Experiment title:

the Structure of Photonic Colloidal Crystals

Experiment number:

SC165

ESRF

Beamline:

BL4/lD2.

Date of Experiment:

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Date of Report:

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Shifts:

12.

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Report:

On January 24-28, 1996, we have done a small angle x-ray scattering (SAXS) study of colloidal crystals [1], that are optically multiply scattering. There are two critical reasons for doing SAXS:
1) We have experimentally found that the optical multiple scattering effects cause a strong shift of the Bragg angle [2]. This effect is much larger [3] than can be interpreted with the dynamic diffraction theory [4]. Hence, obtaining structural information from optical diffraction data is precluded.
2) The physical goal of our research is to study the dispersion relations in the optical spectrum, especially in the vicinity of the lowest stopgaps [4]. This means that one can optically only probe the 1st and maybe 2nd diffraction peak. Such scarce information is completely insufficient to determine the crystal structure, which in turn determines the optical properties. An example is the ongoing discussion in the literature [1] whether dense particles pack in a true f.c.c. structure or in close packed hexagonal planes that are randomly stacked in the c-direction (mixed hexagonal stacking). To investigate such questions, information over a wider range of reciprocal space as provided by SAXS is critical.

The essential features of BL4/1D2 are first the high brightness, which allows to study weakly scattering systems (e.g. polystyrene in water) while maintaining a very high spatial resolution, secondly the 2-dimensional nature of the gas detector, and thirdly the large resolution of $s=2\sin\theta/\lambda\sim10^{-3}$ ri^{m-}l.

We now describe our main results, that are obviously still preliminary at this early stage:
1) Structure identification of the colloidal crystals. By combining the features of BL4/lD2 with angular ω-scans of the sample, we have for the first time been able to literally sweep through reciprocal space of colloidal crystals, that were made of spheres of various sizes and materials, suspended in different media. In Fig. 1, we show diffraction patterns of a crystal of dense (-50 vol%) screened polystyrene spheres in water at ω=0 and 36°. An important feature is immediately visible: clear sharp spots are observed, which indicates that we are now able to grow large crystals at high volume fractions with sizes of the order of the x-ray beam (- 0.5 mm). Closer inspection of the pattern in Fig. la learns that there are many systematic absences of reflections, that are consistent with a 111 cut through an f.c.c. crystal. The six spots nearest to the beamstop

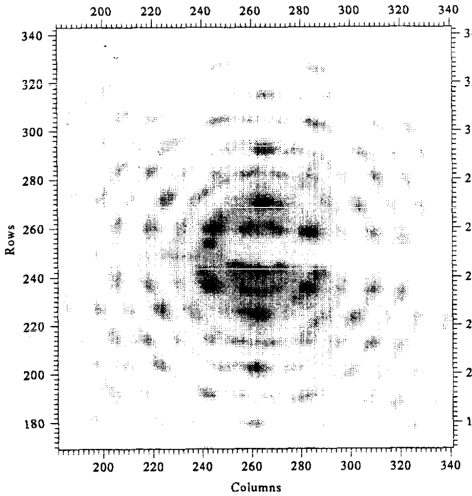

Fig. la. Distraction pattern of a colloidal crystal, oriented to have the 111 axis parallel to the beam.

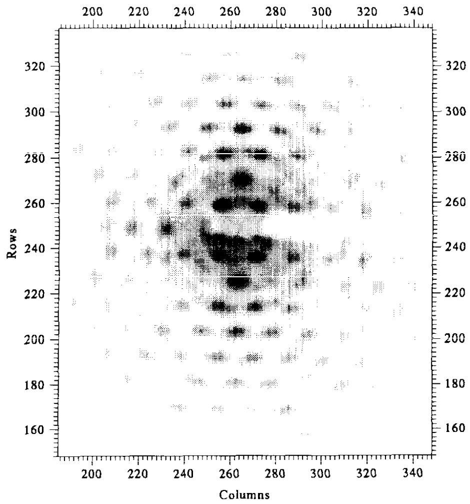

Fig. lb. Distraction pattern of a colloidal crystal, oriented to have the **101** axis parallel to the beam.

are of the 220 class. Upon rotation of the sample, all spots in Fig. 1a disappear, except for those on a vertical line through the origin (1 0-1 direction) and new spots reappear. The pattern in Fig. lb is consistent with a view along the two-fold axis 101: the absences of reflections are particularly noticable at 2, 4, 8, and 10 o'clock. The four spots closest to the beam stop are 1-1-1 like reflections.

Note that mixed hexagonal stacking would reveal a complete hexagonal grid of reflections instead of the patterns in Fig. 1. This was indeed observed on samples of dense screened silica particles suspended in various liquids, and has been observed previously in other systems as well (see also Ref. 5).

2) Knowlegde of the orientations of the colloidal crystals is of importance for optical studies that are aimed at probing the dispersion relations in various crystallographic directions. As discussed above, the data in Fig. 1 clearly reveal the orientations of the crystals in the focus of the x-ray beam. This means that the axes of the hexagonal close packed planes are parallel with the long axis of the capillary (which stands vertically in Fig. 1). This is similar to results of previous experiments on shear alignment of ordered colloids [5].

3) The scattering of dilute colloidal spheres clearly reveals many concentric bright and dark rings, that is due to the Bessel-like form factor. The distance between the rings is a measure of the radius R of the spheres. During the run, it turned out that the radii measured on BL4/ID2 were in excellent agreement (within - 2%) with the radii specified by the producer of the particles. This confirms that the form factors of colloidal spheres are very useful for the calibration of 2D detectors.

Our main results can be summarized as follows:

- We have done a single crystal SAXS study on colloidal crystals with lattice parameters of order 2500 A.
- This technique clearly reveals the difference between fc.c. and mixed hexagonal stacking, which are hard to distinguish by powder diffraction.
- Optical experiments reveal the crystals to be the most photonic [3] 3D crystals made to date.

Papers have been submitted to the Conference on Lasers and Electro Optics, and the IUCr Seattle meeting.

[1] for a review on colloidal crystals, see e.g. P. N. Pusey, in "Liquids, Freezing, and the Glass Transition", eds. D. Levesque, J.-P. Hansen, and J. Zinn-Justin (Elsevier, Amsterdam, 1990).

[2] W. L. Vos, R. Sprik, A. van Blaaderen, A. Imhof, A. Lagendijk, and G. H. Wegdam, Phys. Rev. B (submitted), in *Photonic Band Gap Materials,* ed. C. Soukoulis (Kluwer, Dordrecht, in press).

[3] It is convenient to quantify multiple scattering effects in crystals by the ratio of the polarizability a (the "optical volume" per particle) to the physical volume v per particle: $4\pi\alpha/v$ [2]. For the crystals mentioned, this amounts to about 0.2-0.5. For reference about 0.5 is necessary for optical band gaps, in typical X-ray diffraction situations, this ratio is about 10^{-4}, whereas previous experiments with colloidal crystals have only been done up to 0.05. See also, J. Opt. Sot. Am. **B 10** (February 1993).

[4] see e.g. R. W. James, "the Optical Principles of the Distraction of X-rays" (OxBow, Woodbridge, 1982).

[5] H. Versmold and P. Lindner, Langmuir **10,3043** (1994), and references therein.