Colossal Light-Induced Refractive-Index Modulation for Neutrons in Holographic Polymer-Dispersed Liquid Crystals

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We report strong diffraction of cold neutrons from an only 30 μm thick holographic polymer-dispersed liquid crystal (H-PDLC) transmission grating. The light-induced refractive-index modulation for neutrons is about 10^{-6}, i.e., nearly 2 orders of magnitude larger than in the best photo-neutron-refractive materials probed up to now. This makes H-PDLCs a promising candidate for fabricating neutron-optical devices.

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Holographically produced optical elements are becoming increasingly important in modern telecommunication and data processing. A next generation approach to all optical networks is highly sophisticated diffractive structures, photonic crystals being the best known of them [1–3]. The decisive role in those applications is governed by the proper holographic recording material. The quality demands for and expectations on those photonic media are extremely high, as they frequently are in a competition with the customary outstanding quality of electronic materials that have been developed throughout several decades.

Very attractive candidate materials for next generation holographical optical elements are holographic polymer-dispersed liquid crystals (H-PDLC) [4]. Initially, they consist of a homogeneous mixture of a photosensitive prepolymer and liquid crystals (LC). Upon illumination with a spatially varying light-intensity pattern, e.g., by a holographic two-wave mixing technique, periodic structures in the size of the light-wavelength are recorded. The reason for this is that a photopolymerization reaction takes place more rapidly in the bright regions of the optical interference pattern and consequently the monomers diffuse to these regions while the liquid crystalline molecules congregate in the dark regions [5]. Besides this, when a specific level of photopolymerization is reached locally, demixing of the compounds starts to take place, resulting in formation of LC droplets embedded in a polymer matrix. This complex process produces optical holograms with a very high spatial modulation of refractive index for light. The fact that important parameters like the LC orientation in the droplets and hence the optical properties can be controlled by an electric field represents a unique advantage of H-PDLCs over other materials [4]. Thus, H-PDLCs have enormous potential for applications as active photonic band gap materials or in various devices, e.g., as tunable Fresnel lenses or mirrorless lasers [6–10].

There is very little known about the details of the H-PDLC formation, especially in the stages before and close to the miscibility breakdown. The latter determines the final size and the shape of the LC droplets and consequently the electro-optical properties of the H-PDLCs. The process ideally should be monitored *in situ* during creation of the grating. This is only possible if a nondestructive technique, unlike standard electron microscopy [11] or atomic force microscopy [12], exploring the nanometer range is used such as neutron scattering. A few attempts were made to investigate the structure and texture of anisotropic nematic gels [13] or PDLC systems [14,15] by neutron scattering. Here we present the first neutron diffraction experiment from a H-PDLC transmission grating, which represents a decisive step to explore the associated phase separation process.

In this Letter, we demonstrate and characterize very efficient neutron diffraction from a holographically recorded transmission grating in H-PDLC, which can be observed even for a grating with a thickness as low as 30 μm. This experiment opens up at least two important perspectives in different areas: (1) it proves that the contrast, i.e., the refractive-index mismatch between LC rich and polymer rich regions is strong enough to investigate the phase separation process without the need for deuteration, and (2) it points out the H-PDLC's potential for realizing optical elements for cold and ultracold neutrons.

A series of H-PDLC samples was fabricated from a UV photosensitive mixture prepared from commercially available constituents: a UV curable prepolymer (PN393, Nematel), nematic liquid crystal (TL203, Merck), and 1,1,1,3,3,3,3-Hexafluoroisopropyl acrylate (Sigma-Aldrich). The ratio of different constituents was selected following the formulations previously reported in literature [16]. A drop of the mixture was placed between two glass plates separated by 50 μm Mylar spacers. Two plane waves of wavelength $\lambda_{UV} = 351$ nm were superimposed under a crossing angle $2\Theta = 16°$, resulting in a sinusoidal light-intensity distribution along a single direction z. The corresponding grating spacing thus was $\Lambda = 1.2$ μm. The grating investigated in this study was illuminated for

35 seconds with an intensity of $I = 6$ mW/cm^2 and post-cured with a single laser-beam (half intensity) for 105 seconds. The light-optical properties of the grating have been analyzed in detail and are reported elsewhere [17]. The main characteristics can be summarized as follows: (1) on top of the diffraction signal prominent diffuse scattering is present at ambient temperatures, (2) the grating is anisotropic, i.e., the diffraction efficiency strongly depends on the polarization state of light, with a grating strength of about 2π and $\pi/4$, respectively, for the two eigen polarization states.

In materials that change their refractive index for neutrons upon illumination with light, so called photo-neutron-refractive media, the corresponding variation Δn is expected to reflect the sinusoidal light-intensity variation:

$$\Delta n(z) = n_0 + n_1 \cos\left(\frac{2\pi}{\Lambda} z\right), \tag{1}$$

where $n_{0,1}$ are the mean refractive index and the refractive-index modulation, respectively. In the regime of neutron optics (coherent elastic scattering at low energies) the refractive index of neutrons for nonmagnetic media is predominantly governed by the coherent scattering-length density $\mathcal{B} = Nb_c$. Here, N is the number density and b_c the mean coherent scattering length of the sample. The refractive-index modulation finally reads [18]

$$n_1 = \frac{\lambda^2}{2\pi} \mathcal{B}_1. \tag{2}$$

Small-angle neutron diffraction experiments were performed at the SANS-2 instrument at the Geesthacht Neutron Facility (GeNF). The central neutron wavelength was $\lambda = 1.16$ nm or $\lambda = 1.96$ nm with a wavelength spread of $\Delta\lambda/\lambda = 10\%$. Full collimation distance (16 m) and maximum detector distance (21 m) with diaphragms were used, so that the angular spread was <1 mrad. The diffracted intensities were collected by a 2D detector with 256×256 pixels, each with (2.2×2.2) mm^2.

The neutron diffraction experiments on our particular H-PDLC sample were performed under highly unfavorable conditions, for the following reasons: (1) The samples originally had been prepared for light-optical measurements, so that the two embracing glass plates with a thickness of 1 mm each were supposed to give a tremendous background on the scattering signal from the sample with a thickness of less than 50 μm. (2) Moreover, the grating spacing was quite large, so that despite the long sample-detector distance, the zero and first order diffracted intensities are not easily separated in space. (3) The sample itself contains a big amount of hydrogen that contributes to incoherent scattering, and (4) the suppliers keep the exact chemical formulae of the compounds secret, so that estimations of the expected contrast are difficult. In addition, (5) neutron diffraction samples have usually thicknesses that are at least 2 orders of magnitude larger, and (6) the main contribution to the light-induced refractive-index modulation in H-PDLCs is thought to originate from electronic polarizability changes rather than from density variations as discussed above.

Despite these facts, we succeeded to detect the grating by neutrons, i.e., to observe diffraction. For further characterization, we conducted complete rocking curves, i.e., the angular dependence of the diffraction efficiency $\eta_s = I_s / \sum_{j=0}^{j\,\mathrm{max}} (I_j)$ in the vicinity of the Bragg angle, and extracted the refractive-index modulation n_1 (Eq. (1)). Here, I_s denotes the number of neutrons diffracted to the s-th order reaching the detector and j max the maximum diffraction order.

Figure 1 shows the angular dependence of the first order diffraction efficiencies $\eta_{\pm 1}$ for a central neutron wavelength of 1.16 nm of our H-PDLC sample. From the FWHM of about 40 mrad, we find that the effective thickness $L = \Lambda/\mathrm{FWHM}$ amounts to 30 μm, much less than the Mylar spacer's thickness. This is in agreement with light-optical investigations [17]. Moreover, the angular dependence proves that we are not in the Raman-Nath diffraction regime, yet detecting multiple diffraction orders at the same time. The latter is mainly due to the fact that the ratio λ/Λ is 3 orders of magnitude lower than for light, and thus the Ewald-sphere can be approximated as a plane. A rigorous coupled-wave analysis would be the proper tool to describe the diffraction properties (see e.g. [19]). For the values of the diffraction efficiency measured in our experiment $\eta_{\pm 1} < 3\%$, any theory (phase transparency, two beam coupling) yields $\eta_1(\Delta\theta = 0) \approx \nu_1^2$, where $\nu_1 = \pi n_1 L/\lambda$ is the grating strength for first order diffraction. It can be noted that the shape of the rocking curves is rather close to that expected from a two-wave coupling theory [20]. We reveal such angular dependence by cold neutrons for the first time, as the FWHM of the rocking curve is about 40 mrad and thus much larger than the angular

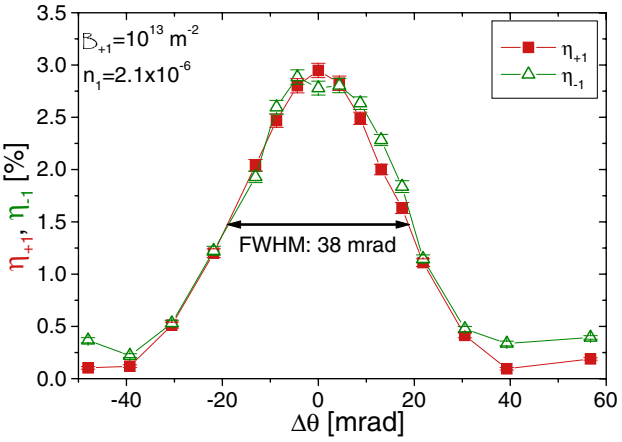

FIG. 1 (color online). Angular dependence of the $\pm$ first order diffraction for neutrons from a grating in 30 μm thick H-PDLC.

spread (≈ 0.5 mrad) of the neutrons, which is in contrast to previous experiments on poly(methylmethacrylate) [21].

From the values of $\eta_{\pm 1}$, we determine the first order light-induced coherent scattering-length density modulation as $\mathcal{B}_1 = (9.89 \pm 0.26) \times 10^{12}/\mathrm{m}^2$, and hence the corresponding light-induced neutron-refractive-index modulation $n_1 = (2.12 \pm 0.05) \times 10^{-6}$ (Eq. (2)). The diffraction efficiency at the Bragg angle can be further increased by simply enlarging the thickness or the wavelength as $\eta_1(\Delta\theta = 0) = (\lambda L \mathcal{B}_1/2)^2$. We therefore measured the diffraction efficiencies using a wavelength of 1.96 nm. The result is depicted in Fig. 2, where the intensities on the detector matrix are shown for diffraction at the Bragg angle. Here, even second order diffraction is strong enough to be observed. From evaluating the diffraction efficiencies $\eta_{+1} = 11.9\%$, $\eta_{-1} = 10.6\%$, $\eta_{+2} = 1.2\%$, $\eta_{-2} = 0.7\%$ with an error $\delta\eta/\eta = 0.1$, the light-induced coherent scattering-length density modulation is $\mathcal{B}_1 = (1.01 \pm 0.10) \times 10^{13}/\mathrm{m}^2$. Thus the light-induced neutron-refractive-index modulation, which depends quadratically on the wavelength, can be calculated to $n_1 = (6.19 \pm 0.05) \times 10^{-6}$.

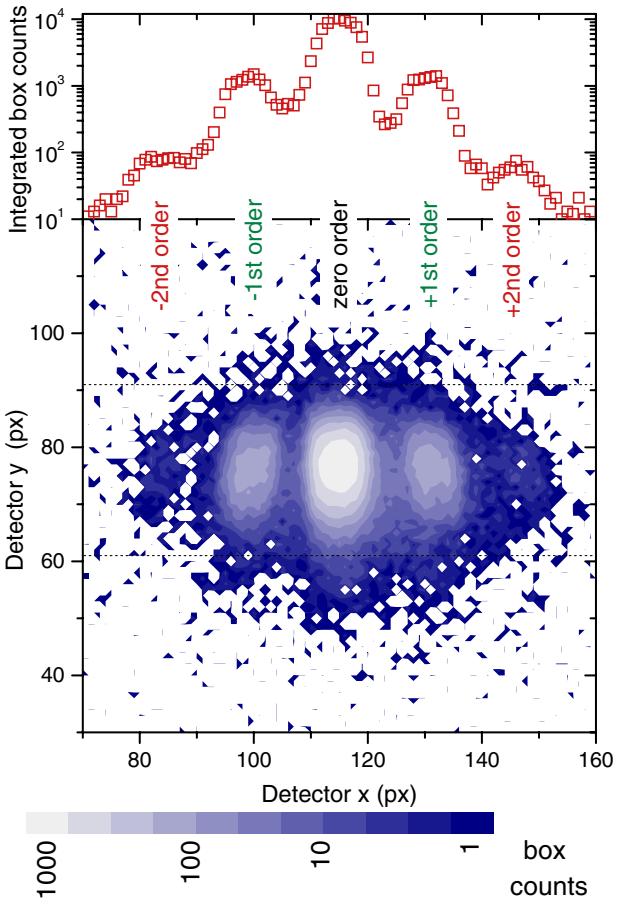

FIG. 2 (color online). Diffraction pattern of an H-PDLC at a wavelength of $\lambda = 1.96$ nm. Diffraction up to the $\pm$ second order is visible (bottom). The data points result from summing up the box counts of 30 pixels along the y-direction around the centers of diffraction spots, so that the second order peaks are clearly visible (top).

The wavelength dependence of n_1 is expected from Eq. (2), so that the ratio of $n_1(\lambda_2)/n_1(\lambda_1) = (\lambda_2/\lambda_1)^2 = 2.85$ when employing wavelengths $\lambda_1 = 1.16$ and $\lambda_2 = 1.96$ nm, respectively. From the experimental values, we obtain 2.92, which is in fair agreement with the prediction.

The first obvious striking feature of our experiments is the fact that despite the completely disadvantageous conditions mentioned above, coherent diffraction could be observed in H-PDLC. The reasons for this are an extremely good contrast between the polymer rich and the liquid crystal rich regions and the fact that the incoherent scattering cross section of the sample had only a minor influence on the transmission (about 0.99) because of the small thickness. These observations encourage us to tackle in future the problem of the phase separation process during recording of the gratings *in situ* employing neutrons and the facility HOLONS, i.e., HOLOgraphy and Neutron Scattering [22].

We establish as a second highlight of these experiments, that the light-induced refractive-index modulation n_1 is nearly 2 orders of magnitude larger as compared to that of any photo-neutron-refractive material probed up to now [18]. To demonstrate that this is exceptionally high, we estimate the mean refractive-index n_0 for 2 nm neutrons in our sample by summing up the mean coherent scattering-length density $\mathcal{B}_0$ of the main (known) constituents according to their volume fraction and using tabulated values of b_c for thermal neutrons [23]. n_0 then deviates from unity by an amount of about -7×10^{-5}. This number relates to the ratio of the neutron-optical potential and the total energy [24]. Thus we are able to modulate the neutron-optical potential via light by about 10%. At present H-PDLCs therefore represent by far the most efficient medium for light-induced, neutron-refractive-index changes.

Finally, let us assume the extreme case of complete separation between polymer and LC, i.e., alternating slices (square wave grating). We estimate the difference of the coherent scattering-length densities for the polymer and the monomer from the spurious information of the commercial suppliers for either component to be $\Delta\mathcal{B} = \mathcal{B}_{0,\mathrm{LC}} - \mathcal{B}_{0,\mathrm{polymer}}$. Then, the maximum achievable contrast for the first Fourier coefficient of a square wave grating would be $\mathcal{B}_1 = (2/\pi)\Delta\mathcal{B} \approx (2/\pi) \times 10^{14}/\mathrm{m}^2$. This is by a factor of 5 larger than experimentally observed and means that we are far from a complete unmixing of the LC and polymer. This finding further supports the assumption that our grating is of sinusoidal shape in accordance with the observations in light-optical experiments [17]. However, ideally sliced structures, which have been recently reported [25,26], can improve the diffraction properties. Full clarification of the problem will be performed on samples with smaller grating spacing and larger thick-

ness, hence ensuring a two-wave coupling regime also for neutron diffraction.

Let us end with a short comment on the higher diffraction orders. For a pure phase grating in the Raman-Nath regime, we expect a strict relation between the diffraction efficiencies for various orders, e.g., $\eta_2/\eta_1 = \mathcal{J}_2^2/\mathcal{J}_1^2 = (\nu_1/2)^2 = \eta_1/4 = 0.028$. From the experimentally obtained values, we find 0.083, i.e., the ratio is a factor of about 4 too low. This simply is attributed to the importance of beam coupling in our diffraction process, which is in accordance with the angular dependence of the diffraction efficiency (see Fig. 1). The observed second order diffraction thus can be simply treated as secondary diffraction of the first order diffracted beam, which leads to $\eta_2 = \eta_1^2$ and fits the experimental values quite well.

We demonstrated that H-PDLCs with a thickness of only 30 μm act as extremely efficient gratings not only for light (cf. [17]) but also for neutrons. Note that the thickness of our sample is typically 2 orders of magnitude less than in standard photo-neutron-refractive materials. Such H-PDLC samples could be useful as new materials for fabricating neutron-optical devices for cold and ultracold neutrons, e.g., as beam splitters, mirrors, lenses, or for an interferometer [27].

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