3.6

Light and Small-Angle X-Ray Diffraction from Opal-Like Structures: Transition from Two- to Three-Dimensional Regimes and Effects of Disorder

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3.6.1 Introduction

In this chapter, we present an overview of the diffraction of visible light and x-rays in opal-like structures. Special attention will be paid to the transformation of diffraction patterns on building up the opal structure from a two-dimensional (2D) single layer of silica particles $\alpha$-SiO$_2$ toward a bulk three-dimensional (3D) opal structure as well as to the effects of disorder such as stacking faults. The consideration here will be limited
to structures with low permittivity contrast $\Delta \varepsilon$. For small-angle x-ray diffraction, this condition is automatically fulfilled for all materials: $\Delta \varepsilon \sim 10^{-5} \text{--} 10^{-6}$. For optical studies, such a situation can be realized for different opal-based structures by filling the voids of the structure with a medium having nearly matching $\varepsilon$. An enhancement of $\Delta \varepsilon$ can lead to broadening of the Bragg reflections and a modification of the relative intensity of different Bragg reflections as well as to significant extinction of the incident wave (see Chapter 3.7), which are not considered here. A different approach considering the full set of Maxwell equations to calculate the electromagnetic eigenmodes and photonic band structure is unavoidable for high $\Delta \varepsilon$, especially if one moves toward the full band-gap materials. This approach is considered in Chapter 3.7 in detail, whereas in this chapter the case of high dielectric contrast is left out.

Opal-like structures are photonic crystals (PhC) that possess stop-bands in the visible range owing to the typical size of the constitutive particles of some hundreds of nanometers. This provides a unique chance to study photonic properties not only by traditional methods such as registering transmission or reflection with a spectrometer but also by directly observing diffraction patterns on a screen disposed behind or around the sample.

For periodic structures made of identical spherically symmetric building blocks, the diffraction intensity $I(q)$ can be written as a product of the squared modulus of form factor $|F(q)|^2$, which describes scattering on a single particle, and the squared modulus of scattering structure factor $|S(q)|^2$, which describes the interference between waves scattered by different particles: $I(q) \propto |S(q)|^2 |F(q)|^2$. Here the scattering vector $q = k_s - k_i$ is the difference between the wavevectors $k_s$ and $k_i$ of the scattered ($s$) and incident ($i$) waves, respectively. Note that for the structures under consideration both $S(q)$ and $F(q)$ magnitudes are real-valued; therefore, the modulus signs are omitted in further text for simplicity. The structure factor $S(q)$ possesses maxima when the condition for constructive interference $q r_{ij} = 2\pi n$ is fulfilled for all pairs of particles, where $r_{ij}$ is the radius vector connecting $i$-th and $j$-th particles and $n$ is an integer.

As the transition from 2D to 3D diffraction regimes is of a particular interest here, let us consider the two limiting cases. A 2D periodic structure (a single monolayer of colloidal particles in our case) can be generated using two primitive vectors $a_1$ and $a_2$. The condition of constructive interference is fulfilled if the projection $q_{\|}$ of the scattering vector on the 2D structure obeys

$$ q_{\|} = g_{hk} \equiv h b_1 + k b_2 $$

(3.6.1)

where $g_{hk}$ is the 2D reciprocal lattice vector, and $b_1$ and $b_2$ are primitive vectors of the 2D reciprocal lattice, which are given by

$$ b_1 = 2\pi \frac{a_2 \times n}{a_1 \cdot (a_2 \times n)}, \quad b_2 = 2\pi \frac{n \times a_1}{a_1 \cdot (a_2 \times n)} $$

(3.6.2)

with $n$ denoting the layer normal.

For a 3D structure, which can be generated by three primitive lattice vectors $a_1$, $a_2$, and $a_3$, the condition of constructive interference leads to a set of Laue equations:

$$ q \cdot a_1 = 2\pi h, \quad q \cdot a_2 = 2\pi k, \quad q \cdot a_3 = 2\pi l, $$

(3.6.3)

where $h$, $k$, and $l$ are integers. The solution of 3.6.3 can be written in the form of the Bragg’s law

$$ q = g_{hkl} \equiv h b_1 + k b_2 + l b_3, $$

(3.6.4)
where \( \mathbf{g}_{\text{hkl}} \) is a 3D reciprocal lattice vector normal to \((hkl)\) lattice planes (see Figure 3.6.1a) and \( \mathbf{b}_1, \mathbf{b}_2, \) and \( \mathbf{b}_3 \) are primitive vectors of the 3D reciprocal lattice, which are given by\(^1\):

\[
\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.
\]

As we consider only elastic scattering (\(|\mathbf{k}_i| = |\mathbf{k}_f|\)), Equation 3.6.4 implies that in ordered 3D crystals Bragg diffraction follows the law of *specular reflection* from \((hkl)\) crystallographic planes with surface normal parallel to \( \mathbf{g}_{\text{hkl}} \). Moreover, the end of scattering vector \( \mathbf{q} \) must lie on the so-called Ewald sphere (a sphere of radius \( 2\pi/\lambda \) in reciprocal space, where \( \lambda \) is the radiation wavelength).\(^2\) Diffraction is observed only when the Ewald sphere crosses at least two reciprocal lattice nodes.

Let us first consider the diffraction of visible light on an opal lattice. The lattice spacing is determined by the diameter of close-packed spheres \( D \sim 10^2\text{–}10^3 \text{ nm} \), which is of the order of the typical visible light wavelength \( \lambda \sim (4\text{+}7)\times10^2 \text{ nm} \). Diffraction is then observed at large diffraction angles between \( \mathbf{k}_i \) and \( \mathbf{k}_f \) (Figure 3.6.1c). Moreover, optical Bragg diffraction can only be observed for low Miller index planes. For example, for a face-centered cubic (FCC) lattice, the interplanar spacing is given by \( d_{\text{hkl}} = D/\sqrt{(h^2 + k^2 + l^2)/2} \).

**FIGURE 3.6.1**

(a) Illustration of the light Bragg diffraction on a system of \((hkl)\) planes in real space. (b) Illustration of the small-angle x-ray diffraction on a system of \((hkl)\) planes in real space. Owing to the large difference between the structure period and the wavelength the diffracting incident beam propagates almost parallel to the \((hkl)\) planes. (c) The Ewald sphere construction in reciprocal space for the Bragg diffraction of light. (d) The Ewald sphere construction in reciprocal space for incident x-ray wave propagating along the \((hkl)\) planes of an ideal infinite opal-like structure (\(|\mathbf{k}_i| >> |\mathbf{g}_{\text{hkl}}|\)). (e) The same as in (d) but including broadening of the reciprocal lattice nodes for a realistic structure. Broadening of the reciprocal lattice nodes and the curvature of the Ewald sphere are exaggerated for clarity. (f) Photonic band structure of low-contrast opal-like photonic crystals for the near-infrared, visible, and near-ultraviolet range of the spectrum, that is, the theoretical dependences of the Bragg wavelength versus angles of light incidence onto the \((hkl)\) planes in the face-centered cubic lattice (see details in Figure 3.5.5 of Chapter 3.5). (g) Extrapolation of the photonic band-gap structure into the x-ray range of the spectrum.
diffraction can only be observed on sets of crystal planes with low Miller indices such as
\{111\}, \{200\}, and \{220\} as for higher Miller indices the factor \(\sqrt{(h^2 + k^2 + l^2)}/2\) makes \(d_{\text{hkl}}\) smaller than half of the visible light wavelength in the medium. This result is also reflected in Figure 3.6.1f, where the dependence of the Bragg wavelength on the angle of incidence is shown. This scheme can be also presented as the dependence of the energy of photonic stop-bands on the diffraction wavevector \(q\). Such a representation known as the photonic band structure is discussed in detail in Chapter 3.5.

To get access to Bragg reflections with high Miller indices, one can use radiation with a shorter wavelength \(\lambda\). In the ultraviolet part of the spectrum the Bragg diffraction is precluded for many materials, which become opaque as a result of the presence of numerous electronic resonances. One has to go all the way to hard x-rays, where the photon energy \((\hbar \omega > 10 \text{ keV})\) is significantly higher than the energy of electronic transitions. Here the transparency increases sufficiently for all materials to allow Bragg diffraction experiments again. The change of the photon energy by almost four orders of magnitude between visible light and x-rays implies several important consequences. For x-rays the permittivity of materials differs from 1 by as little as \(|1 - \varepsilon| \sim 10^{-5} - 10^{-6}\). This means that the contrast is intrinsically very weak and the Born approximation is fulfilled with very high accuracy. Diffraction on sets of crystal planes with high Miller \((hkl)\) indices can now be accessed as a result of the short wavelength of x-rays, \(\lambda \sim 0.1 \text{ nm}\). On the other hand, Bragg angles for opal-like structures become very small, in the range of 0.1–10 \(\mu\text{rad}\) as illustrated in Figure 3.6.1b. Measuring diffraction experimentally at such small angles is a challenge and one usually needs to use synchrotron x-rays. In addition, the radius of the Ewald sphere \(2\pi/\lambda\) is very large for x-rays in comparison to the scale of interest. As discussed in more detail in Section 3.6.5, for most cases of practical interest the curvature of the Ewald sphere is negligible in comparison, for example, with the broadening of the crystal reflections due to the finite size effects as schematically sketched in Figure 3.6.1e. As a result, many Bragg reflections can be observed simultaneously in a single diffraction pattern. It is also reflected in Figure 3.6.1g, where the photonic band structure is extrapolated into the x-ray spectrum. One can see that here many bands converge at a single value of the incident angle.

Bragg diffraction of light was studied experimentally and theoretically on different opal-like structures, including bulk samples of synthetic opals\(^3\)\(^-\)\(^5\) and opal films.\(^6\)\(^-\)\(^11\) These works involved studies of both specular reflection spectra and diffraction patterns, which were observed on screens, captured and processed using various software. In particular, for an opal film in case of normal beam incidence, either three or six diffraction reflections are observed depending on the sample quality, thickness, the “matrix-filler” contrast of the permittivity and its other parameters. The main features of the \(k\)-resolved spectra of 3D PhCs can be successfully analyzed in terms of single or multiple Bragg diffraction. The possibility of the visual study of the formation and alteration of photonic band structure during the diffraction experiments was demonstrated by Baryshev et al.\(^4\) by comparing diffraction patterns and synthetic opals’ transmission spectra. The theory of 3D Bragg polarized light diffraction from opals based on Green’s electrodynamic functions method is presented in the study by Baryshev et al.\(^5\) This theory takes into account the effects of random packing of growth (111) layers in opal structures.

In general, self-assembled opal-like crystals contain disorder of various types. The stacking disorder is one of the most common and intensively studied types of disorder. Colloidal opal-like crystals are composed of close-packed layers, which can form different structures depending on their stacking sequence: FCC structure (…ABCABC…),
hexagonal close-packed (HCP) structure (…ABABAB…), as well as random hexagonal close-packed (RHCP) structure, in which close-packed layers are arranged in a random fashion. The colloidal crystals synthesized by the sedimentation method (bulk opals) often demonstrate RHCP structure. The colloidal crystals grown by vertical deposition (film opals) are composed of large-scale FCC fragments separated by stacking faults or HCP fragments.

The optical diffraction method is distinguished by its simplicity and informativity. Wide capabilities of optical diffraction for studying different types of structure disorder in opal-like PhCs is demonstrated in Figure 3.6.2 where four diffraction patterns are shown. They are obtained during the studies of opals with different degrees of lattice disorder—from a virtually “non-twinned” sample to a fully disordered sample.

In this chapter, we present a detailed study of 2D diffraction of light from thin opal films (Section 3.6.2) and the transition from 2D to 3D diffraction (Section 3.6.3). Then we discuss the selective switching of (hkI) reflections in diffraction patterns of thick opal films depending on the value of permittivity of infiltration material (filler) εf (Section 3.6.4). The effects of the sample thickness in x-ray diffraction are discussed in Section 3.6.5. The order and disorder of opal-like structures of bulk and film samples will be considered using the example of microradian x-ray diffraction (Section 3.6.6). The advantage of this approach stems from the intrinsically low contrast for x-rays, which leads to clear single scattering data. Moreover, x-rays can be applied to characterize opaque inverse opals as well as the samples with a periodicity less than 300 nm, whose structure cannot be investigated by conventional optical methods. An example of how x-ray diffraction can serve the technology of opal growth will be given in Section 3.6.7. In Section 3.6.8, the principles of 3D reciprocal space reconstruction of large-scale opal-like structures will be presented on the basis of microradian x-ray diffraction patterns. The chapter concludes with a discussion of the complementarity of visible light diffraction and microradian x-ray diffraction for investigation of photonic opal-like structures (Section 3.6.9).

**FIGURE 3.6.2**
Top row: diffraction patterns from various opal samples in the k·||[101] incidence geometry: (a), (b) are the best-ordered monodomains of the face-centered cubic (FCC)-I (…ABCABC…) and FCC-II (…ACBACB…) lattices; (c) is a slightly disordered region of FCC twins; (d) is a strongly disordered region made up of numerous microcrystallites with their growth axes oriented randomly relative to one another. Bottom row: a schematic arrangement of the crystal planes involved in diffraction, together with the incident and diffracted beams. (Reprinted from M. V. Rybin et al., Photonics Nanostruct. Fundam. Appl. 4, 146 (2006), Copyright (2006), with permission from Elsevier.)
3.6.2 Two-Dimensional Optical Diffraction from Thin Opal Films

In this section, we focus primarily on the experimental and theoretical study of 2D diffraction from thin opal films. We should emphasize two key features of the diffraction studies reported in the literature.\textsuperscript{9,10} First of all, a novel technique of recording the diffraction patterns is proposed. The commonly used scheme\textsuperscript{5,7,13} is illustrated in Figure 3.6.3a–c. It involves investigating diffraction patterns displayed on a flat screen positioned before or after the sample. Among the disadvantages of this scheme are pattern distortions due to the nonsphericity of the screen and, more importantly, the limitation of the spatial angle where the diffraction pattern is registered. It should be mentioned that in most cases one

**FIGURE 3.6.3**

(See color insert.) (a) The reciprocal lattice of a two-dimensional (2D) hexagonal layer placed in the XZ plane normally to the incident beam. The lattice consists of an array of nodes, the position of each determined by the 2D vector $g_{hk} = hb_1 + kb_2$, where $b_1$ and $b_2$ stand for the basis vectors of the reciprocal lattice, and $h$ and $k$ are integers. The nodes defining the first order of diffraction for the beam incident along the film normal (along the Y axis) are marked with circles. (b) A schematic illustration of the experimental setup designed to observe transmitted or reflected light on a flat screen. (c) The experimental pattern of monochromatic ($\lambda = 532$ nm) light diffraction from a thin opal film observed on a flat screen positioned behind the sample. Six observed reflections are marked with the respective pairs of 2D diffraction indices $(hk)$. (d) A schematic illustration of 2D diffraction conditions in the XY plane $q_i = g_{i1}$ and $q_f = g_{f1}$ with the incident white light beam propagating along the Y axis and the hexagonal layer positioned in the XZ plane. For $\Theta = 140^\circ$ and $\Theta = 140^\circ$. (e) A sketch of the experimental setup designed to observe light diffraction in the XY plane on a cylindrical screen. Six diffracted beams are shown. Three of them are scattered forward with respect to the incident beam (i.e., the Y axis), whereas the other three are scattered backward. The angle of incidence $\theta$ and the angle of scattered light registration $\Theta$ are indicated. Oblique incidence is exemplified here: $\theta = 5^\circ$. (f) A surface development of the white light diffraction pattern from opal film observed on the cylindrical screen in the XY plane at $140^\circ \leq \Theta \leq 140^\circ$. (Adapted from A. K. Samusev et al., Phys. Solid State 53(5), 1056 (2011). With permission.)
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does not necessarily need the information about light diffraction in full solid angle ($4\pi$).
The method considered in the study by Samusev et al.\textsuperscript{9} is suggested as a tool to investigate
the diffraction in the horizontal plane containing the incident beam. Diffraction patterns
are displayed on a cylindrical screen with a sample fixed in its center using a vertical holder
as shown in Figure 3.6.3e. In this approach, diffraction reflections are displayed on the
cylinder surface in the full angle ($2\pi$) in the XY plane without any distortion. Therefore, at
the near-normal incidence one observes five diffraction reflections lying in the horizontal
plane on the cylindrical screen, as can be seen in Figure 3.6.3e. Note that the sixth diffraction
spot (00) at $\Theta = 180^\circ$ is out of the experimentally investigated range of $-140^\circ \leq \Theta \leq 140^\circ$
(Figure 3.6.3f). Rotating the sample holder allows us to change the angle of incidence $\theta$
within the range $-90^\circ \leq \theta \leq 90^\circ$. The diffraction pattern on the narrow cylindrical screen is
photographed from three different fixed points. The full diffraction pattern (Figure 3.6.3f)
is formed by processing the obtained images onto a flat stripe line. Note that in the diffraction
literature angle $\theta$ is usually used for the Bragg angle. Here, however, $\theta$ denotes sample
orientation to comply with notations used in the majority of photonics literature and the
notation used in other chapters of this book.

The second key feature of these studies is the experimental data presentation.\textsuperscript{9,10} Most
commonly, 2D diffraction patterns are presented as recorded on a flat screen. Here an
alternative approach is used: a collection of a large number of the cylindrical screen color
photographs are presented as a function of the angle of light incidence $\theta$ and the angle of
diffracted light registration $\Theta$. The diffraction patterns are collected for the angles of incidence
within the range $-90^\circ \leq \theta \leq 90^\circ$ with the angular step size of $\Delta \theta = 2.5^\circ$. Hereby, 72
narrow “strip patterns,” similar to those presented in Figures 3.6.3f and 3.6.4a, are obtained
and joined together into a single image similar to the one presented in Figure 3.6.4b.

The advantage of this presentation is that one can easily distinguish 2D and 3D diffraction,
along with singling out a variety of effects induced by the disorder in the sample. Indeed,
in the case of 2D diffraction, Equation 3.6.1 produces a complex dependence between $\Theta$ and $\theta$ angles for the allowed, that is, experimentally observed, reflections. At the same
time, the case of 3D Bragg diffraction reduces to the specular reflection of the beam from a
set of (hkl) crystallographic planes, and is thus described by a simple equation $\Theta = 2(\theta - \theta_{hkl})$
as discussed in more detail in the next section. Therefore, in the $(\theta, \Theta)$ coordinates the allowed
Bragg reflections will be represented by parallel straight lines, and any deviation or broadening
of the lines will be associated with some kind of sample disorder.

Let us now consider light diffraction from thin opal films. It is worth recalling that a com-
monly observed diffraction pattern with the incident beam perpendicular\textsuperscript{6} to the sample
surface ($\theta = 0$) has the $C_6$ symmetry and consists of six intensive reflections symmetrical
with respect to the incident beam (see Figure 3.6.3c). Note that six diffraction reflections in
the given geometry can be observed in two cases. The first one is first-order 2D light diffraction
from the hexagonal layer with the $C_6$ symmetry; the second is 3D Bragg diffraction
from the twinned FCC lattice\textsuperscript{6} oriented so that the [111] axis coincides with the incident
beam direction. Each FCC twin has the $C_3$ symmetry in the direction [111] and defines a
triplet of diffraction reflections. As the twins in the FCC lattice turn into each other after a
rotation by 60$^\circ$ about the [111] axis, the result will bear the $C_6$ symmetry and will look like
the image shown in Figure 3.6.3c.

To distinguish 2D and 3D diffraction cases, one should investigate light scattering pat-
terns for arbitrary incident angles ($-90^\circ \leq \theta \leq 90^\circ$) and present the result in the $(\theta, \Theta)$ coor-
dinates. Let us use the scheme with a cylindrical screen described above and register the
reflections formed as a result of 2D diffraction in the XY plane (see Figure 3.6.3d–f). In
these experiments, the investigated film should be oriented so that two out of six
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reflections observed on the flat screen are situated strictly along the X axis. On the cylindrical screen, one can then observe the reflections that correspond to the zeroth order of 2D diffraction (diffraction condition being $q_\parallel = 0$), the first order (diffraction conditions being $q_\parallel = 1\beta_1$ and $q_\parallel = 1\beta_2$), the second order ($q_\parallel = 2\beta_1$ and $q_\parallel = 2\beta_2$), and so on. Note that according to the 2D diffraction condition each reciprocal lattice node $g_{hk}$ gives rise to a pair of diffraction reflections, one corresponding to forward scattering with respect to the incident beam $k_i$, the other to backscattering (see Figure 3.5.3). The possibility of the experimental observation of a certain reflection in the visible spectral range is determined by a-SiO$_2$ particle diameter and the order of diffraction.

The experimental results presented in Figure 3.6.4b are obtained using a six-layer-thick opal film consisting of a-SiO$_2$ particles with diameter $D = 720$ nm. With the incident beam normal to the sample surface ($\theta = 0$), diffraction reflections, which are specified by the zeroth and the first-order diffraction, are observed on the cylindrical screen. Note that the intensity of the “forward-scattered” ($|\Theta| > 90^\circ$) reflections is higher than the intensity of the “backscattered” ($|\Theta| < 90^\circ$) ones. This can be associated with the nature of Mie scattering on a spherical particle, which has an asymmetric radiation pattern with the forward scattering being dominant (see Figure 3.5.3 in Chapter 3.5 and the study by Bohren and Huffman).

Also, in Figure 3.6.4b one can distinguish three types of diffraction features: (i) a straight line of white light corresponding to the scattering angles $\Theta = 2\beta$; (ii) two intense color curves (ovals) formed by diffracted white light with ruptures in the vicinity of the angles $\Theta = \pm 90^\circ$,
marked with dashed lines; and (iii) less intense diffraction features situated within the intensive color curves, which are also interrupted at the angles close to $\Theta = \theta \pm 90^\circ$. From Figure 3.6.4b it follows at once that light diffraction from the six-layer-thick opal film differs strongly from the 3D Bragg diffraction considered in more detail in Section 3.6.4. For experimental data interpretation we will use the results of two calculations—numerical and analytical, illustrated in Figure 3.6.4c and d, which are described below.

For diffraction pattern calculation in the case of low-contrast PhCs (which include synthetic opals), it is usually sufficient to use the Born approximation. Main features of light diffraction are then determined by the scattering structure factor and the scattering form factor. The calculations show that for interpretation of the experimental data (Figure 3.6.4b) it is sufficient to consider only the scattering structure factor $S(q)$. In the Born approximation, its square is given by the following expression:

$$S^2(q) = \frac{1}{NLM} \cdot \frac{\sin^2(Nqa_1/2)}{\sin^2(qa_1/2)} \cdot \frac{\sin^2(Lqa_2/2)}{\sin^2(qa_2/2)} \cdot \frac{\sin^2(Mqa_3/2)}{\sin^2(qa_3/2)},$$

(3.6.6)

where $q = k_s - k_i$ is the scattering vector, and $a_1$, $a_2$, and $a_3$ are the translation vectors of FCC opal lattice primitive cells. Equation 3.6.6 allows one to calculate $S(q)$ for different angles of scattering and sample orientation determined by the $k_s$ and $k_i$ vector directions. The size of the sample is the calculation variable and is determined by the number of scatterers $N$, $L$, $M$ along the directions of $a_1$, $a_2$, and $a_3$ vectors, respectively. For the calculations, we used the values $D = |a_i| = 720$ nm, $N = 1$, $L = M = 1500$, which correspond to the linear dimensions of the sample being about a millimeter and the sample thickness being one layer of $a$-SiO$_2$ particles. The results of the numerical calculation are in excellent agreement with the experimental results, as seen in Figure 3.6.4b and c. However, this calculation cannot interpret all the features observed in the diffraction patterns.

Equation 3.6.1 describing diffraction from a 2D periodic system of scatterers allows us to perform a detailed analysis of experimental data. Let us place the centers of spheres at the nodes of the hexagonal Bravias lattice with a nearest-neighbor distance $D$. One can then obtain a simple formula for the diffracted light wavelength:

$$\lambda_{hk} = \frac{D}{2} \sqrt{\frac{\varepsilon_{av}}{h^2 + hk + k^2}} \left(\frac{3}{h^2 + hk + k^2}\right)^{1/2} \left|\sin(\Theta - \theta) - \sin\theta\right|,$$

(3.6.7)

where $\theta$ and $(\Theta - \theta)$ are the angles of incidence and scattering counted from normal to scattering plane, $h$ and $k$ are integers, $\varepsilon_{av}$ stands for the average permittivity, and $D$ is the $a$-SiO$_2$ particle diameter, which in the first approximation can be equated to the modulus of translation vectors $|a_i|$. Expression 3.6.7 implies that the zeroth-order diffraction $(h = k = 0)$ can be observed only when $\sin(\Theta - \theta) = \sin \theta$, that is, $\Theta = 2\theta$ or $\Theta = 180^\circ$. The first condition corresponds to specular reflection of white light from film surface, whereas the second corresponds to directly transmitted beam (two (00) beams in Figure 3.6.3e). The first-order diffraction meets the condition $(h^2 + hk + k^2)^{1/2} = 1$, which is satisfied for the pairs of $(h,k)$ indices being equal to $(\overline{1}1), (1\overline{1}), (0,0), (0,1), (0\overline{1}), \text{ or } (0\overline{0})$, whereas the investigated diffraction in the XY plane corresponds to $(\overline{1}1)$ and $(1\overline{1})$ pairs of indices. The second-order diffraction meets the condition $(h^2 + hk + k^2)^{1/2} = 2$, whereas the diffraction in the XY plane is defined by $(\overline{2}2)$ and $(2\overline{2})$ pairs of indices. Higher orders of diffraction can be treated similarly.
data can be interpreted as solutions $\Theta = f(\theta, \lambda)$ of Equation 3.6.7 for the first three orders $(0,0), (1\overline{1}), (2\overline{2}), (2\overline{2})$ of diffraction as illustrated in Figure 3.6.4d for monochromatic light with wavelengths $\lambda = 415, 500, \text{and} 585 \text{ nm}$.

Comparing the results presented in Figure 3.6.4b and d, one can easily interpret all observed features. The zeroth-order diffraction corresponds to the specular reflection from the hexagonal plane on all wavelengths and is observed experimentally as a bright white stripe at $\Theta = 2\theta$, which splits Figure 3.6.4b into two areas. These areas correspond to light diffraction of $(1\overline{1})$ and $(2\overline{2})$ orders, that is, “to the right” with respect to $k$, and of $(\overline{1}1)$ and $(\overline{2}2)$ orders, that is, “to the left” (see Figure 3.6.4d). Theoretical dependences $\Theta = f(\theta, \lambda)$ for a nonzero order of diffraction represent ovals, with the oval corresponding to a higher order of diffraction lying within the oval of the lower order for the given wavelength. Note that on the experimental pattern diffraction is not observed close to the angle values $\Theta = \theta \pm 90^\circ$, which are marked with dashed lines in Figure 3.6.4b. This diffraction geometry implies propagation of diffracted light inside the film and exit of light from the film edge that significantly decreases the intensity of the registered light. Therefore, we can conclude that light diffraction from a six-layer-thick opal film has a vivid 2D nature.

### 3.6.3 Two-Dimensional to Three-Dimensional Transition in Optical Diffraction

The alteration of physical properties with the transition from 2D to 3D objects creates tremendous interest for researchers, and optical diffraction is no exception.\textsuperscript{17} When considering 2D diffraction patterns, represented in $(\theta, \Theta)$ coordinates as in Figure 3.6.4, a challenging question arises: What is the mechanism of transformation of the continuous ovals into a set of straight parallel lines expected in the case of Bragg diffraction from a low-contrast 3D photonic structure?

To answer this question one can use numerical modeling of the diffraction patterns computing the square of scattering structure factor $S^2(q)$ using Equation 3.6.6 as a function of the film thickness. Thickness is determined by the varying number of layers $N$ whereas the other geometrical parameters are fixed: $L = M = 3000$ and $D = 330 \text{ nm}$, which corresponds to the linear dimensions of the sample of about a millimeter. As is well known, most opal samples have twinned FCC structure. To describe the diffraction patterns observed in the experiment, the computation is performed for the twinned structure assuming that both twins (FCC-I and FCC-II) contribute equally to the diffraction patterns.\textsuperscript{10}

Light scattering from a single hexagonal layer formed by close-packed $a$-SiO$_2$ spheres corresponds to the 2D diffraction case ($N = 1$) (Figure 3.6.5a). The calculated diffraction pattern presented in the $(\theta, \Theta)$ coordinates and in the range $-90^\circ \leq \theta \leq 90^\circ$ of angles consists of two interrupted ovals and a straight line $\Theta = 2\theta$ separating them that corresponds to the specular reflection from the hexagonal layer. A presentation of the same result in the range of angles $0^\circ \leq \theta \leq 180^\circ$ would merge the semiovals into one solid oval that represents 2D diffraction from a single hexagonal layer for a given wavelength range. In this calculation, the diameter of $a$-SiO$_2$ particles was assumed to be equal to $330 \text{ nm}$, which corresponds to the diameter of the particles of the sample studied by Samusev et al.\textsuperscript{10} Note that the 2D diffraction pattern shown in Figure 3.6.5a differs significantly from the one given in the previous section for the sample with the diameter of particles of $720 \text{ nm}$ (Figure 3.6.4).
most important difference is the lack of the inner diffraction oval in Figure 3.6.5a, which falls into the ultraviolet spectral range and is therefore not shown in Figure 3.6.5.

Increasing the sample thickness leads to a transition from 2D to 3D diffraction regimes. A 2D structure is constructed with only two primitive vectors so that the diffraction condition should satisfy only two Laue equations (3.6.3) out of three. In contrast, for a 3D structure all three equations are to be used, thus implying additional limitations to the diffraction conditions and reducing the number of solutions.

The transformation of the diffraction patterns in the $(\theta, \Theta)$ coordinates during the transition from 2D to 3D is presented in Figure 3.6.5. With increasing number of layers, certain regions of both the semiovals and the diagonal fade out, unlike the initial 2D diffraction pattern. First, the closed semiovals break up into bands, then the bands narrow down, and, finally, in the case of the bulk sample consisting of $3000 \times 3000 \times 3000$ unit cells, these regions turn into a set of straight segments parallel to the $\Theta = 2\theta$ line (see Figure 3.6.5d). Note the transformation of the line $\Theta = 2\theta$ itself. It changes from a strip of reflected white light into colored segments formed by diffracted light. As a result, the expected Bragg diffraction pattern is indeed reached. A detailed interpretation of the 3D diffraction pattern represented in the $(\theta, \Theta)$ coordinates is given in the following section.

3.6.4 Three-Dimensional Optical Diffraction and Selective Switching of Diffraction Reflections

In Chapter 2.7, a calculation of photonic stop-band width in low-contrast multicomponent photonic crystals (MPhCs) was presented. MPhCs are structures composed of three or more homogeneous or inhomogeneous components. The calculation results indicate that different $[hkl]$ stop-bands can be selectively “switched off” in MPhCs while varying the permittivity of one of the components. In Chapter 3.5, it was demonstrated that
opal-based PhCs belong to the class of MPhCs. The multicomponent nature of the opal structure is created by the fact that the constitutive a-SiO\textsubscript{2} particles consist of smaller amorphous silica dioxide grains and possess an inhomogeneous inner structure: the porous nucleus covered by a denser thin coat.\textsuperscript{18,19} The opal transmission spectra studies have established that the parameters of photonic stop-bands corresponding to the different \{hkl\} families of crystal planes have different dependences on the permittivity of the filler \(\varepsilon_f\).\textsuperscript{18} For the bulk opal sample, the stop-bands of the \{111\} family significantly weaken when the filler permittivity approaches the value of \(\varepsilon_f(\mathbf{g}_{111}) = 1.82\), whereas the intensities of the dips corresponding to the \{220\} family stop-bands significantly decrease when \(\varepsilon_f\) approaches \(\varepsilon_f(\mathbf{g}_{220}) = 1.92\). Note that at the critical points \(\varepsilon_f(\mathbf{g}_{hkl}) = \varepsilon_f\) the stop-bands in opal spectra do not vanish, but undergo a complex transformation leading to the formation of pass-bands. This effect was discussed in the context of the Fano resonance model\textsuperscript{19,20} and is described in Chapter 3.5.

In low-contrast PhCs, stop-bands in transmission spectra and the reflections in the diffraction patterns both originate from the Bragg light reflection from certain \{hkl\} crystallographic plane sets. Taking into account the effects discovered in opal transmission spectra, one can expect some nontrivial transformation of the Bragg \{hkl\} reflections in the diffraction patterns, depending on the dielectric contrast. Such effects are indeed experimentally observed in light diffraction from bulk opal samples while varying \(\varepsilon_f\).\textsuperscript{10} The experimental setup illustrated in Figure 3.6.3e is used. An opal sample is fixed on a holder in the center of a cylindrical flask serving as a screen for observing and capturing the diffraction patterns. The experiments are performed using the immersion spectroscopy method, which implies consecutive acquisition of the diffraction patterns as a function of the permittivity of a liquid filling the opal matrix.\textsuperscript{18} The cylindrical flask was filled with the liquid serving as the opal filler as well as the ambient medium. During the experiment distilled water (\(\varepsilon_{\text{H}_2\text{O}} = 1.78\)), glycerine (\(\varepsilon_{\text{gl}} = 2.16\)), and their mixtures were used. This allows us to vary the filler permittivity within the range \(1.78 \leq \varepsilon_f \leq 2.16\).

The results of the experimental studies of white light diffraction from bulk opal samples as a function of the filler permittivity \(\varepsilon_f\) are presented in Figure 3.6.6. We are primarily concerned with the behavior of the Bragg reflections corresponding to the different \{hkl\} plane sets. For the experimental data analysis, one must associate the reflections shown in Figure 3.6.6 in the \((\theta, \Theta)\) coordinates with specific \{hkl\} plane sets of the FCC opal lattice. For this purpose, the Bragg wavelength \(\lambda_{hkl}(\theta)\) of the light beam reflected from the \{hkl\} plane set was calculated as a function of the incident angle \(\theta\), which is counted from the normal to \{111\} growth plane set. The expression for \(\lambda_{hkl}(\theta)\), which is also used in Chapter 3.5 (see Equation 3.5.3), is given by

\[
\lambda_{hkl}(\theta) = 2d_{111}\sqrt{\varepsilon_{av}\left(\frac{3}{h^2 + k^2 + l^2}\right)^{1/2}} |\cos(\theta - \theta_{hkl})|,
\]

where \(d_{111} = \sqrt{(2/3)D}\) stands for the distance between neighboring \{111\} planes, \(\varepsilon_{av} = 0.74\varepsilon_{\text{SiO}_2} + 0.26\varepsilon_f\) is the average permittivity of the opal FCC structure, and \(\theta_{hkl}\) is the angle between the \{111\} and \{hkl\} directions. The calculation is performed for \{111\}, \{200\}, and \{220\} plane families of the twinned FCC lattice (see Figure 3.6.6a). Bragg wavelengths \(\lambda_{hkl}(\theta)\) corresponding to higher-index \{hkl\} plane sets for the sample formed by 330 nm a-SiO\textsubscript{2} particles fall within the ultraviolet spectral range (\(\lambda_{hkl}(\theta) < 400\) nm) that was not studied experimentally by Samusev et al.\textsuperscript{10} The calculation of the dispersion curves \(\lambda_{hkl}(\theta)\) was performed for the incident wavevector \(\mathbf{k}\), lying in the scanning plane \(X \rightarrow L_x \rightarrow K_x \rightarrow L\).
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of FCC-I Brillouin zone, as this case was realized in the experiment. In the Brillouin zone of FCC-II opal twin, this plane coincides with the $L \rightarrow K_g \rightarrow L_g \rightarrow X$ scanning plane. The representation of the Brillouin zone of the FCC lattice and its cross sections can be found in Chapter 3.5 and in the study by Samusev et al.\textsuperscript{10}

The angle of the specular Bragg reflection from different $(hkl)$ plane sets is given by

$$\Theta = 2(\theta - \theta_{hil}).$$ \hfill (3.6.9)

The angles of interest $\theta_{hil}$ between $[111]$ and $[hkl]$ directions are $\theta_{111} = 70.5^\circ$, $\theta_{200} = -54.7^\circ$, and $\theta_{022} = 35.3^\circ$ for the FCC-I lattice and $\theta_{111} = -70.5^\circ$, $\theta_{200} = 54.7^\circ$, and $\theta_{022} = -35.3^\circ$ for the FCC-II lattice. Therefore, Bragg diffraction reflections associated with different $(hkl)$ plane sets are expected to appear in the $(\theta, \Theta)$ diagram as a set of parallel straight lines shifted by $\theta_{hil}$ along $\theta$ axis with respect to the $\Theta = 2\theta$ diagonal corresponding to the $(111)$ reflection common for both FCC-I and FCC-II twins ($\theta_{111} = 0$).

By comparing the upper panels (a–e) in Figure 3.6.6, which contain the Bragg wavelength dispersion relations $\lambda_{hil}(\theta)$ for $[111]$, $[200]$, and $[220]$ families, with the lower panels (f–j), one can interpret all the observed diffraction reflections. Note that in the lower panels theoretical (Figure 3.6.6f) and experimental (Figure 3.6.6g–j) data are presented only for the visible range, which form segments rather than continuous straight lines passing through the entire image. The interruptions correspond to diffraction in either the ultraviolet or infrared range.

The effect of the selective weakening of the reflections corresponding to $[111]$ and $[220]$ families of planes appears to be the most important experimental result. Let us first

**FIGURE 3.6.6**
(See color insert.) (a)–(e) The dispersion relations $\lambda_{hil}(\theta)$ of the Bragg wavelengths for the twinned face-centered cubic (FCC) opal lattice formed by $a$-SiO$_2$ particles with $D = 330$ nm. $\lambda_{111}(\theta)$ are indicated by solid curves, $\lambda_{200}(\theta)$ by dashed curves, and $\lambda_{220}(\theta)$ by dot-dash curves (see Equation 3.6.8). Panel (c) misses the dispersion curves $\lambda_{111}(\theta)$ and panel (d) misses the dispersion curves $\lambda_{220}(\theta)$. The visible spectral range of electromagnetic waves is separated out by two horizontal lines; the ultraviolet and infrared spectral ranges are darkened. (f) The calculated intensity of visible (400–700 nm) light diffraction from the twinned FCC opal structure consisting of $3000 \times 3000 \times 3000$ scatterers immersed in water. (g)–(j) The experimental patterns of light diffraction from the synthetic opal sample immersed in fillers with dielectric permittivity $\varepsilon_f = 1.78$ (g), 1.86 (h), 2.05 (i), and 2.16 (j). $\theta$ is the angle of incidence counted from growth $(111)$ plane set of opal FCC lattice and $\Theta$ is the angle of scattered light registration. (From A. K. Samusev et al., Phys. Solid State 53(7), 1415 (2011). With permission.)
consider this effect for (022) reflections, which are observed as blue stripes at \(-50° \leq \theta \leq -15°\) (FCC-I), \(15° \leq \theta \leq 50°\) (FCC-II), and \(\Theta = 2(\theta \pm 35.3°)\) (“+” for FCC-I, “−” for FCC-II) angles within the range of registration angles \(-40° \leq \Theta \leq 40°\). Note that outside of this range (022) reflections are not visible as \(\lambda_{022}(\theta)\) falls within the ultraviolet range, as clearly seen in Figure 3.6.6a–c and e. From the dispersion curves \(\lambda_{hkl}(\theta)\) represented in Figure 3.6.6d (\(\epsilon_f = 2.05\)), both branches of the (022) plane set are eliminated. This simplifies singling out the diffraction associated with the other \{hkl\} families. The intensity of (022) reflections are seen to significantly depend on \(\epsilon_f\). The lowest intensity of (022) reflections corresponds to the value of \(\epsilon_f \approx 2.05\), whereas the reflections of \{111\} and \{200\} families are still clearly observed on a diffraction pattern with the same \(\epsilon_f\) (Figure 3.6.6i).

Let us now discuss the immersion dependence of \{111\} family reflections, marked with solid lines in Figure 3.6.6. The \{111\} family of planes is represented by reflections from (111) and (111) crystal planes. The position of the (111) reflection meets the requirement \(\Theta = 2\theta\) and therefore coincides with the specular reflection of incident white light. Nevertheless, the (111) reflection is experimentally observed within the range of angles \(-55° \leq \theta \leq -20°\) and \(20° \leq \theta \leq 55°\), while its color changes through the entire visible range from blue to red in full accordance with the computational dependence shown in Figure 3.6.6f. Within the range of angles \(-20° \leq \theta \leq 20°\), (111) reflection is not registered as \(\lambda_{111}(\theta)\) falls within the infrared range, whereas within the range of angles \(\theta < -55°\) and \(\theta > 55°\), \(\lambda_{111}(\theta)\) falls within the ultraviolet range so this reflection is also not visible.

The intensity of all reflections of the \{111\} family exhibits pronounced dependence on the dielectric contrast with a minimum at \(\epsilon_f(\{111\}) = 1.86\). From the dispersion curves \(\lambda_{hkl}(\theta)\) represented in Figure 3.6.6, all branches of the \{111\} family are eliminated. This simplifies singling out the diffraction associated with the other \{hkl\} families, specifically with \{200\} (these reflections are of virtually all colors of the visible range—from blue to orange) and with \{220\} (only blue reflections).

**FIGURE 3.6.7**
The filler permittivity \(\epsilon_f^0(\text{g})\) that corresponds to the immersion condition for an opal structure as a function of the reciprocal lattice vector modulus \(\text{g}\) calculated from Equation 3.5.4 for the permittivity profile \(\epsilon_s(r)\) simulating the \(a\)-SiO\(_2\) spheres. The \(\epsilon_s(r)\) profile is given in the inset. The moduli of the shortest reciprocal lattice vectors \(\text{g}_{hkl}\) are shown by vertical lines. Open circles represent values of \(\epsilon_f^0(\text{g}_{hkl})\) obtained in the transmission experiments (Figure 3.5.9 in Chapter 3.5); black squares represent the diffraction data. The gray region is for the experimental range of \(\epsilon_f\).
The fitting of the $\varepsilon_f(\mathbf{g})$ function to experimental data is discussed in detail in Chapter 3.5. The result is presented in Figure 3.6.7 where both transmission and diffraction experimental data are displayed. It should be mentioned that the values of $\varepsilon_f^0$ obtained in diffraction experiments on opal films differ from the values derived from the transmission spectroscopy of bulk opal samples (Chapter 3.5) because of a technological difference in the preparation of $a$-SiO$_2$ particles forming opal structures for transmission and diffraction experiments.

Therefore, one can conclude a possibility of selective control over the intensity of Bragg diffraction reflections in low-contrast MPhCs. It is important to note that the phenomenon of selective stop-band switching discussed in Chapter 3.5 and the effect of selective attenuation of $[hkl]$ diffraction reflections are complementary.

3.6.5 Sample Thickness Dependence in Small-Angle X-Ray Diffraction

X-ray diffraction is described by the same laws as light diffraction. However, about four orders of magnitude difference in the wavelength results in a number of essential differences in the appearance of the diffraction phenomenon. To illustrate the differences, let us consider the effects of the sample thickness in x-ray diffraction. Figure 3.6.8a–c illustrates the modification of the reciprocal lattice of the opal-like structure. If only a single close-packed layer is deposited on the substrate, the reciprocal lattice consists of scattering rods normal to the crystal plane XZ (Figure 3.6.8a). In this case, the scattering structure factor $S(\mathbf{q})$ does not change along the rods and the decay of the scattering intensity is solely determined by the particle form factor $F(\mathbf{q})$. On increase of the number of layers, the interference between their contributions will lead to appearance of additional structure in $S(\mathbf{q})$ along these Bragg scattering rods, which eventually will split into separate reflections, which are broadened along the layer normal Y (Figure 3.6.8b). With further increase of the number of layers, these reflections will transform into delta-function-like Bragg reflections characteristic for an ideal large 3D crystal (Figure 3.6.8c).

The appearance of the diffraction pattern depends on the sample orientation, which is illustrated in Figure 3.6.8d and e in the $(\theta, \Theta)$ coordinates introduced above. Here only monochromatic x-rays with a wavelength of $\lambda = 0.1$ nm are considered. The crystal is assumed to consists of $N$ hexagonal close-packed layers of touching spheres with the diameter $D = 400$ nm. One can see that x-ray diffraction is very much concentrated around the forward direction, that is, around $\Theta = 180^\circ$. For a single ($N = 1$) crystal plane (Figure 3.6.8d), observation angle $\Theta$ slowly varies on sample rotation by angle $\theta$. For a crystal consisting of $N = 15$ layers, the interference between them splits the monotonic lines in Figure 3.6.8d into segments, where most of the diffraction intensity is concentrated (Figure 3.6.8e). Note an essential difference between the intensity distributions for visible light diffraction in Figures 3.6.3 through 3.6.6, and that for x-ray diffraction in Figure 3.6.8d and e. For x-rays, the diffraction “traces” appear to be nearly symmetric with respect to $\Theta = 180^\circ$. The diffraction peaks at $\Theta > 180^\circ$ and $\Theta < 180^\circ$, which correspond to $\mathbf{q} = \mathbf{g}_{hkl}$ and $\mathbf{q} = -\mathbf{g}_{hkl}$ can be simultaneously observed at a single $\theta$ value, even in the case of a multilayer crystal (Figure 3.6.8e). Moreover, multiple diffraction orders, $2\mathbf{g}_{hkl}, 3\mathbf{g}_{hkl}$, and so on, can be simultaneously detected. Such observations are impossible with visible light. The reason for these effects is that for x-rays the radius $2\pi/\lambda$ of the Ewald sphere is very large in comparison to the scale of interest. As a result, for a crystal with $N = 15$ layers the Ewald sphere can be simply approximated by a plane. However, on further increase of the crystal thickness and
Further sharpening of the crystal reflections, effects of the curvature of the Ewald sphere should show up.\textsuperscript{21}

Let us now estimate the sample thickness at which the curvature effects can be observed and the possible effect of the curvature of the Ewald sphere in x-ray diffraction. Let us assume that the x-rays are incident exactly along the \((hkl)\) crystallographic plane set as sketched in Figure 3.6.1b and d. From a simple geometrical consideration one can see that the \(hkl\) site of the reciprocal lattice of an FCC crystal will deviate from the Ewald sphere by

\[
\Delta = \frac{\lambda g_{\text{id}}^2}{4\pi} = \frac{\pi\lambda(h^2 + k^2 + l^2)}{2D^2}.
\]

Because of this deviation the Ewald sphere should miss the reciprocal lattice node and no Bragg diffraction should be observed in a perfect infinite opal-like crystal. In practice, however, the nodes of the reciprocal lattice of a real opal-like crystal are usually broadened because of finite thickness of the sample, presence of disorder, and so on.

Just to give a few typical numbers, let us consider diffraction of x-rays with \(\lambda = 0.1\) nm on an FCC crystal of spheres with diameter \(D = 400\) nm. For the \((220)\) reflections the deviation

\[
\Delta = \frac{\lambda g_{\text{id}}^2}{4\pi} = \frac{\pi\lambda(h^2 + k^2 + l^2)}{2D^2} = \frac{\pi\lambda(400^2 + 400^2 + 400^2)}{2(400^2)} = \frac{\pi\lambda(1200000)}{2(160000)} = \frac{3.14 \times 0.1 \times 1200000}{320000} = 0.117.
\]

The length of the segments in panel (e) is selected to display the full-width at half-maximum of every maximum in \(S^2(q)\). It is assumed in panel (e) that the crystal consists of two twin domains in equal proportion, whereas in (b) and (c) only a single domain with unique stacking direction is illustrated.
of the Ewald spheres from a plane is \( \Delta = 8 \cdot 10^{-6} \text{ nm} \). For a crystalline film of a finite thickness \( L \) the broadening of the reciprocal lattice nodes is of the order of \( 2\pi/L \) (full-width at half-maximum). To observe the effect of the curvature of the Ewald sphere, one requires \( 2\pi/\lambda < \Delta \), or \( L > 800 \mu \text{m} \), that is, 2000 times the sphere diameter!

In practice, the thickness of opal crystals is usually far too small to observe the effects of the curvature of the Ewald sphere. The diffraction pattern is then equal to the squared modulus of the Fourier transform of the 2D projection of the electron density in the sample on a plane normal to the x-ray beam.

### 3.6.6 Order and Disorder from Microradian X-Ray Diffraction

Here one can find examples of the characterization of structure and disorder in PhCs using small-angle x-ray diffraction with microradian resolution (microradian x-ray diffraction). For more detailed interpretation of the microradian diffraction patterns and the analysis of structural order and disorder of opals, we refer the readers to our previously published articles.\(^{21-26}\)

To characterize the 3D crystal structure one usually needs to measure the microradian x-ray diffraction patterns with different sample orientations. Some typical examples of diffraction patterns are presented in Figure 3.6.9a–c for film opals recorded at different angles of rotation \( \theta \). As shown in Section 3.6.5, the Ewald sphere curvature is negligible, so many subsequent diffraction orders can be observed simultaneously. The patterns are measured at normal incidence \( \theta = 0^\circ \) (a) and after sample rotation by \( \theta = -35^\circ \) (b) and \( \theta = 55^\circ \) (c). Figure 3.6.9d–f presents the expected Bragg reflections for an FCC crystal with corresponding orientations. One can see that most of the Bragg peaks in Figure 3.6.9a–c correspond to an FCC structure with the size of the conventional cubic unit cell of \( a = \sqrt{2D} = d_{\text{hhkl}} \sqrt{h^2 + k^2 + l^2} \), where \( d_{\text{hhkl}} = 2\pi/q_{\text{hhkl}} \) is the interplane distance corresponding to an \( (hkl) \) Bragg reflection.

The diffraction peak intensities are proportional to the product of the squared structure factor \( S^2(q) \)—as a result of scattering from the structure—and the squared form factor \( F^2(q) \)—as a result of scattering from a particle that is the base element of this structure. Figure 3.6.10 shows the squared form factor of the homogeneous spherical particles described by \( F^2(q) = [\sin(qR) - qR\cos(qR)]^2/(qR)^4 \), where \( R \) is the radius of a colloidal particle. The strength of the form factor for a number of Bragg reflections is illustrated by points at the corresponding \( q \)-values. This allows us to clarify not only the positions of the Bragg peaks but also their relative intensities. It is clear from Figure 3.6.10 that the form factor for the (111) reflection is slightly higher than that for the (220) reflection, whereas both are two orders of magnitude higher than that for the (200) reflection. Furthermore, the low visibility of the (422) and (222) in Figure 3.6.9a and b, respectively, can be explained by their proximity to the form factor minima (Figure 3.6.10). Such theoretical calculations are in good agreement with the results obtained from the experiment (Figure 3.6.9a–c).

In addition, in Figure 3.6.9a–c there are a number of additional peaks that do not correspond to an ideal FCC structure. These features can be caused by the stacking faults parallel to the substrate as well as by finite crystal thickness. The more striking are the rods of diffuse scattering seen in Figure 3.6.9b. These Bragg scattering rods are parallel to the (111) crystallographic directions and indicate the presence of planar defects parallel to two types of HCP layers that make an angle of 70.5° with the substrate.
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Figure 3.6.10
The theoretical squared scattering form factor $F^2(q)$ of a single uniform sphere (solid line). The symbols display the squared form factor values for different $(hkl)$ reflections of a face-centered cubic structure of touching uniform spheres.

Figure 3.6.9
(See color insert.) Microradian x-ray diffraction patterns of opal-like photonic films of polystyrene colloidal spheres. The film is about 20 layers thick. The patterns are measured at normal incidence $\theta = 0^\circ$ (a) and after sample rotation by $\theta = -35^\circ$ (b) and $55^\circ$ (c). The sketches (d–f) below each pattern (a–c) present the expected Bragg reflections for a face-centered cubic crystal with corresponding orientations.
Figure 3.6.11 presents the intensity distribution along the rods between the (111) and (200) reflections in Figure 3.6.9b. The intensity distribution along the Bragg scattering rods is usually described by Wilson's theory,\(^2\) which assumes that the probability \(\alpha\) of finding a close-packed FCC layer is independent of the stacking environment of the neighboring layers. In this model, the fraction of FCC-type layers in a crystal is labeled \(\alpha\). Figure 3.6.11 shows the measured intensity profile along a first-order Bragg rod. It also shows the profile along a Bragg rod, calculated within Wilson's theory for a crystal with dominant FCC stacking (\(\alpha = 0.9\)). One can see that the theory predicts two times more maxima than experimentally observed. The reason for this discrepancy is related to the fact that in the Wilson model a single HCP layer changes the direction of the FCC growth from the . . .ABCABC. . . to . . .ACBACB. . .-type stacking, giving rise to an additional set of Bragg reflections along the Bragg rod (dashed line in Figure 3.6.11). If stacking disorder is caused by pairs of HCP layers and only one growth direction dominates, then Wilson’s theory should be modified by adapting Paterson’s model\(^{27}\) to fit the data correctly (solid line in Figure 3.6.9). In this model, each subsequent layer is stacked with a probability \(\beta\) in a particular direction. With the probability \((1 - \beta)\), however, a fault is created by selecting alternative stacking direction. For \(\beta\) close to 1 the original stacking direction will most probably be restored in further layers, leaving behind a stacking fault, for example, in the sequence . . .ABCACABC . . . the central two layers are in an HCP environment with a deformation stacking fault between them. Such a “double”-stacking fault is equivalent to sliding one part of a perfect FCC crystal ( . . .ABC| in the example above) relative to the other part along the stacking fault ( |BCAB . . . becomes then |CABC . . .). One can see that the intensity profile \(I(q) \propto S^2(q) \cdot F^2(q)\) along the first-order

\[ \begin{align*}
(111) & \quad \text{Wilson, } \alpha = 0.9 \\
(200) & \quad \text{Paterson, } \beta = 0.9 \\
(022) & \quad \text{Experiment}
\end{align*} \]

**FIGURE 3.6.11**
Intensity profile along one of the Bragg scattering rods in Figure 3.6.9b. The corresponding piece of the diffraction pattern is reproduced above the graph. The coordinate \(q_{\text{rod}}\) along the Bragg rod is normalized to the length of \(q_{111}\) wavevector corresponding to the spacing \(d_{111} = a/\sqrt{3}\) between close packed layers. \(q_{\text{rod}} = 0\) corresponds to the point closest to the origin of the reciprocal space. The dashed and solid lines display results of model calculations using the Wilson theory and Paterson model, respectively.
Bragg rod, calculated with the modified theory\textsuperscript{27} for $\beta = 0.9$ (Figure 3.6.11), closely follows the experimental result, confirming the presence of 10% double-stacking faults in at least two out of four $\{111\}$ directions in this crystal with a dominating FCC structure.

### 3.6.7 How X-Ray Diffraction Can Serve the Technology of Opal Growth

Here we present an example of a study where x-ray diffraction is used to properly adjust the fabrication process of opal films. A direct current electric field is applied normal to the substrates during vertical deposition of colloidal crystals. The external electric field is shown to be an excellent tool to control the crystallization process of the opal-like structures. It can act as the driving force, which moves colloidal particles to the substrate or induces dipole–dipole interparticle interactions, and therefore can improve the crystal quality and even change the crystal structure.\textsuperscript{28}

Colloidal crystals made of polystyrene microspheres were grown by the vertical deposition technique in the presence of an external electric field $U = -1.5 \div +1.5$ V.\textsuperscript{24} Negatively charged polystyrene spheres were deposited onto indium tin oxide glass vertically aligned electrodes (substrates) in a cylindrical glass cell (5 cm diameter) using a Solartron 1287 potentiostat. The distance between the electrodes was 3 cm. The electrodes were fixed precisely parallel to each other. X-ray studies were performed using a microradian x-ray diffraction setup.\textsuperscript{26} To achieve angular resolution needed to study these large-period structures, the beam was focused at the detector by a set of compound refractive lenses.\textsuperscript{29} The colloidal films were first mounted perpendicular to the x-ray beam. Samples were then rotated around the vertical axis (the $[101]$ axis of the crystal) within the range $-75^\circ \leq \theta \leq 75^\circ$, and the diffraction patterns were recorded at each degree of rotation.

Figure 3.6.12 shows typical examples of microradian diffraction patterns measured at $\theta = 0^\circ$ (Figure 3.6.12a, d, and g) and at $\theta = -35^\circ$ (Figure 3.6.12b, e, and h) for colloidal crystals synthesized at $U = -1.5, 0,$ and $+1.5$ V. In the diffraction patterns one can clearly identify a large number of Bragg reflections, which can be assigned to the reciprocal lattice of an ideal FCC crystal structure with lattice constant $a = 750$ nm. Corresponding indices are shown in Figure 3.6.12. In addition to the assigned Bragg peaks, the diffraction patterns also show features that cannot be assigned to the FCC structure. They can be truly Bragg reflections (e.g., corresponding to an HCP structure coexisting with FCC), or can be sections of diffuse objects in the reciprocal space. The latter can be related to the finite film thickness and/or to the presence of stacking faults along the $[111]$ direction. Complete information on this type of disorder could be inferred from the distribution of diffracted intensity in the 3D reciprocal space (see Section 3.6.8).

Figure 3.6.12c, f, and i show the intensities of (220), (111), and (202) reflections observed in Figure 3.6.12a and b, d and e, as well as g, and h, respectively, as functions of the sample rotation angle $\theta$. We note that in contrast to the example considered in the previous section, where we dealt with a single crystal with unique stacking direction, here one observes the coexistence of twin domains with different stacking directions. The relative amounts of $\ldots$ABCABC$\ldots$ and $\ldots$ACBACB$\ldots$ stacking sequences can be estimated by comparing the integral intensities of the corresponding peaks: (111)-type at $\theta = -19.5^\circ$ ($\ldots$ABCABC$\ldots$) and $\theta = +19.5^\circ$ ($\ldots$ACBACB$\ldots$); (202)-type at $\theta = -54.7^\circ$ ($\ldots$ABCABC$\ldots$) and $\theta = +54.7^\circ$ ($\ldots$ACBACB$\ldots$).
(See color insert.) The diffraction patterns obtained at rotation angles $\theta = 0^\circ$ (a, d, g) and $35^\circ$ (b, e, h) for samples synthesized at a few selected voltage values $U = -1.5$ V (g, h), 0 V (d, e), and $+1.5$ V (a, b). Panels (c), (f), and (i) present corresponding rocking curves: the $\theta$ dependence of the intensity for (220) (circles), (111) (triangles), (1T1) (squares), and (202) (rhombs) Bragg reflections. Panel (j) displays the longitudinal ($\Delta q$) and transversal ($\delta q_{\text{azim}}$) width of (1T1) reflection (measured at $\theta = 19^\circ$) as a function of the potential applied on colloidal film synthesis. The dependence of stacking probability $\alpha$ of a colloidal film on applied voltage $U$ is given in panel (k). Negative (positive) values of $U$ correspond to cathode (anode) polarizations.
The variation of the crystal quality can also be derived from the width of the diffraction reflections. The results obtained from the patterns measured at \( \theta = 0^\circ \) are summarized in Figure 3.6.12j. The full-width at half-maximum of the diffraction maxima in the azimuthal (\( \delta q_{\text{azim}} \)) and radial (\( \Delta q \)) directions characterizes the mosaicity of the colloidal films and the average crystallite size (\( \Lambda \)), respectively. One can see that the mosaicity \( \delta q_{\text{azim}} \) of the colloidal crystals decreases from 8° to 3° when the applied voltage changes from +1.5 to −1.5 V. Higher values of applied potential lead to significant disorientation of the domains in colloidal films grown at anode polarizations. One can see in Figure 3.6.12c, f, i, and j that the optimum value of an applied voltage \( U \) for the conditions we have used (given concentration of the suspension, pH, charge of colloidal particles, temperature, distance between electrodes, etc.) is around −1.5 V.

### 3.6.8 Three-Dimensional Reciprocal Space Reconstruction

The collected 2D images shown in Figure 3.6.9 or Figure 3.6.12 can be compiled to reconstruct a full 3D reciprocal space of the sample. This process, called 3D reciprocal space reconstruction, allows one to reveal full details of the Bragg reflections, that is, their broadening in different directions, their integrated intensities, and so on.

An example of a 3D map in reciprocal space is shown in Figure 3.6.13a for the colloidal crystal formed on a cathode at \( U = 1.5 \) V, described in Section 3.6.7. One clearly sees the presence of the extended rods of diffuse scattering and of localized reflections with well-defined round shapes. This reciprocal lattice is typical for a close-packed structure with stacking faults.

![Figure 3.6.13](image)

**Figure 3.6.13**

(a) Three-dimensional reconstruction of the reciprocal space for the colloidal crystal obtained on the cathode at \( U = 1.5 \) V. Only the reflections within \( q < 0.03 \) nm\(^{-1} \) are shown. Hexagonal basis is depicted by the vectors \( b_1, b_2, \) and \( b_3 \). The inset illustrates a view on the reciprocal space along \( b_3 \) (i.e., at \( \theta = 0^\circ \)). (b) Normalized intensity variation along Bragg rods for two samples prepared on electrodes with two opposite polarizations at ±1.5 V. Intensity profile calculated within Wilson’s theory for \( \alpha = 0.85 \) and 0.60 are shown by solid and dashed lines, respectively. (Reprinted with permission from K. S. Napolskii et al., Langmuir 26, 2346 (2010). Copyright 2010 American Chemical Society.)
To reconstruct the total reciprocal space, a program for the 3D reconstruction of an object from a set of its 2D cross sections was developed in the MathCad worksheet. The Ewald sphere in the reconstruction region can be considered as planar for the case of small-angle scattering. The set of the initial data consists of (i) diffraction maxima located at the nodes of the reciprocal lattice, (ii) diffuse rods as a result of the stacking faults, and (iii) small-angle diffuse background with a maximum at \( q = 0 \), which is determined by the scattering of x-rays on the imperfections of the sample structures and on the elements of the optical scheme. As the intensity of the diffuse rods is low, the correct subtraction of the background is an important task determining the possibility of the correct quantitative reconstruction of the reciprocal space pattern.

We analyze the distribution of the diffracted intensity along the Bragg rod with the help of Wilson’s theory. Figure 3.6.13b shows the normalized intensity profiles along a Bragg rod extracted from 3D reconstruction for colloidal crystals grown at \( U = 1.5 \) V on the cathode and the anode. These profiles are compared to the predictions of Wilson’s theory with different values of probability \( \alpha \) of finding an FCC sequence of stacked layers. The calculated intensity profiles \( I(q) \propto S^2(q) \cdot F^2(q) \) are shown by lines in Figure 3.6.13b. One can see that while for the crystal grown on the cathode the stacking is mostly FCC (\( \alpha \approx 0.85 \)), a nearly RHCP structure is found on the anode (\( \alpha \approx 0.6 \)). The dependence of parameter \( \alpha \) on the applied potential is shown in Figure 3.6.12k.

Thus, microradian x-ray diffraction provides extremely valuable information on the real structure of mesoscopic materials, which cannot be easily obtained by other analytical approaches. Our results based on the analyses of diffraction patterns, 3D reconstructions of the reciprocal space, and Wilson’s theory unambiguously show that application of a negative potential can significantly improve the quality of opal-like photonic structures. The suggested synthetic approach is a highly reproducible way for the formation of large-scale high-quality dry colloidal crystals with controllable thickness on conducting substrates.

3.6.9 Conclusions

To summarize, in this chapter diffraction of light and x-rays on opal-like structures is considered. New methodological approaches to collection, processing, and interpretation of experimental data are presented.

In particular, a novel representation of the light diffraction data in the “incident angle–registration angle” \( (\theta, \Theta) \) coordinates is shown to be an effective tool of data analysis. This representation allows one to easily distinguish the reflections originating from 2D diffraction from the ones governed by 3D Bragg diffraction. In addition, structural disorder becomes apparent in the \( (\theta, \Theta) \) representation. It is also demonstrated that the immersion spectroscopy method can be used to selectively switch diffraction reflections. This phenomenon is caused by inhomogeneity of the \( a-SiO_2 \) particles that form synthetic opals.

Furthermore, it is demonstrated that microradian x-ray diffraction is a powerful technique that is able to reveal the dominating structure and the presence of disorder in opal-like structures. Short acquisition times, modern 2D detectors, and progress in computing techniques make 3D reconstructions of reciprocal space routinely available. This method provides extremely valuable information on the real structure of mesoscopic materials that cannot be easily obtained by other analytical approaches.
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References

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