X-Ray Diffraction on Photonic Colloidal Single Crystals

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We have performed X-ray diffraction on colloidal single crystals with lattice parameters in the order of several hundred nanometers on ID2. These crystals are optical photonic crystals, i.e. crystals that modify the propagation of light and may lead to novel optical phenomena, analogous to semiconductor electronics.

In photonic crystals, the refractive index varies periodically on length scales comparable to optical wavelengths. This has an effect on light similar to the effect that the periodic potential of atomic crystals has on electrons [1,2]. The periodicity causes optical Bragg reflections: directions in the crystal where waves with certain frequencies are reflected. Figure 1 shows a Bragg reflection for green light in a photonic colloidal crystal. If the light is very strongly coupled to the crystal, an optical photonic band gap may occur, i.e. a frequency band in which no light can be transmitted in any direction. This can be interpreted as a Bragg reflection that extends over a full 4π solid angle. Photonic band gaps for light are expected to have unusual properties: spontaneous emission of excited atoms with a resonance in the forbidden frequency band is inhibited, and light can be localised [1]. Thus, with photonic band gap crystals one may achieve control over photons similar to that over electrons in microelectronics [1,2].

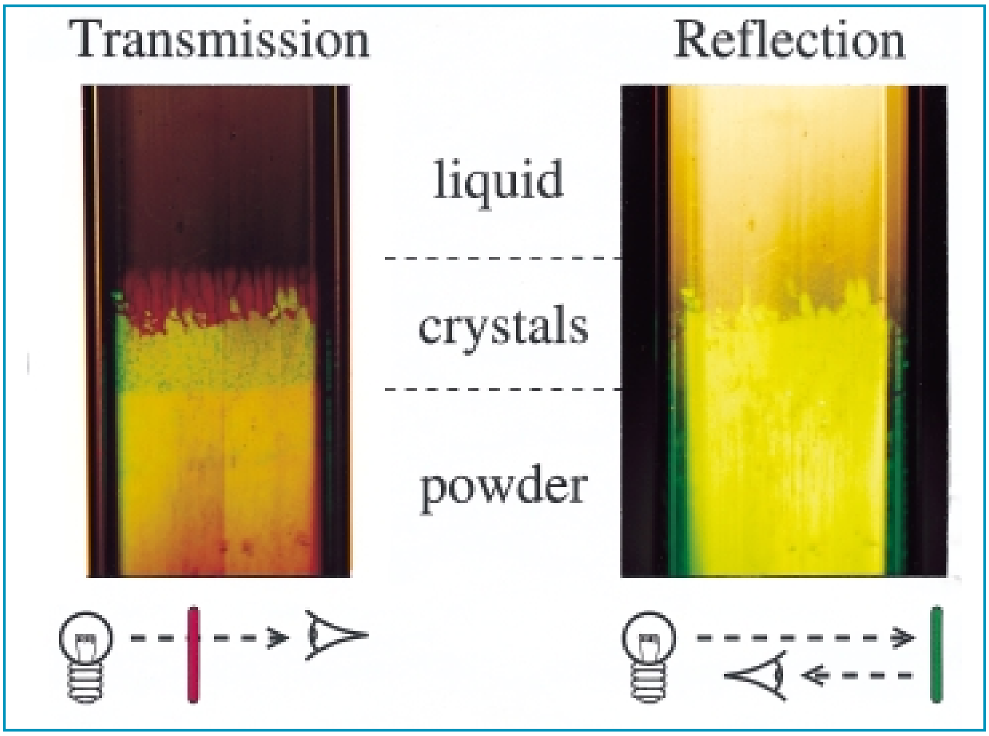

Fig. 1: Photomicrographs of a sample of polystyrene colloids in methanol in a 4 mm wide glass capillary. The pictures were taken with white light, in transmission (left) and reflection (right). The bright green Bragg reflections are caused by the fcc (111) planes oriented parallel to the capillary wall. Red light is still transmitted through the crystals. At the top of the sample, the density of the colloids is lower, hence they form a disordered liquid. This results in random multiple scattering of the light and thus appears dark in transmission and white in reflection.

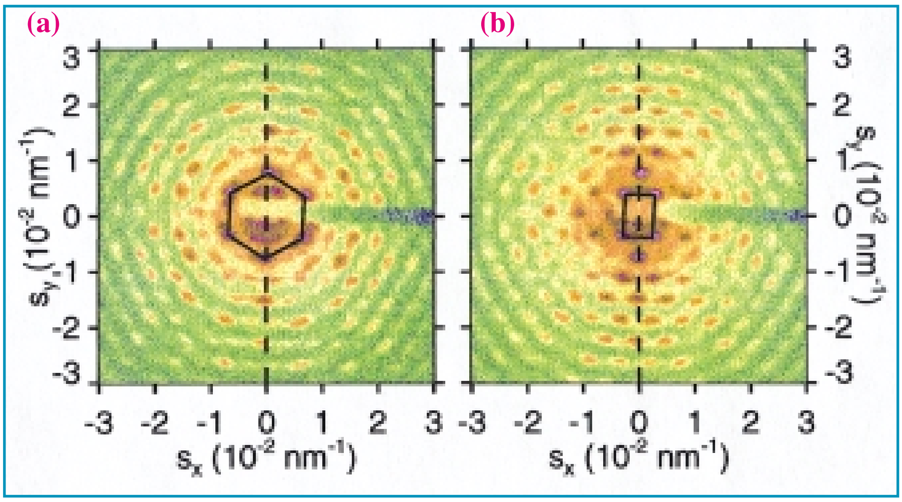

Fig. 2: Small-angle X-ray scattering patterns from a crystal of 242 nm diameter polystyrene colloidal spheres in water. The spheres have formed an fcc crystal with the (111) planes parallel to the wall of the capillary. In (a) the X-ray beam is parallel to a [111] axis. In (b), the X-ray beam is parallel to a [110] axis. The large number of rings further out in the scattering pattern is caused by the form factor of the monodisperse colloidal spheres [3].

The realisation of three-dimensional periodic structures with lattice parameters of the order of optical wavelengths presents a major challenge [2]. We study colloidal suspensions of particles that are so small (10-1000 nm) that they execute Brownian motion. Familiar examples of colloids are fog, milk or paint. It is currently possible to synthesise colloidal spheres with a very small variation in size [3]. Such colloids can self-organise into bulk three-dimensional crystals, that are a natural realisation of photonic crystals for light. Thus, colloidal crystals are promising building blocks for crystals with optical photonic band gaps.

Because the optical properties of photonic crystals are intimately related to the crystal structure, it is crucial to know their structure [4]. Usual optical techniques such as light scattering and microscopy are not suited for photonic crystals however, for several reasons. First, a strong interaction between the light and the crystals results in multiple scattering. We have observed that the Bragg spacings then strongly deviate from the real lattice spacings [5]. Second, the required lattice spacings allow only a few Bragg reflections to be observed in the available optical spectrum. These points are remedied by small-angle X-ray scattering. Beamline ID2 has several key features for X-ray diffraction experiments on photonic colloidal crystals: the narrow focus allows a single crystal to be isolated for study, and the high brilliance allows experiments in reasonably time scales.

Figure 2 presents X-ray diffraction patterns from a colloidal single crystal [6]. The diffraction patterns show symmetric patterns of Bragg peaks, thus the spheres are ordered in a crystalline array. If we translate the sample relative to the X-ray beam, we observe doubling or tripling of each peak or even powder rings, which means that the beam then irradiates two, three, or many crystallites respectively. This confirms that the diffraction patterns in Figure 2 indeed result from a large single crystal, with a size larger than the beam diameter (0.2 x 0.5 mm). The diffraction peaks are well explained with an fcc structure with a lattice parameter of 370 nm, a remarkable value for an X-ray diffraction study.

We see many Bragg spots simultaneously in Figure 2, in contrast to usual single crystal X-ray studies on atomic crystals. The reason is that the X-ray wavelength is much smaller than the lattice spacing, hence the Ewald sphere is almost a plane. This Ewald “plane” simultaneously intersects many reciprocal lattice vectors. By rotating the sample, we sweep the Ewald “plane” through reciprocal space (cf. Figure 2). For Figure 2a, the X-ray beam was perpendicular to the window of the sample, while for Figure 2b, the sample was rotated 34° around the long axis of the capillary (vertical), which results in a very different diffraction pattern. The pattern in Figure 2a has approximately a six fold symmetry, which is expected because dense colloids often arrange in hexagonal planes (fcc 111) parallel to a window. The pattern in Figure 2b is characteristic of an fcc crystal aligned with the 110 planes perpendicular to the beam. Such a pattern has not been observed before [6].

In previous experiments on dense charge stabilised colloids, random stacks of hexagonal planes or glass formation have been observed. The present observation of fcc agrees with *a priori* statistical physical predictions. The observation of the fcc structure is exciting for photonics, because theoretical calculations show that photonic band gaps can be made with this structure. To achieve photonic band gaps, crystals must be made of materials with high refractive indices, which we are currently pursuing.

The present experiments demonstrate that X-ray diffraction is a powerful tool to investigate systems with length scales comparable with optical wavelengths. In particular the two-dimensional detection is an attractive feature as shown in Figure 2. The large number of diffraction peaks in Figure 2 suggest that the Debye-Waller factors of the crystals are small and that the particles never wander far from their lattice positions. It is expected that a detailed study of the Debye-Waller factors will provide information about the mesoscopic interparticle forces, which are currently a subject of debate. ■

References

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