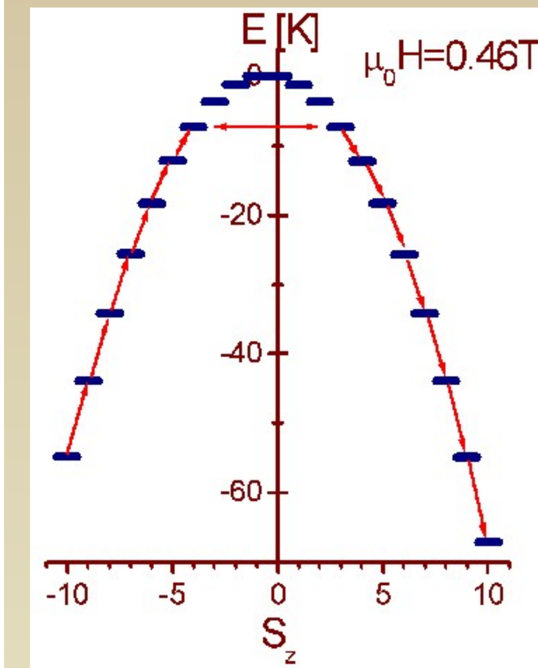


Termički potpomognuto tuneliranje

Arrhenius + rezonancija

naseljenost + brzina tuneliranja

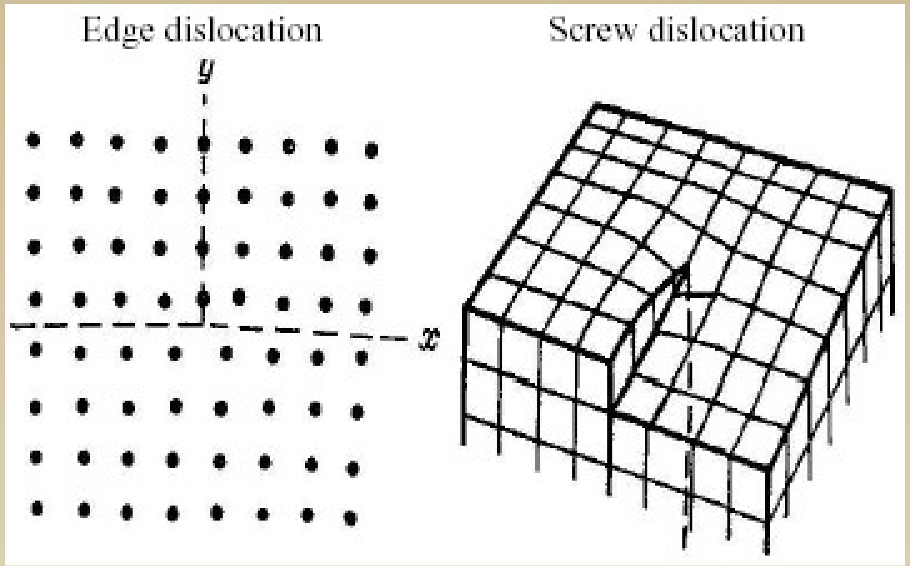




Nešto tu nedostaje ...

* Problemi
  - H_x preslabo
  - odstupanje od $M \propto e^{-t/\tau}$
  - "smjesa dvaju uzoraka" ?

Dislokacije



* Glavni razlog tuneliranja: dugodosežna izobličenja
* Lokalno zakretanje osi anizotropije
* Longitud. polje ima lokalnu transverz. komponentu

Magneto-elastično vezanje

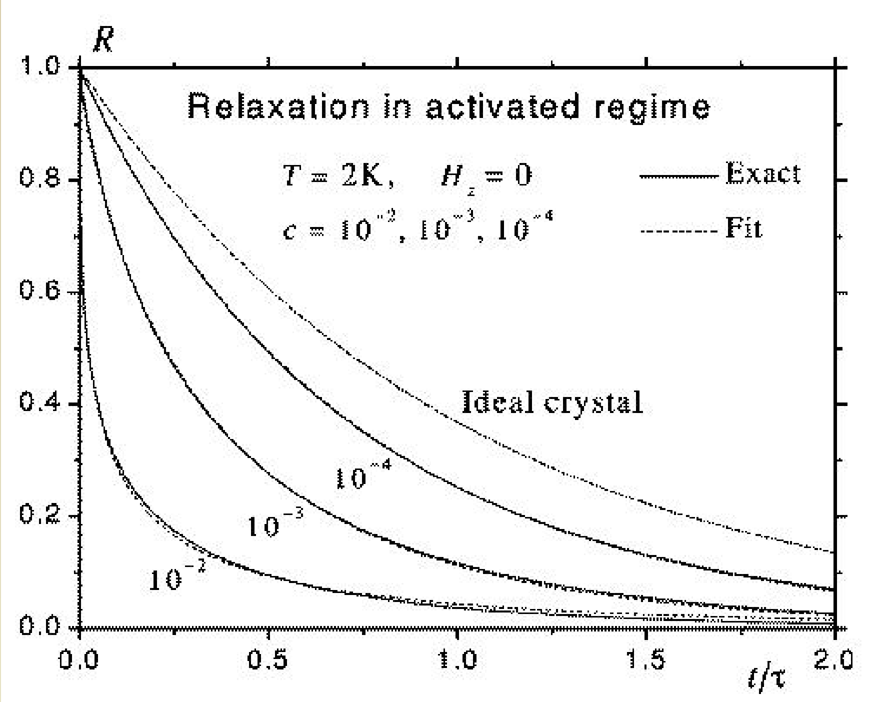
* $\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z + \mathcal{H}_{m-e}$
* Garanin & Chudnovsky, PRB **65** (2002) 094423
* $\mathcal{H}_{m-e} = g_1 D(\epsilon_{xx} - \epsilon_{yy})(S_x^2 - S_y^2) + g_2 D\epsilon_{xy}\{S_x, S_y\} + D((g_3\epsilon_{xz} + g_4\omega_{xz})\{S_x, S_z\} + (g_3\epsilon_{yz} + g_4\omega_{yz})\{S_y, S_z\})$
* ("rubna"+"vijčana")x("transverz."+"longitud.")
* $\mathcal{H} = \mathcal{H}_0(z, \mathrm{ili} z') + E(S_{x'}^2 - S_{y'}^2) - H_{x'}S_{x'} - H_{y'}S_{y'}$
* $E = 2D\frac{g(\phi)}{r}$ i $H_\perp = H_z\frac{g_H(\phi)}{r}$

Rezultat magneto-elastičnog vezanja

* Dobivena su "bolja" transverzalna polja

* Objašnjeno postojanje raspodjela rezonantnih polja i visina barijera

* Temperatura prijelaza kvantno-klasično široko raspodijeljena



Drugi jednomolekulski magneti

* "Fe_8"
* Mn_{12}-formijat
* Prstenovi $LiFe_6$, Fe_{10}, Fe_{18} u kompleksnoj strukturi
* Kompleksi Cr uokvireni u CN

Eksperimentalne tehnike

* MPMS5 magnetometar *: (1.8K-300K, 5T)
* AC susceptibilnost
* EPR
* NMR
* Mössbauer
* Toplinski kapacitet

Zaključak

* Bogatstvo instantonskih rješenja za tuneliranje magnetizacije
* Predviđanje eksperimentalnih mogućnosti, ali ne i kako ih izvesti
* Uočavanje prelaska na kvantni režim relaksacije magnetizacije kod magnetskih nanočestica
* Tuneliranje magnetizacije kod jednomolekulskih magneta vidljivo na makroskopskoj skali
* Dislokacije u objašnjavanju magnetske relaksacije

Da, i?

* Kvantni superparamagnetizam?
* Makroskopska kvantna koherencija?
* Opis relaksacije magnetizacije pri rezonanciji?
* Kvantitativna veza između dislokacija i magnetskih svojstava?
* Utjecaj kristalne vode i octene kiseline na neuređenost?

* Ograničenost magnetskih mjerenja?
* Suradnja eksperimentalnih i teorijskih tehnika?
* Kvantno računalo? $\smile$