Experimental report

30/03/2021

Proposal: 9-12-559 **Council:** 10/2018

Title: Assessing the production process of holographic nanoparticle-polymer composite gratings using polarized SANS

Research area: Materials

This proposal is a new proposal

Main proposer: Juergen KLEPP

Experimental team: Juergen KLEPP

Local contacts: Robert CUBITT

Samples: nanoparticle-polymer composite

Instrument	Requested days	Allocated days	From	To
D22	2	0		
D33	2	1	23/09/2019	24/09/2019

Abstract:

We use materials that are sensitive to light and apply holographic techniques to develop diffraction gratings for light as well as for long-wavelength neutron optics. These nanoparticle-polymer composite gratings consist of mixtures of monomers, photostarter and particular species of nanoparticles. Under illumination with a periodic light intensity pattern, the raw materi-als exhibit a periodic refrac-tive-index pattern arising from a light-induced redistribution of the con-stituents. In this process, monomers are drawn into bright regions where they are consumed by the polymerization initiated by the illuminated photostarter chemical. The resulting chemical potential gradient draws nanoparticles to the dark regions. A hologram of the periodic light pattern is recorded, which is a nearly sinusoidal density modulation pattern with typical period of some 100 nm. Our goal is to optimize the already elaborate production process by obtaining better understanding of its details. In particular, the experiment described in this proposal aims at testing the efficiency of the nanoparticle redistribution by holographic methods using polarized SANS.

Assessing the production process of holographic nanoparticle-polymer composite gratings using polarised SANS

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We use materials that are sensitive to light and apply holographic techniques to develop diffraction gratings for light as well as for long-wavelength neutron optics [1]. These nanoparticle-polymer composite (NPC) gratings consist of mixtures of monomers, photostarter and particular species of nanoparticles, carefully chosen for the application one has in mind. Under illumination with a periodic light intensity pattern, the materials exhibit a periodic refractive-index pattern arising from a light-induced redistribution of the constituents: Monomers are drawn into bright regions, where they are consumed by polymerization initiated by the photostarter that emits radicals under ilumination. The resulting chemical potential gradient draws nanoparticles to the dark regions. A hologram of the near-plane wave, aperiodic light pattern is recorded, which is a nearly sinusoidal density modulation pattern of nanoparticles and polymer with typical period of some 100 nm (the period of the illuminating pattern). Our goal is to optimize the already elaborate production process by obtaining better understanding of its details. In particular, the experiment described in this proposal aimed at development of a method to test the efficiency of the nanoparticle redistribution by holographic methods, using polarised SANS at the instrument D33 [2].

Holographic gratings can be modeled by the refractive index modulation denoted as $n(x) = n_0 + n_1 \cos(2\pi/(\Lambda)x)$, where n_0 is the average refractive index, n_1 is the modulation amplitude of the refractive index, Λ is the grating period and x is the spatial coordinate along the 1 D modulation (parallel to the direction of the grating vector). For neutrons, $n_1 = \lambda^2 b\Delta\rho/(2\pi)$, with the neutron wavelength λ and the coherent scattering length density modulation amplitude $b\Delta\rho$. For NPC gratings, $b\Delta\rho$ can be viewed as split up into two terms so that we have $b\Delta\rho \rightarrow (b\Delta\rho)_{poly} - (b\Delta\rho)_{NP}$, where "poly" and "NP" are referring to the polymer matrix and the nanoparticles, respectively. The minus sign originates from the naive view that our gratings might be regarded as consisting of two entangled structures of nanoparticle-free (containing only polymer) and polymer-free (containing only nanoparticles) grating structures, shifted by π relative to each other. Clearly, the above is a simplification and this view is not appropriate for accurate determination of $(b\Delta\rho)_{NP}$. Nevertheless, for a given polymer, $(b\Delta\rho)_{NP}$ is a decisive parameter of the production process and, in particular, for nanoparticle redistribution. Since light and also neutron diffraction are not capable of giving a clear answer here and, because of Electron microscopy is not effective with bulk samples, we employed polarized SANS in the following way: We incorporated superparamagnetic nanoparticles (magnetite, for instance) in the NPC material, instead of the species ultimately desired (SiO_2 [1] or nanodiamond [3], for instance). The neutron refractive index modulation amplitude of the grating changes to $b\Delta\rho \rightarrow (b\Delta\rho)_{poly} - (b_{NP} \pm b_m)\Delta\rho_{NP}$, where the latter term – containing the magnetic scattering length density of the nanoparticles – depends (for small q) only on the neutron spin state, the presence of an external magnetic field and the nanoparticle density modulation amplitude, which we desire to study. The former two can be set by experimenters in polarized SANS measurements, the latter can be extracted by measuring with orthogonal spin states separately and subtracting the two signals.

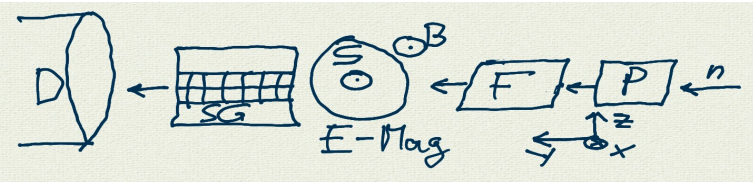
From what was said above, a difference between the curves for different neutron spin states is expected, from which – ultimately – one should be able to draw certain conclusions about the refractive-index profile shape of the gratings and, therefore, the nanoparticle distribution. The proposed diffraction experiment aimed at measuring the neutron DE of holographic gratings recorded in NPC containing magnetite nanoparticles for an unpolarized beam (as reference) and for up- and down-spin to determine the density modulation amplitude of nanoparticles in holographic gratings.

For a first short test of the method, a holographic grating of about 33 microns thickness, 0.5 micron period and about 100 mm^2 circular area recorded in magnetite-NPC material was prepared[1]. We used the D33 sample table as rotation stage for variation of the angle of incidence θ for measuring rocking curves in the range from -3° to 3° in steps of 0.2° (rotation axis in x-direction as shown in Fig. 1, 15 min/position) with and without magnetic field (electromagnet E-Mag in Fig. 1, field strength in x-direction ≈ 1.05 T @ 45 Amps, pole shoe gap of about 25 mm, and pole shoe diameter of 76 mm; measured ≈ 1.7 mT @ 0 Amps at the sample position). To observe magnetic diffraction, the grating vector was set perpendicular to the field direction- The sample rotation axis was parallel to the latter.

For setting the polarization (spin state) of the neutrons, two options were available: *(i)* The cavity polarizer of the instrument and *(ii)* a device using the spin-separating effect of a magnetic field gradient (Stern-Gerlach effect) [see Fig. 1 (b)]. We refer to this device as SG. Using SG, it is not the incident beam that is polarized, but the beam is spatially (laterally) split into two beams in orthogonal spin states after interaction with the sample. Using the 2 D detector of the instrument D33, the diffraction patterns for both spin states can be observed at the same time (see Fig. 2). The polarizer P was

[1] Note for the authors: sample # 123-08

a)



b)

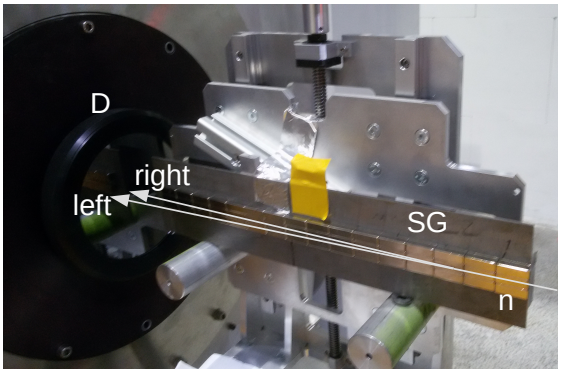


Figure 1: a) Sketch of the SANS setup we used for the experiment at D33. The neutrons enter from the right (in y-direction), are polarized by polarizer P (if needed for adjustment), the polarization flipped by flipper F (if needed for adjustment). The sample S is mounted within the magnetic field (horizontal direction) created by the electromagnet E-Mag. The electromagnet is mounted on the sample table of D33 (not shown) to vary the angle of incidence by rotation about the x-direction. A Stern-Gerlach device (SG, see text and Fig. on the right) seperates the two neutron spin states and enables us to detect the diffraction signals for both spin states simultaneously on the 2 D detector of D33. b) SG is a Halbach array of permanent magnets arranged in parallel and at a distance of a few mm along the neutron flight path to create a horiziontal (x-direction) magnetic field gradient perpendicular to the beam direction [4]. SG splits the beam coming from the sample into two beams prepared in orthogonal spin states (here referred to as 'left' and 'right') after the interaction with the sample.

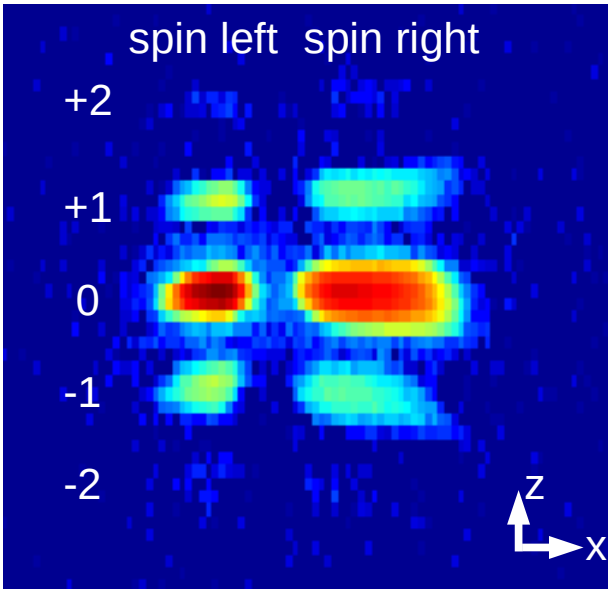


Figure 2: A typical detector image as obtained only using SG (P was not used) and the sample in place at a particular θ. The diffraction spots corresponding to one spin direction are arranged vertically in two columns. The various diffraction orders of the grating (-2,. . . ,+2) are observed in five rows.

mostly used for checking the adjustment of SG.

Note that we also measured the transmitted (forward-diffracted) beam to calculate the diffraction efficiency (DE, defined as the counts in a particular diffraction order divided by the sum of counts in all observed diffraction orders for given θ). The beam divergence for the rocking curves was about 10^{-4} mrad set by choosing collimation distance and apertures accordingly. The wavelength was $\lambda = 1.4$ nm. As measurement result, the DE is plotted as a function of the angle of incidence, i.e. rocking curves were measured.

Some results can be seen in Figs. 3 to 6, where rocking curves measured with the electromagnet turned off and on are shown for the two orthogonal spin states (again referred to as "left" and "right"). It is observed that the diffraction peaks are practically identical for orthogonal spin states with the B field turned off. However, only the ± 1 diffraction orders are left unchanged for the two spin states with the B field turned on. There seems to be a miniscule difference in the ± 2 diffraction orders between spin left and spin right when the B field is on. Since the weak asymmetry in the ± 2 order peak heights switches places from spin left to spin right, which is meaningful, we believe that the effect is really there. However, the experiment could be repeated with at least twice the measurement time/angular position and a smaller sample grating to be able to reach higher field strengths of up to 1.6 T by decreasing the distance between pole shoes, as additional material analysis suggests that there is room for improvment in this respect.

[1] Y. Tomita, E. Hata, K. Momose, S. Takayama, X. Liu, K. Chikama, J. Klepp, C. Pruner, and M. Fally, J. Mod. Opt. **63**, S1 (2016).

[2] C. D. Dewhurst, I. Grillo, D. Honecker, M. Bonnaud, M. Jacques, C. Amrouni, A. Perillo-Marcone, G. Manzin, and R. Cubitt, Journal of Applied Crystallography **49**, 1 (2016).

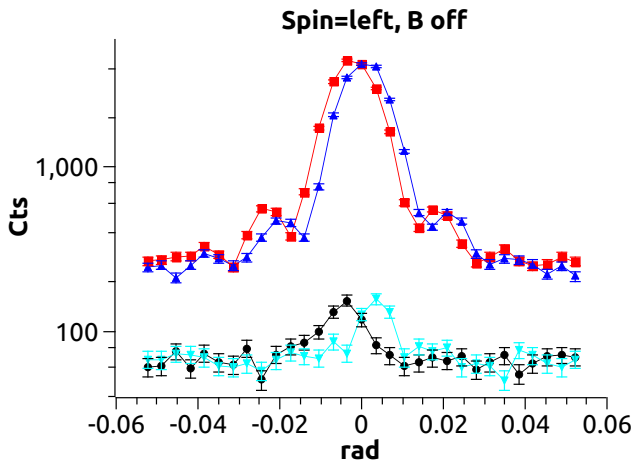


Figure 3: Rocking curve of a magnetite NPC grating (thickness $\approx$ 33 μm, grating spacing = 0.5 μm) with the electromagnet turned off for spin "left".

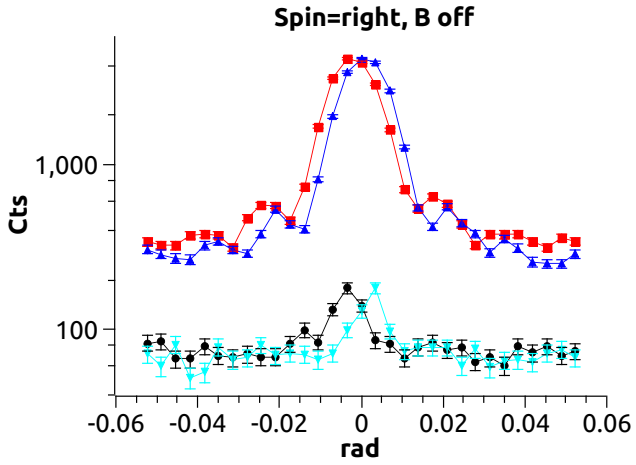


Figure 4: Rocking curve of the same magnetite NPC grating as in Fig. 3 (with the electromagnet turned off also) for spin "right". The curves are practically identical to what is shown in Fig. 3.

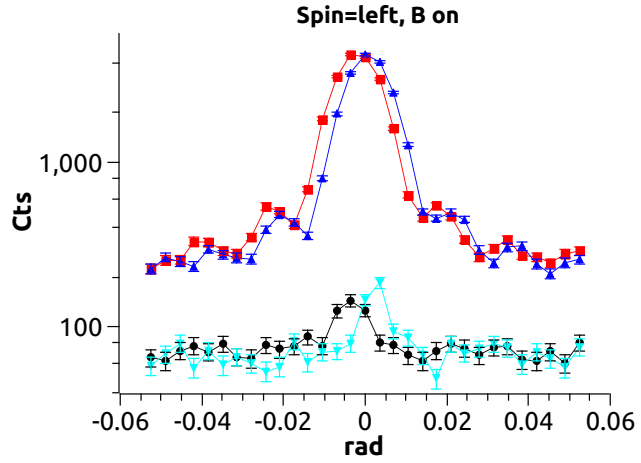


Figure 5: Rocking curve of the same magnetite NPC grating as in Fig. 3 with the electromagnet turned on for spin "left". Note the small asymmetry in the peak heights of the ± 2 diffraction orders.

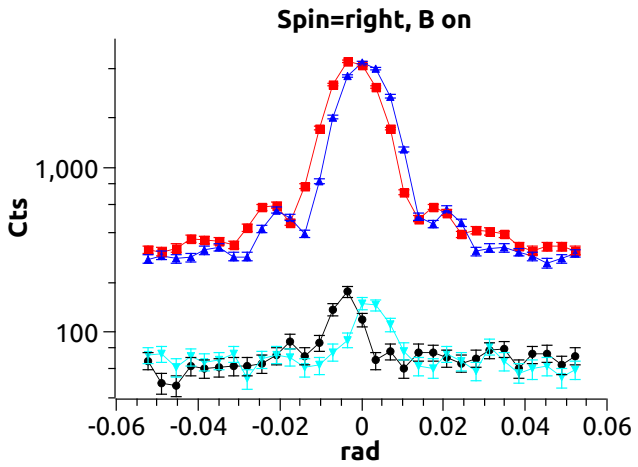


Figure 6: Rocking curve of the same magnetite NPC grating as in Fig. 3 with the electromagnet turned on for spin "right". Note that the small asymmetry in the peak heights of the ± 2 diffraction orders is inversed as compared to Fig. 5.

[3] Y. Tomita, A. Kageyama, Y. Iso, K. Umemoto, A. Kume, M. Liu, C. Pruner, T. Jenke, S. Roccia, P. Geltenbort, M. Fally, and J. Klepp, Phys. Rev. Applied **14**, 044056 (2020).

[4] R. Cubitt, "A neutron Stern-Gerlach device for polarisation analysis," (2019), unpublished.

Proposal-number: 9-12-559
Instrument: D33