Magnetic Properties of Iron Nanoclusters in Silver

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Outline

- Previous experiments
- Fe location at Ag host
- Nanoparticles
- Kondo Effect
- Magnetic behavior
Absorption spectra and XMCD - LNLS
• Recent Donation from Germany

Produces well defined magnetic nanoclusters and embedded in different matrix to study TMR or GMR.
preparation of films

films of Fe in Metals

vapor condensation
pressure: $5 \times 10^{-8}$ mbar

Tantalum crucibles
evaporation control: quartz crystals

Mössbauer spectroscopy: *in situ*

Resistivity: *in situ*
Our group have been working with dilute alloys of Fe impurities embedded in several non magnetic metals (RE, M) with low or no miscibility: Fe$_x$M$_{1-x}$, M={Ag, Yb, Pb, Cd e Zn.} and $x < 1$ at. %.

FCC hosts {Ag, Yb, Pb} ; HCP host {Cd, Zn}

Location of iron ions
- Systematics ISOMER SHIFT

- Magnetism and location of Fe: Ag, Fe: Yb and Fe: Pb

- Magnetism of Fe: Cd and Fe: Zn
Fe:Pb, Fe:Yb; Ts=15K (Phys. Rev. B 60, 1111, 1999)

Fig. – In situ Mössbauer spectra of the film Fe$_{0.005}$Pb$_{0.995}$, Fe$_{0.005}$Yb$_{0.995}$
Films of diluted Fe alloys in non-magnetic metals - $M$ deposited at $15K$

$\text{Fe}_x\text{M}_{1-x}$, $M=$\{Ag, Yb, Pb, Cd, Zn\}

• (monomers, dimers)

• By product -> aging effects -> Nanoparticles
evidence for Kondo effect: Cd/Fe

films: 0.5 at.% Fe  
1.5 at.% Fe
• for 1.5 at.% no Kondo effect observed

R vs T

R vs lnT

T_K = 5 K
RESUMÉ

position of impurities

formation of clusters

study of Kondo effect

Cd/Fe: substitutional sites

M.A. Morales, E. Baggio-Saitovitch, S. Frota Pessôa

Zn/Fe: substitutional sites

Cd/Fe: \( D = 0.5 \) nm; 5 atoms

Ag/Fe: \( D = 0.75 \) nm; 13 atoms

Zn/Fe: Kondo effect due to Fe monomers

Cd/Fe: Kondo effect also with nanoclusters
Previous studies: co-evaporation of 1 at% Fe in Ag onto He-cooled substrate, monomers, dimers, clusters.
Subsequent annealing: increased formation of clusters.

$^{57}\text{Fe:Ag ; } T_s=15\text{K}$

Evaporation onto substrate at 285K and 80K for conc. below 3 at% Fe:

with decreasing % Fe concentration and T monomers fraction increases.
$\text{Fe}_x\text{-Ag}_{1-x}$ (0.003 $< x < 0.03$) deposited at 285K
Fe in Ag

$R/R_0(1.5K)$ vs Temperature (K)

- $0.3\%$
- $0.4\%$
- $0.5\%$
- $0.8\%$
- $1.0\%$
- $1.5\%$
- $3.0\%$

Temperature range: 3 to 33 K
For 1 at % Fe only clusters: 2 quadrupole doublets

<table>
<thead>
<tr>
<th></th>
<th>S1 (mm/s)</th>
<th>ΔE_Q1 (mm/s)</th>
<th>A1(%)</th>
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</thead>
<tbody>
<tr>
<td>T = 260 K</td>
<td>0.29</td>
<td>0.41</td>
<td>90</td>
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<tr>
<td>T = 140 K</td>
<td>0.35</td>
<td>0.73</td>
<td>10</td>
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<tr>
<td>T = 80 K</td>
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<td>T = 40 K</td>
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<td>T = 20 K</td>
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Above 20K: Curie-Weiss behavior

Deviations below ~20K

Can be approximated with a distribution of magnetic moments

From magnetization curves above 20K:

\[ <\mu> \approx 35-40 \, \mu_B \]

i.e. about 15-20 atoms per cluster
Ag/Fe: T dependence of Mössbauer spectra

Mössbauer vs T

average hyperfine field vs T

Simple approach
distribution of $B_{hf}$

$T_B$

$B_{hf} \text{sat} = 32 \text{ T}$
1 at% Fe

More detailed fits

2 sites with fixed ratio from high T

below 6K: Bhf distribution, slow dynamics of cluster magnetization
alignment of $B_{hf}$ in plane of substrate

above 6K: fast dynamics of cluster magnetization in a molecular field created by neighboring clusters, uniaxial fluctuations assumed

The hyperfine field was kept fixed to the value found at 1K!
The fits work well only for magnetically interacting clusters!

Each cluster sees a molecular field created by the other clusters.
Further support for size of average moment of clusters from average field as a function of applied field at $T > 20K$

$<\mu> = 40(5) \mu_B$ agrees with magnetization
Tentative picture of clusters:

- Estrutura ferromagnética
- Estrutura antiferromagnética

Magnetic moment of free cluster $\text{Fe}_{13}$

Theory: $34 - 44 \mu_B$

Experimental: $\sim 40 \mu_B$

On surface 12 atoms
Inside 1 atom

Exp. found 2 spectra with intensity ratio 10:1

G. Rollmann, P. Entel, S. Sahoo
Ag/Fe

<table>
<thead>
<tr>
<th>Atomic Radius</th>
<th>Atomic Volume</th>
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<tbody>
<tr>
<td>Ag</td>
<td>Fe</td>
</tr>
<tr>
<td>$R_{Ag} = 1.44 , \text{Å}$</td>
<td>$V_{Ag} = 10.36 , \text{cm}^3/\text{mol}$</td>
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<tr>
<td>fcc</td>
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<tr>
<td>$R_{Fe} = 1.26 , \text{Å}$</td>
<td>$V_{Fe} = 7.10 , \text{cm}^3/\text{mol}$</td>
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<td>bcc</td>
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$V_{Ag} / V_{Fe} = 1.46$

fcc structure of Ag

Free clusters of Fe
X-ray Absorption Near Edge Structure

Extended X-Ray Absorption Fine Structure

Absorção(normalizada)

7100 7200 7300 7400 7500 7600

Energia

EXAFS Fe-Ag (0.5% Fe)
XANES Fe bulk

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XANES Fe bulk
NANO - RIO

9th International Conference on Nanostructured Materials

June 1-6, 2008
Rio de Janeiro
The fits work well for magnetically interacting clusters!
Each cluster sees a molecular field created by the other clusters

Estimates:
From the cusp in $\chi$ and the onset of magnetic hyperfine interaction we may estimate via

$$\gamma = \gamma_0 e^{-\frac{KV}{k(T-\theta)}}$$

$$\theta \approx 6K, \quad KV/k \approx 19K$$
Some more estimates:

size of clusters: about 15-20 atoms (assumed moment per iron about 2-3 $\mu_B$)

$$V \approx 0.25 \text{ nm}^3$$

From $KV/k \approx 19K$:

$$K \approx 10^6 \text{ J/m}^3$$

which is a bit higher than usually found for iron particles contributions from surface anisotropy?