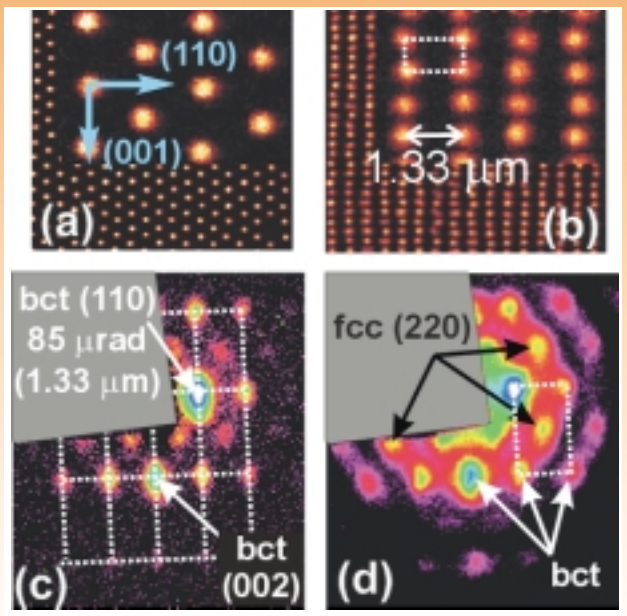


Fig. 1: Body-centred tetragonal colloidal crystal: (a) A confocal laser microscope xy-image of a single hexagonal plane. (b) A z-average of lateral particle positions in four crystal planes. 11 keV µrad-XRD patterns of a crystal before (c) and after (d) drying and silicon infiltration. (a)-(c) are measured in the same crystal while for the sample used in (d) optical techniques are not applicable.

Scientific article

3D STRUCTURE AND (DIS–)ORDER IN PHOTONIC CRYSTALS BY MICRORADIAN SYNCHROTRON X–RAY DIFFRACTION

A.V. Petukhov *Van't Hoff laboratory, Debye Institute, Utrecht University, The Netherlands*
J.H.J. Thijssen, A. Imhof, A. van Blaaderen *Soft Condensed Matter, Debye Institute, Utrecht University, The Netherlands*
I.P. Dolbnya *BM26 DUBBLE CRG, ESRF*
A. Snigirev, I. Snigireva, M. Drakopoulos *ESRF*

X-ray diffraction at microradian angles (µrad-XRD) is readily achievable at the ESRF and is able to characterise 3D structure and order of photonic crystals with a lattice spacing above one micrometre.

Photonics: large–scale crystals

In photonic crystals the refractive index varies periodically on length scales comparable to optical wavelengths *[1]*. With a sufficient contrast and a proper 3D lattice a photonic band gap can be opened, which will allow one to manipulate light similar to semiconductors manipulating electrons. An important area of application is infrared telecommunications, operating at wavelengths of 1.3 and 1.5 µm, where silica fibres display high transport performance. Fabrication of such materials is challenging and one possible route is through self-organisation of colloidal particles. By tuning the interparticle interaction potential, various lattices can be achieved *[2]*. By filling dried colloidal crystals with silicon and etching out the silica, 'inverted crystals' of silicon can be made, which have the desired band gap *[3]*.

To check whether the photonic crystal still possesses the intended structure and a high degree of order, one can no longer rely on optical tools since the light/lattice coupling is too strong. X-rays are therefore one of the few tools, if not the only one, available to elucidate the internal 3D structure and order *[4,5]*. The issue addressed here is: can one further extend XRD to include crystals with spacing above 1 µm? Moreover, can one exploit diffraction to probe order on distances of tens to hundreds of periods?

Microradian 3D Crystallography

At **BM26B** (DUBBLE) X-ray crystallography methods were successfully applied to photonic super-micrometre

structures. An example is given in Figure 1c, which presents a diffraction pattern of a wet body-centred tetragonal (bct) crystal, which is self-assembled in an external electric field *[2]*. The rectangular arrangement of bright reflections (highlighted by white dotted lines) reflects the bct-stacking of close-packed layers (cf. panel 1b). By measuring patterns at different orientations, the full 3D structure was accessed. Panel 1d presents a diffraction pattern obtained from a similar bct crystal, which was dried and then filled with silicon. The rectangular arrangement of the strongest reflections is still recognisable, but reflections typical for close-packed (fcc, rhcp) structures *[4,5]* are also apparent. Furthermore, one can see about 6% reduction of the average period and a strong increase of the scattering background, which indicates creation of defects in the crystal. Moreover, one can detect broadening of the intrinsic 2σ width of the crystal reflection to about 0.6 μm^{-1} (or, 11 µrad in angular terms). The latter, however, is at the edge of the resolution power of **BM26B**.

Pushing the limit further

The middle sketch in 'Diffraction and Coherence' points out the bottleneck of the setup at **BM26B**. Due to beam focusing, the coherence properties of the X-ray beam degrade towards the sample position and l_{tr} shrinks to about 10 µm. A simple solution is to let X-rays freely propagate to the sample. With typical ESRF parameters ($d/L \sim 10^{-6}$), a transverse coherence length l_{tr} up to 50 - 100 µm can be reached, which is sufficient to determine the order parameters of photonic crystals in great detail. Figure 2 illustrates that a few microradians resolution can indeed be achieved *[6]*. The experiment was performed at **BM05** using a test 2D Ni grid with a period as large as 12.5 µm.

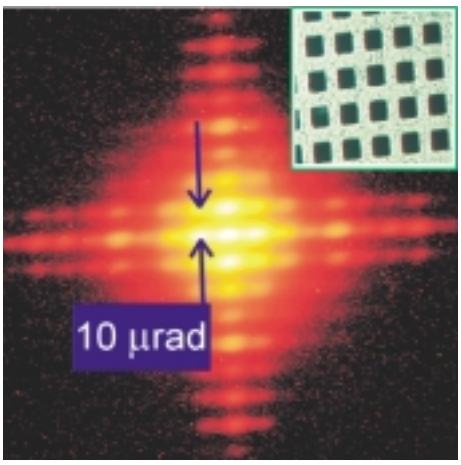
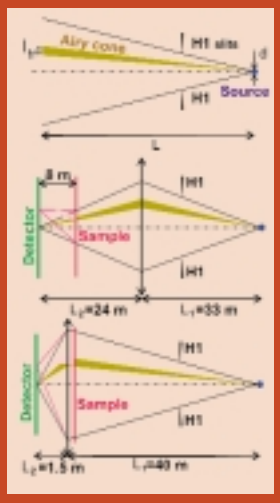


Fig. 2: 10 keV µrad-XRD pattern and optical microscope image of a Ni grid with 12.5 µm pitch and 5 µm bar.

Diffraction and Coherence

Diffraction appears as a result of interference of scattered X-ray waves, which must be coherent with each other. This can be fulfilled easily in the longitudinal direction (*i.e.*, along the beam) for a small diffraction angle *[5]*. Troublesome are the random fluctuations of the phase front in the transverse direction, which must be much smaller than the tiny X-ray wavelength (λ ~ 1 Å) in order to probe positional correlation of scattering objects. A freely-propagating X-ray wave is coherent within the so-called Airy cone of size $l_{tr} = L\lambda/d$ (see the top sketch).



To resolve diffraction at µrad angles, one has to focus the beams at the detector. As illustrated in the middle panel, at BM26B the focusing element is far upstream from the sample. Another scheme utilising a compound refractive lens *[7]* with a much shorter focal length was used in the experiment at BM5 as sketched at the bottom.

To summarise, our results demonstrate that µrad-XRD is readily achievable at the ESRF even without a Bonse-Hart camera, which is typically used in an ultra-small-angle X-ray scattering (USAXS) setup. µrad-XRD was shown to fully cover the needs of photonics and to yield a wealth of information on the 3D structure and (dis)order.

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[1] J. D. Joannopoulos et al., Photonic Crystals: Molding the Flow of Light (Princeton University Press, Princeton, 1995).
*[2] A. Yethiraj and A. van Blaaderen, Nature, **421**, 513 (2003).*
*[3] Y. A. Vlasov et al., Nature **414**, 289 (2001).*
*[4] M. Megens et al., ESRF Newsletter **29**, 8 (1997); W. Vos et al., Langmuir **13**, 6004 (1997).*
*[5] A.V. Petukhov et al., PRL, **88**, 208301 (2002); PRL, **90**, 028304 (2003); ESRF Highlights 2002, p. 19.*
[6] M. Drakopoulos et al., submitted to PRL (2003).
*[7] A. Snigirev et al., Nature, **384**, 49 (1996); B. Lengeler et al., APL, **74**, 3924 (1999).*