National Institute for Research & Development of
Isotopic and Molecular Technologies
Cluj-Napoca, Romania

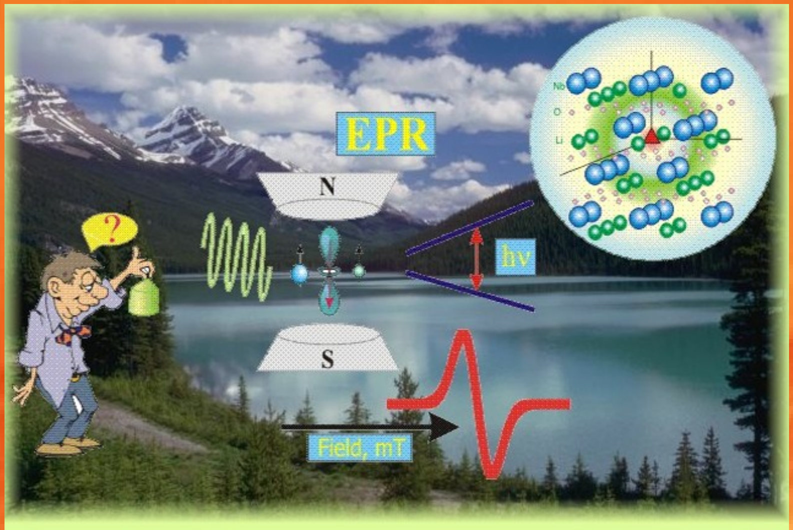
AL VII- LEA SEMINAR DE NANOSTIINTA SI NANOTEHNOLOGIE , 20 MARTIE 2008 , ACADEMIA ROMANA, BUCURESTI

MAGNETIC RESONANCE, PNCDI-II AND THE TRANSYLVANIANS

LIVIU MIHAIL GIURGIU


Primavara… o picatura parfumata
cu vibrari de violet.
G. Bacovia

MAGNETIC RESONANCE
ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY



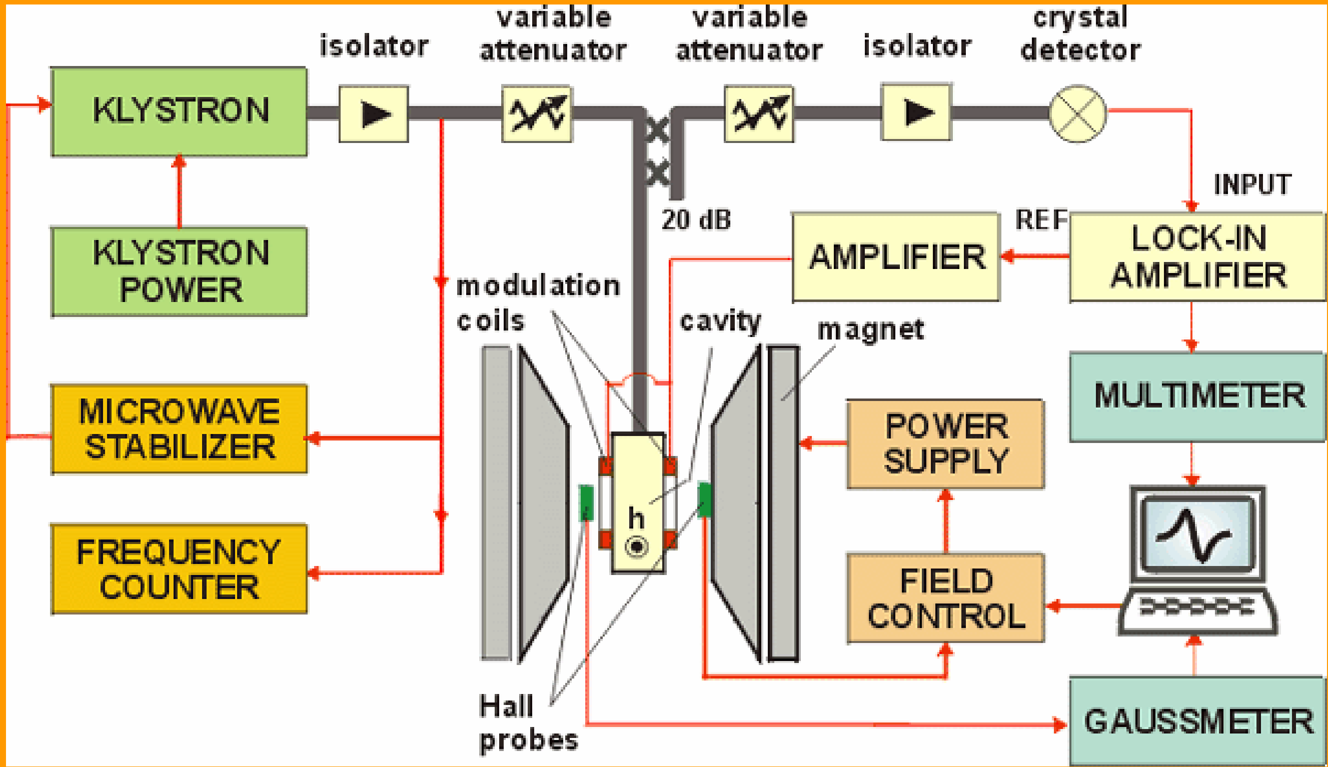
- ***ESR*** **is a powerful non-nondestructive and non-intrusive tool for studying microscopic details of novel materials.**

- ***ESR spectroscopy*** **yields meaningful dynamic**
  -information in a wide range of applications areas:
  -physics, materials research, chemistry, biology, medicine and environment.

- **Including *multi-frequency ESR investigations* among the objectives or activities of the complex and exploratory research projects within the framework of PNCDI – II, it could increase the novelty and original degree of the proposed projects.**

APLICATII PRINCIPALE ALE RES

RES este o metoda spectroscopica care detecteaza prezenta electronilor neimperechiati din proba



FIZICA

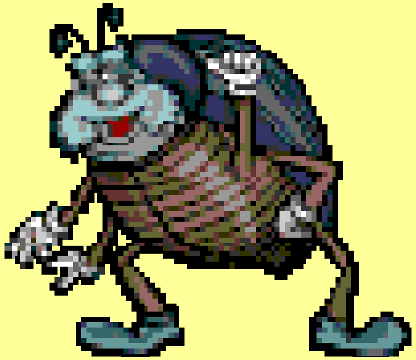
- concentratii de spin
- ioni paramagnetici ai metalelor de tranzitie, pamanturilor rare si actinidelor
- defecte paramagnetice, centrii de culoare, deformari locale
- electroni de conductie in conductori si semiconductori
- interactii magnetice si cristaline
- procese de recombinare la temperature scazute

CHIMIE

- radicali liberi
- cataliza
- procese de oxidare si reducere
- stari de triplet a moleculelor
- compusi organo-metalici si zeoliti
- cinetica de reactie si reactii de polimerizare

BIOLOGIE, MEDICINA, MEDIU

- markeri de spin
- antioxidanti si agenti de contrast
- oximetrie
- radicali liberi in tesuturi, radicali ai oxigenului, NO in sisteme biologice
- fotosinteza
- detectie droguri, metabolism si toxicitate
- factori poluanti



APLICATII INDUSTRIALE

- controlul calitatii produselor alimentare irradiate
- dozimetrie pentru procesele de iradiere
- varste si datari de materiale cu aplicatii in arheologie, geologie
- detectia radicalilor in polimeri iradiati si procese de coroziune
- prospetimea uleiurilor vegetale
- controlul calitatii sticlelor optice speciale
- procese oxidative in vopsele utilizate in industria auto

CARACTERIZARI MATERIALE

- proprietati ale polimerilor
- defecte in fibre optice
- materiale laser
- conductori organici si anorganici cu dimensionalitate redusa
- influenta impuritatilor si defectelor in semiconductori
- proprietati ale noilor materiale magnetice
- proprietati ale materialelor utilizate in spintronica, optoelectronica manganiti cu magnetorezistenta colosala
- supraconductori oxidici cu temperature de tranzitie ridicata semiconductori

NANOMATERIALE, NANOSTIINTE

- efecte ale reducerii dimensionalitatii
- dinamica de spin in nanomateriale, nanocompozite
- efecte miez interior - strat superficial ale nanoparticulelor magnetice
- proprietati ale nanoparticulelor si nanofirelor magnetice
- interactii magnetice dipolare si de schimb: efectele dimensiunii
- nanometrologie: dimensiune medie a nanoparticulelor metalice si magnetice
- caracterizare nanotuburi de carbon, fullerene si compusi derivati
- proprietati ale conductiei electrice si transportului polaronic

THE APPLICATION OF ESR IN NANOSCIENCE

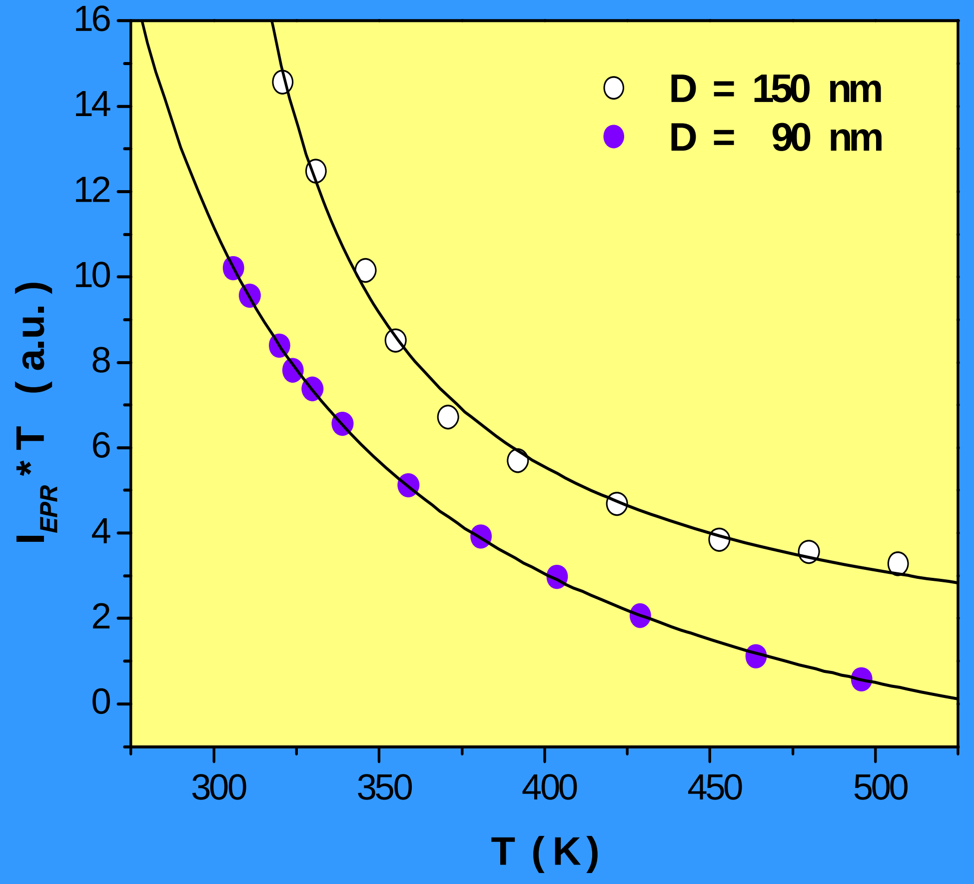
OUR RESULTS

- **SPIN DYNAMICS IN NANOSTRUCTURED MATERIALS WITH COLOSSAL MAGNETORESISTENCE**

- **NANOMETROLOGY OF METALLIC AND MAGNETIC NANOPARTICLES**

- **MAGNETIC INTERACTIONS IN FERROMAGNETIC NANOWIRES**

COMPARISON OF THE TEMPERATURE DEPENDENCIES OF $I_{ESR} * T$ FOR NANOSIZED $La_{0.67} Ca_{0.23} Mn O_{3-\delta}$ MANGANITES



Exchange coupling integral J between Mn spins as function of grain size

$La_{0.67}Ca_{0.33}MnO_{3-\delta}$	J (K)
ceramic	116
nanosized	
D = 150 nm	87
D = 90 nm	39

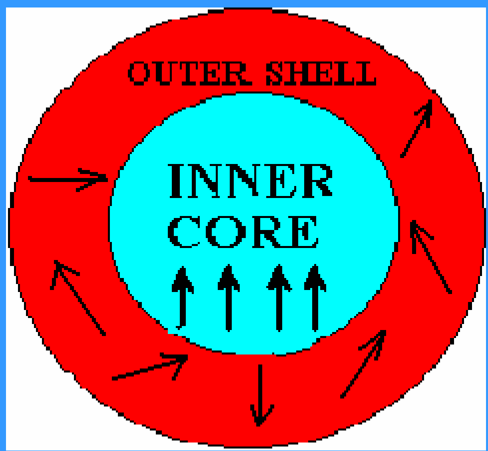
EXCHANGE COUPLING INTEGRAL J BETWEEN Mn SPINS IN NANOSIZED $La_{0.67}Ca_{0.33}MnO_{3-\delta}$

J decreases with D ↓

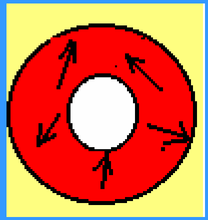
Reasons for the degradation of DE interaction

Two similar contributions

(inner core , outer shell)



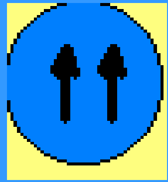
A) OUTER SHELL OS →



- Increased influence of OS in *smaller grains*
- J in OS much weaker than in IC

Exchange coupling J in OS decreases when D ↓

B) INNER CORE IC →



- T_C ↓ with D ↓

Exchange coupling J in IC decreases with D ↓

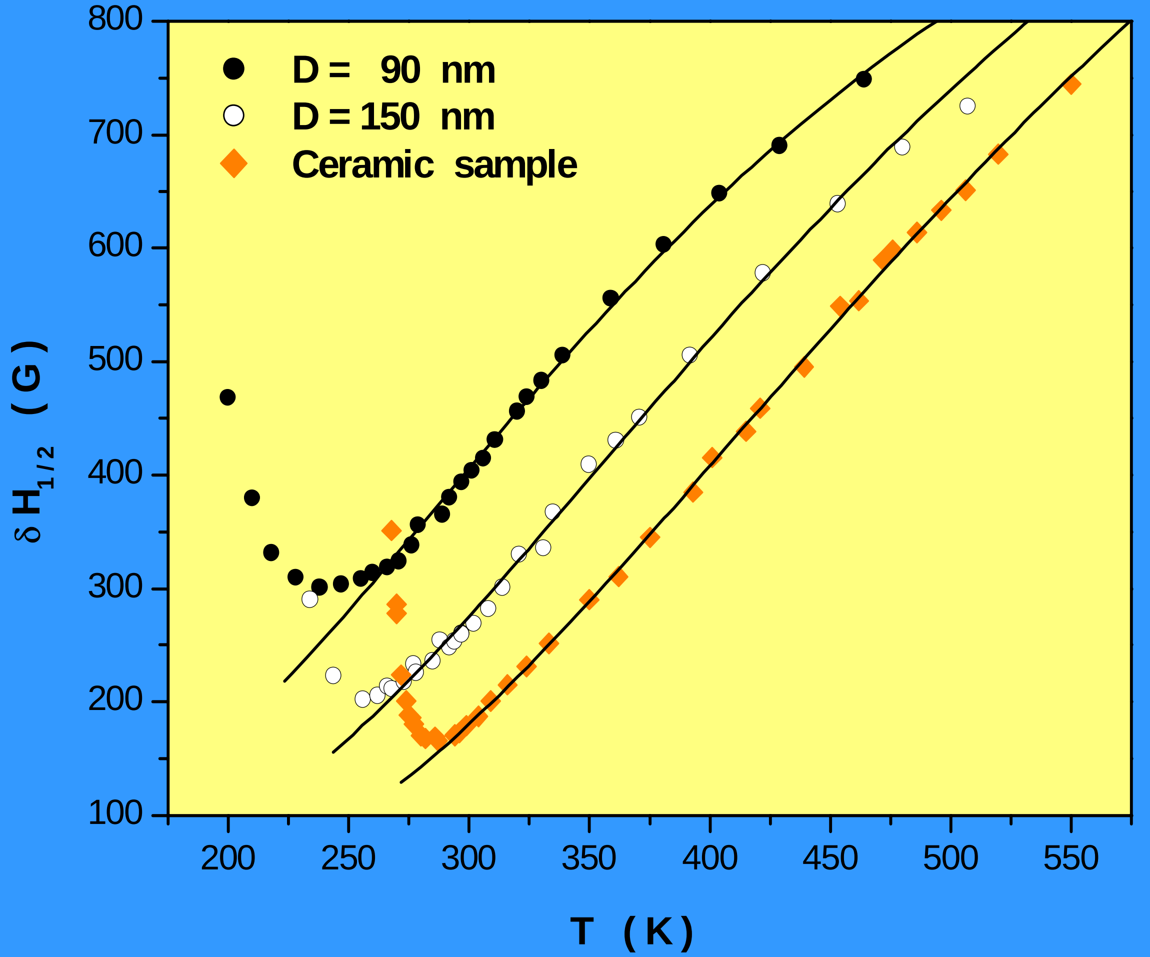
IINFLUENCE OF STRUCTURAL CHANGES ON J

Increase Mn – O bond

Decrease of Mn – O - Mn bond angle ⇒ J ↓

(de Gennes : Phys. Rev. 118, 141, 1960)

TEMPERATURE DEPENDENCIES OF THE LINEWIDTH $\delta H_{1/2}$ FOR $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ SAMPLES FITTED WITH THE SMALL POLARON MODEL



$$\delta H_{1/2}(T) = \delta H_0 + AT^{-1}\exp(-E_a / k_B T)$$

Polaron activation energy E_a and the residual linewidth δH_0 as function of grain size in the paramagnetic regime of

nanostructured $La_{0.67} Ca_{0.33} Mn O_{3-\delta}$

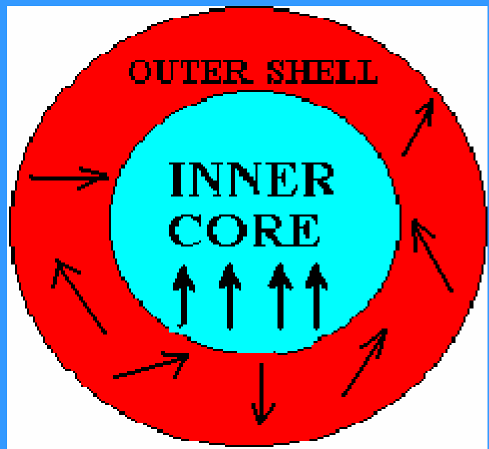
$La_{0.67} Ca_{0.33} Mn O_{3-\delta}$	E_a (meV)	δH_0 (G)
ceramic	120	24
nanosized		
D = 150 nm	104	42
D = 90 nm	83	70

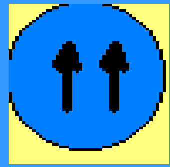
POLARONIC EFFECTS IN NANOSTRUCTURED $La_{0.67}Ca_{0.33}MnO_{3-\delta}$

E_a decreases with D ↓

Two opposite contributions

(inner core , outer shell)

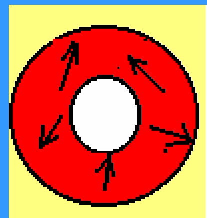


A) **INNER CORE IC →** 

Mn^{4+} content ↑ (Mn^{3+}↓) with D↓

E_a ↑ when Mn^{3+} content ↑

E_a ↓ with Mn^{4+} content ↑ or D ↓

B) **OUTER SHELL OS →** 

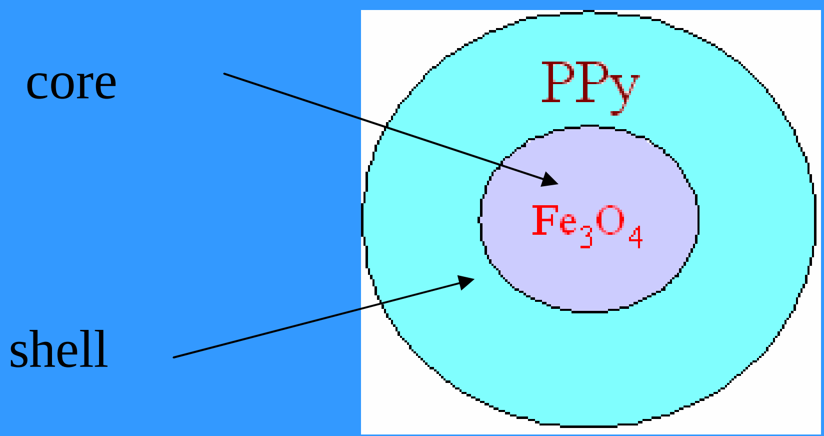
- **Mn^{3+} and Mn^{4+} spins are disordered**
- **defects, oxygen vacancies ⇒ higher energy barrier for e_g polarons to hope over**

E_a ↑ as disorder in OS ↑ in smaller grain

Inner-core contribution to E_a is dominant

MAGNETITE:

CORE – SHELL Fe_3O_4 / PPy NANOPARTICLES



Nanometrology by ESR:

size determination of core-shell Fe_3O_4 / PPy nanoparticles

TEMPERATURE DEPENDENCE OF ESR LINEWIDTH

P.C. Morais et. all. Phil. Mag. Letters ***55****, 181 (1987)*

$$\Delta H = \Delta H_R^0 \tanh\left(\frac{\Delta E}{2k_B T}\right)$$

$$\Delta E = \left(K_B + k_{eff} T\right) V$$

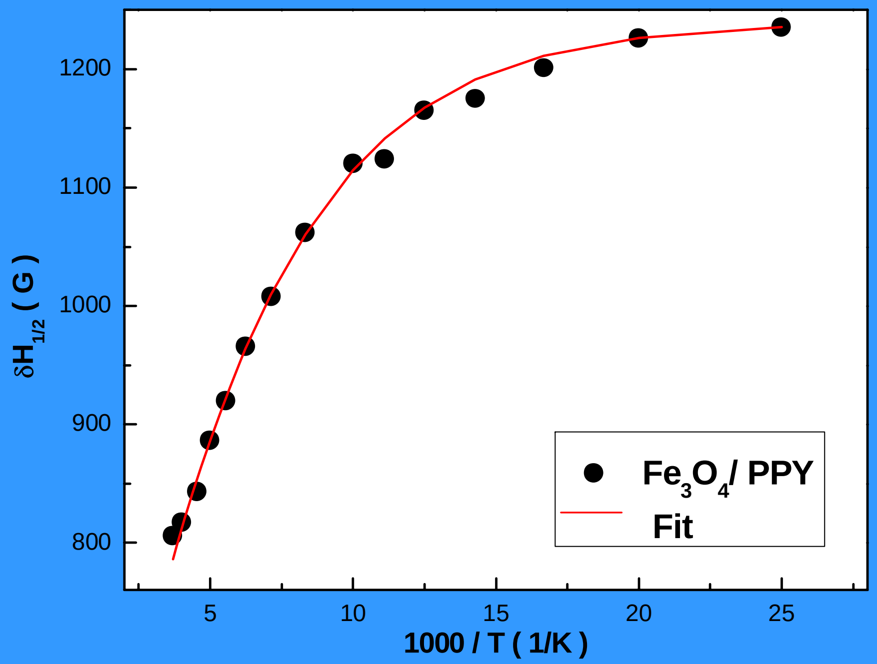
$$\Delta H = \Delta H_R^0 \tanh\left(\frac{K_B}{2k_B T} V + \frac{k_{eff}}{2 k_B} V\right)$$

V – nanoparticle's volume

$$D_m = \sqrt[3]{\frac{6V}{\pi}}$$

D_m – mean diameter

$\Delta H = f(T)$ FOR PPy-Fe_3O_4 CORE-SHELL NANOPARTICLES



K_B = 6.4 x 10^4 erg cm^{-3} ⟶ bulk value

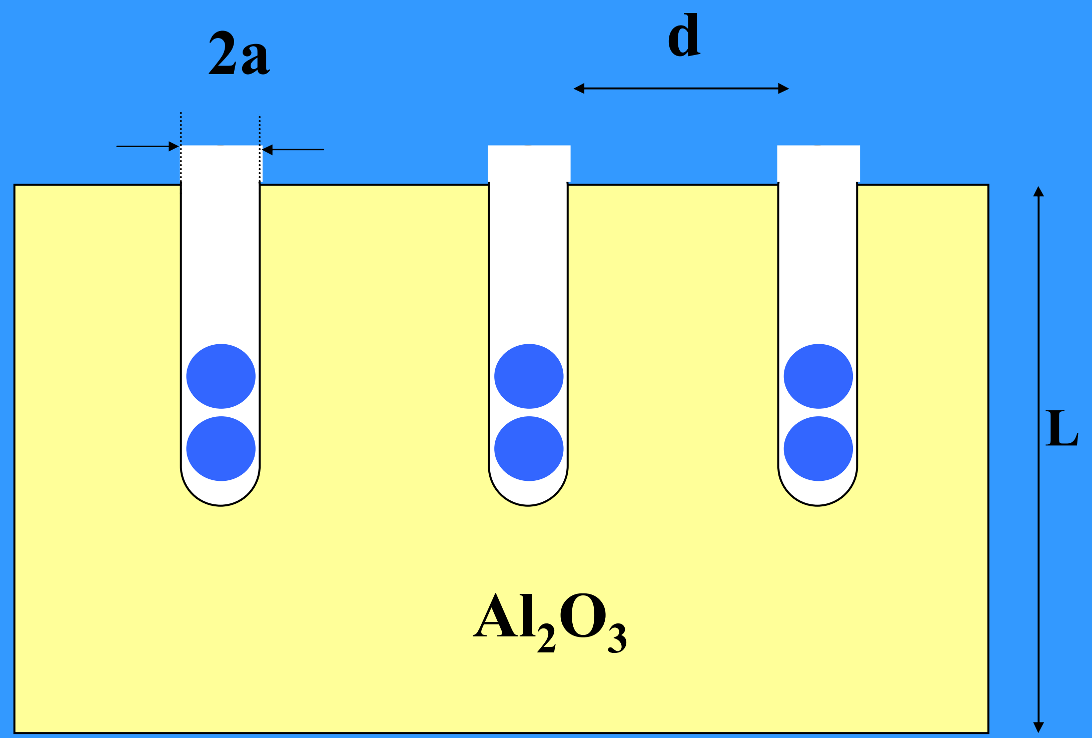
k_{eff} = 229 G^2 K^{-1} ⟶ from $H_R = f(T)$

Mean diameter of PPy-Fe_3O_4 nanoparticles

D_m (ESR) ≈ 12 nm **compared with D_m (TEM) ≈16 nm**

Nanometrology by CESR

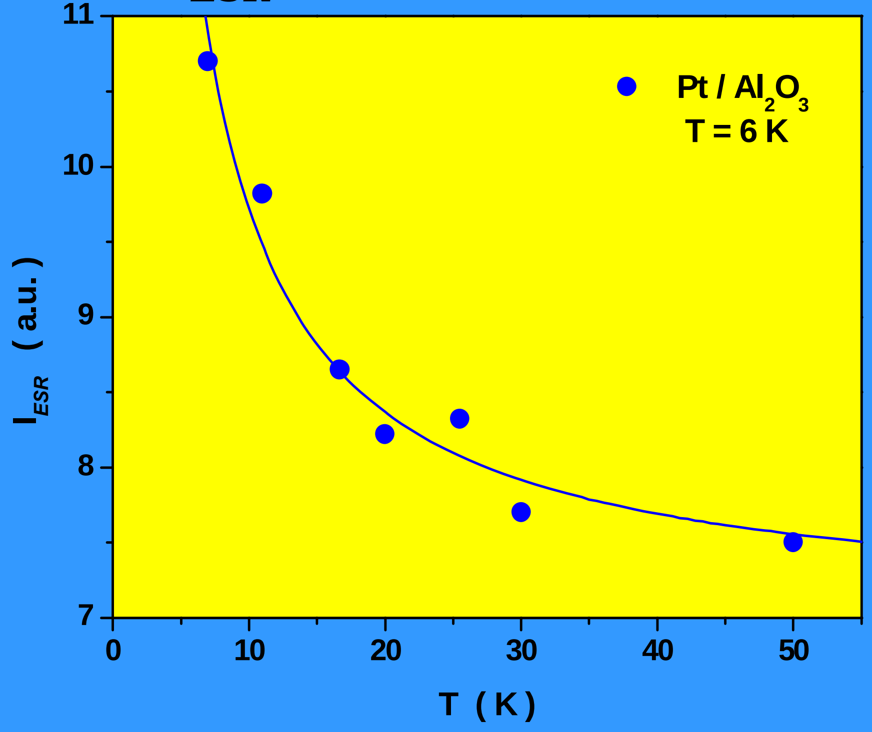
- *Pt – nanoparticles* electrodeposited in the channels of porous Al $_2O_3$



2a = 12 nm
d = 30 nm

QUANTUM SIZE EFFECTS IN Al_2O_3 / Pt

1. I_{ESR} follows a Curie law



2. *g – factor* and *ESR linewidth* *are temperature independent*

g = 2.092 **$\Delta H_{1/2}$ = 242 (G)**

3. Observation of *Pt –ESR* signals : large spin-orbit coupling

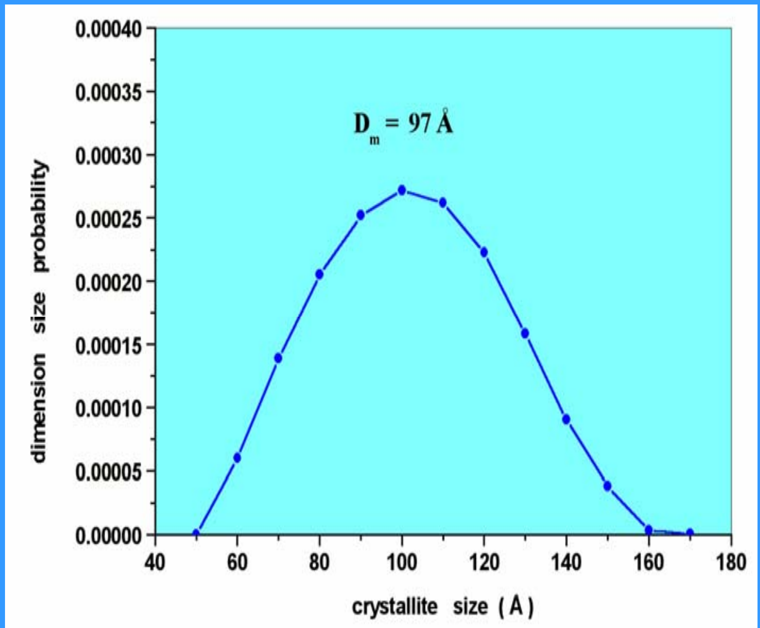
Pt – metallic nanoparticles

$$\Delta H_{1/2}\,(\,G\,) \approx 7.776\, d_m^{\,2}\ (nm\,)$$

Experimental $\Delta H_{1/2} = 242$ (G) for Al_2O_3 / Pt

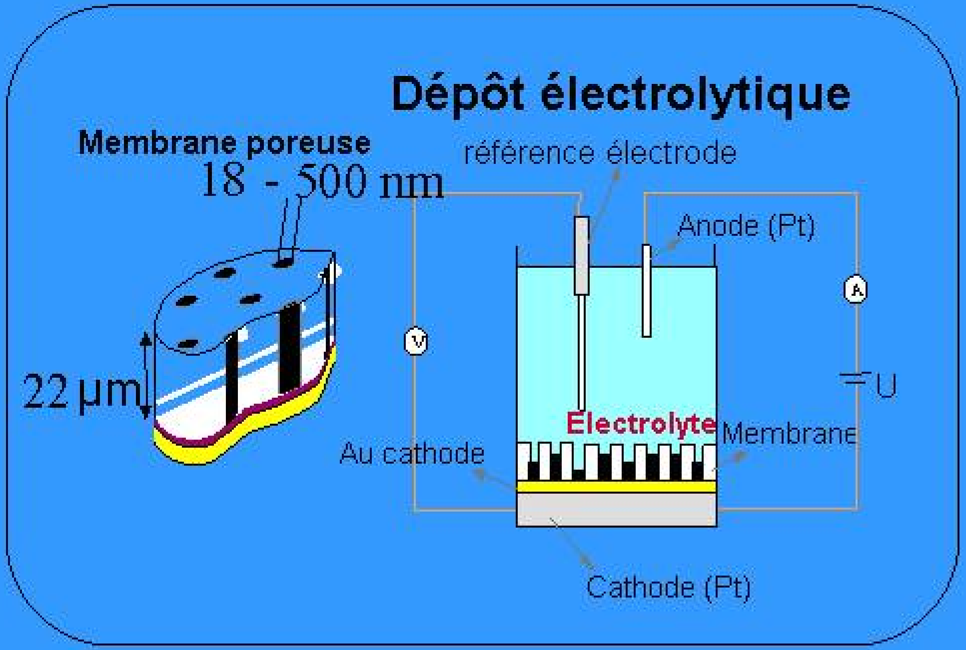
d_m (Pt-CESR) ≈ 6 nm

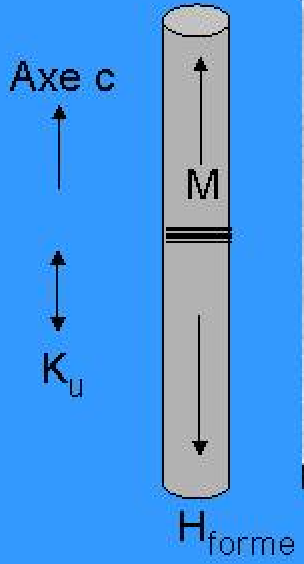
Crystallite size distribution function

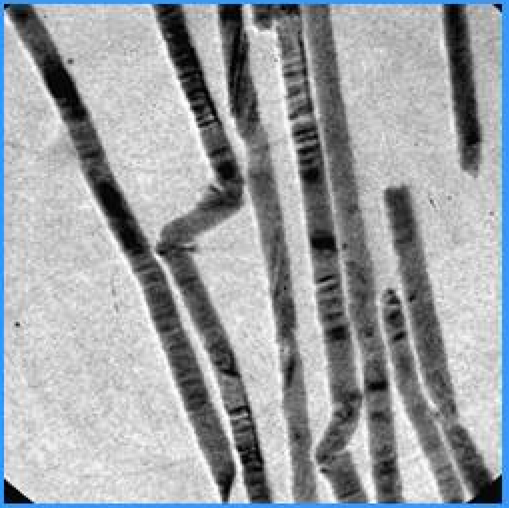


Compared with
crystallite size
$D_m = 9.7$ nm

1D – CHAINS OF FERROMAGNETIC NANOWIRES





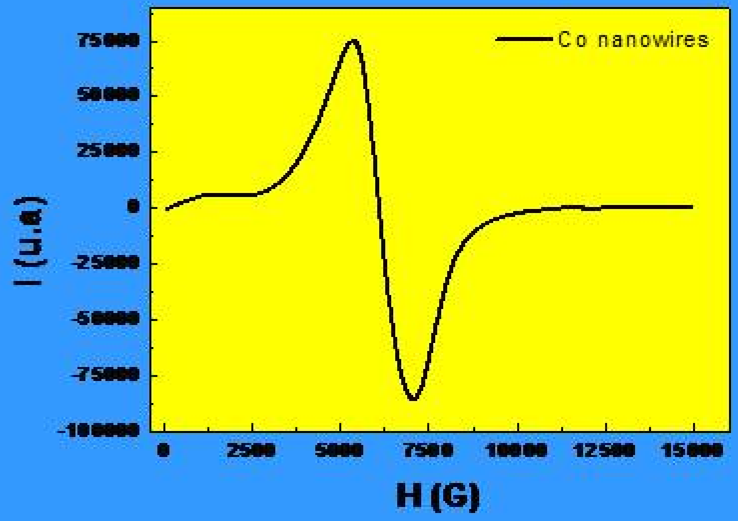


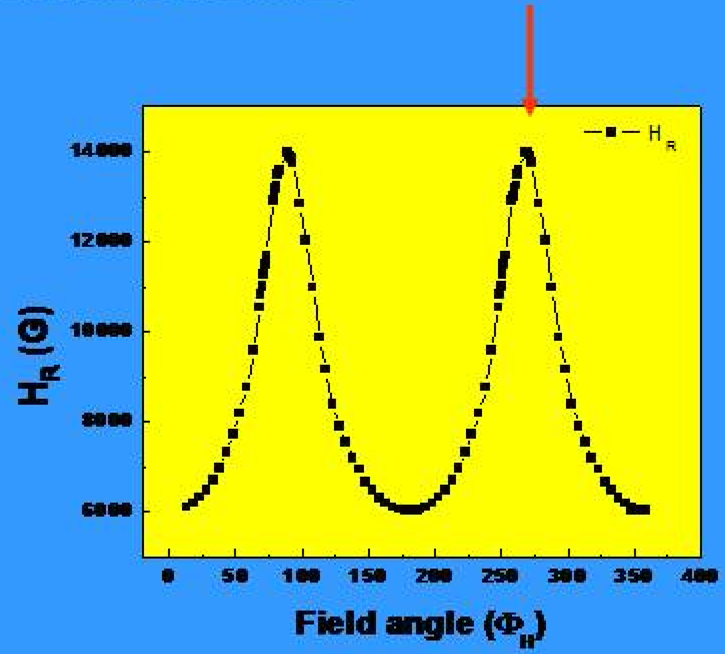
Co , Ni - ferromagnetic nanowires

Porous membranes : Al_2O_3 , polycarbonates

Q- BAND ESR: ANISOTROPY MAGNETIC FIELD

CO NANOWIRES IN POLYCARBONATES





$$\frac{\omega}{\gamma} = \left[\left\{H_{eff}\cos 2\theta_0 + H_{res}\cos(\theta_0 - \theta_H)\right\} \times \left\{H_{eff}\cos^2\theta_0 + H_{res}\cos(\theta_0 - \theta_H)\right\}\right]^{1/2}$$

$$H_{eff} = H_u + 2\pi M_S$$

H_u - anisotropy field

H_u = 5.2 kOe

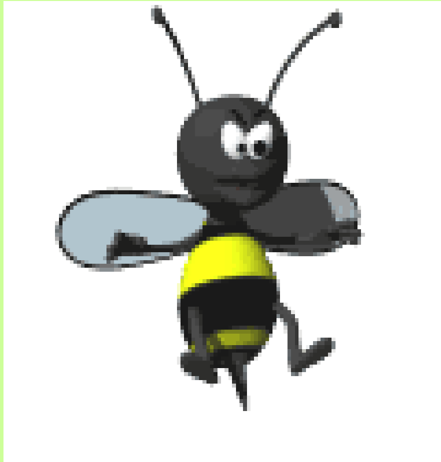
Spectrometru

REZONANTA ELECTRONICA DE SPIN IN MULTIFRECVENTA

Achizitionat in cadrul PNCDI-II, programul de capacitati
proiect nr. 127CP / I / 14.09.2007

Benzi de frecventa* X - *9.8 GHz ;* Q - *34 GHz
***Domenii de temperatura variabila* 4 - 300 K; 300 - 600 K**
LINUX Workstation , pachet software pentru control, achizitie date si procesari 1D si 2D

Specificitati ale RES in multifrecventa / frecventa inalta



-**caracteristici ale dinamicii de spin in functie de frecventa**

-**identificarea, separarea si caracterizarea proceselor de interactie si relaxare magnetica dependente de frecventa**

- separarea contributiilor provenind de la miezul interior si stratul superficial al nanoparticulelor magnetice

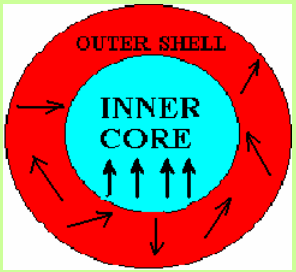
-**identificarea centrilor paramagnetici cu valori apropiate ale campurilor magnetice de rezonanta**

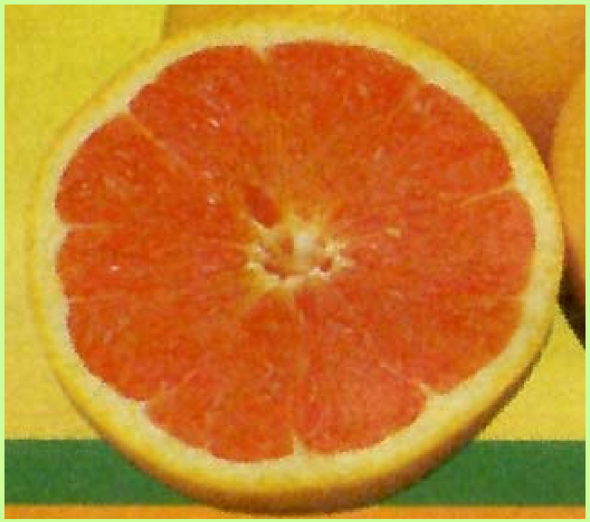
MULTIFREQUENCY ESR (10 AND 34 GHZ)

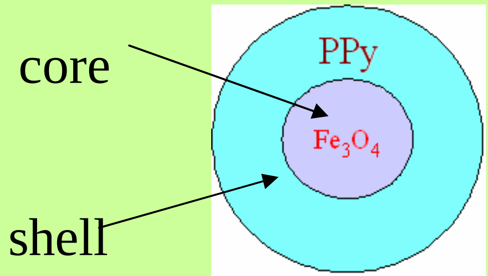
PROVIDES AN EXPERIMENTAL ROUTE TO STUDY CORE – SHELL EFFECTS IN NANOPARTICLES

Model

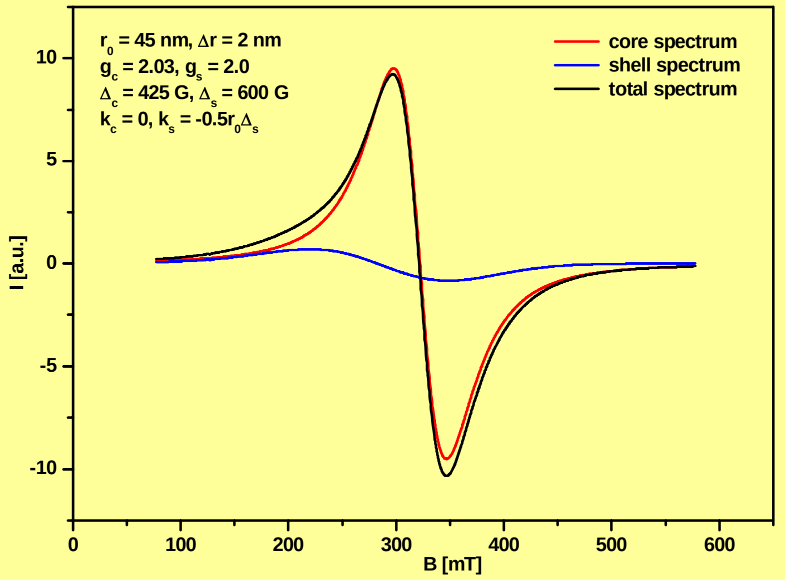
Inner Core - Surface Layer



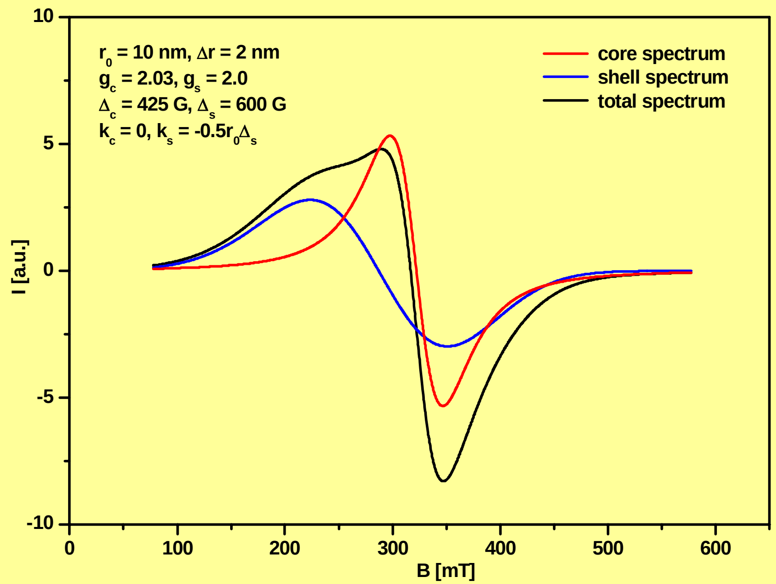




$d = 90\ nm$ $k_c = 0$; $k_s \neq 0$



$d = 20\ nm$ kc = 0; ks≠ 0



Critical size $d_0 \approx 20\ nm$

RES IN MULTIFRECVENTA

Relaxari magnetice de spin

$$(\Delta H)_{RES} \approx (T_2)^{-1}$$

T_2 – viteza de relaxare spin-spin

$(T_2)^{-1}$ → $(T_2)_d^{-1}$, $(T_2)_h^{-1}$

$(T_2)_d^{-1}$ - Fluctuati locale dipolare

$(T_2)_h^{-1}$ - Fluctuatiile campului hiperfin

$$(T_2)_d^{-1} \propto C_d(T)\left[(1-3\cos^2\theta)^2 J(0) + 10\sin^2\theta\cos^2\theta J(\omega) + \sin^4\theta J(2\omega)\right]$$

$$(T_2)_h^{-1} \propto C_h(T)\left[4(1-3\cos^2\theta)^2 + 18\sin^2\theta\cos^2\theta\right]J(0) + \left[(1-3\cos^2\theta)^2 + 36\sin^2\theta\cos^2\theta + 9\sin^4\theta\right]J(\omega)$$

$J(\omega)$ – functia de densitate spectrala

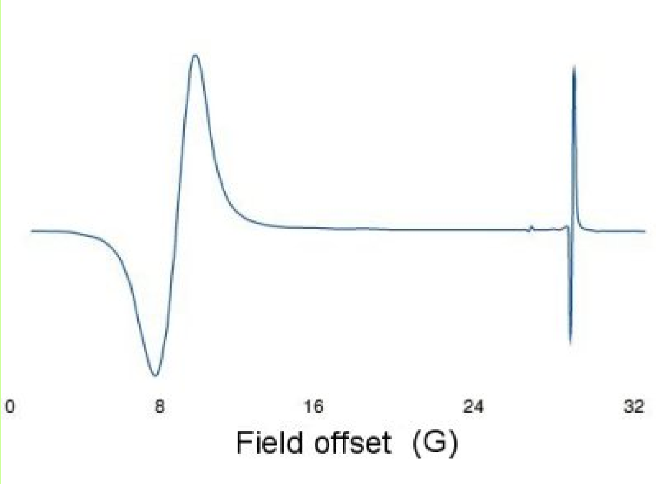
Investigatii RES = f(ω)

Identificarea mecanismului dominant in procesul de relaxare magnetica spin-spin

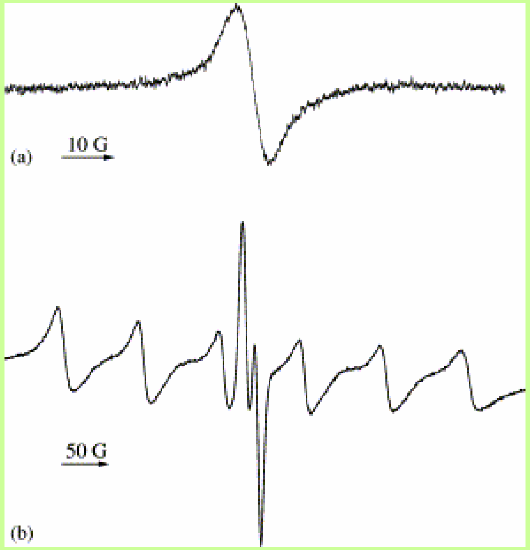
HIGH – FREQUENCY Q –BAND ESR

ABILITY TO STUDY VERY SMALL SAMPLES

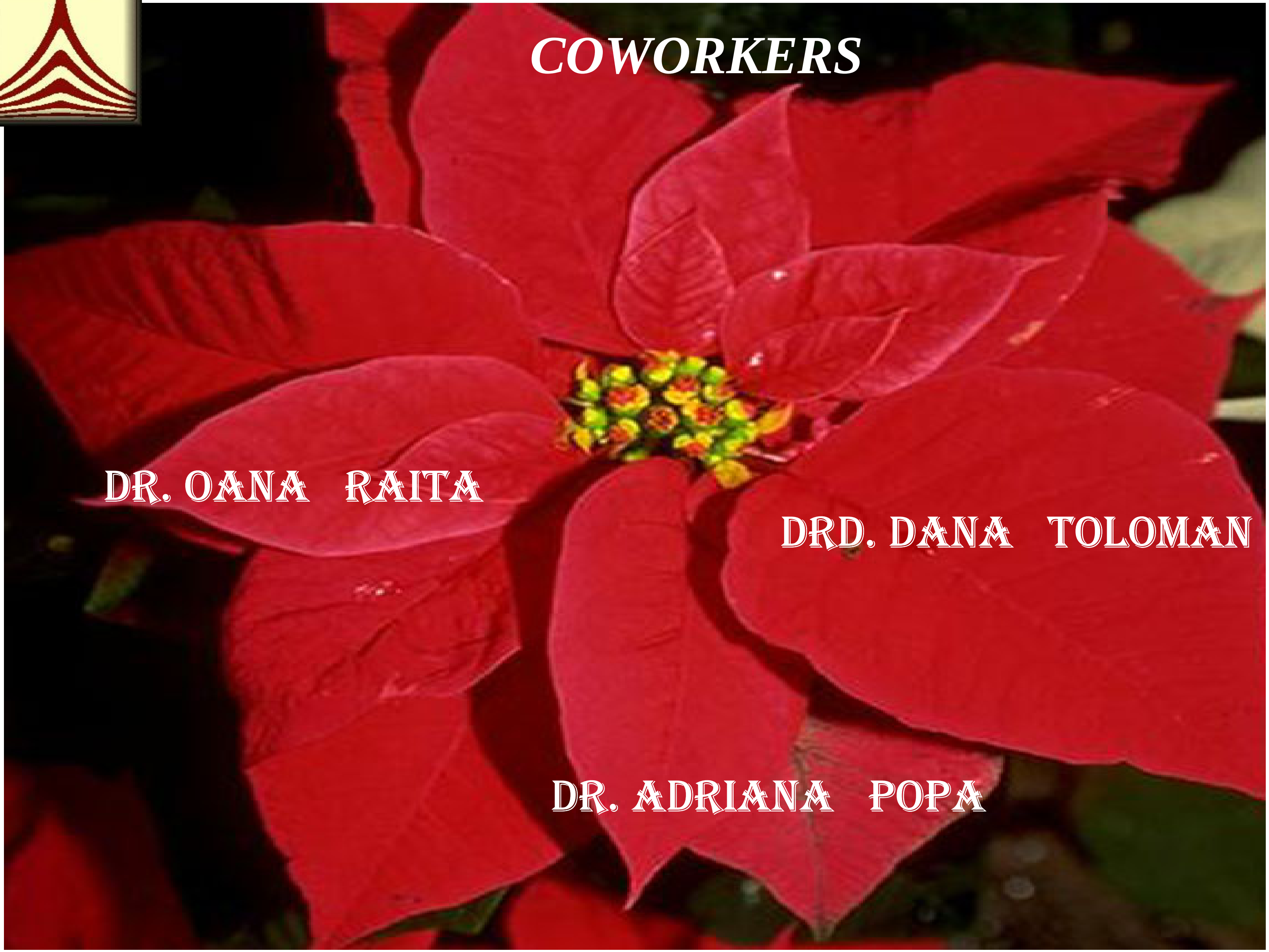
HIGH RESOLUTION AND DISCRIMINATION BETWEEN SIMILAR SPECIES



At 10GHz, these two features would not be separated, so high field ESR allows us to detect a small amount of one material in the presence of another



Transylvanian point of view referring to the implementation of the projects within the framework of PNCDI-II-capacities programme


COWORKERS
DR. OANA RAITA
DRD. DANA TOLOMAN
DR. ADRIANA POPA

- *Gabriel Garcia Marquez - ultima scrisoare din “veacul de singurătate”.*

- ***Unui copil i-aş da aripi, dar l-aş lăsa să înveţe să zboare singur.***

ACKNOWLEDGEMENTS

We thank for financial support from MEdCT,

CAPACITIES PROGRAMME

✓ **Project nr.127CP / I / 14.09.2007**


TO OUR LADIES
Gérard Mulot
ST-GERMAIN PARIS
アンブル（6号） 2,400円
アーモンド風味のスポンジ、チョコカスタード、チョコレートスポンジ
プラリネクリームと4層になったナッツのケーキです

TO

GENTLEMANS

Johnnie Walker


•Gabriel Garcia Marquez - ultima scrisoare din “veacul de singurătate”.
Întotdeauna există ziua de mâine
şi viața ne dă, de fiecare dată ,
altă oportunitate pentru a face lucrurile bine...,