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Volume 397 Issues 1–2 15 July 2007 ISSN 0921-4526

PHYSICA B

Recognized by the European Physical Society

CONDENSED MATTER

PNCMI 2006

Proceedings of the Sixth International Workshop on Polarised Neutrons in Condensed Matter Investigations

# PNCMI 2006

held in Berlin, Germany
25–28 September 2006

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Physica B 397 (2007) 23–26
PHYSICA B
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# Topology constrained magnetic structure of Ni photonic crystals

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**Abstract**

We report the small angle polarized neutron scattering study of nickel inverse opals, prepared by templating colloidal crystals made of polystyrene microspheres.


*PACS:* 42.70.Qs; 75.75.+a; 75.25.+z

*Keywords:* Small angle polarized neutron scattering (SAPNS); Photonic crystals; Inverse opals; Frustrated magnetism; Electrodeposition

## 1. Introduction

Photonic crystals (PCs), the materials with a periodic modulation of dielectric constant, have recently attracted a great attention due to their unusual optical properties and promising applications [1]. Self-assembly of monodisperse submicron microspheres provides a convenient tool for synthesis of colloidal crystals, also referred to as artificial opals, which are widely used for modeling of PC optical properties. Another important class of PCs is inverse opals, usually prepared by filling the voids of opal templates with desirable materials and removing of the initial microspheres to leave three-dimensionally ordered porous frameworks [2]. The structure quality is a key parameter for PCs, because only PCs well-ordered on a macroscale could be used for fabrication of optoelectronic devices. The local ordering of microspheres or spherical voids is usually verified by scanning electron microscopy (SEM). Recently, laser diffraction was demonstrated to be effective for characterization of PC structure quality on a scale up to several millimeters [3,4]. The significant limitation of this method is that the diffraction can be observed only if the laser wavelength is less than PC lattice period. Meanwhile, important PCs for visible region possess a periodicity in a range of 200–300 nm, making laser diffraction method not applicable to their study. One can overcome this limitation by using radiation of another type than laser one with a wavelength short enough for recording diffraction patterns from PCs with any periodicity.

Although small angle neutron scattering (SANS) is extensively used for the study of spatially ordered materials, to the best of our knowledge, it was never applied to characterization of PCs. In this work we report the preparation and small angle polarized neutron scattering (SAPNS) study of nickel inverse opals.

## 2. Experimental part

The Ni PC films with an inverse opal structure were prepared using a templating technique. Colloidal crystal films made of 450 nm polystyrene microspheres were grown onto polished Cu substrates by the vertical deposition method [5].

Electrochemical crystallization of nickel in the voids between the spheres was carried out in three-electrode cell at room temperature. The counter electrode was a Pt wire and the reference electrode was saturated Ag/AgCl

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0921-4526/$ - see front matter 
doi:10.1016/j.physb.2007.02.072

electrode connected to the cell via a Luggin capillary; 0.1 M $NiCl_2$, 0.6 M $NiSO_4$, 0.1 M $H_3BO_3$ and 4 M $C_2H_5OH$ solution was used for potentiostatic Ni deposition at $E_d = -0.85$ V versus reference electrode. In order to obtain free-standing Ni structure onto Cu substrate, the polystyrene microspheres were dissolved in toluene.

SEM images of Ni PCs were recorded by LEO Supra 50 VP instrument. The structure and magnetic properties of the samples have been studied by SAPNS with the SANS-2 instrument at the Geesthacht Neutron Facility (GeNF). The beam of polarized neutrons with initial polarization $P_0 = 0.96$, wavelength $\lambda = 0.58$ nm ($\Delta\lambda/\lambda = 0.1$) and divergence of 1.0 mrad was used. The scattered neutrons were detected with a position-sensitive detector with $256 \times 256$ pixels. In SAPNS experiments the PC sample was oriented perpendicular to the incident beam. An external magnetic field (0 and 800 mT) was applied in the plane of the sample.

## 3. Results and discussion

According to the SEM observations, all synthesized samples possess an ordered porous structure with uniform spherical pores (Fig. 1). Cross-section SEM images reveal a face-centered cubic structure of spherical pores in the

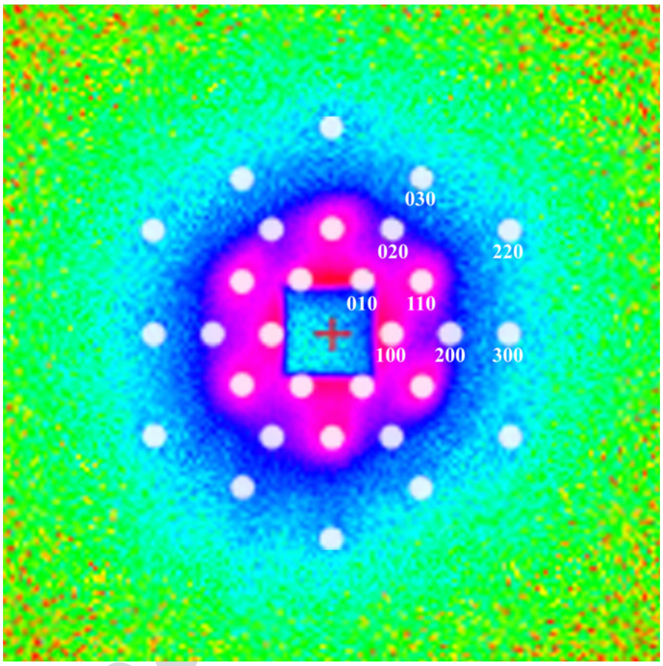


Fig. 2. Typical experimental SAPNS diffraction pattern from Ni PC. The square in the center marks a beam-stop, white circles represent theoretical diffraction pattern.

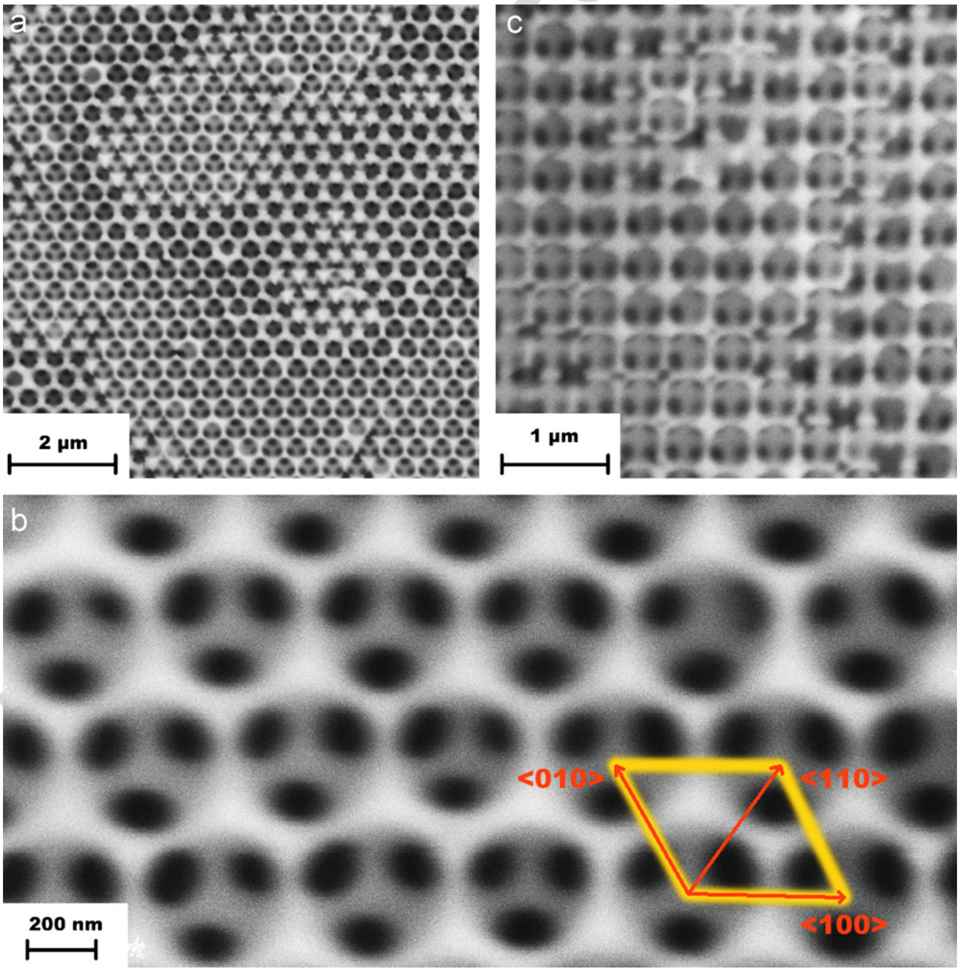


Fig. 1. Low (a) and high (b) magnification SEM images of Ni inverse opals; (c) cross-section SEM image.

nickel framework (Fig. 1c). The average center-to-center distance between close-packed voids is 450 nm, suggesting no structure shrinkage during the fabrication process.

Typical SAPNS diffraction pattern is shown in Fig. 2, demonstrating several clearly resolved sets of hexagonally arranged reflections. In similar laser diffraction experiments, the patterns were interpreted considering each layer of close-packed spherical voids in the PC as an individual two-dimensional (2D) diffraction grating [4]. We can introduce a 2D basis shown in Fig. 1b . For the considered geometry the interplanar spacings ($d_{hk0}$) can be calculated as

$$d_{hk0} = \frac{\sqrt{3}a}{2\sqrt{h^2 + hk + k^2}}.$$

Using $a = 450$ nm, we have found the interplanar distances for the first diffraction maxima ({1 0 0}, {1 1 0}, etc.) and calculated the corresponding values of $q$ -vectors ($q_{hk0} = 2\pi/d_{hk0}$), which were used for plotting the theoretical diffraction pattern (white circles in Fig. 2). It can be seen that the calculated positions for the most intense {1 0 0} and {1 1 0} reflections perfectly match the experimental maxima. The other diffraction reflections are not so well-resolved onto the diffuse scattering background. Meanwhile, high-order diffraction maxima can be seen in $q$-dependences of the neutron intensity $I(q)$ for defined directions. For instance, $q$-dependence in [1 1 0]-direction demonstrates diffraction peaks at $q_{110} \approx 0.028\,\mathrm{nm}^{-1}$ and $q_{220} \approx 0.056\,\mathrm{nm}^{-1}$ (Fig. 3). This result differs from the common laser diffraction experiments, in which only sixfold diffraction patterns are usually observed [3,4].

It is worth noting that the patterns, typical of single crystals, were recorded using a large beam spot area (about 1 cm$^2$), suggesting the well-ordering of Ni PCs on a macroscale.

The increase in a magnetic field results in decrease in the small-angle scattering from the multidomain structure

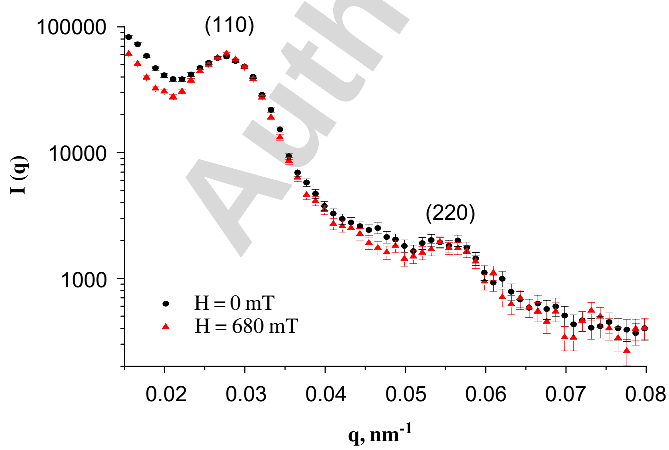


Fig. 3. SAPNS intensity profile for Ni PC in [1 1 0] direction.

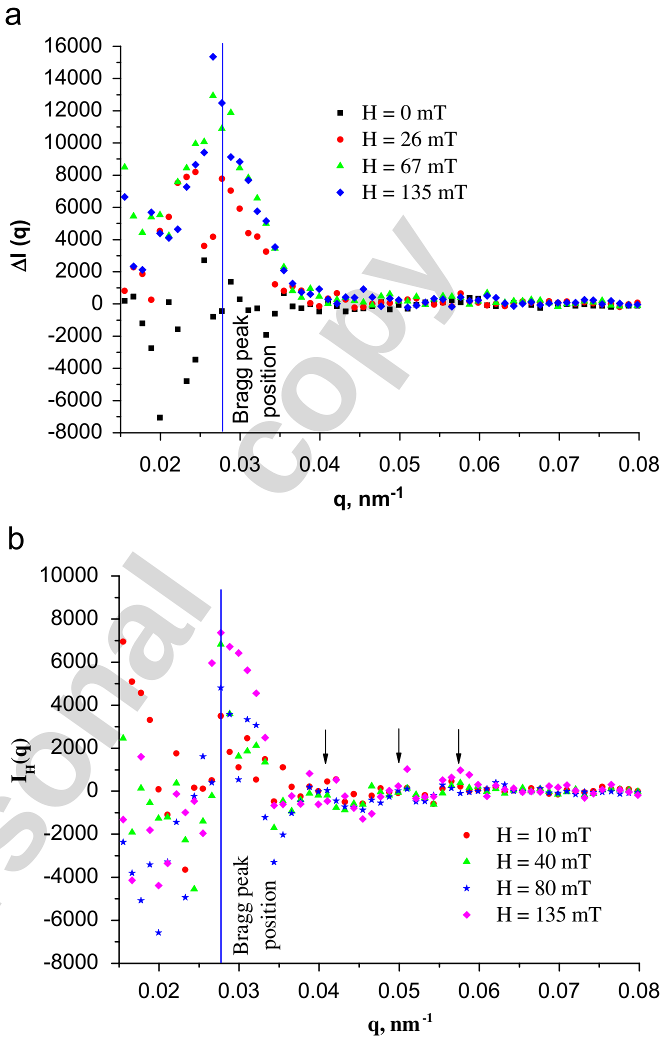


Fig. 4. $q$-Dependence of the nuclear–magnetic interference (a) and magnetic contribution to the scattering $I_H(q)$ (b).

($q < 0.023\,\mathrm{nm}^{-1}$; magnetic domain size more than 270 nm) constrained by elementary blocks of Ni PC, while intensity of Bragg peaks increases.

According to the polarization-dependent part of scattering $\Delta I(q) = (I^{-}(q) - I^{+}(q))$, nuclear and magnetic structures are well-correlated (Fig. 4a). The two types of contributions to the interference scattering, the diffuse small angle scattering and Bragg reflection, with domination of the second one are clearly seen.

The pure magnetic contribution to the scattering, also referred to as field-induced scattering, was extracted as $I_H(q) = I(q,H) - I(q,0)$ (Fig. 4b). In addition to the decreasing of the small-angle scattering described above, the magnetic reflections are clearly observed. It testifies to transition from multi- to single-domain magnetic structure at $H > 50$ mT. The nature of the several additional magnetic reflections (indicated by arrows) with rather small intensities and positions not connected to the Bragg peaks demands the future investigation.

## 4. Conclusions

It was first demonstrated that SAPNS technique is effective for the study of features of the nuclear and magnetic structures of PCs. Magnetic inverse opals can be promising model objects for the investigation of highly frustrated magnetism and artificial spin ice effects.

## Acknowledgment

This work is supported by RFBR (Grant nos. 06-03-33052, 06-03-08157 and 05-03-32778) and Federal Target Science and Engineering Programme. The authors thank A.G. Veresov for SEM studies.

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