Pushing the Limits of Coherent X-ray Diffraction: Imaging Single Submicrometer Silver Nanocubes

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Introduction

X-ray crystallography has proven to be an extremely efficient investigation method to solve the structure of matter at the atomic scale. Although several methods have been employed to circumvent the intrinsic phase problem, other limitations do exist for classical x-ray crystallographic methods. In particular, disordered materials, single nanostructures, or noncrystalline and/or nonrepetitive biological structures (e.g., some important viruses or proteins) cannot be accessed by this approach.

As first considered by Sayre et al. [1], a combination of coherent x-ray diffraction with a so-called "oversampling" phasing method can overcome these limitations. In a first demonstration experiment, Miao et al. used that method to invert the soft x-ray forward-scattering pattern measured from a fabricated object [2]. More recently, the reconstruction of 2-D and 3-D crystalline and noncrystalline structures has been reported [3, 4]. In particular, the latest results from Williams et. al [5], where the complete 3-D phase and shape information of a micrometer-sized gold crystal could be retrieved, impressively demonstrate the high potential of this nondestructive method.

Methods and Materials

Chemically synthesized, single-crystalline silver nanocubes with an average size of 175 nm (Fig. 1) were prepared as suitable samples by using a polyvinyl pyrrolidone (PVP) capping agent [6]. The crystals were suspended in an aqueous solution that was evaporated onto glass plates. The cubes were then attached by a combination of mild heating and the application of various gluing agents.

In order to have both sufficient flux and the opportunity to select single nanocrystals, an intense x-ray beam focus with a spot size on the order of a few square micrometers is required for the coherent x-ray diffraction experiment. In these experiments, carried out at beamline station ID-34-C at the APS, we used Kirkpatrick-Baez (KB) mirror optics to focus the x-ray beam to typically 1.0×1.5 μm^2 at the position of the sample. The entrance aperture of the KB mirror system was set to 50×50 μm^2.

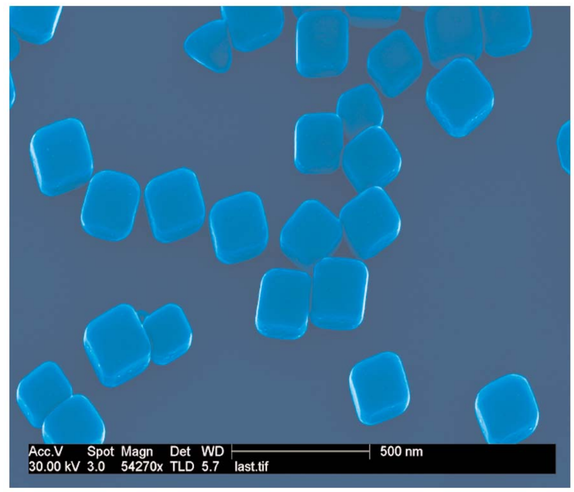

FIG. 1. Monodisperse, single-crystalline silver nanocubes with an average edge length of 175 nm.

Results

The diffraction patterns of the nanocubes have been inverted to images, as shown in Fig. 2. This demonstrates that the coherence is not seriously affected by the introduction of optics. Nevertheless, it is interesting to consider the possible implications of incident wave curvature effects [7]. These can be predicted by straightforward ray tracing, as shown in Fig. 3. To a first approximation, the finite focus size can be attributed to demagnification of the source alone and hence ignored for a sample that is much smaller in size. Nevertheless, it must be assumed that the sample does not sit at the exact focus of the mirror but away at a defocus distance d.

If the illuminating wave passing through the center of the sample is taken to have a phase of zero, then the phase shift at a lateral distance x away from the center can be found to be $\varphi(x) = kD1\ [1 - \cos(x/d) \approx \_\ kDx^2/d^2$, where D is the focal length of the mirror and k is the x-ray wave vector. The curvature effects can be considered important when $\varphi(x)$ reaches a significant fraction of π at the edges of the sample, $x = a/2$, where the sample size a is 162 nm. For the horizontal mirror (D = 200 mm), this occurs at a defocus d = 3.0 mm,

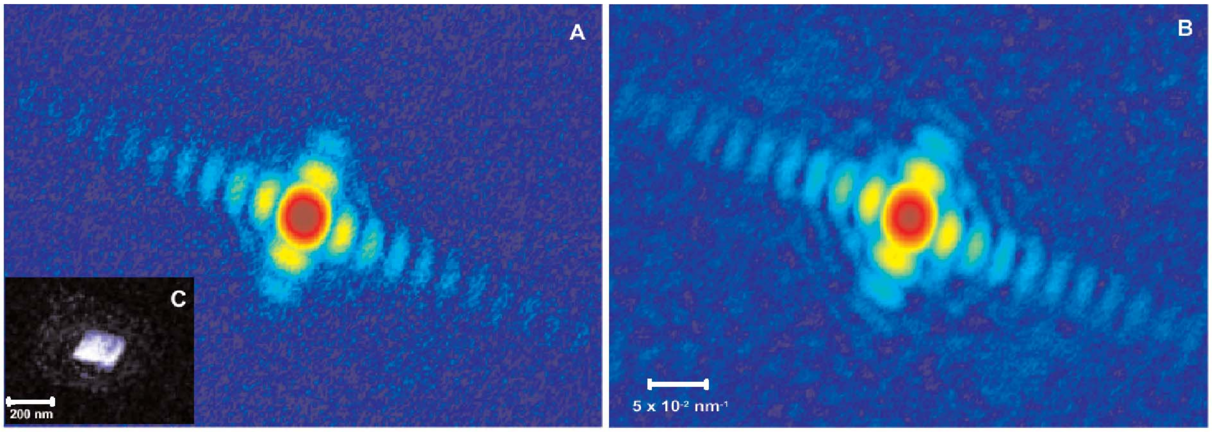

FIG. 2. A shows a charge-coupled device (CCD) image of the measured single-crystal coherent diffraction pattern around the 111 Bragg peak of a single silver nanocube (8.5-keV x-rays). The image has been corrected for background, averaged, and symmetrized. In B, the best-fitting result was obtained after 2000 iterations of the reconstruction algorithm. During the fitting procedure, we alternated between 150 cycles of the ***hybrid-input-output*** *(HIO) mode and 100 cycles of the* ***error reduction*** *(ER) mode. C shows a reconstructed real-space image of the silver nanocube. The image corresponds to a projection of the electron density onto a plane perpendicular to the outgoing scattering vector. From the data, we estimate a resolution of ~15 nm.*

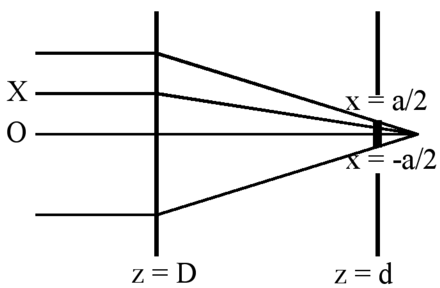

FIG. 3. Schematic ray tracing of the focusing geometry. The KB mirror is at a distance z = D if it is in front of the focus, while the illuminated sample (thick vertical bar) is at z = d, the defocus distance. Ray O is the central ray, while ray X crosses the sample a distance x above the axis.

while for the vertical mirror (D = 100 mm), this occurs at d = 2.1 mm. In spite of the careful focusing procedures used, it is conceivable that the mirrors were defocused by this amount in our experiment because of the depth of field of the sample mount.

Figure 4 shows calculations of the diffraction patterns for an ideal cube-shaped sample, corresponding to the experimental conditions. Different amounts of wave curvature have been included, as indicated. The phase of the incident wave is assumed to vary quadratically across the sample. We note this is the smallest-order contribution that can affect the diffraction, since linear phase terms simply shift the position of the image. Even if the sample were

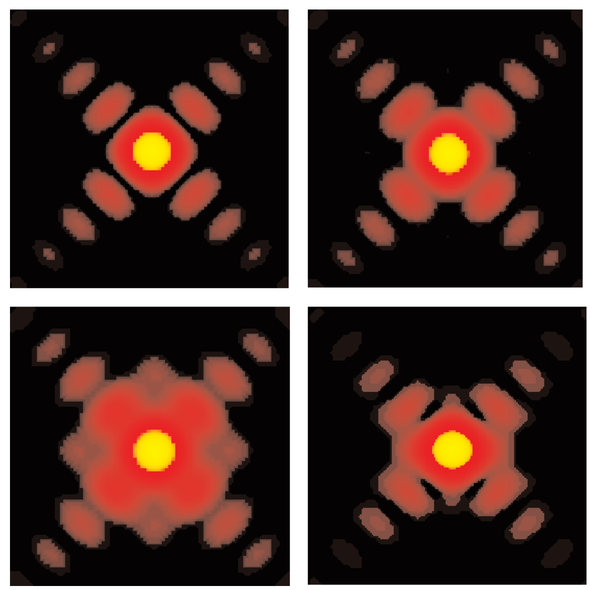

FIG. 4. Calculated far-field diffraction patterns for a cube, oriented diagonally, under different illumination conditions. Top left shows a plane wave. Top right shows a spherical wave with a phase shift of π/4 at the cube edges. Bottom left shows a spherical wave with a phase shift of π/2. Bottom right shows a cylindrical wave with a phase shift of π/4 in the horizontal only.

significantly off axis in the experiment, this would only cause its diffraction pattern to appear shifted on the detector but have the same amount of wavefront curvature. The magnitude of the curvature in Fig. 4 is specified by the total phase shift from the center to the edges of the sample.

Our calculations show that the introduction of this small amount of wavefront curvature is sufficient to change the diffraction patterns significantly. We can estimate that, in the experimental data of Fig. 2, no strong curvature effects, beyond about $\varphi(a/2)$ of $\sim\pi/4$, have been seen so far. Future experiments will attempt to look for the effect, which, as our calculations suggest, should be easy to see. In particular, the case of a cylindrical wave field, where the foci of the two KB mirrors need to be separated by a millimeter or so, should lead to particularly dramatic effects on the diffraction patterns.

Discussion

Once the curvature effects have been observed experimentally, it will open the possibility of new phasing methods based on the "transport of intensity" equation (TIE) [8] that have the potential of resolving chiral structures and breaking the "twin" symmetry inherent in current iterative phasing methods. Specifically, the degrees of curvature would be separately varied in the horizontal and vertical directions by adjustment of the two independent KB mirrors. Two through-focal series would be used in a difference calculation that would result directly in a measured phase [8]. It is believed that just three diffraction patterns would be sufficient to determine the phase uniquely.

These experiments clearly demonstrated the feasibility of measuring the coherent x-ray diffraction pattern formed by nanocrystals with sizes on the order of 100=200 nm at currently available third-generation synchrotron sources. In the future, we plan to extend the work by investigation of Fresnel zone plate optics in place of the KB system.

Acknowledgments

This work was supported by the National Science Foundation (NSF) under Grant No. DMR 03-08660. The 34-ID-C coherent x-ray diffraction facility was built with funds from NSF Grant No. DMR 97-24294 and is operated by UNI-CAT. UNI-CAT is supported by the UICU Materials Research Laboratory (U.S. Department of Energy [DOE]; State of Illinois Board of Higher Education, Higher Education Cooperation Act; and NSF); Oak Ridge National Laboratory (DOE under contract with UT-Battelle, LLC); National Institute of Standards and Technology (U.S. Department of Commerce); and UOP LLC. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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