MAGNETIC SCATTERING DETERMINATION FROM SANS CONTRAST VARIATION EXPERIMENTS AT IBR-2 REACTOR

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Received September 14, 2015

Separate determination of the nuclear and magnetic contributions to the scattering intensity by means small angle neutron scattering (SANS) method is analyzed. The possibility of simultaneous and separate investigation of nuclear and magnetic structures of a system by means of neutron scattering gives especially valuable the use of neutrons in magnetic materials characterization. The experimental necessity of a magnetic field application during the SANS measurements change the initial state of the colloidal disperse system, unlike in the case of the bulk materials. The SANS method with the use of contrast variation technique for studying the structure of magnetic colloidal particles solve this problem and eliminates the need for a magnetic field application during the measurements.

Key words: small angle neutron scattering, magnetic nanoparticles, ferrofluids.

1. INTRODUCTION

Magnetic nanoparticles are one of the most interesting classes of material due to their numerous technical applications. There is a continuing interest in the development of magnetic nanoparticles, especially because of their applications in the fields of high-density recording, [1, 2, 3], catalysis [4], ferrofluids, sensors, transducers, imaging and therapy, for example hyperthermia [5, 6, 7, 8, 9, 10]. A growing interest recently emerged for investigating effects of magnetic nanoparticles on biological and artificial lipid membranes [11], on microorganism cells [12] and for targeted delivery of DNA into tissues and cells [13].

Different synthesis processes have been proposed, such as the sol–gel method [14], chemical co-precipitation [9, 10, 15, 16, 17, 18], spraying co-precipitation [19], forced hydrolysis in a polyol medium [20, 21], forced hydrolysis and combustion method [22], synthesis in oil-in-water micelles [23], synthesis in reverse micelles [24] or thermal decomposition of mixed complexes [25, 26], hydrothermal preparation [27].

The development and optimization of the obtaining process requires knowledge about their characterization.
The use of neutrons in magnetic materials characterization has the advantage of allowing to be obtained simultaneously the information on the physical and magnetic structure of the investigated system.

In the present paper, the possibility of separate investigation of nuclear and magnetic structures of a system by means of small angle neutron scattering (SANS) method is reviewed.

The method with the use of contrast variation technique [28–30], studying the structure of magnetic colloidal particles, performed on the small angle scattering facility installed at the IBR-2 high pulsed reactor of the Joint Institute of Nuclear Research, Dubna, Russia, is discussed. This method eliminates the need for the magnetic field application and the use of polarized neutrons in the process to separate the nuclear and magnetic scattering from a colloidal disperse system.

2. THEORY

The effective cross section for the general scattering process relative to a scatterer nucleus according to [31] is defined as:

$$\frac{d\sigma}{d\Omega} = b^2 + 2bpq \lambda + p^2q^2$$  \hspace{1cm} (1)

where,

- $b$ is the nuclear scattering length;
- $p$ is the magnetic scattering length;
- $\lambda$ is the versor of the incident to the sample neutron polarization direction;

where, $q$ is the vector of the magnetic interaction:

$$q = \vec{\varepsilon} (\vec{\varepsilon} \cdot \vec{K}) - \vec{K}$$  \hspace{1cm} (2)

$\vec{K}$ and $\vec{\varepsilon}$ are the unit vectors of the magnetization direction of the sample, respectively of the orthogonal direction to the scattering plan (scattering unit vector).

Several methods for separate determination of nuclear and magnetic components of neutron scattering derived from relation (1) using polarized and unpolarized neutrons are known [32].

It is obvious from (2) that the vector $q$ is in the plane formed by the unit vectors $\vec{\varepsilon}$ and $\vec{m}$, and is perpendicular to $\vec{\varepsilon}$, and $|q| = \sin \alpha$, where, $\alpha$ – is the angle between the unit vectors $\vec{\varepsilon}$ and $\vec{K}$.

If the neutrons are not polarized, then the unit vector of the spin direction of the incident neutrons $\vec{\lambda}$ can have any orientation. In this case $\langle q \cdot \lambda \rangle = 0$, therefore, the average over the central term of (1) is zero, and the expression (1) becomes:
\[
\frac{d\sigma}{d\Omega} = b^2 + p^2 q^2 = b^2 + p^2 \sin^2 \alpha .
\] (3)

In the absence of magnetic field, the average \( q^2 \) is equal to:
\[
\langle q^2 \rangle = \langle \sin^2 \alpha \rangle = \frac{2}{3}
\]
\[
\frac{d\sigma}{d\Omega} \text{ becomes:}
\]
\[
\frac{d\sigma}{d\Omega} = b^2 + \frac{2}{3} p^2
\] (4)

For the extraction of proper information about the magnetic and nuclear microstructure of the studied system, the magnetic and nuclear contributions of the differential effective scattering cross section must be identified and studied separately. All methods of separately determination of the nuclear and magnetic contributions to the differential effective scattering cross-section from SANS experimental data on magnetic materials, use one of the following three expressions (1), (3) or (4) [32].

In the case of polarized neutrons, for the separate determination of the nuclear and magnetic contributions, to the investigated sample is applied a saturation magnetic field and for the differential effective scattering cross section is used the expression (1). Experimentally, the scattering of neutrons in two cases, when \( \vec{\lambda} \parallel \vec{K} \) and \( \vec{\lambda} \perp \vec{K} \) are parallel and antiparallel is measured. Therefore, the differential effective scattering cross-section in one and another case is described as follows:
\[
\frac{d\sigma}{d\Omega} = (b + p)^2 \quad \vec{\lambda} \parallel \vec{q}
\] (5)
\[
\frac{d\sigma}{d\Omega} = (b - p)^2 \quad \vec{\lambda} \perp \vec{q}
\] (6)

Using simple mathematical operations from the relation (5) and (6) it is possible to determine separate the nuclear and magnetic contributions to the differential effective scattering cross-section in the magnetized sample.

In case of nonpolarized neutrons, for the separate determination of the nuclear and magnetic contributions to the differential effective scattering cross-section are carried out two measurements using one of the following of 3 schemes:

a) in case of a magnetic field applied to the sample and directed parallel to the scattering vector, \( \vec{H} \parallel \vec{q} \), the differential effective scattering cross section is,
\[
\frac{d\sigma}{d\Omega} = b^2, \quad (7)
\]

b) In the case of an applied magnetic field perpendicular to the scattering vector \( \vec{H} \perp \vec{e} \), the differential effective scattering cross section is,
\[
\frac{d\sigma}{d\Omega} = b^2 + p^2, \quad (8)
\]
c) In case of no magnetic field, \( \vec{H} = 0 \), the differential effective scattering cross section is,
\[
\frac{d\sigma}{d\Omega} = b^2 + \frac{2}{3} p^2. \quad (9)
\]

For the separate determination of the nuclear and magnetic contribution values using unpolarized neutrons, it is enough to accomplish the measurements using the two of three above presented experimental configuration variants (a, b, c) and to apply simple mathematical operations.

In the case of a colloidal system of magnetic particles, another method, which eliminates the need for the magnetic field application can be used. This method represents an extended variant of the contrast variation method [28, 29, 30] for nanoparticulate suspensions with magnetic properties.

### 3. MAGNETIC SCATTERING DETERMINATION FROM SANS CONTRAST VARIATION METHOD

The contrast variation method represents a particularization of the isomorphic substitution method, initially used in the X-ray technique by Bragg & Perutz [33]. This method was first applied to neutrons by Stuhrmann and Kirstie works [28, 29]. They found out that hydrogen and deuterium were always susceptible of being substituted isomorphic and had different nuclear scattering lengths: \( b_H = -3.741 \times 10^{-15} \) m and \( b_D = 6.674 \times 10^{-15} \) m. In all these experiments, the contrast variation method was used to extract structural information only from the neutron scattering nuclear single component present in the case of non-magnetic scatterers system.

Starting from this idea they developed series of experiments in which being involved hydrogenated substances (mainly organic substances), the analysis of these materials by neutron scattering method have shown to be effective by using the substitution of hydrogen with deuterium.

Thus, they showed that for diluted suspension of particles, the efficient macroscopic scattering cross-section per particle in vacuum is:
Magnetic scattering determination from SANS contrast variation experiments at IBR-2 reactor

\[ \frac{d\Sigma(\hat{Q})}{d\Omega} = \left\langle |F(\hat{Q})|^2 \right\rangle = \left\langle \left| \int V \rho(\vec{r}) \exp(i\hat{Q} \cdot \vec{r}) d^3r \right|^2 \right\rangle \]  

(10)

where \( F(\hat{Q}) \) represents the particle form factor.

However, the particle is not in vacuum but in an homogenous solvent, having average scattering density, \( \rho_s \). Then \( \frac{d\Sigma}{d\Omega} \) shall be [34]:

\[ \frac{d\Sigma(\hat{Q})}{d\Omega} = \left\langle |F(\hat{Q})|^2 \right\rangle = \left\langle \left| \int V (\rho(\vec{r}) - \rho_s) \exp(i\hat{Q} \cdot \vec{r}) d^3r \right|^2 \right\rangle \]  

(11)

Volume \( V \), occupied by the molecules of a particle, represents the volume that is inaccessible to the solvent. The contrast \( K \) between the particle and the solvent can be written as follows:

\[ K = \frac{1}{V} \int V (\rho(\vec{r})d^3r - \rho_s) = \rho_v - \rho_s \]  

(12)

whereas, \( \rho_v \) represents the average scattering density of the particle.

When we consider the particles to be polydisperse or nonspherical, the form factor varies from particle to particle. If the particle size and orientation are uncorrelated with the positions of the particles, the relation (10) can be written [35] as

\[ \frac{d\Sigma(\hat{Q})}{d\Omega} = \frac{1}{V} \left\langle \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} \left\langle F(\hat{Q})F^*(\hat{Q}) \right\rangle \times \exp \left[ i\hat{Q} \cdot (\vec{R}_i - \vec{R}_j) \right] \right\rangle. \]  

(13)

Where the inner brackets represent an average weighted by the distribution of particle sizes and orientations.

Therefore, the cross-section reduces to

\[ \frac{d\Sigma(\hat{Q})}{d\Omega} = n_p \left\{ \left\langle |F(\hat{Q})|^2 \right\rangle - \left\langle |F^*(\hat{Q})|^2 \right\rangle \right\} + n_p \left| \left\langle F(\hat{Q}) \right\rangle \right|^2 S(\hat{Q}), \]  

(14)

where \( n_p = \frac{N_p}{V} \) is the average number density of particles in the sample and \( S(\hat{Q}) \) is the interparticle structure factor defined by

\[ S(\hat{Q}) = \frac{1}{N_p} \left\langle \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} \exp \left[ i\hat{Q} \cdot (\vec{R}_i - \vec{R}_j) \right] \right\rangle. \]

To observe the effects of polydispersity and orientational averaging on the scattering cross section, the relation (17) can be rewritten as
\[
\frac{d\Sigma(Q)}{d\Omega} = n_r P(Q) S'(Q)
\]  
(15)

where \( S'(Q) = 1 + \beta(Q) \left[ S(Q) - 1 \right] \), \( \beta(Q) = \frac{\left\langle |F(Q)|^2 \right\rangle}{\left\langle |F(Q')|^2 \right\rangle} \) \( = \frac{\left\langle |F(Q)|^2 \right\rangle}{\left\langle |F(Q')|^2 \right\rangle} \) and \( P(Q) = \left\langle |F(Q)|^2 \right\rangle \).

For the case of a system with monodisperse particles, \( \beta(Q) = 1 \) and the
relation (15) acquires a simple form

\[
\frac{d\Sigma(Q)}{d\Omega} = n_r P(Q) S(Q).
\]  
(16)

For a very low particle density \( S'(Q) = S(Q) = 1 \) and

\[
\frac{d\Sigma(Q)}{d\Omega} = n_r P(Q).
\]  
(17)

In the case of isotropic systems containing homogeneous particles, the scattering vector \( Q \) can be replaced with its magnitude \( Q \).

The contrast variation method, applied to the investigation of colloidal isotropic and homogeneous magnetic nanoparticles by means of small angle neutron scattering (SANS) experiments, consist in measuring \( \frac{d\Sigma_c(Q)}{d\Omega} \), the differential cross-section of the coherent elastic neutron scattering as a function of \( Q \), the momentum transfer, \( Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \) where \( \lambda \) is the wavelength of the neutron while \( \theta \) is the scattering angle, for each investigated sample [36].

The samples are composed of a dilute suspension (about 0.6% volume concentration) of nanoparticles in a liquid matrix, with a given value of \( x \), the volume fraction of deuterated substance in the fluid carrier formed from the combination H-D (deuterated substance – the same substance non deuterated). The value \( x \) is chosen to have at least six equidistant values ranging from 0 \( \div \) 1 (0.0; 0.2; 0.4; 0.6; 0.8; 1.0). Measurements must be also performed on all the compositions of the carrier liquids, free of particles, measuring in such way \( \frac{d\Sigma_c}{d\Omega} \) for the same values of \( x \). The difference \( \frac{d\Sigma(Q)}{d\Omega} = \frac{d\Sigma_c(Q)}{d\Omega} - \frac{d\Sigma_c}{d\Omega} \) represents the excess scattering power of the colloidal particles.

Neglecting interparticle correlations and size polydispersity, on one hand, and presuming approximately spherical particles, on the other, for values of \( Q \)
small enough to ensure the Guinier’s law \([37]\), \(Q \cdot R \leq 1\), to be valid and magnetic particle magnetic form factor \(f \sim 1\), the differential scattering cross-section for unpolarized neutrons may be written as

\[
\frac{d\Sigma(Q)}{d\Omega} = \frac{d\Sigma_n(Q)}{d\Omega} + \frac{d\Sigma_m(Q)}{d\Omega}
\]  

(18)

Further there are determined the curves \(\frac{d\Sigma(Q)}{d\Omega}\) versus of \(Q^2\) for each value of \(x\). From the extrapolation of these curves to \(Q = 0\) the values of \(\frac{d\Sigma(0)}{d\Omega}\) for each value of \(x\) are obtained. The graph of the \(\frac{d\Sigma(0)}{d\Omega}\) is represented as a function of \(x\). The existence of a minimum point at \(x = x_0\) is determined.

In the relation (18), only the nuclear component \(\frac{d\Sigma_n(Q)}{d\Omega}\) can be dependent on the isotopic composition of the sample, therefore, the value of \(x\). The magnetic component \(\frac{d\Sigma_m(Q)}{d\Omega}\) does not depend on \(x\). Due to the contrast variation, the general theory consider that this minimum is about zero, because the contrast is compensated.

![Graph](image)

**Fig. 1** – The dependence of the scattering cross-section value extrapolated to \(Q = 0\), \(\frac{d\Sigma(0)}{d\Omega}\), depending on the volume fraction of deuterated solvent, \(x\).
Given the physical system is defined statistically, meaning that although the alleged identical colloidal particles may be small variations in density, ability to rigorously equal to zero contrast value is excluded. However, for \( x = x_0 \) the nuclear contrast it is very small in comparison with the density of magnetic scattering, so in this respect the residual contribution of nuclear scattering can be neglected relative experimental the error of 5% of the method of small angle neutron scattering.

So, it can be considered that at \( x = x_0 \) is present only the magnetic scattering and \( \frac{d \sum_m(Q)}{d \Omega} \) becomes [36, 38, 39]:

\[
\frac{d \sum_m(Q)}{d \Omega} = \frac{d \sum(Q)}{d \Omega} \bigg|_{x = x_0} .
\]  

The relation (19) allows to be determined the magnetic component of the effective macroscopic differential neutron scattering cross-section and from the relations (18) and (19) is determined the nuclear component of the neutron scattering cross-section [36, 38, 39]

\[
\frac{d \sum_n(Q)}{d \Omega} = \frac{d \sum(Q)}{d \Omega} - \frac{d \sum(Q)}{d \Omega} \bigg|_{x = x_0} .
\]  

Thus, the separate nuclear and magnetic components of the small angle scattering of unpolarized neutrons are determined [40].

Further, using relations (17) and (18) we obtain

\[
\frac{d \sum(Q)}{d \Omega} = n_p P'(Q) ,
\]  

where \( P'(Q) = P_n(Q) + P_m(Q) \).

Analyzing the \( P_n(Q) \) and \( P_m(Q) \) for \( Q \rightarrow 0 \), features of the physical or magnetic structure of the system can be obtained: forms, sizes, size distributions. In the range Guinier [37], where \( Q \cdot r \ll 1 \) the relation (10) can be rewritten as

\[
\frac{d \sum(Q)}{d \Omega} = \frac{d \sum(0)}{d \Omega} \exp \left[ - \frac{R^2 Q^2}{3} \right]
\]  

where, \( \frac{d \sum(0)}{d \Omega} = (\rho V)^2 ; \rho \) and \( V \) are the scattering density, respectively the particle volume; \( R_g \) is the gyration radius characterizing the particle dimension.

Therefore, the relation (18) becomes [36, 39]:

\[
\frac{d \sum(Q)}{d \Omega} = \frac{d \sum_{nm}(0)}{d \Omega} \exp \left[ - \frac{R^2 Q^2}{3} \right] + \frac{d \sum_n(0)}{d \Omega} \exp \left[ - \frac{R^2 Q^2}{3} \right] + \frac{d \sum_m(0)}{d \Omega} \exp \left[ - \frac{R^2 Q^2}{3} \right]
\]  

(23)
where, $R_{nm}$ and $R_{gm}$ are the nuclear and magnetic gyration radii and

$$
\frac{d \sum_n(0)}{d \Omega} = n_p (\rho_n V_n)^2 \quad \text{and} \quad \frac{d \sum_m(0)}{d \Omega} = \frac{2}{3} n_p (\rho_m V_m)^2
$$

with, $\rho_n$, $\rho_m$ and $V_n$, $V_m$ are the scattering nuclear and magnetic densities, respectively the nuclear and magnetic particle volumes.

4. CONCLUSIONS

The possibility of simultaneous and separate investigation of nuclear and magnetic structures of a system by means of small angle neutron scattering (SANS) gives especially valuable the use of neutrons in magnetic materials characterization.

The experimental necessity of a magnetic field application during the SANS measurements change the initial state of the colloidal disperse system, unlike in the case of the bulk materials. Thus, the usual data processing considering the system isotropic is not properly valuable.

The SANS method with the use of contrast variation technique studying the structure of magnetic colloidal particles solve this problem eliminating the need for a magnetic field application during the measurements. Different type of magnetic nanoparticles can be prepared as low concentration dispersion and analyzed in such a way.

Acknowledgements. The finance support from the Romania-JINR Cooperation Programme on 2014–2015 and Grants of Romanian Governmental Plenipotentiary Representative at JINR Dubna for 2015 is acknowledged.

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