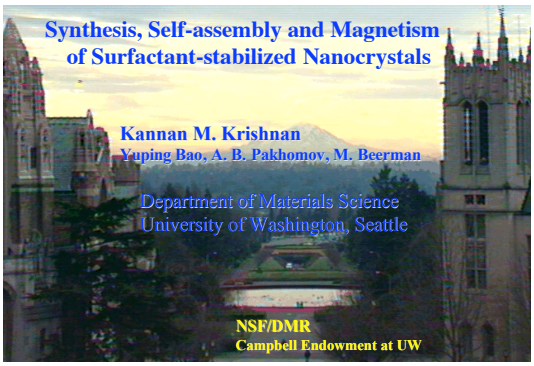
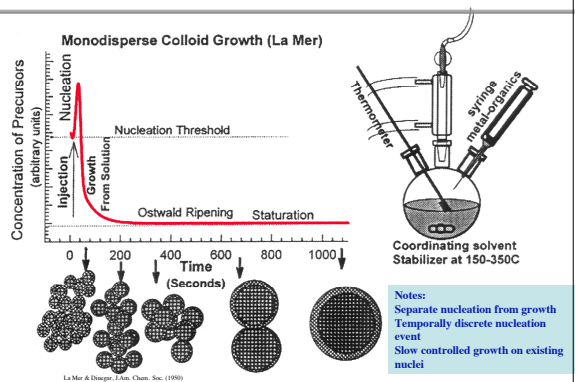


depts.washington.edu/kkgroup
faculty.washington.edu/kannanmk

Preparation of Colloidal Metals in Constrained Environments

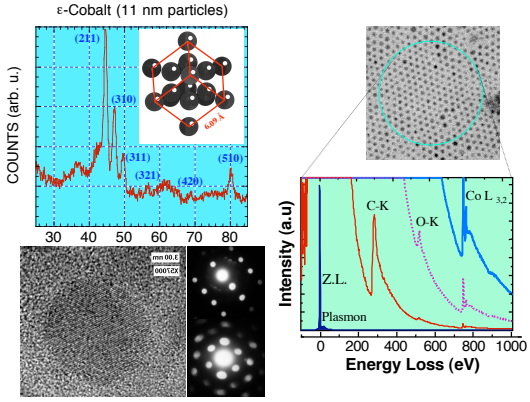


Notes:
Separate nucleation from growth
Temporally discrete nucleation event
Slow controlled growth on existing nuclei

V. F. Puntes, Kannan Krishnan and A. P. Alivisatos. *Science* **2001**, 291, 2115;

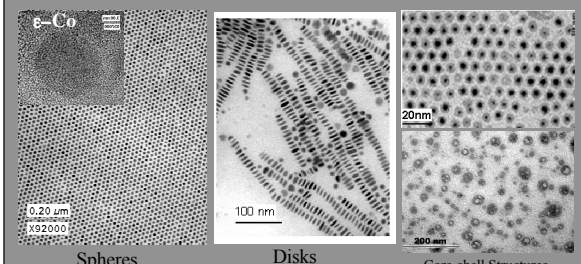
Microstructure of Cobalt Nanocrystals

ε-Cobalt (11 nm particles)



La Mer Synthesis of Cobalt Nanocrystals

Control - size, size distribution, shape & morphology



Spheres
5-25 nm

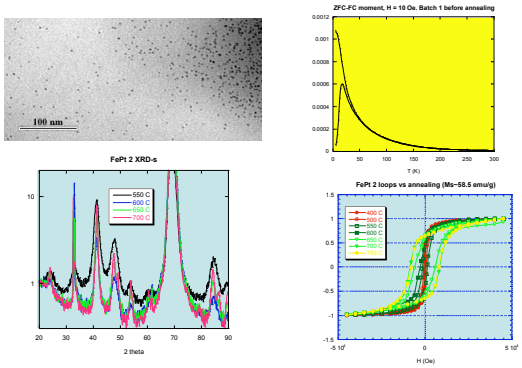
Disks
4/8 - 5/25nm

Core-shell Structures

Core shell structures: surface modification , water solubility

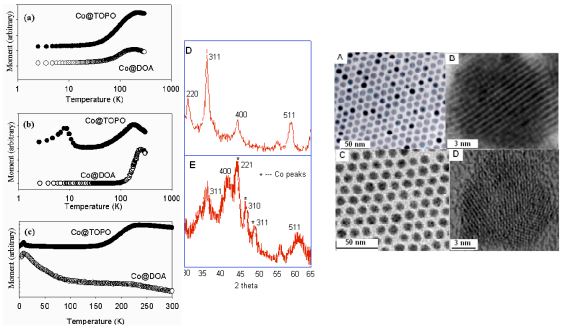
Y. Bao and Kannan Krishnan , *Advanced Materials* (submitted)

Synthesis and magnetic properties of FePt alloy NCs



Yuping Bao, A.B. Pakhomov, K. M. Krishnan, *Jour. Appl. Phys.*, (submitted)

Stability of Nanocrystals



Y.Bao, M. Beerman, A.B. Pakhomov and , *Nanoletters* (submitted)

Weak Forces Involved in the Self-assembly Process

Van der Waals: (1.6×10^{-21}J)

$$V(D) = -\frac{A}{6}\left\{\frac{2R^2}{(2R+D)^2-4R^2}+\frac{2R^2}{(2R+D)^2}+\ln\left(\frac{(2R+D)^2-4R^2}{(2R+D)^2}\right)\right\}$$

Steric repulsion: (1-2×10^{-21}J)

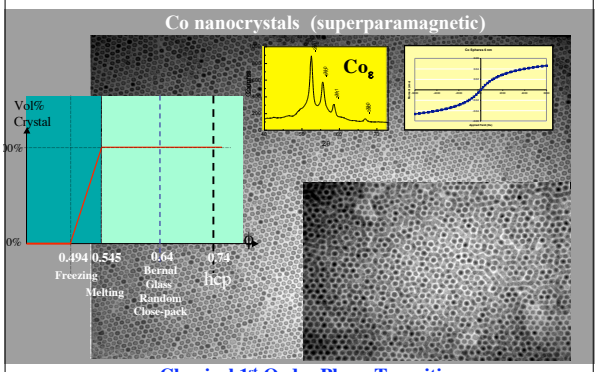
$$E_S = \frac{k_B T}{a^3}\left(\ln\left(\frac{1}{1-\phi}\right)-\phi\right)\cdot\left(\frac{\pi\delta^2}{12}\left[6(R+L)-\delta\right]\right)$$

k_B is the Boltzman constant
T is temperature
a is the monomer dimension (~0.5 nm)
ϕ is the volume fraction of the surfactant
δ is extent of overlap of surfactants ($2L - D$)
L is the surfactant length

Magnetostatic or dipolar Interaction:~ (10^{-21}J)

"Entropy" Forces

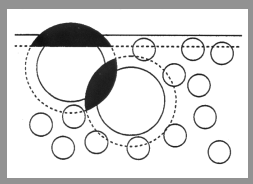
Self-assembly of intermediate size (8-10 nm)

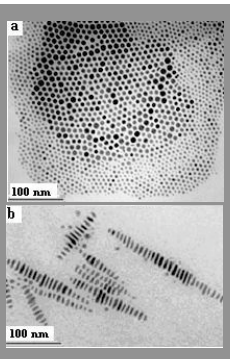


Classical 1st Order Phase Transition

Self-assembly of Bimodal size distributions

Two different NC Sizes
Role of Surfaces

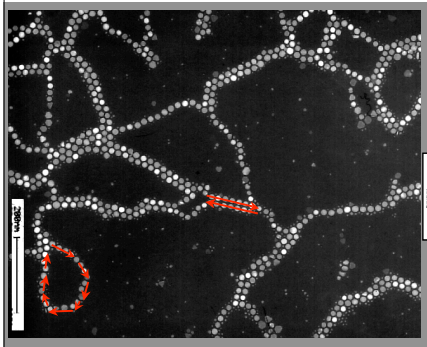


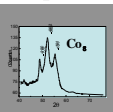


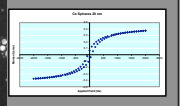
Y. Bao, M. Beerman and Kannan M. Krishnan, *Jour. Mag. Mag. Mat.*, **266**, L245-L249 (2003)

Entropy-induced Wetting: Depletion forces determine self-assembly

Self Assembly of Co Nanoparticles: Large FM particles

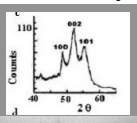


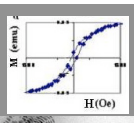


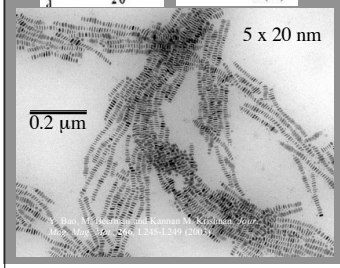


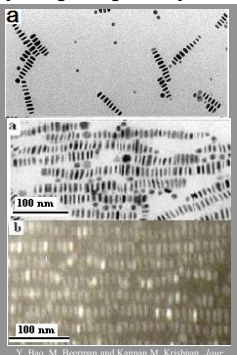
Magnetostatic interactions dominate self-assembly

Self Assembly of Co Nanodisk: Lyotropic liquid crystals





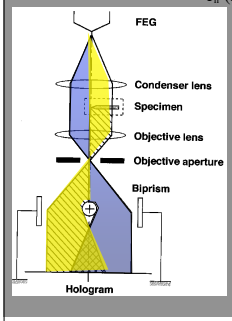




Y. Bao, M. Beerman and Kannan M. Krishnan, *Jour. Mag. Mag. Mat.*, **266**, L245-L249 (2003)

Do magnetostatic interactions dominate self-assembly ?

Introduction to Electron Holography



$$I_h(\mathbf{r}) = 1 + A(\mathbf{r})^2 + 2\,A(\mathbf{r})\,\mathrm{Cos}\left(2\pi \frac{\alpha_h}{\lambda} x - \phi(\mathbf{r})\right)$$

(intensity of the hologram)

$$F\,[I_h(\mathbf{r})] = \delta(u) + F\,[A(\mathbf{r})^2] +$$

(auto correlation)

$$F\,\{A(\mathbf{r})\exp[-i\,\phi(\mathbf{r})]\}^* \,\delta(u - \tfrac{\alpha_h}{\lambda}) +$$

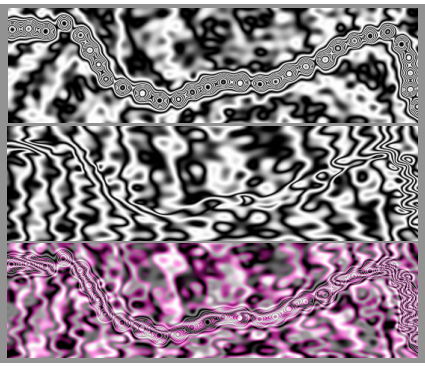
$$F\,\{A(\mathbf{r})\exp[i\,\phi(\mathbf{r})]\}^* \,\delta(u + \tfrac{\alpha_h}{\lambda})$$

(side bands)

Select 3rd term
Shift by α_h/λ
Carry out inverse FT

⇨ Phase Information

Transmission Electron Holography: Spherical Co Nanocrystals



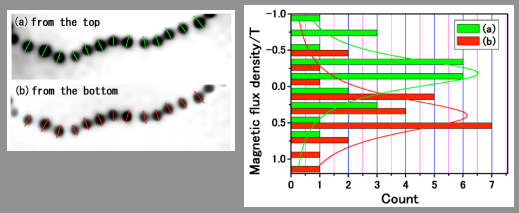
a) Reconstructed Hologram

b) Magnetic Component Only

a) and b) superimposed

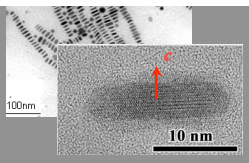
Collaborators: Shindo Group (IMRAM, Tohoku University)

Quantitative estimation of magnetic flux density from the reconstructed phase images



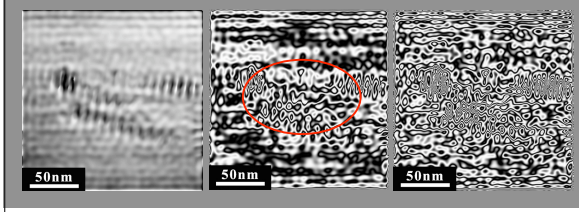
Magnetic flux density B on the Co nanoparticle chain was estimated to be 0.30T.

Transmission Electron Holography: Co Nanodisks



Magnetostatic Energy Dominates

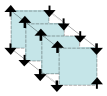
Magnetocrystalline Energy Dominates



Work in Progress: Dipolar Ferromagnets ?

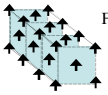
Ferromagnetism in the absence of exchange interactions

Ground State



SCL

Columnar Antiferromagnet

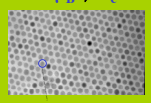


FCC /BCC

Dipolar Ferromagnet ?

$$T_c = \frac{\mu_o \, \mu^2}{4 \pi k_B d^3} \sim \frac{\mu_o}{4 \pi k_B} \mu M_s \phi$$

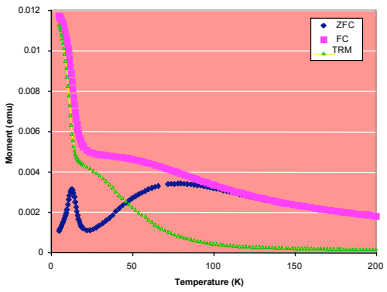
$\mu \sim 1\text{-}2\ \mu_B \Rightarrow T_c \sim mK$



$\mu > 3000 \mu_B \Rightarrow T_c \sim ??$

Luttinger and Tisza (1946)
Roser and Corrunccini (1990)
Bouchaud and Zerah (1993)

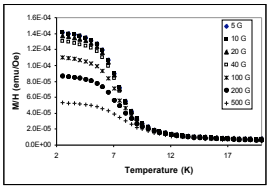
ZFC - FC- TRM measurements



6nm spheres + TOPO/OA in powder form

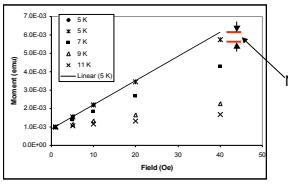
Collaborators: Per Norblad and Petra Jonsson, Uppsala University

Non-linear susceptibility : Spin glass transition ?



Total susceptibility as a function of temperature.

6 nm spheres



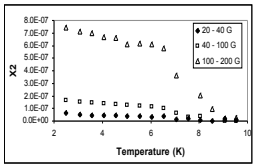
$$\frac{M}{H} = \chi_0 - \chi_2 H^{\alpha}$$

Nonlinear Moment

For it to be a spin-glass transition, α should be a minimum at T_G

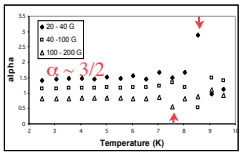
Novak et al, PRB **33**, 343 (1986)

The current status of our measurements



Log – log plot gives χ_2 and α.

$$\log\left(\chi_0 - \frac{M}{H}\right) = \log \chi_2 + \alpha \log H$$



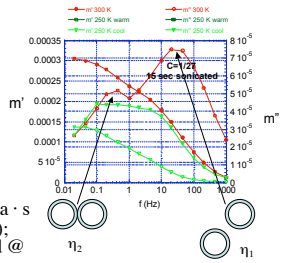
Nonlinear exponent α as a function of temperature

α is constant below the critical temperature, but decreases as field increases

Not a bulk spin glass transition !

Relaxation Dynamics: Effect of Surfactant Friction

- Neel relaxation for 20 nm cobalt particles blocked:
- $f_N = f_{0N}\exp[-E_A V/k_B T] << f_m$ (very long relaxation time);
- Brownian relaxation:
- $f_B = k_B T/3\eta V$
- f_{B1}~20 Hz; f_{B2}~0.45 Hz;
- Handbook data: η_1 ~ 1.32 mPa · s (1,2-Diclorobenzene @ 25°C); η_2 ~ 27.64 mPa · s (Oleic acid @ 25°C)
- f_{B1}/f_{B2}~40; η_2/η_1 ~ 20;



A. B. Pakhomov, Yuping Bao and Kannan M. Krishnan "*Jour. Appl. Phys.*, (submitted);