FIELD INDUCED STRUCTURES IN COLLOIDAL SOLUTION OF HEXAFERRITE NANOPARTICLES

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Outline

- Motivation

- The morphology and chemical composition of the colloidal hexaferrite particles

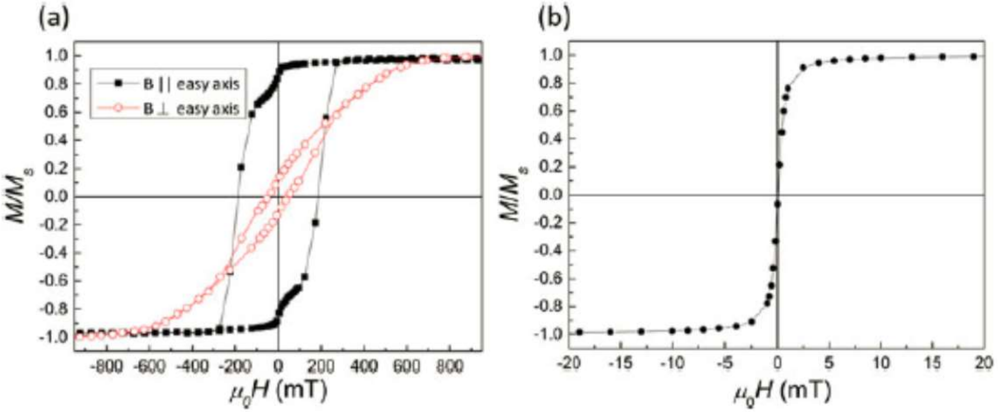
- Small-angle X-ray scattering

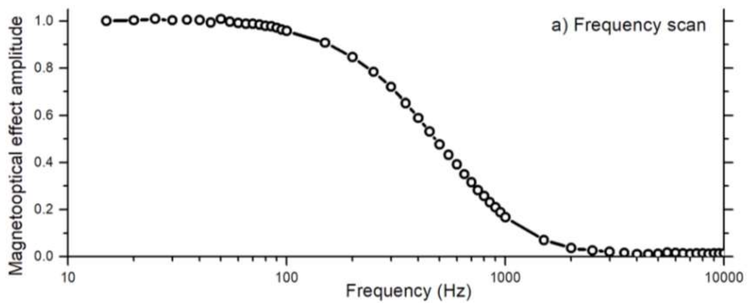
- Small angle scattering of polarized neutrons

- Conclusions

Motivation

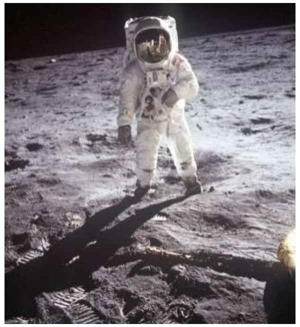
Plate-like strontium hexaferrite particles have about 5000 Oe coercive force and a large magnetic moment. When dissolved in water, magnetic SrFe12O19 particles disperse in space with random orientations, but cause of anisotropic (electrostatic and magnetic) interactions readily turn and align in magnetic fields demonstrated phase transition isotropic-nematic liquid.



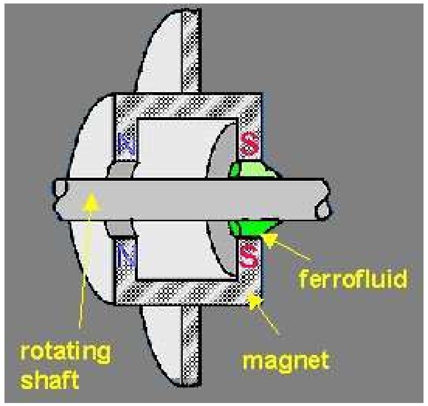


A. Mertelj and D. Lisjak, Liq. Cryst. Rev. 5, 1 (2017)
Art. Eliseev, Andr. Eliseeev, et al, Appl. Phys. Lett. 113, 113106 (2018) - Rotational dynamics of colloidal hexaferrite nanoplates.

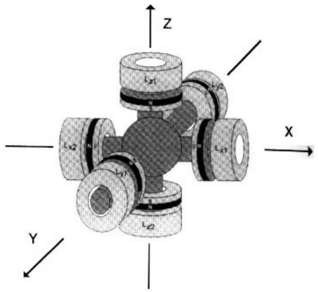
Ferrocolloidal systems: technical applications



Vacuum rotating seals and bearings

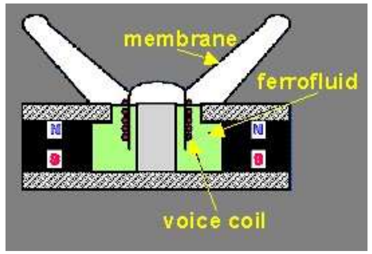


Acceleration sensors



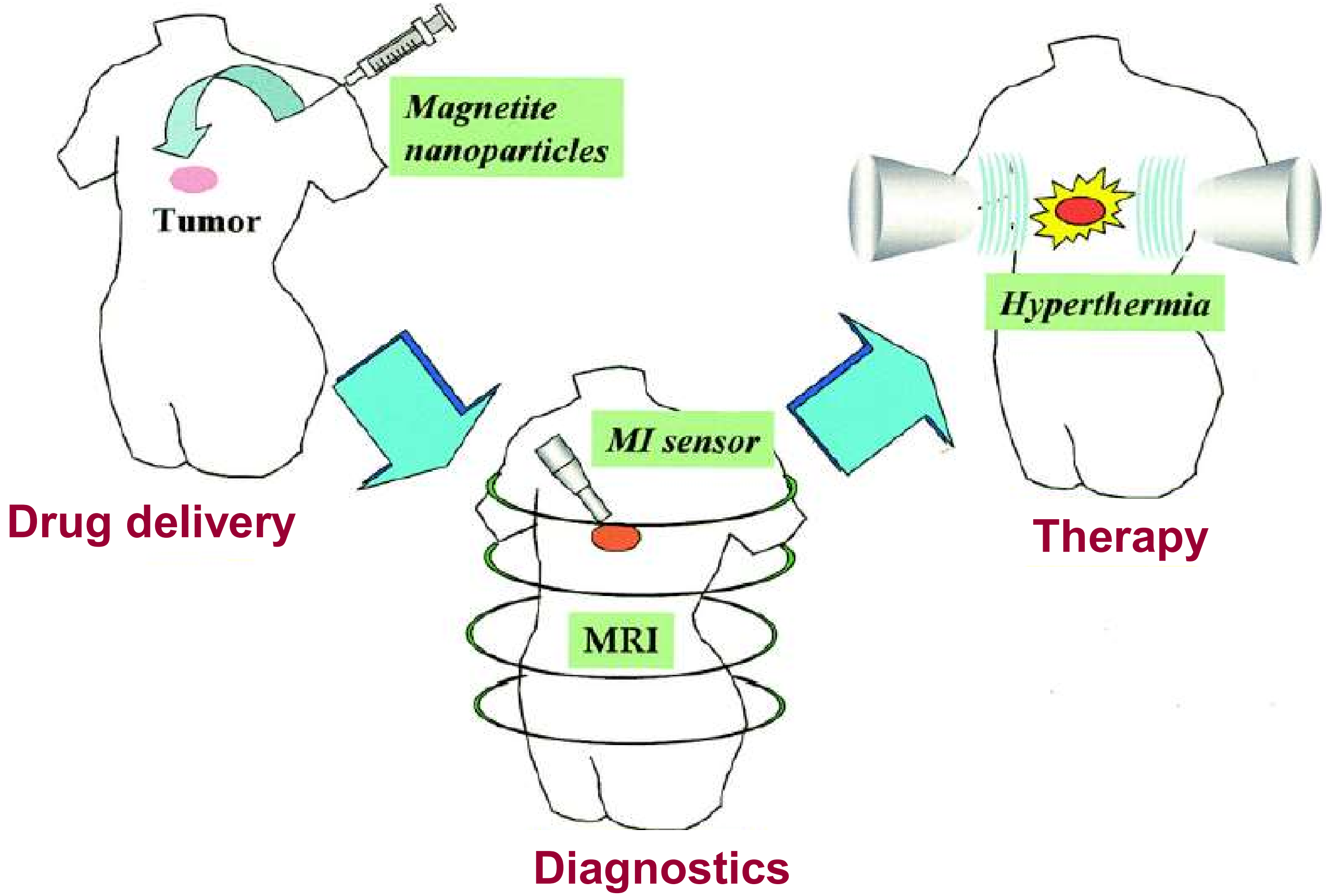
Inductive aerodynamic sensors

Loud speakers



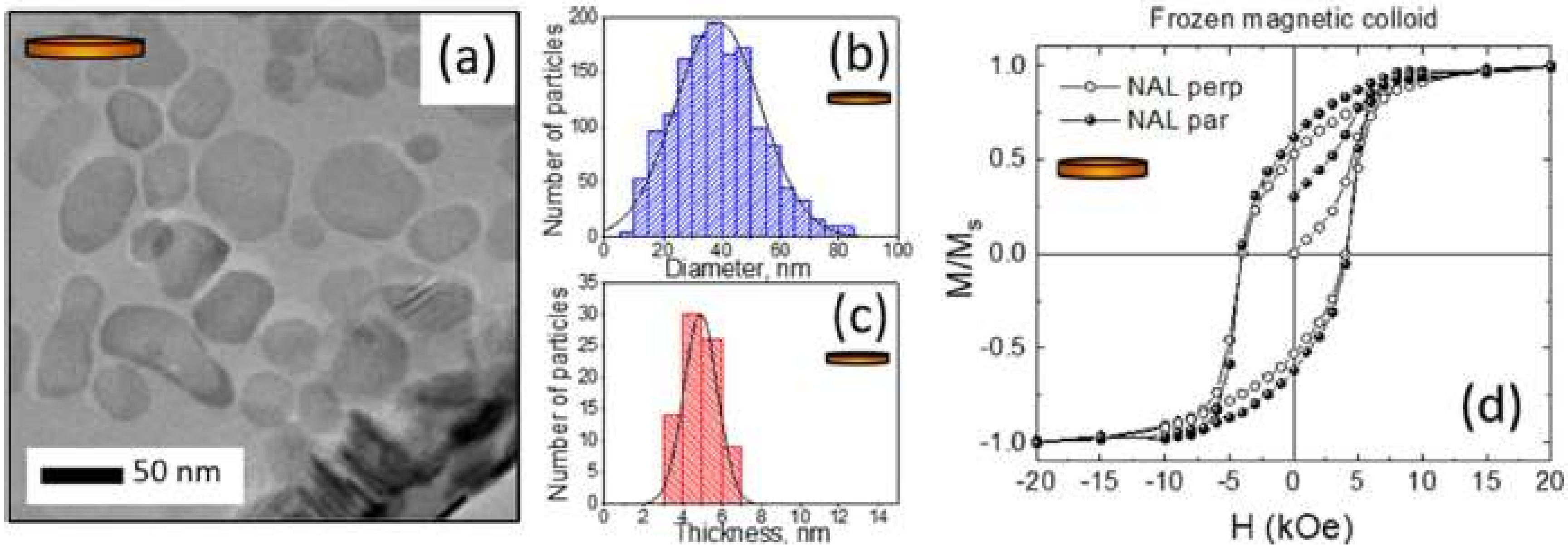
Ferrocolloidal systems: medical applications

Main activities are related with cancer treatment!



K.M. Krishnan, *IEEE Trans. Magn.* 46 (2010) 2523 - 2558

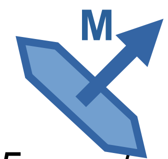
Plate-shaped single-domain nanoparticle $SrFe_{12}O_{19}$



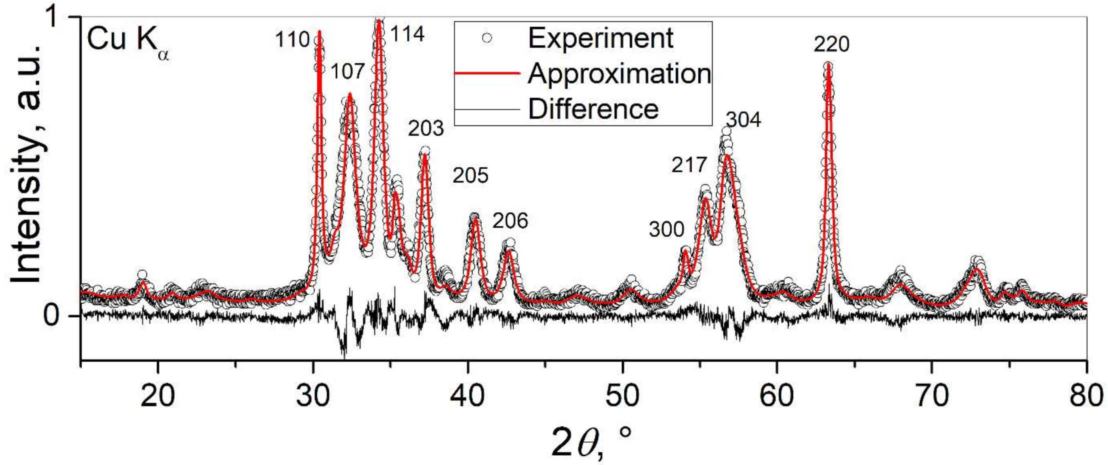
Dried colloid nanoplates:

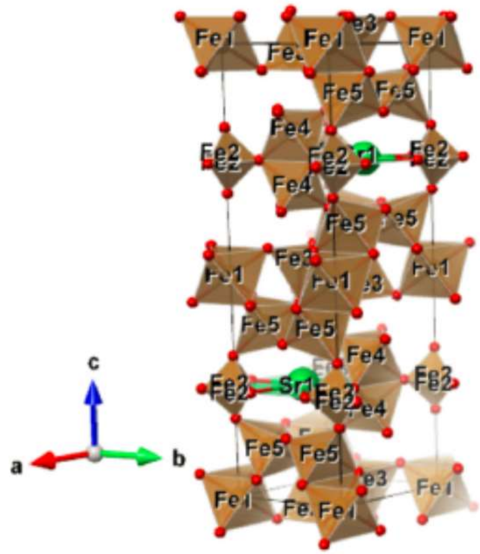
- diameter of 50 nm, thickness of 5 nm
- surface of nanoplates is charged producing electrostatic mutually repulsion

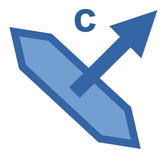
- strong magnetocrystalline anisotropy
- coercive force of 4700 Oe
- saturation magnetization 51.5 emu/g
- remanent magnetization 23 emu/g



XRD analysis







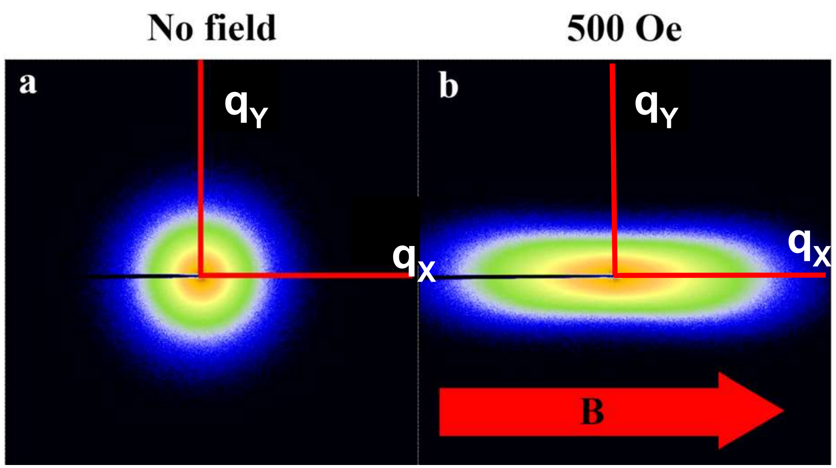
- Hexaferrite phase (PDF 84-1531). Space group $P6_3/mmc$
- The cell parameters a_0 = 5.873(1) Å, c_0 = 23.03(1) Å
- Significant broadening of l-index -- a highly anisotropic particles shape with smaller dimension along c-axis
- Rietveld analysis: Average diameter of the particles is 44.1 nm, thickness is 6.5 nm

Small-angle X-ray scattering

ID-02 beamline, European Radiation Facility, Grenoble

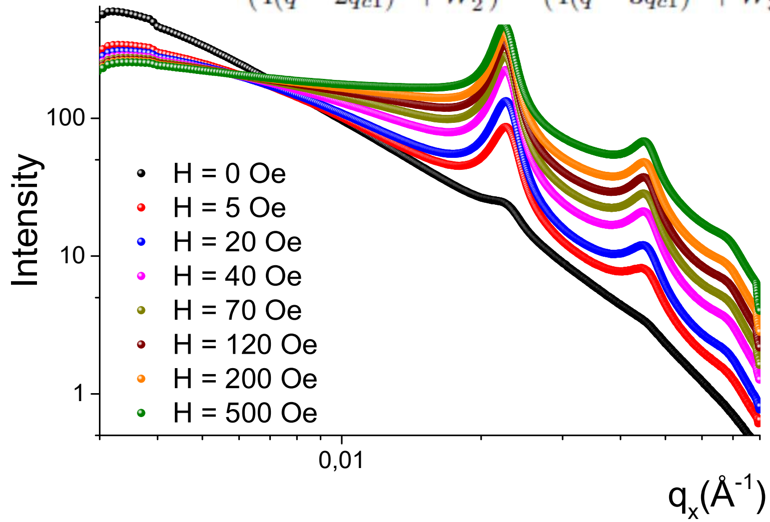
Concentration of the hexaferrite colloid -130 mg/l.

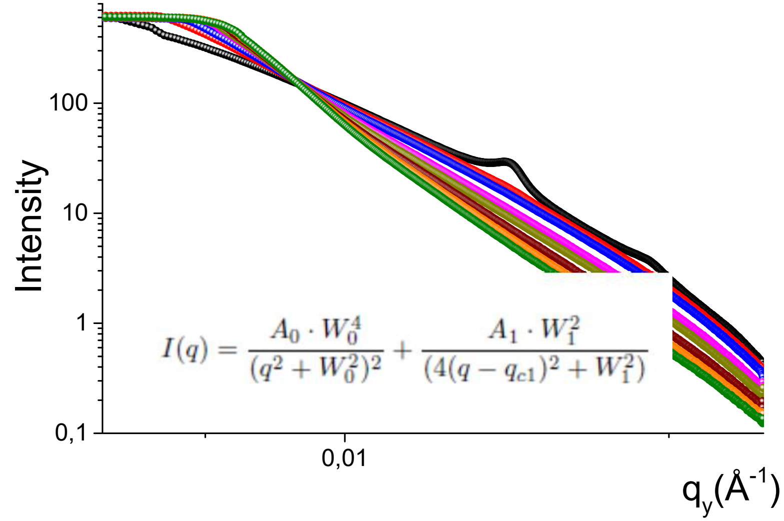
H = 0 ÷ 500 Oe



The two dimensional maps of the intensity reveal a diffuse isotropic scattering at small q and a series of diffraction reflections appeared along the field axis, which corresponds to the particle ordering at a distance of 28 nm, approximately.

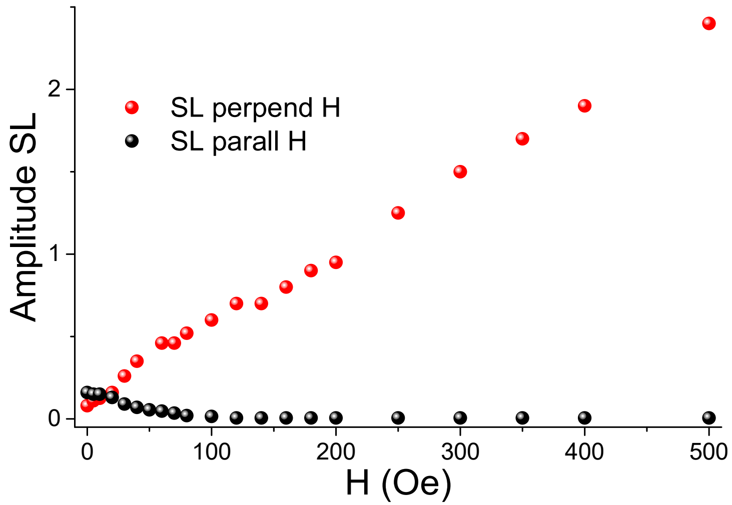
$$I(q) = \frac{A_0 \cdot W_0^4}{(q^2 + W_0^2)^2} + \frac{A_1 \cdot W_1^2}{(4(q - q_{c1})^2 + W_1^2)} + \frac{A_2 \cdot W_2^2}{(4(q - 2q_{c1})^2 + W_2^2)} + \frac{A_3 \cdot W_3^2}{(4(q - 3q_{c1})^2 + W_3^2)}$$

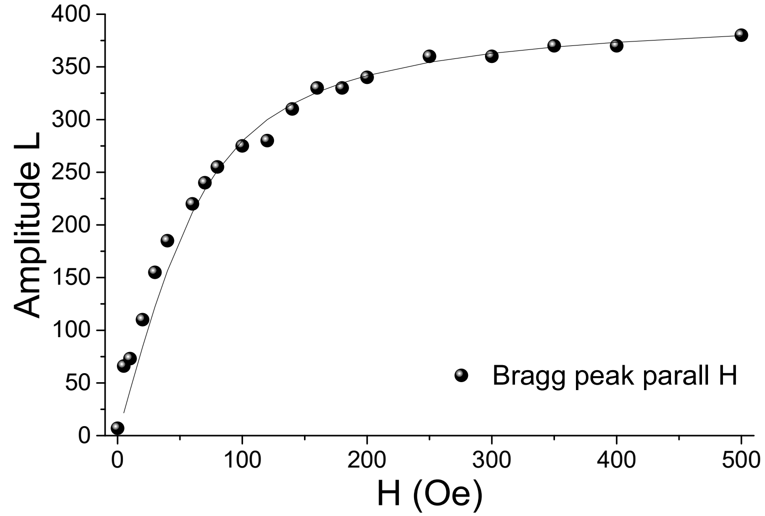


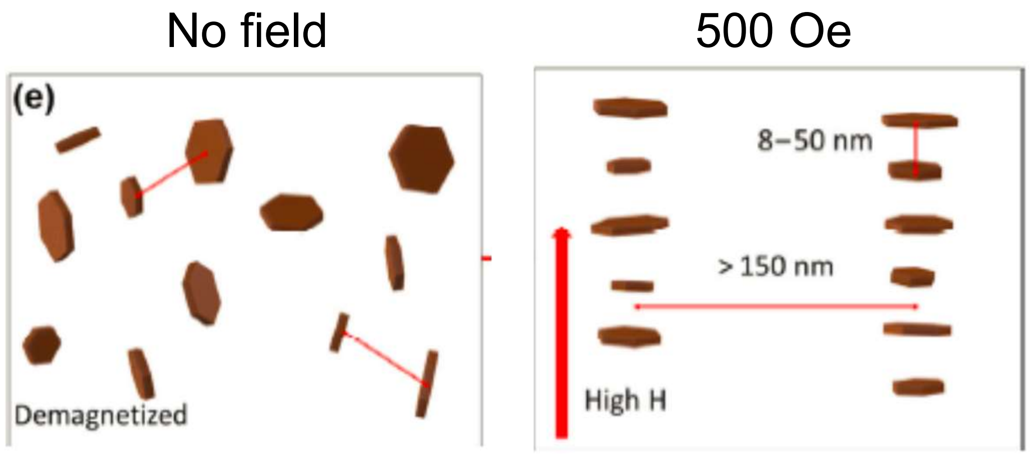


Small-angle X-ray scattering

X-ray small-angle scattering was fitted by Lorentzian (L) for Bragg peaks and Squared Lorentzian (SL) for small q. Field dependences of Lorentzian amplitude and squared Lorentzian amplitude were analized



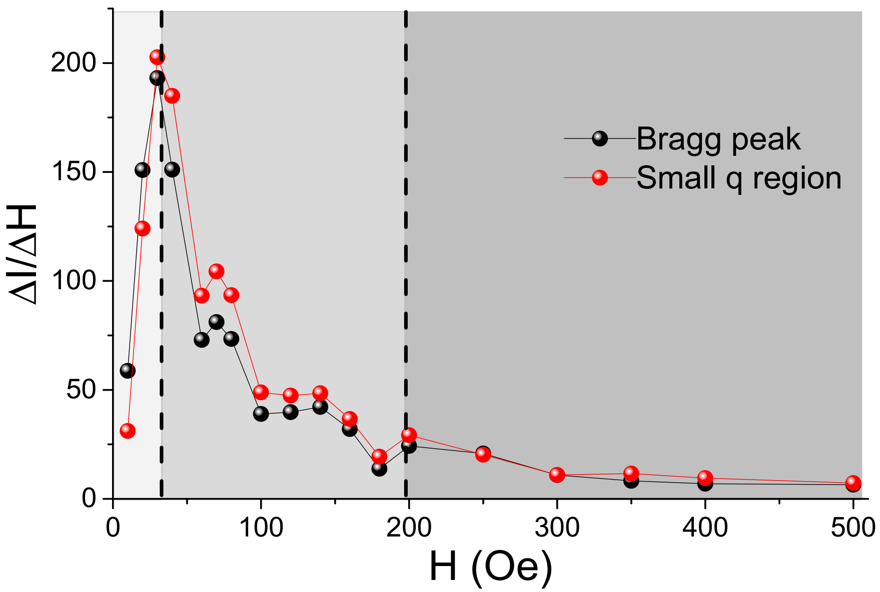




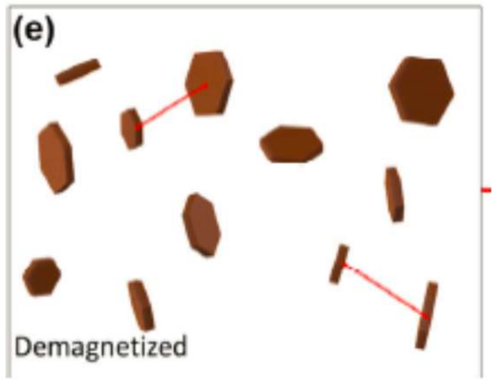
Phase transition of isotropic-nematic liquid

Small-angle X-ray scattering

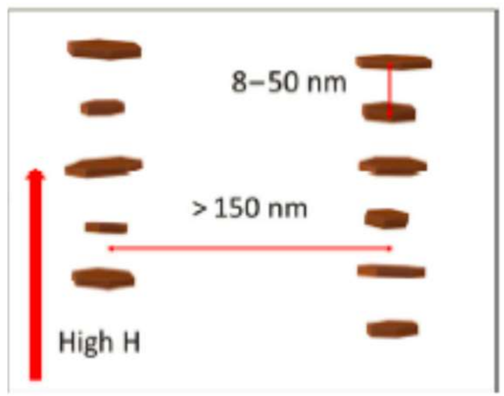
Field dependence of the increase in the scattering curve intensity ΔI/ΔH along the applied field



No field



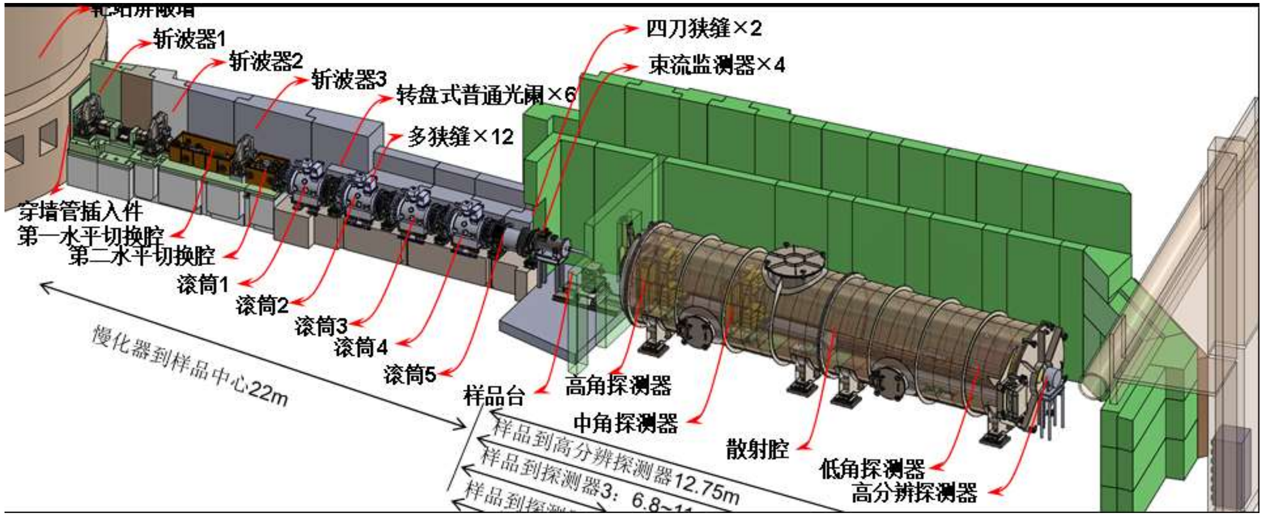
500 Oe



Phase transition of isotropic-nematic – smectic (?) liquid

The small angle scattering of polarized neutrons

BL14: Very Small-Angle Neutron Scattering at CSNS.



Currently operating at 160 kW,

$f_{proton} = 25$ Hz

λ: 2.2 ÷ 6.7 nm

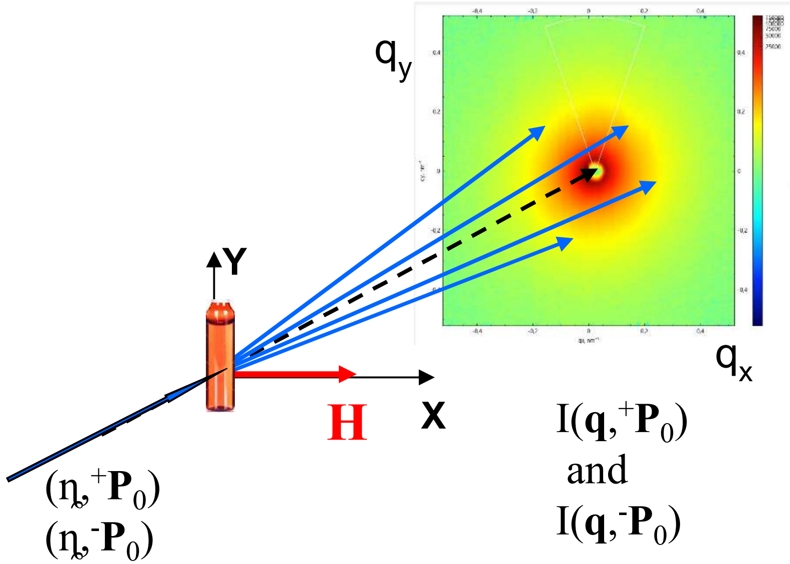
Δλ: 3%

q range: 0.007 ÷ 0.25 Å

Δq/q: 5-10%

SDD: 11.5 m

Neutron flux at sample $10^6 \div 10^7$ n $s^{-1}cm^{-2}$ at 100 k



The small angle scattering of polarized neutrons

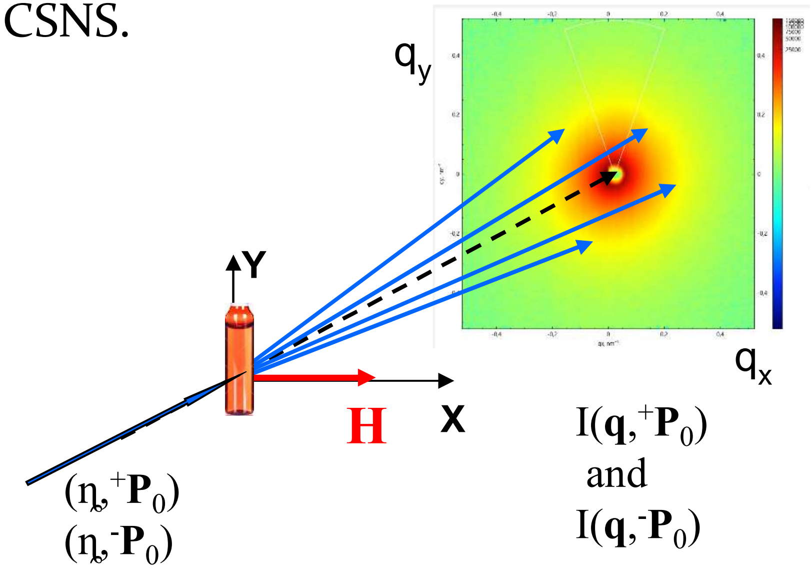
Proposal entitled as “Study of magnetic properties of colloidal liquids based on anisotropic hard magnetic nanoparticles SrFe12O19”

BL14: Very Small-Angle Neutron Scattering at CSNS.

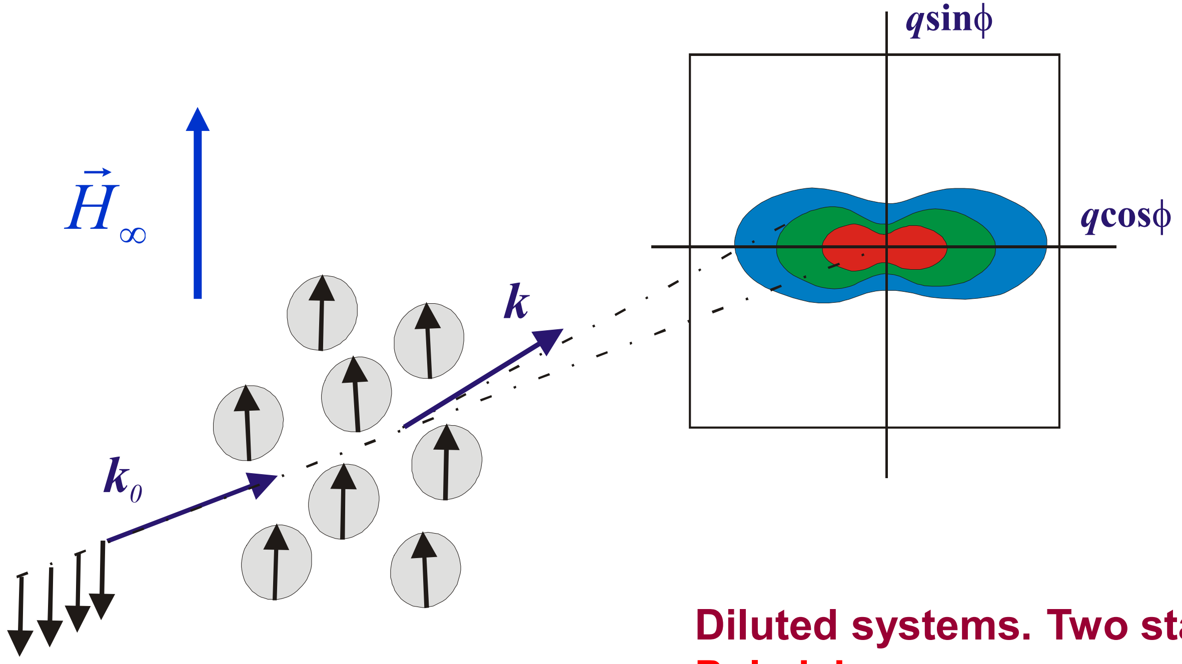
Half polarized option.

Double-V cavity polarizer,
Radio-frequency adiabatic spin-flipper,
Electromagnet 1.5 T
Temperature 5 – 400 K

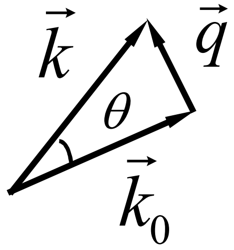
Many thanks to the
Sample Environment group and
Neutron Polarization Facility group



SANS with half polarized option: effect of magnetic field



Incident beam of polarized neutrons



$$\vec{q} = \vec{k} - \vec{k}_0$$

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

Diluted systems. Two states of neutron polarization.
Polydsisperse case

$$\frac{d\sigma^+}{d\Omega}(\vec{q}) \approx < F_N^2(q) > + \{ < F_M^2(q) > -2 < F_N(q) F_M(q) > \} \sin^2\varphi$$

$$\frac{d\sigma^-}{d\Omega}(\vec{q}) \approx < F_N^2(q) > + \{ < F_M^2(q) > +2 < F_N(q) F_M(q) > \} \sin^2\varphi$$

Nuclear form-factor

Magnetic form-factor

Polarized SANS methodology

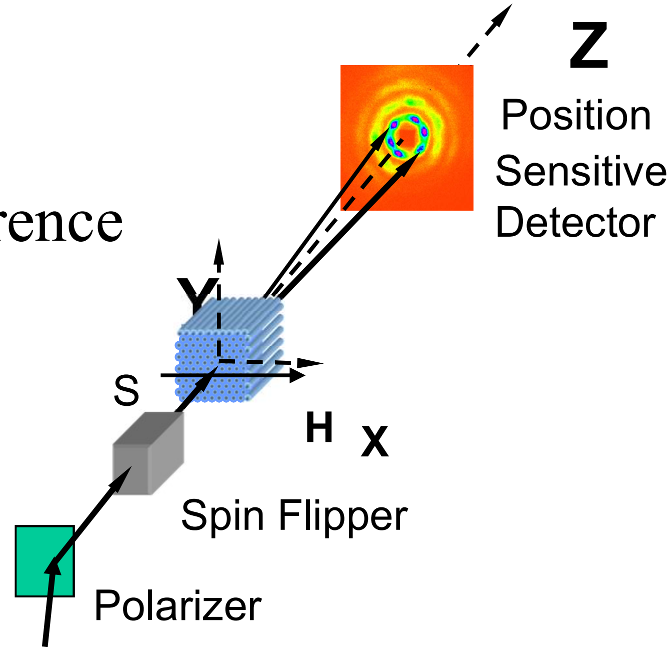
$$|f_Q|^2 = \Sigma_n + \Sigma_m + \Sigma_i$$

Nuclear +Magnetic + NM interference

$$\Sigma_n = |A_n S(\mathbf{Q}) F(Q)|^2$$

$$\Sigma_m = |A_m \mathbf{m}_{\perp\mathbf{Q}} S(\mathbf{Q}) F(Q)|^2$$

$$\Sigma_i = 2(P_0 \langle \mathbf{m} \rangle_{\perp\mathbf{Q}}) A_n A_m |S(\mathbf{Q}) F(Q)|^2$$



$$\mathbf{m}_{\perp q} = \mathbf{m} - (\mathbf{m}\mathbf{q}_e)\mathbf{q}_e$$

Imagine that $Am = 0.1An$ $\quad I = N^2 + F_M^2 = N^2 + (0.1 \times N)^2 = 1.01 \times N^2.$

$$I^+ = N^2 + F_M^2 + 2\,N\,F_M = N^2 + (0.1 \times N)^2 + (2 \times 0.1 \times N^2) = 1.21 \times N^2$$

$$I^- = N^2 + F_M^2 - 2\,N\,F_M = N^2 + (0.1 \times N)^2 - (2 \times 0.1 \times N^2) = 0.81 \times N^2.$$

Polarized SANS methodology

$$I(\mathbf{Q}) = (I(\mathbf{Q},+P_0) + I(\mathbf{Q},-P_0))/2 \sim \sum_n(\mathbf{Q}) + \sum_m(\mathbf{Q})$$

$$I_H(\mathbf{Q}) = I(\mathbf{Q},H) - I(\mathbf{Q},0) \neq I_m(\mathbf{Q},H) - I_m(\mathbf{Q},H=0),$$

$$\Delta I(\mathbf{Q}) = (I(\mathbf{Q},+P_0) - I(\mathbf{Q},-P_0)) \sim 2\sum_i(\mathbf{Q})$$

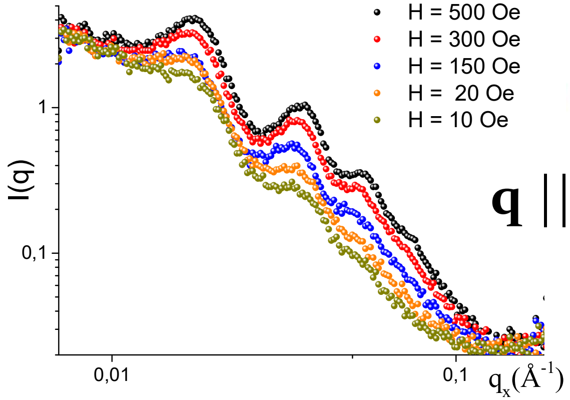
$$\Sigma_n = |A_n S(\mathbf{Q}) F(Q)|^2$$

$$\Sigma_m = |A_n \mathbf{m}_{\perp\mathbf{Q}} S(\mathbf{Q}) F(Q)|^2$$

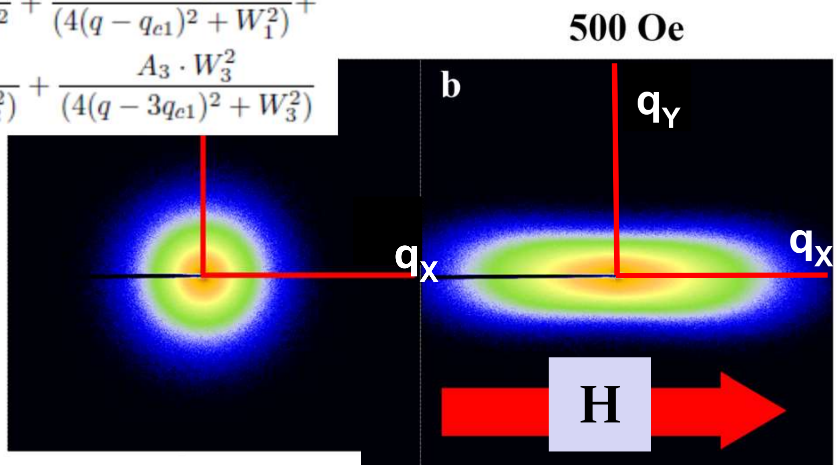
$$\Sigma_i = 2(P_0 \langle\mathbf{m}\rangle_{\perp\mathbf{Q}})\, A_n A_m\, |S(\mathbf{Q}) F(Q)|^2$$

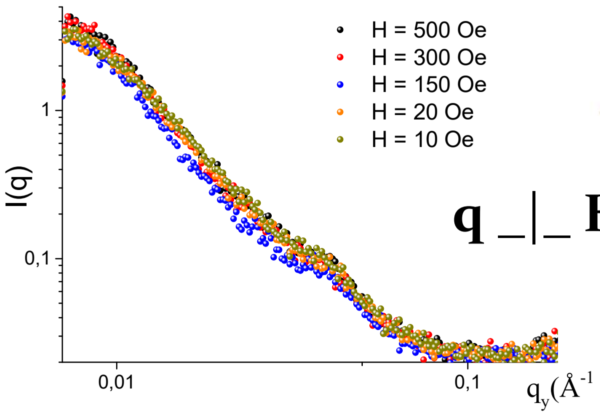
The small angle scattering of *non*-polarized neutrons for hexaferrite nanoparticles

$$I(q) = \frac{1}{2}\left(I(q,+P_0) + I(q,-P_0)\right) \sim \left|A_n S(q) F(q)\right|^2 + \left|A_m m_{\perp q} S(q) F(q)\right|^2$$



$$I(q) = \frac{A_0 \cdot W_0^4}{(q^2 + W_0^2)^2} + \frac{A_1 \cdot W_1^2}{(4(q - q_{c1})^2 + W_1^2)} + \frac{A_2 \cdot W_2^2}{(4(q - 2q_{c1})^2 + W_2^2)} + \frac{A_3 \cdot W_3^2}{(4(q - 3q_{c1})^2 + W_3^2)}$$



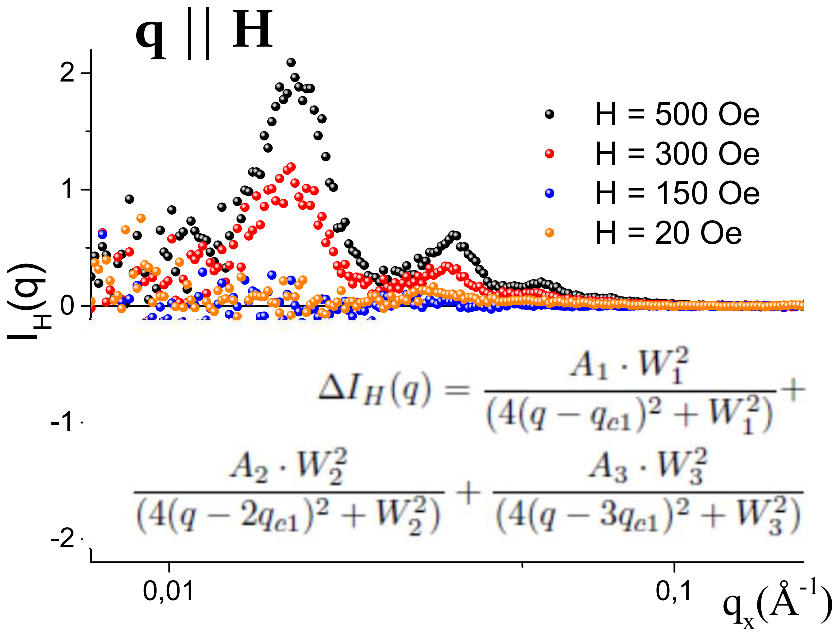


$$I(q) = \frac{A_0 \cdot W_0^4}{(q^2 + W_0^2)^2} + \frac{A_1 \cdot W_1^2}{(4(q - q_{c1})^2 + W_1^2)}$$

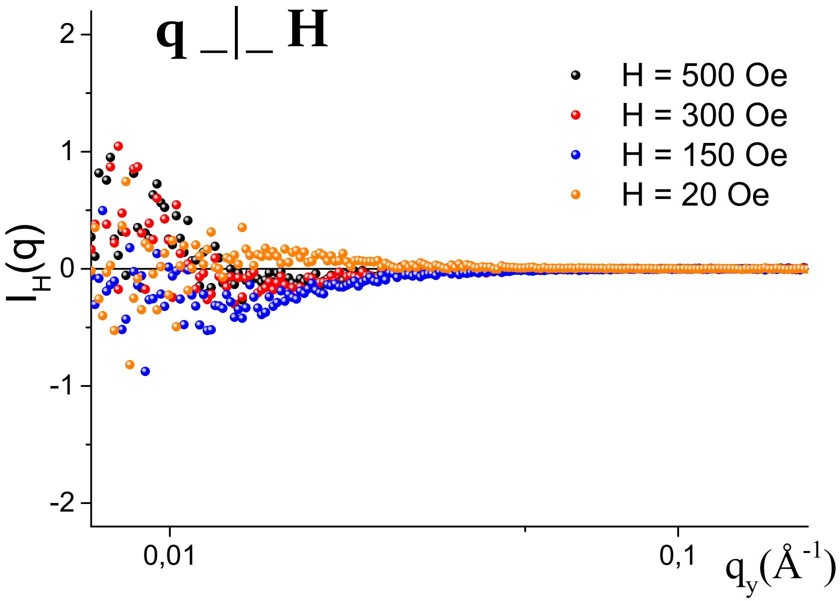
Momentum transfer dependencies of the total cross section intensity I(q)

The small angle scattering of *non*-polarized neutrons for hexaferrite nanoparticles

$$I_H(q) = \mathrm{I}(q, \mathrm{m}(H)) - \mathrm{I}(q, \mathrm{m}(H_c)) \sim \left|A_n S(q) F(q)\right|^2$$



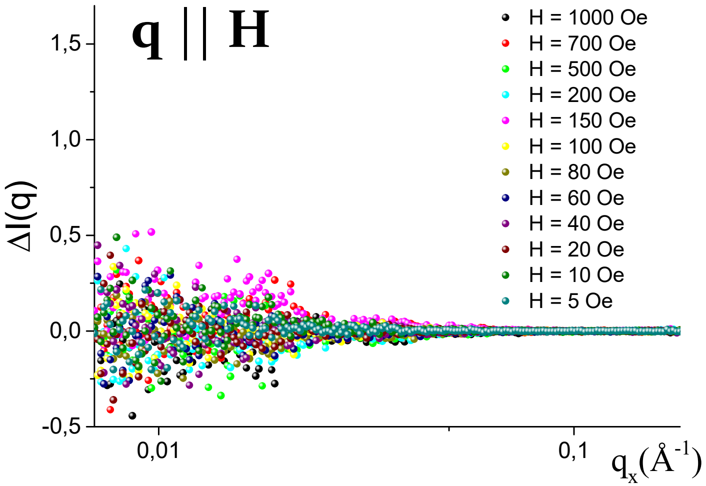
$$\Delta I_H(q) = \frac{A_1 \cdot W_1^2}{(4(q-q_{c1})^2 + W_1^2)} + \frac{A_2 \cdot W_2^2}{(4(q-2q_{c1})^2 + W_2^2)} + \frac{A_3 \cdot W_3^2}{(4(q-3q_{c1})^2 + W_3^2)}$$

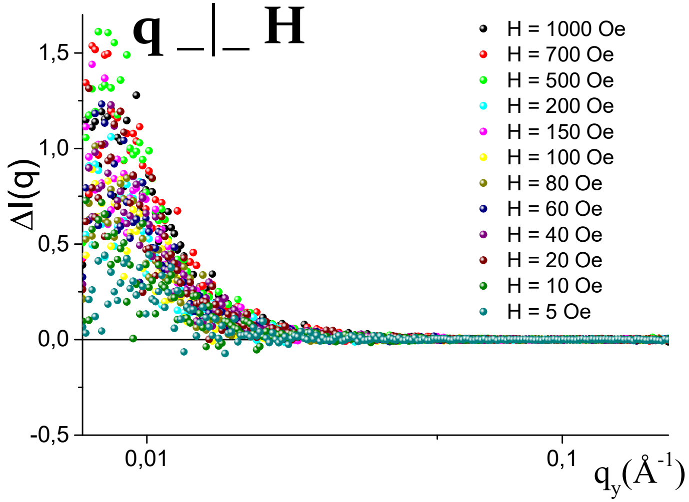


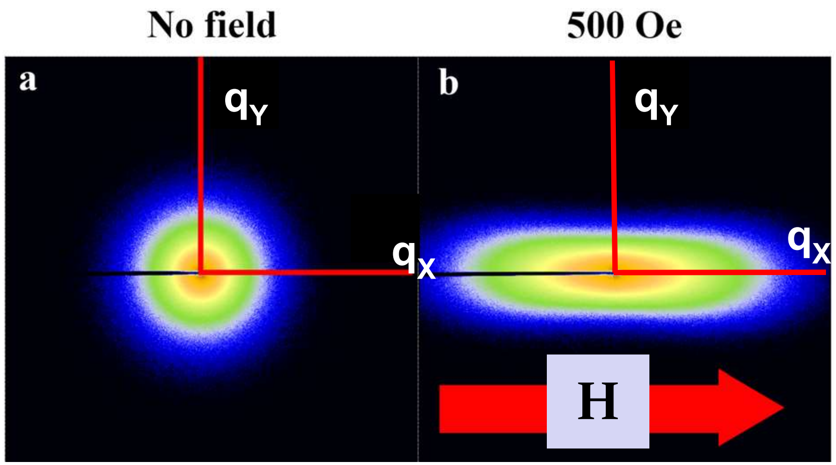
Magnetic-field-dependent neutron cross section $I_H(q)$, *being in fact the nuclear scattering*, reflects structural changes in the colloid.

The small angle scattering of polarized neutrons for hexaferrite nanoparticles

$$\Delta I(q) = (I(q,+P_0) - I(q,-P_0)) \sim 4(P_0 m_{\perp q})A_n A_m |S(q)F(q)|^2$$

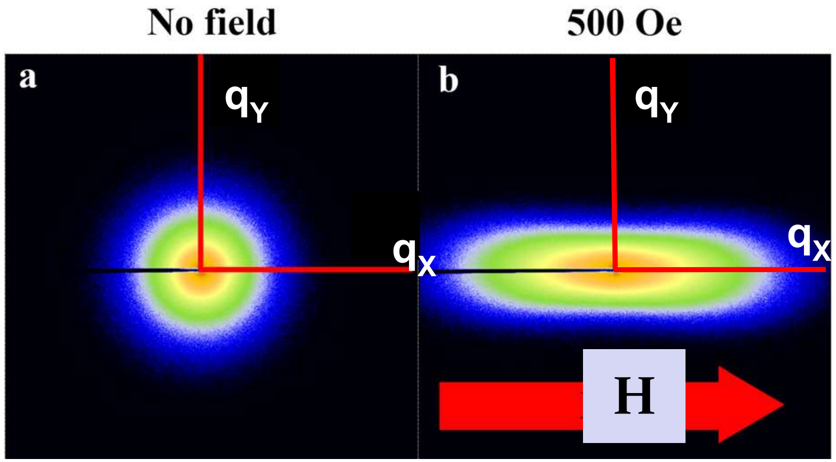






Momentum transfer dependencies of the interference nuclear – magnetic scattering ΔI(q)

The small angle scattering of polarized neutrons for hexaferrite nanoparticles

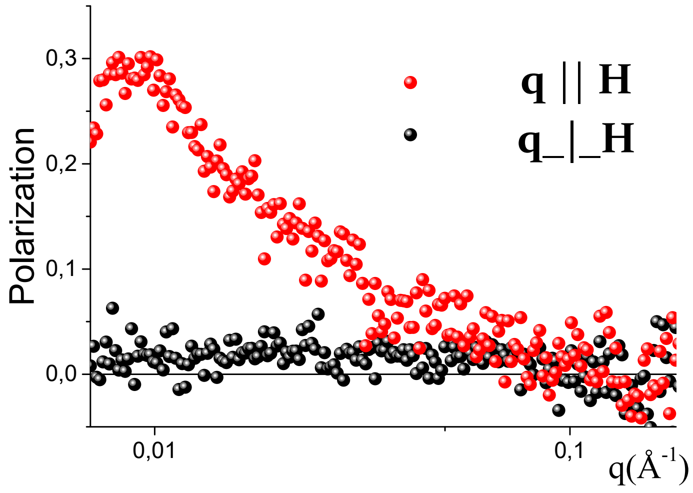


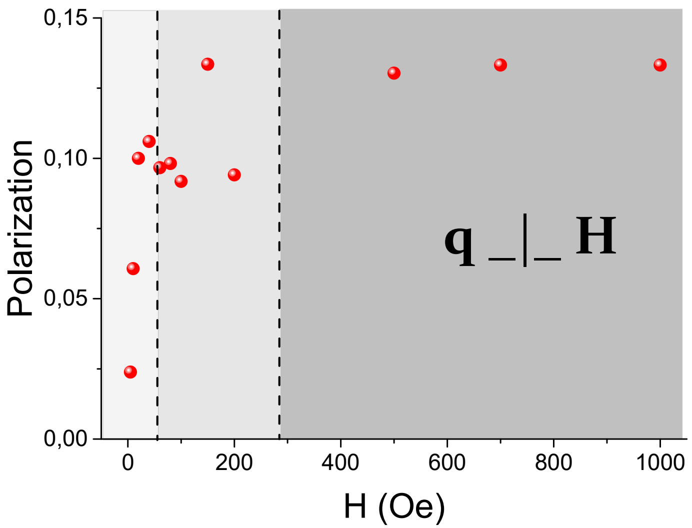
$$P(q) = \frac{\Delta I(q)}{I(q)} \sim 4(\mathbf{P}_0 \mathbf{m}_{\perp q})\frac{A_n A_m}{A_n^2 + A_m^2}) \sim$$

$$4\sin^2\alpha \frac{A_m}{A_n} = 4\frac{A_m}{A_n}$$

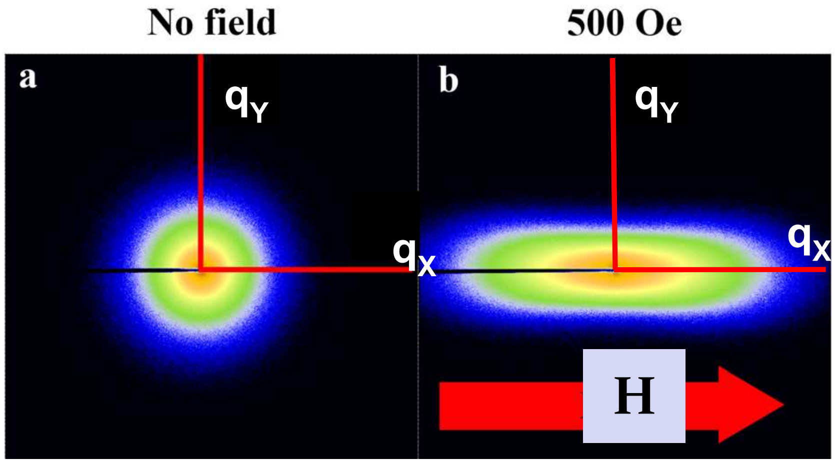
$$\langle P \rangle(q) = \frac{1}{N}\Sigma_{i=1}^{N} P(q, H_i)$$

$$\langle P \rangle(H) = \frac{1}{M}\Sigma_{i=1}^{M} P(q_i, H)$$



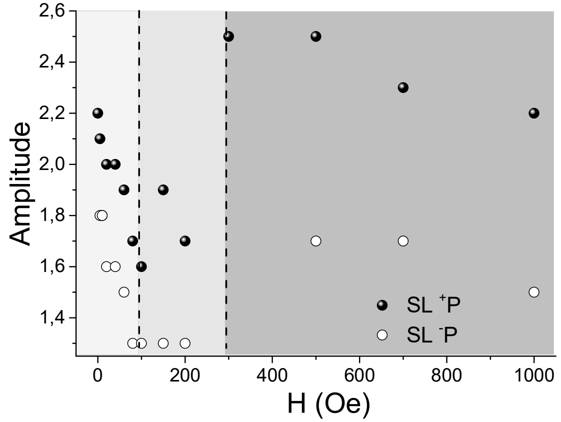


The small angle scattering of polarized neutrons for hexaferrite nanoparticles



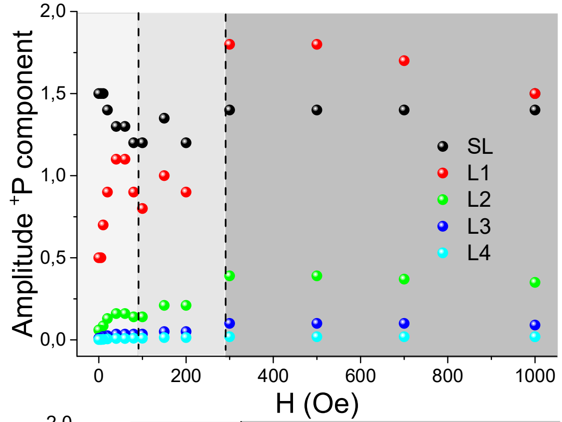
$$I(q) = \frac{A_0 \cdot W_0^4}{(q^2 + W_0^2)^2} + \frac{A_1 \cdot W_1^2}{(4(q - q_{c1})^2 + W_1^2)}$$

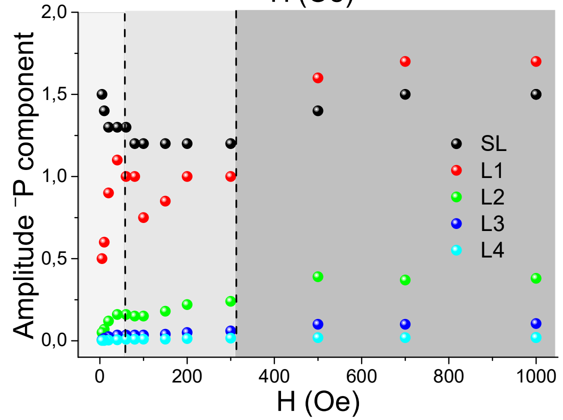
q _|_ H



$$I(q) = \frac{A_0 \cdot W_0^4}{(q^2 + W_0^2)^2} + \frac{A_1 \cdot W_1^2}{(4(q - q_{c1})^2 + W_1^2)} + \frac{A_2 \cdot W_2^2}{(4(q - 2q_{c1})^2 + W_2^2)} + \frac{A_3 \cdot W_3^2}{(4(q - 3q_{c1})^2 + W_3^2)}$$

q || H





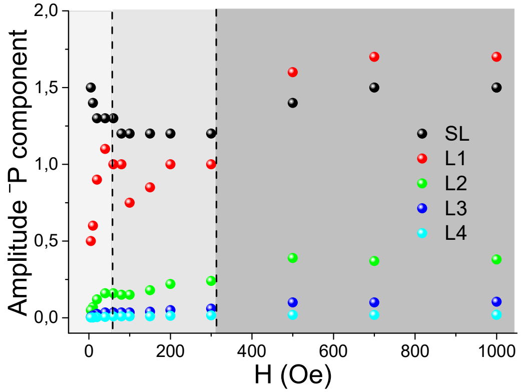
The small angle scattering of polarized neutrons for hexaferrite nanoparticles

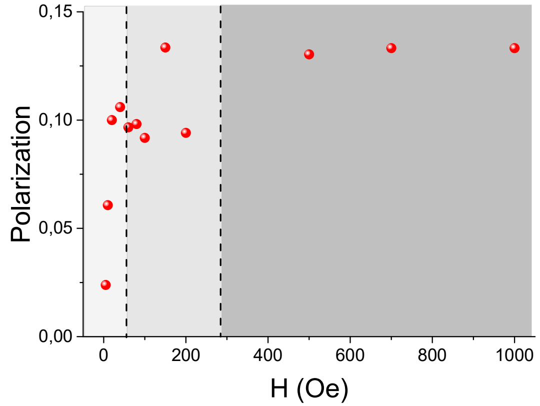
MODEL: electrostatic force (repulsive) + magnetostatic (attractive) = equilibrium of nanoparticles in colloidal solution in 3D box at

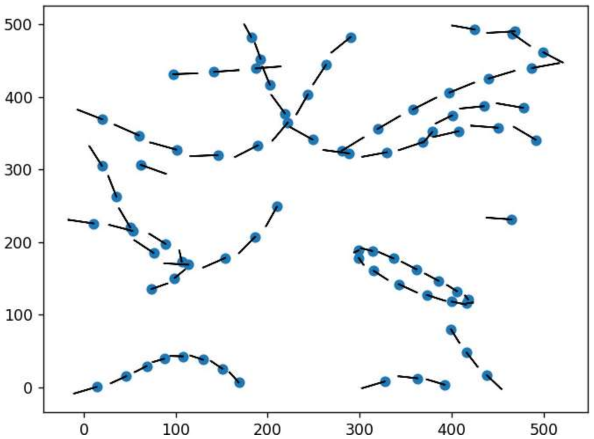
(i) $H < H_C$;

(ii) $H_C < H < H_{sat}$

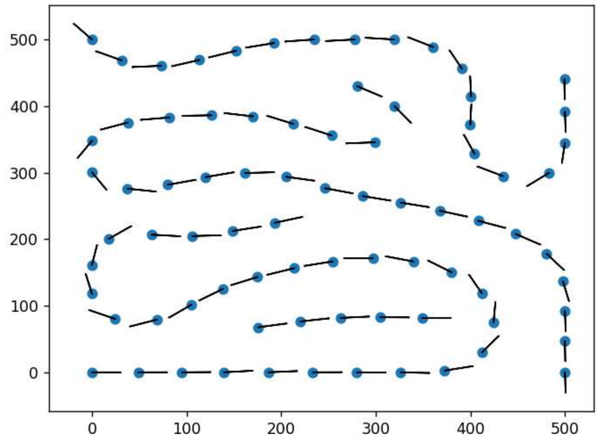
(iii) $H_{sat} < H$



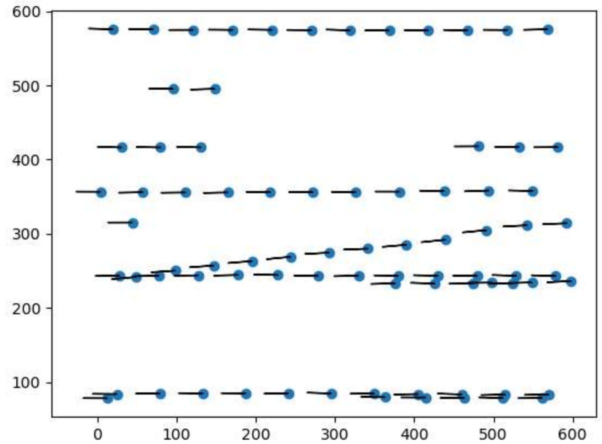




$0 = H < H_C$



$H_C < H < H_{sat}$



$H > H_{sat}$

Conclusions

At the magnetization process three structural states of the hexaferrite ferrofluid can be identified in different magnetic field regions:

- disordered magnetic chains of hexaferrite particles at low fields
- spiral-like structures oriented along the magnetic field
- short strait columns of the 10-12 particles directed rigidly along the magnetic field.

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