Magnetic Properties of Self-Assembled Ferritin Arrays*

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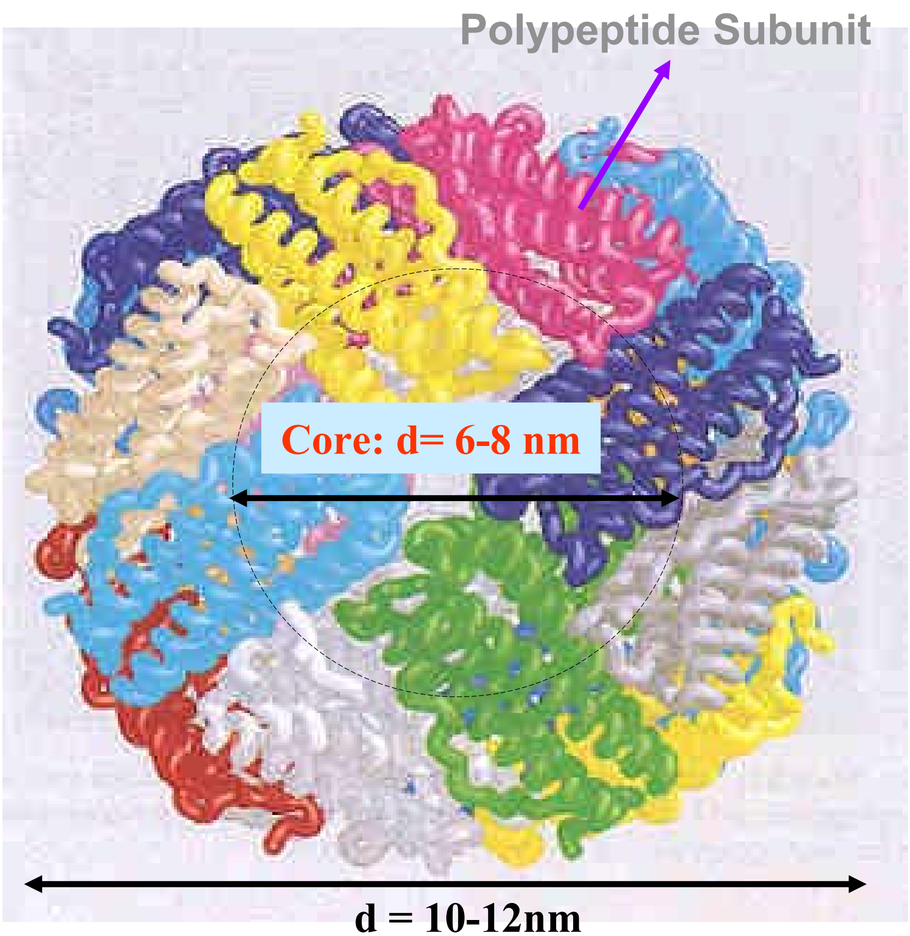
Basic Properties of Ferritin



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- **Iron-storage/Controlled Release Protein**
  - plays a key role in the iron metabolism of mammals
- **Apoferritin** (without the iron core)
  - **spherical shell**
  - **24 subunits (peptide chains) connected through strong non-covalent links**
  - **combined molecular weight: 474,000Da**
  - **stable up to 75-80°C, pH 4-10**
- **Iron Core**
  - **spherical core**
  - **mineral ferrihydrite core:** $[FeO(OH)]_8[FeO(H_2PO_4)]$
  - **can store up to about 4500 iron atoms**
  - **metallic and magnetic properties**

Magnetic Properties of Ferritin

Néel suggested that in a monodomain antiferromagnetic cluster of N spins, approximately $(N)^{1/2}$ spins will remain uncompensated. Since we have ~4500 iron atoms per core, that means ~380μ_B in uncompensated spins.

L. Néel, C.R. Acad. Sci., 1961

In accordance with Néel's picture, superantiferromagnetism and hysteretic behavior (due to the uncompensated spins) in the core develop for temperatures below 'T_N' ≈ 500 K.

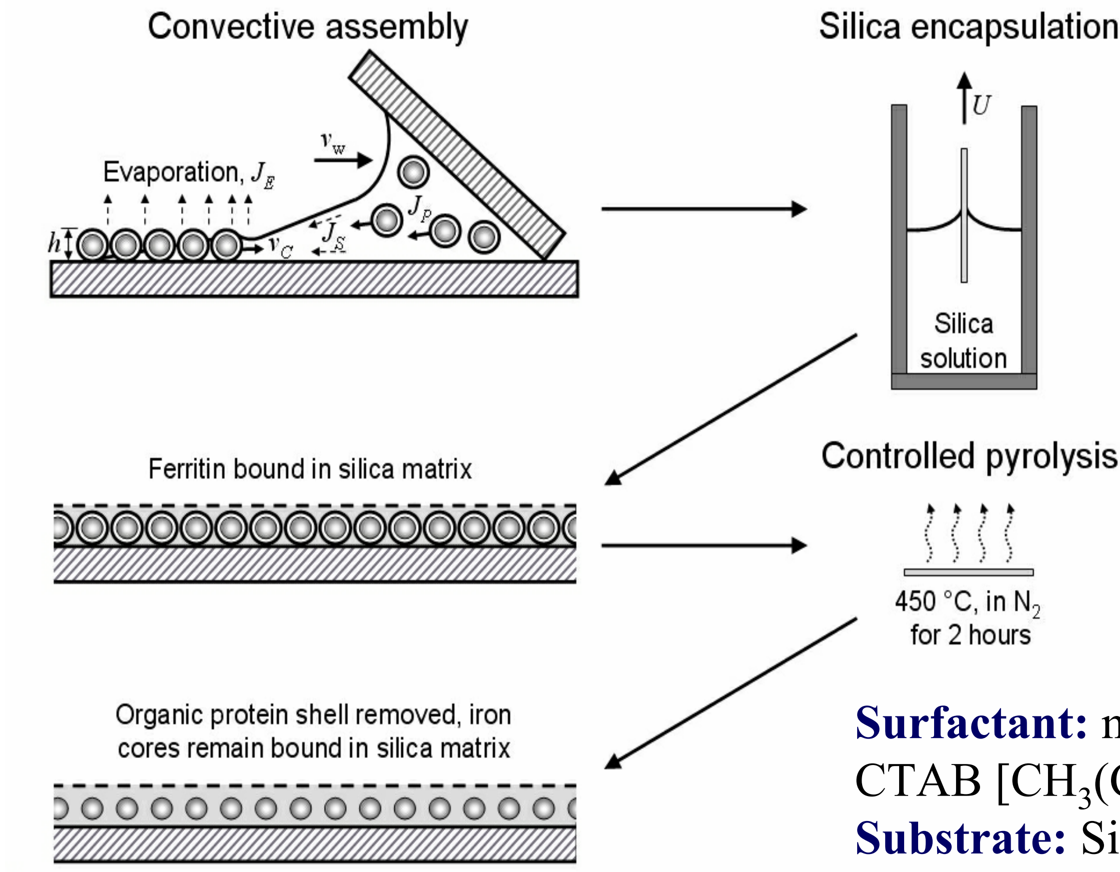
S.H. Kilcoyne and R. Czywinski, J. Magn.Magn.Mater, 1995

C. Gilles et al., J.Magn.Magn.Mater., 2002

Mössbauer studies reveal an additional hyperfine splitting below 240K.

E.R. Bauminger and I. Nowik, Hyperfine Interactions, 1989

Convective Self-Assembly and Treatment of Ferritin Arrays



Control parameters:

- surfactant composition
- volume fraction of ferritin in suspension
- substrate material
- spread-coating velocity
- atmosphere during pyrolysis
- core content and material

Surfactant: mixture of water, ethanol and CTAB [$CH_3(CH_2)_{15}N^+(CH_3)_3Br$]
Substrate: Si wafers or glass

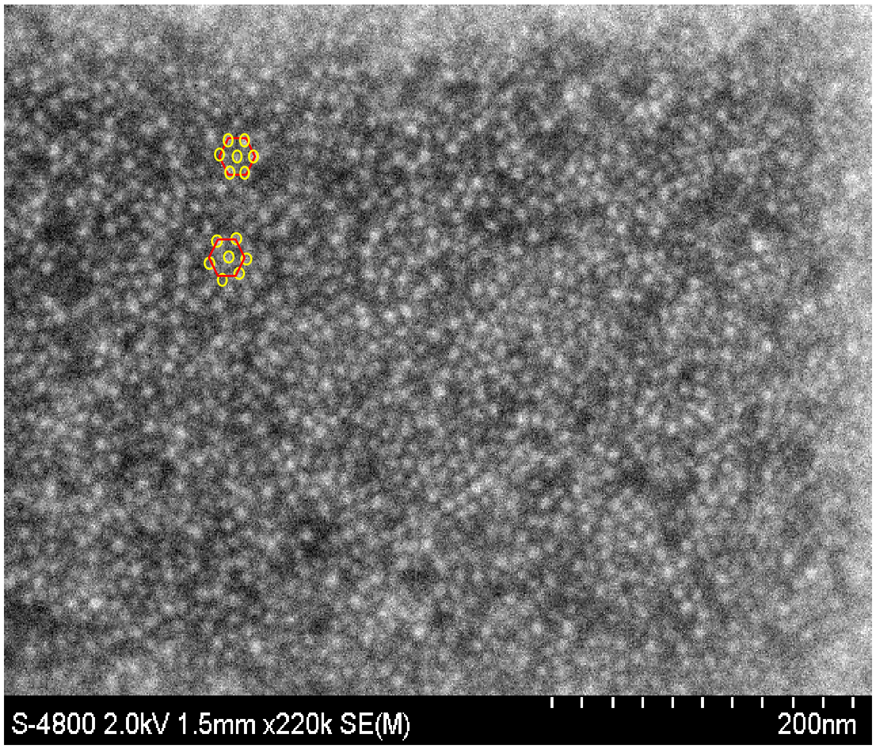
Depending on the growth conditions, regular arrays with core-core separations ranging from about 10 nm up to almost 1 μm (!) can be achieved.

NNSA

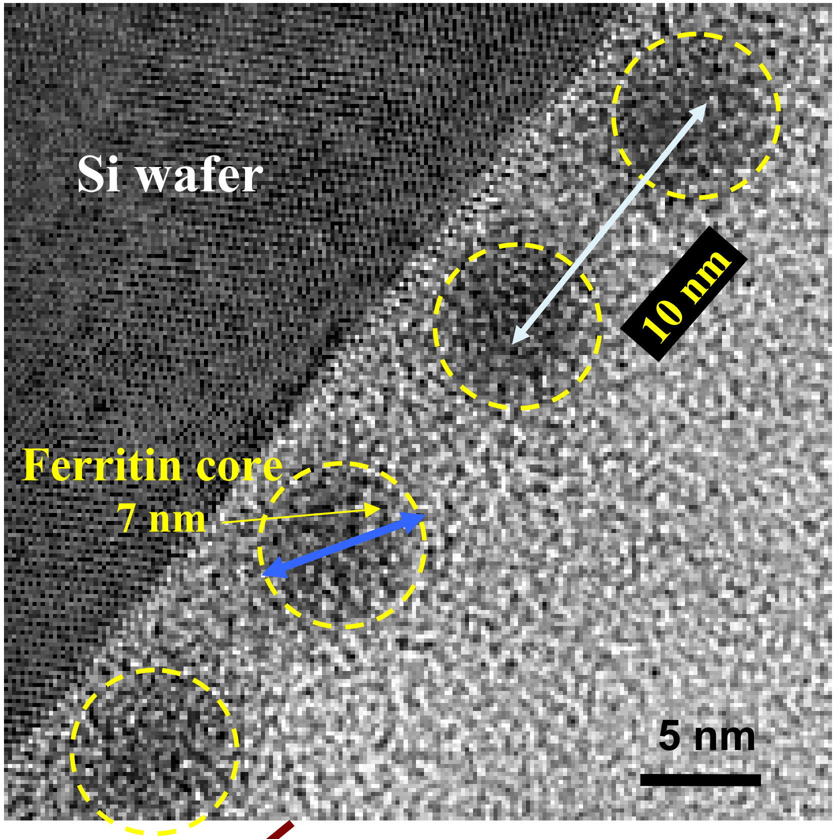
Los Alamos

Self-Assembled Ferritin Arrays

SEM

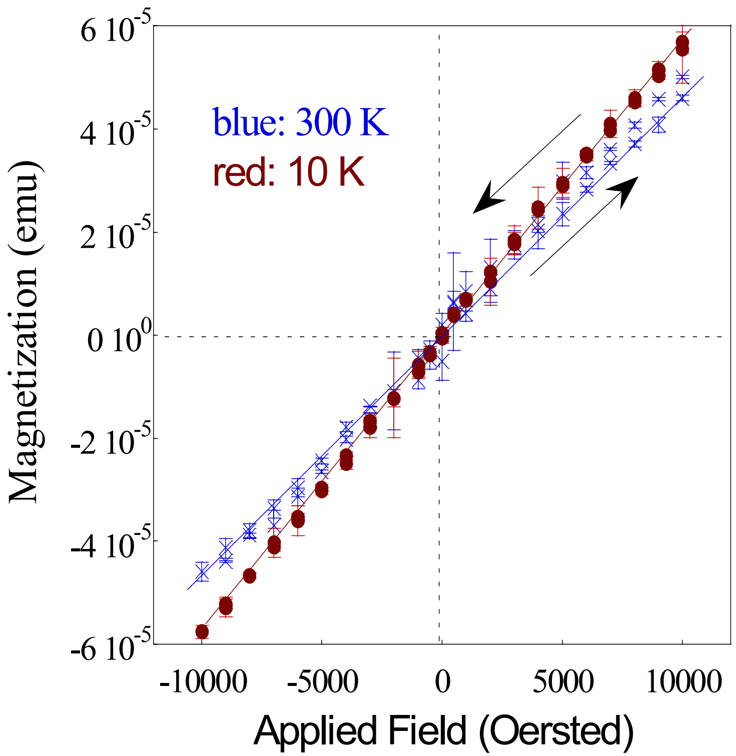


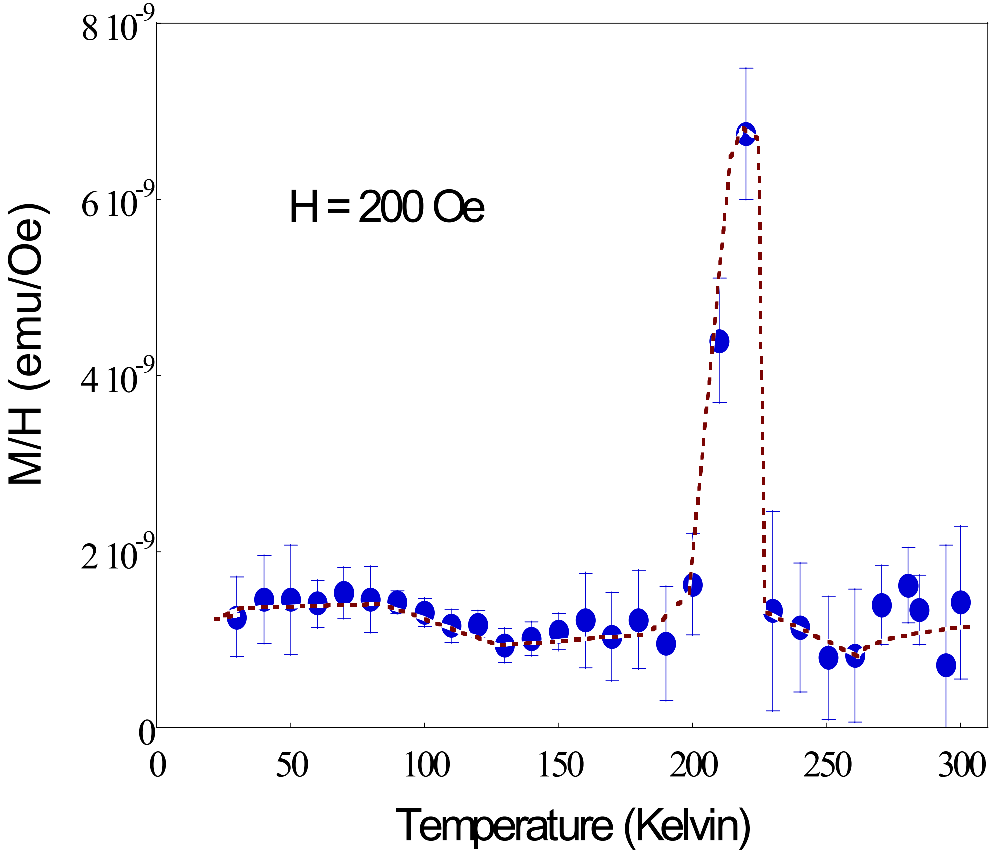
high-resolution TEM



2-D array with 'hexagonal' in-plane configuration

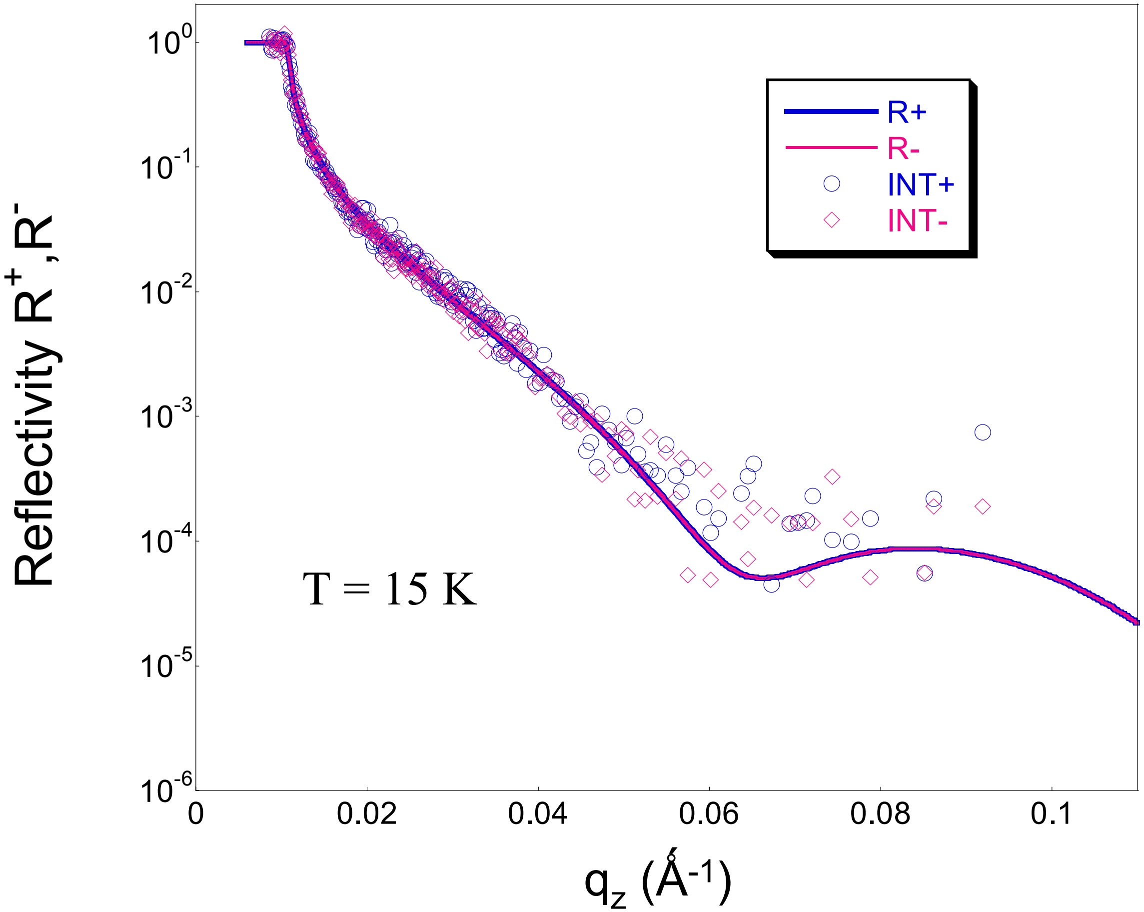
SQUID Results for treated Ferritin-Core Arrays in Silica





- pronounced peak for M/H at around 220 K
- no evidence for hysteretic behavior at low temperatures

Polarized Neutron Reflectometry Study on POSY I (IPNS)



Layer Thickness

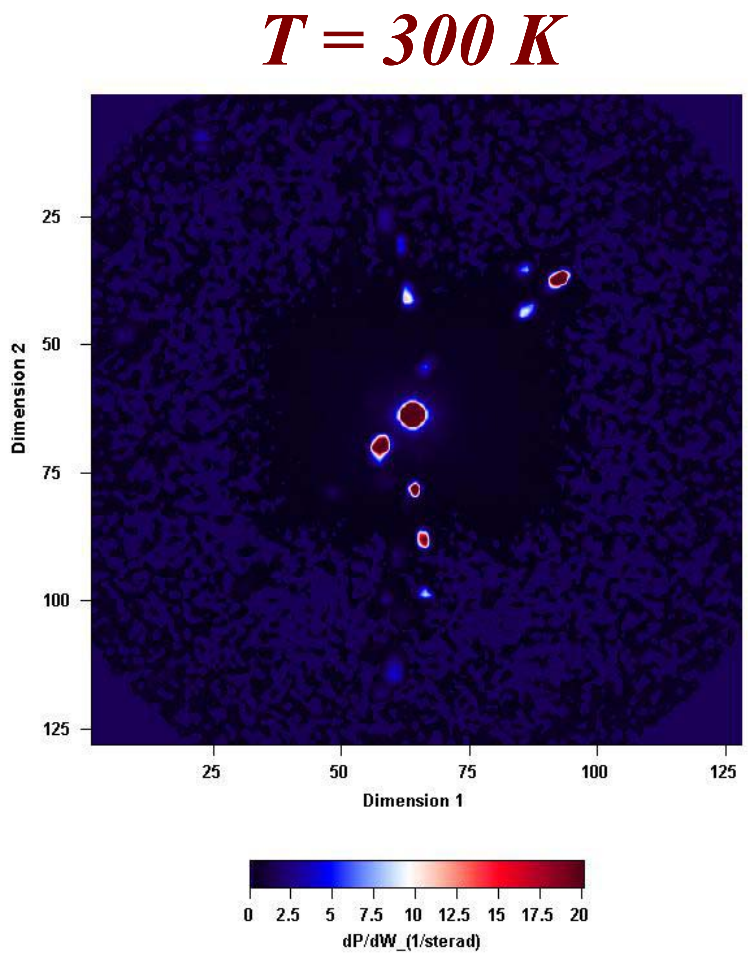
3 nm

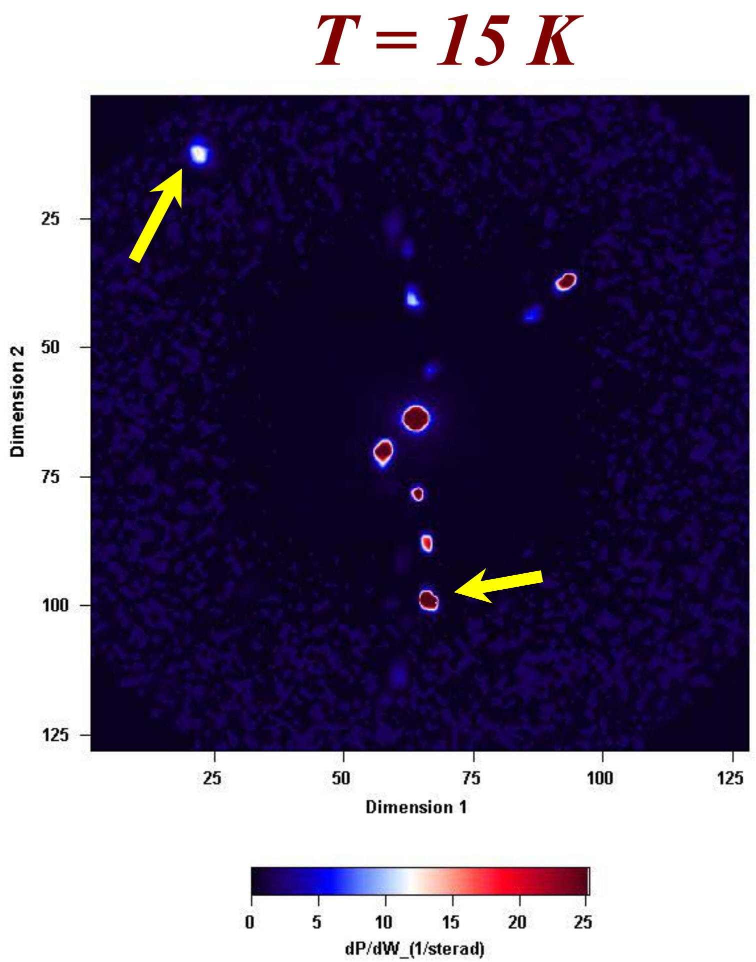
7 nm

The total in-plane magnetization at 8 Oe is less than 0.02 μ_B.

Thicknesses are consistent with HRTEM results.

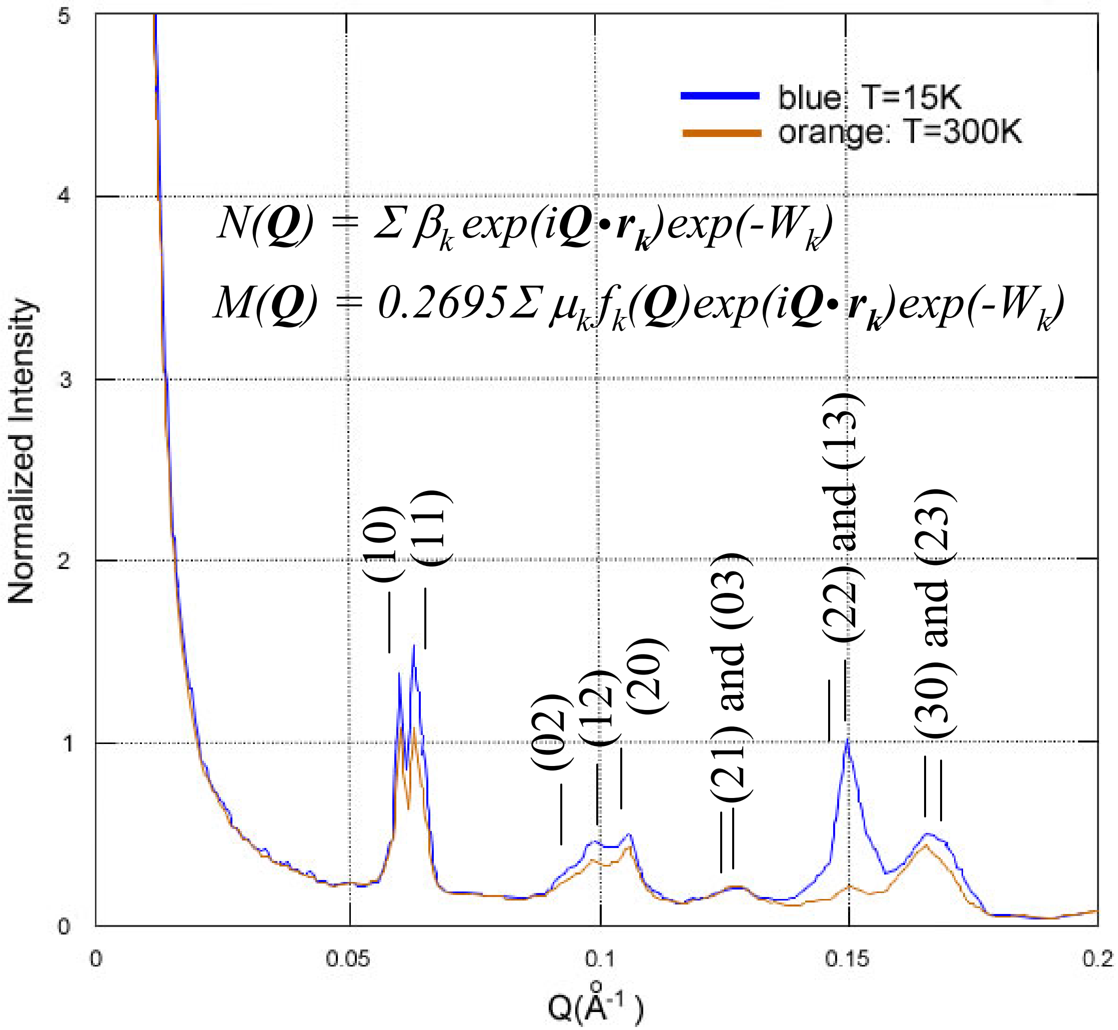
LQD results (LANSCE)





There are additional (magnetic?) contributions to some of the peaks!

Integrated Intensities



- **no additional short-range correlations at low T; magnetic contributions on Bragg peaks only**

- **peaks can indexed in an orthorhombically distorted lattice** (a=10.5nm and b=14.5nm)

- **assume ferromagnetic coupling for Q=0.15Å^{-1}, take the scattering length length *b* of iron (9.45) and *f(Q)* ≈ *1*, then**

$0.2695^2 * \mu^2 * f(Q)^2/b^2 = I_{mag}/I_{nuc} = 23$

This yields a rough estimate for the moment of ~185 μ_B per core.

Summary and Future Plans

1.) Evaporation-induced self-assembly of ferritin and adequate treatment leads to a formation of a regular array of their cores. The diffraction pattern is consistent with an almost hexagonal array of such ferritin cores.

2.) At low temperatures, additional (presumably magnetic) contributions are found on top of some of the nuclear intensities.

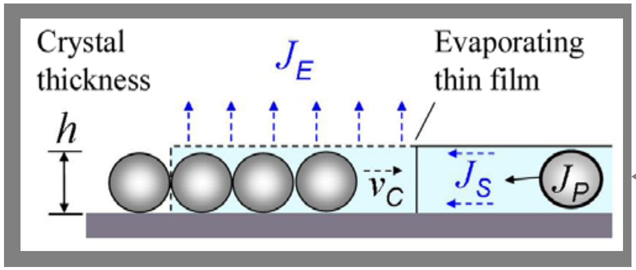
3.) We find evidence for large out-of-plane moments that exhibit some kind of antiparallel coupling.

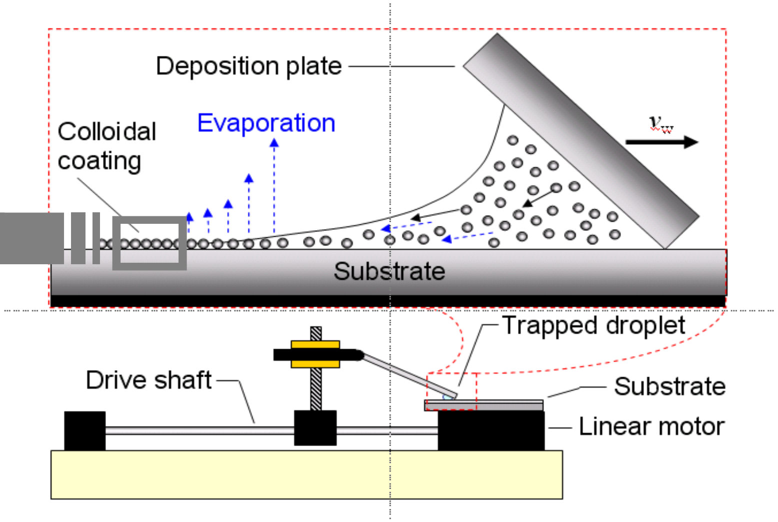
The studies will be extended to ferritin-core arrays with vastly different separations and different core material.

Backup Slides

Controlled Deposition by Convective Self-Assembly

Volumetric Flux Balance





J_S: entrant flux of the carrier solvent
J_P: resulting hydrodynamic flux
J_E: evaporative flux of solvent leaving drying region
ν_C: rate of colloidal crystal formation
ε: porosity
h: height of deposited colloidal crystal
ϕ_p: volume fraction of the particles in suspension
K: $j_e\beta l$

$$v_C = \frac{K\phi_P}{h(1-\varepsilon)(1-\phi_P)}$$

Conditions:

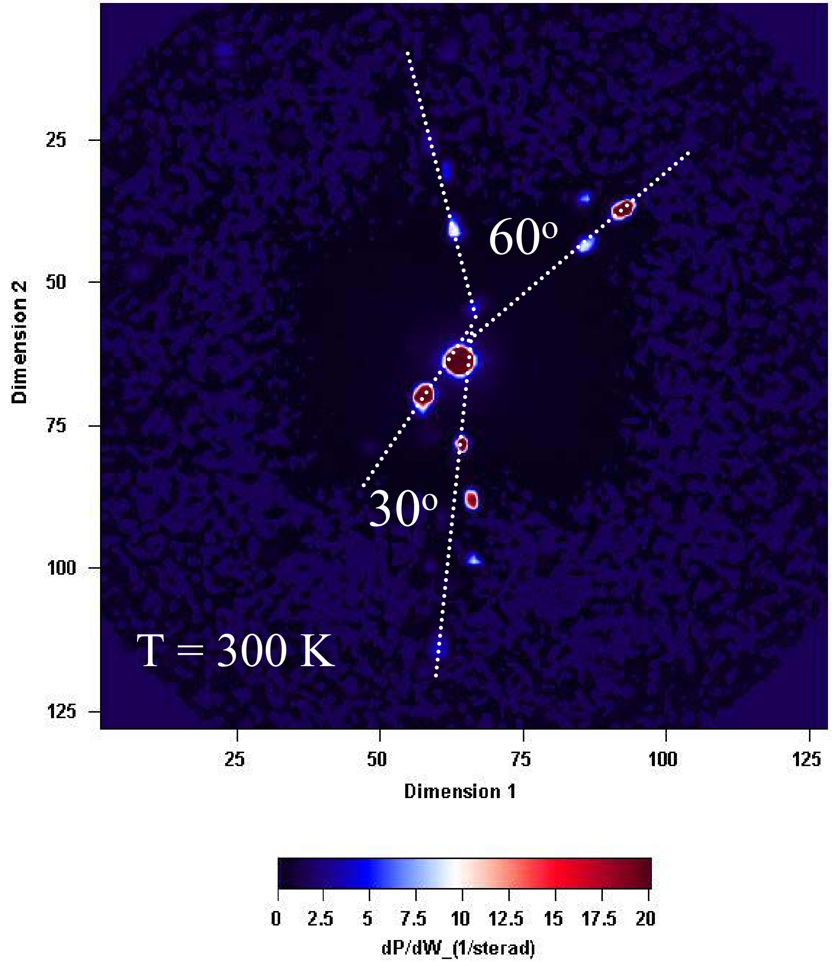
- concentration: 10-25 mg/ml
- volume fraction: 2-4%
- pH = 8
- deposition speed: 1.05-4.22 μm/s
- humidity: 30% - 40%
- temperature: 25°C

Advantages:

- coating time-scale reduced to minutes
- material consumption decreased
- single surface coating
- scalable & controllable

Small-angle Scattering on LQD

Raw Data

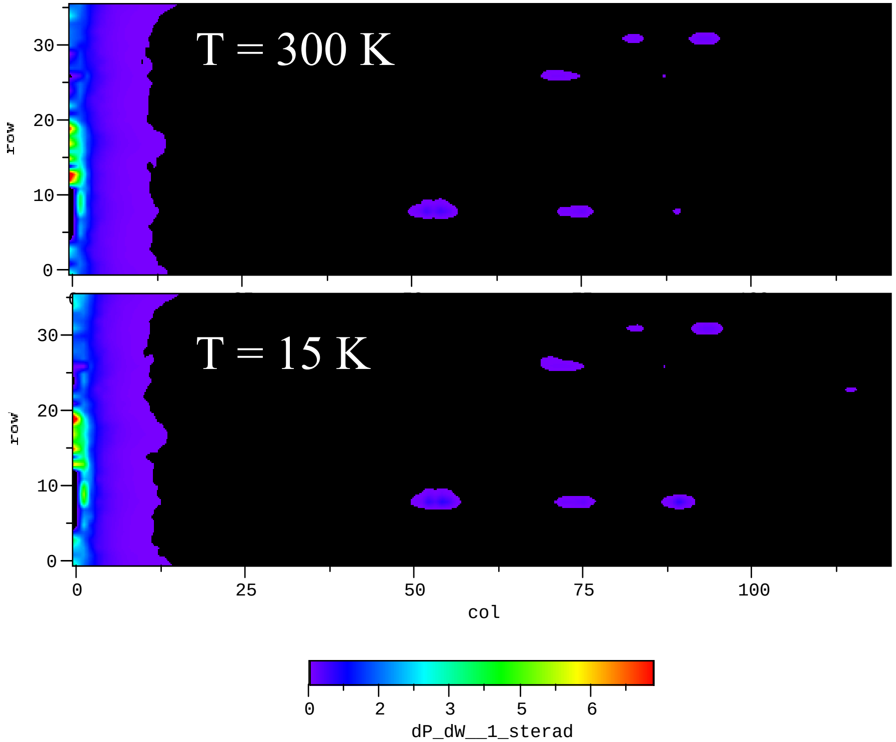


Experimental Details:

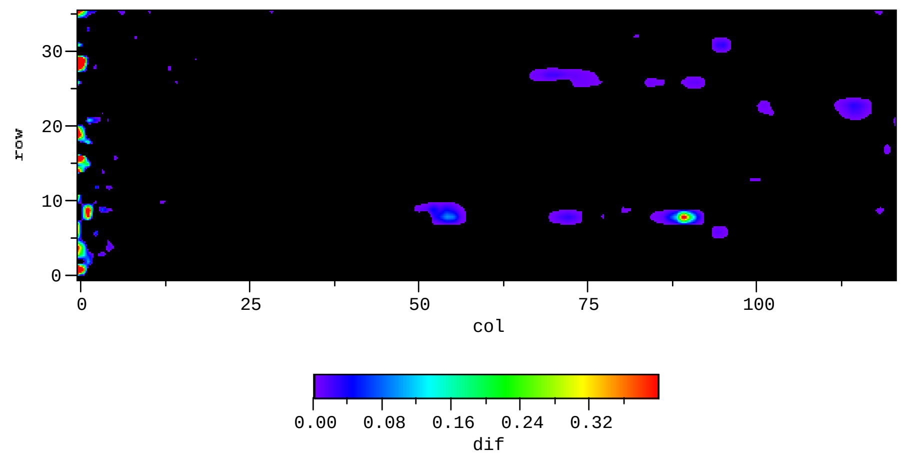
- stacked 6 ferritin-coated wafers, separated by thin Al foil (to ensure heat conductance)
- assembly was wrapped with Al foil and mounted onto the cold finger of a displex
- neutron beam was aligned perpendicular to the wafers

At room temperature, we observe **Laue diffraction spots** consistent with (almost) hexagonal symmetry.

Q-ϕ maps of LQD Data



Difference Map (15K-300K)



- The occurrence of higher-order peaks is consistent with the picture of a periodic lattice.
- The additional intensities at low temperatures exhibit some **Q** dependence, as would be expected for magnetic scattering.