

NOVEL X-RAY TECHNIQUES & INSTRUMENTATION



PUSHING THE LIMITS OF COHERENT X-RAY DIFFRACTION: IMAGING SINGLE SUBMICROMETER SILVER NANOCUBES

X-ray crystallography has been proven to be an extremely efficient investigation method for solving 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 non-repetitive biological structures (e.g., some important viruses or proteins) cannot be accessed by this approach.

A combination of coherent x-ray diffraction with a so-called oversampling phasing method can overcome these limitations. In a first demonstration experiment, that method was used to invert the soft x-ray forward-scattering pattern measured from a fabricated object. More recently, the reconstruction of two-dimensional and three-dimensional (3-D) crystalline and noncrystalline (!) structures has been reported. In particular, the latest results, 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.

The experiment described here focused on applying that technique to even smaller nanocrystals in order to investigate the feasibility of pushing the limits of imaging by using coherent x-ray diffraction into the nanometer range.

Chemically synthesized, crystalline silver nanocubes were used as demonstration samples, with a typical size of 90–150 nm. The coherent x-ray diffraction experiments were carried out at the UNI-CAT 34-ID beamline by using monochromatic x-rays with an energy of 8.5 keV.

In order to have both sufficient flux and the opportunity to select single nanocrystals, a Kirkpatrick-Baez (K-B) mirror system was used to focus the x-ray beam to typically $1.0 \times 1.5 \mu\text{m}^2$ at the position of the sample. The diffraction data were recorded using a charge-coupled-device detector placed at a position corresponding to the 111 Bragg reflection of the silver crystal lattice.

The following major conclusions could be drawn from the experimental results. First and most important, the high-resolution reciprocal diffraction patterns clearly demonstrate the feasibility of carrying out such measurements on single nanocrystals at sizes in the 100-nm range (Fig. 1). Depending on the orientation of the individual nanocrystals, the measured diffraction patterns showed nice three- and four-fold symmetry and up to, typically, 5–10 high-contrast interference fringes in directions corresponding to the facets of the cubic structure. Furthermore, no negative effects on the transverse coherence were found by using the experimentally crucially important K-B focusing optics. Finally, the obtained results agree well with some model calculations based on a simple Fourier transform of a two-dimensionally projected single silver nanocube (Fig. 2).

Encouraged by this successful first demonstration experiment of coherent x-ray diffraction on submicrometer single crystalline nano-objects, researchers are currently working on

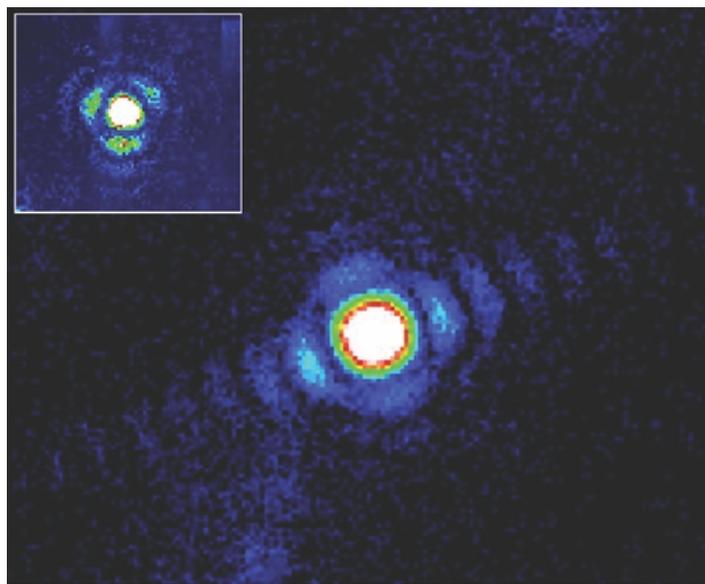


Fig. 1. Charge coupled device image of the measured single crystal coherent diffraction pattern around the 111 Bragg peak of a silver nanocube (8.5 keV x-rays). The two diffraction images are taken for slightly different Q-values and correspond to the Fourier transform of different projections of the cubic crystal.

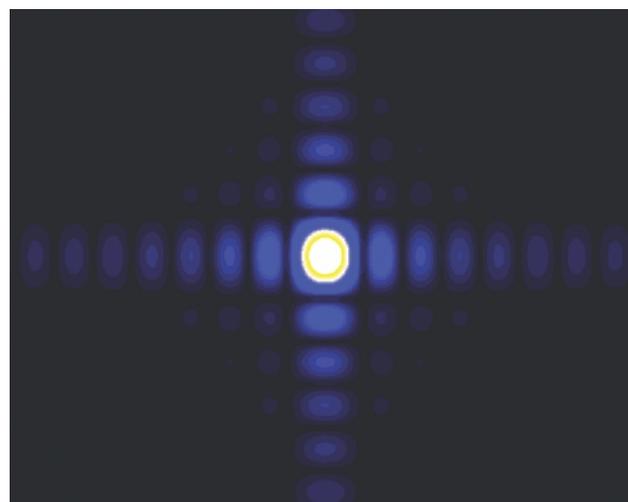


Fig. 2. Calculated coherent diffraction pattern of a single nanocube assuming the simplest possible diffraction geometry (detector plane perpendicular to the surface normal of one of the cubes facets).

the direct reconstruction of full 3-D diffraction data using the oversampling phasing method. ○

See: I. Robinson¹, F. Pfeiffer^{1,2}, I. Vartanyants¹, Y. Sun³, Y. Xia³, "Enhancement of coherent X-ray diffraction from nanocrystals by introduction of X-ray optics," *Opt. Express* **11**(19), 2329-2334 (September 2003).

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COHERENT X-RAY DIFFRACTION IMAGING DETAILS THE 3-D MICROSTRUCTURE OF AU NANOCRYSTALS

Coherent x-ray diffraction (CXD) is an emerging technique that has considerable potential for revealing many structural and dynamic characteristics of nanocrystalline materials. The method is enabled by high-brilliance third-generation x-ray sources because the technique depends entirely on the coherence volume of the x-ray beam being large enough to enclose the crystal under study; the coherence volume is directly proportional to source brilliance.

The penetrating power of a hard x-ray beam allows scientists to look below the surface of materials, while the ability to distinguish the diffraction patterns from neighboring nanocrystalline grains is retained, making it possible to image the full volume of a grain with negligible absorption effects. In principle, even three-dimensional (3-D) real-space strain maps of the interiors of materials should be feasible. This prospect was advanced by researchers from the University of Illinois at Champaign-Urbana (UIUC), who used CXD to obtain 3-D images of the interiors of gold (Au) nanocrystals that were formed by high-temperature coalescence from an evaporated polycrystalline thin film (Fig. 1).

In an x-ray crystallographic experiment, x-rays interact with electrons in a crystal to produce a diffraction pattern that is the Fourier transform of the desired electron density distribution. A Fourier transform can be reversed to reconstruct the 3-D distribution of the electrons (and, hence, the atoms) in the crystal, but to do this, one needs not only the amplitudes of the diffracted waves, which are obtained from the intensity distribution of the diffraction pattern, but also their relative phase shifts, which cannot be measured directly. Generally one gets phase data from supplementary information of some sort. The UIUC researchers obtained the needed information by oversampling the diffraction patterns, which is possible with small crystals because they generate continuous patterns.

The CXD experiment was conducted at the UNI-CAT 33-ID undulator beamline at the APS, where the transverse coherence length was greater than 5 μm and the longitudinal coherence length was determined to be

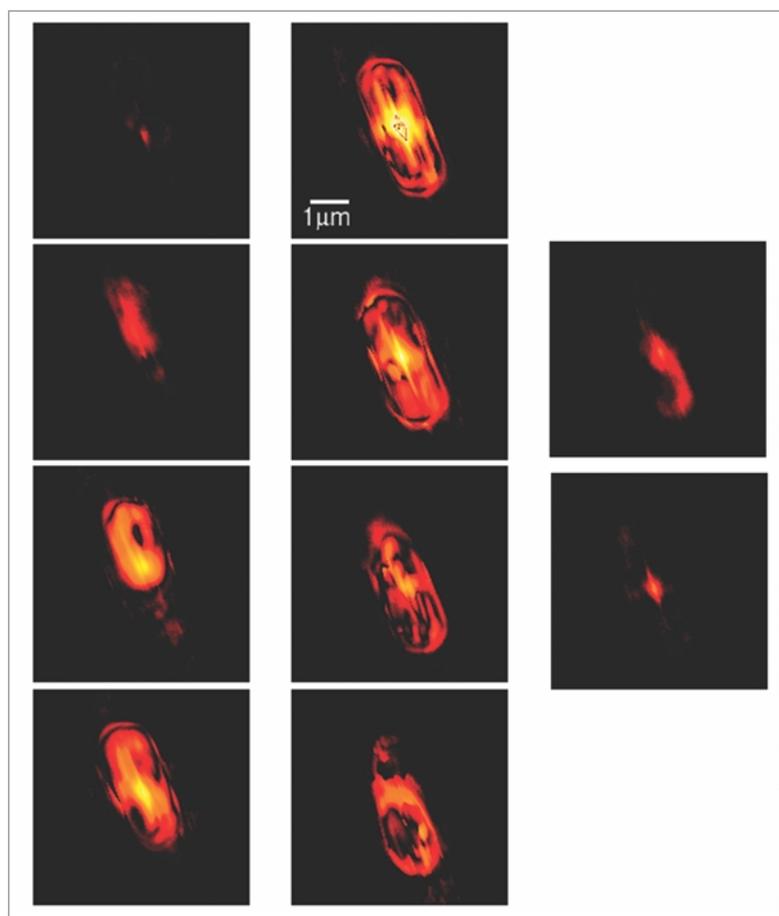


Fig. 1. Slices through a 3-D reconstruction of the internal density for a micron-sized gold nanocrystal, measured with the new CXD method. The striping effects, which follow the crystallographic directions, indicate the presence of internal microstructure in the crystal.

6 μm by a Si(333) monochromator at 9.5 keV. Two-dimensional diffraction patterns were collected with a direct-reading charge-coupled device. To construct full 3-D patterns, each sample was rotated through the Bragg condition in steps of 0.002° , thus acquiring a sequence of nearly parallel 2-D slices, which were then stacked to obtain the sampled 3-D patterns.

It proved possible to draw some conclusions about the size and shape of the Au grains directly from the CXD patterns before they were phased. The flares in reciprocal space were seen to correspond to facets of the crystal, while the modulation of these flares indicated the spacing of parallel facets. Phasing of the oversampled diffraction patterns was accomplished through the use of an iterative method, utilizing known information to find a set of phases consistent with the measured data. This cycle was repeated until the search converged to a solution.

The 3-D images of the interiors of the Au nanocrystals showed 50-nm-wide bands of contrast with $\{111\}$ orientation that probably arose from internal twinning by dynamic recrystallization during their formation at high temperature. In the method

used by the researchers, entire patterns were measured directly. Because Bragg diffraction was involved, all artifacts due to air or slit scattering and the presence of other grains were avoided, and a strong sensitivity to strain was manifested. \circ

See: G.J. Williams, M.A. Pfeifer, I.A. Vartanyants, and I.K. Robinson, "Three-Dimensional Imaging of Microstructure in Au Nanocrystals," *Phys. Rev. Lett.* **90**(17), 175501-1 to 175501-4 (2 May 2003).

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A HIGH-REPETITION-RATE LASER SYSTEM FOR TIME-RESOLVED X-RAY ABSORPTION FINE STRUCTURE

X-ray absorption fine structure (XAFS) is a valuable technique for probing materials dynamics, because (in contrast to x-ray diffraction), with XAFS, one can determine the behavior of a sample directly without dependence on long-range order. The dynamics of heating and phase changes induced by laser excitation may, therefore, be directly monitored by XAFS regardless of a material's state. In addition, the near-edge portion of the XAFS (the XANES) contains electronic information about the material, and it is, for example, sensitive to the shielding between the core hole and photoelectron, which can be modified by the laser pulse in a semiconductor, since the excited carrier density can be initially similar to that of a metal. As a result, XANES has the potential for use in studies of dynamics of this type of phenomenon, regardless of material state.

Researchers from the University of Washington and the Pacific Northwest National Laboratory, using the PNC/XOR facility at sector 20, have developed a high-repetition-rate laser system for time-resolved pump-probe XAFS studies on sub-nanosecond to microsecond time scales. A schematic diagram of the timing electronics and laser system is shown in Fig. 1. The 800-nm Ti:sapphire pulsed-laser system repeats at the APS P0 frequency of 272 kHz with $\sim 4\mu\text{J}/\text{pulse}$, allowing researchers using the PNC/XOR apparatus to collect data from a given bunch at each appearance. This provides an increase in data-collection efficiency of more than an order of magnitude when compared to typical pulsed-laser systems and data collection times similar to those of typical non-time-resolved

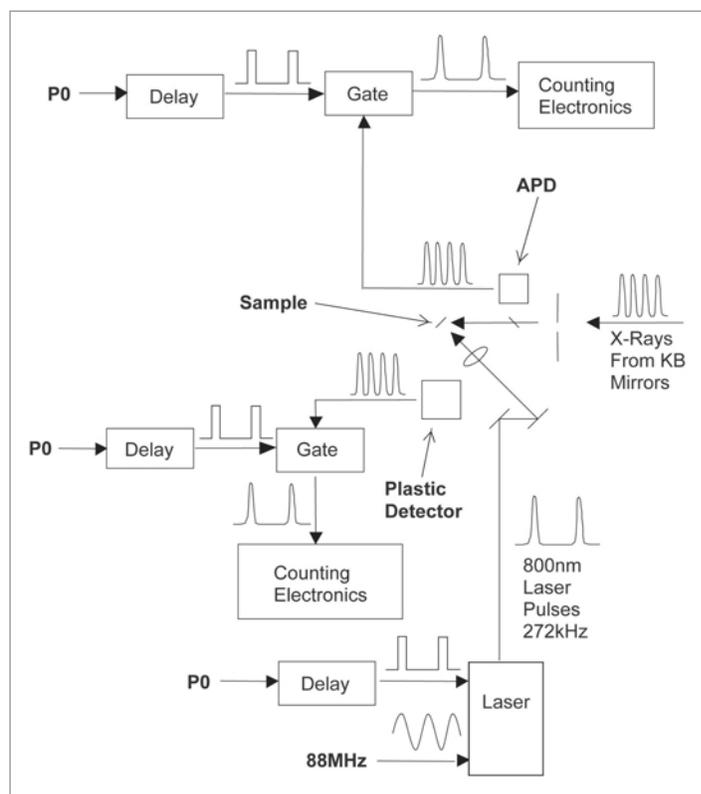


Fig. 1. Schematic of system timing electronics and laser.

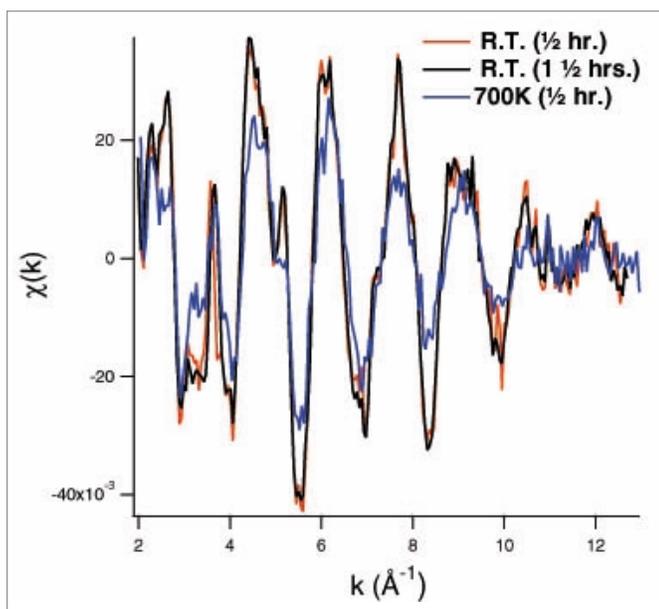


Fig. 2. Single EXAFS spectrum from a sample at room temperature, with the average of three similar scans, and data collected from the same sample while laser-heated to $\sim 700\text{K}$.

experiments. Diffraction measurements can also be made concurrently with the same time resolution.

The PNC/XOR laser system is used in conjunction with Kirkpatrick-Baez x-ray focusing mirrors to enable time-resolved micro-XAFS on a $10\text{-}\mu\text{m}$ scale. Focusing both the x-rays and the laser also provides the ability to perform experiments not inherently microscopic in nature but requiring extremely large fluences. The current timing resolution is limited by the finite electron-bunch width to ~ 90 ps. To date, the PNC/XOR team has utilized the laser system to investigate the time-resolved extended x-ray absorption fine structure (EXAFS) of laser-heated germanium, but it could be utilized in a wide range of time-resolved pump-probe experiments that are currently impractical due to the long data collection time required by lower-repetition-rate systems.

Experiments have been performed using a $10\text{-}\mu\text{m}$ x-ray beam to obtain micro-EXAFS from a 200-nm -thick Ge film that was initially amorphous and crystallized by heating with the laser beam. Micro-EXAFS was obtained from the heated film after crystallization. Figure 2 shows a single EXAFS spectrum from the sample at room temperature, along with the average of three similar scans, and data collected from the same sample as it was heated by the laser to $\sim 700\text{K}$. The temperature of the heated film was measured by determining the vibration amplitude of the Ge-Ge bond revealed in the EXAFS. The vibrations cause the amplitude of the EXAFS oscillations to decrease with increasing temperature, as seen for the 700K plot. A comparison of the single room-temperature spectrum with the averaged spectra illustrates the excellent noise level and reproducibility for a data collection time of $\sim 1/2$ hour, from a sample with very small absorption ($\sim 2\%$).

The spectra in the figure were collected in pulse-counting mode, which required a reduction of the potentially available signal to avoid saturation caused by pulse pile-up. The addition of radio-frequency-derived lock-in detection of the gated signal should allow use of the entire available flux, an increase over the current configuration by a factor of at least five. Use of an avalanche photodiode array for the fluorescence signal would provide an alternative approach for increasing data quality, by keeping the signal on each element low enough to remain within the pulse-counting regime, with a much larger total collected signal.

Figure 3 shows preliminary results for the time dependence of the EXAFS from the laser-heated film for times within a few ns of the laser excitation. Future plans call for an increase of the laser fluence to heat the Ge film to the melting point and a study of the dynamics of the transition from the four-fold coordinated solid to the six-fold coordinated liquid by directly monitoring the EXAFS, thus using the ability of this probe to look at local atomic structure independent of the material state. \circ

See: E.A. Stern, D.L. Brewster, K.M. Beck, S.M. Heald, Y. Feng, "Sub-nanosecond time-resolved XAFS of laser excited thin Ge films", invited paper at XAFS 12, June 2003.

PNC/XOR facilities and research at these facilities is supported by the U.S. DOE Office of Science grant no. DE-FG03-97ER45628. Additional support was provided by Battelle-Pacific Northwest National Laboratory's (PNNL) Laboratory Directed Research Directorate.

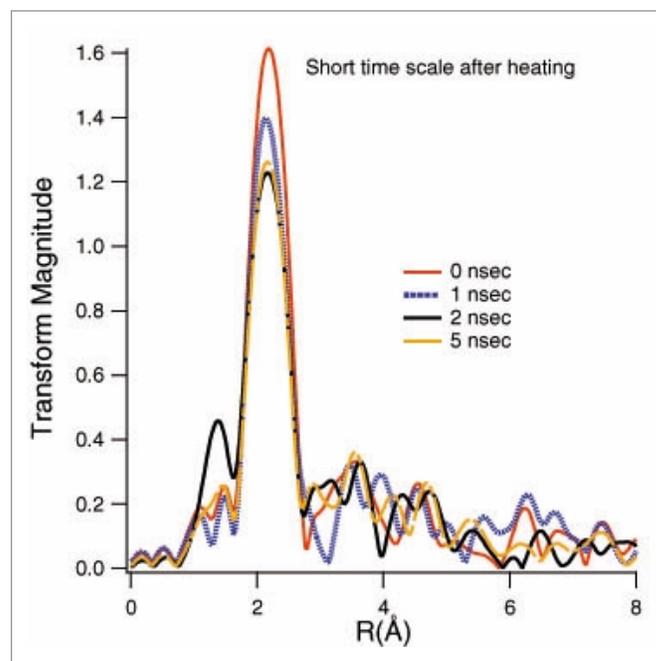


Fig. 3. Preliminary results for the time dependence of the EXAFS from the laser-heated film for times within a few ns of the laser excitation.

UPGRADE OF THE INELASTIC SPECTROMETER AT 3-ID-C

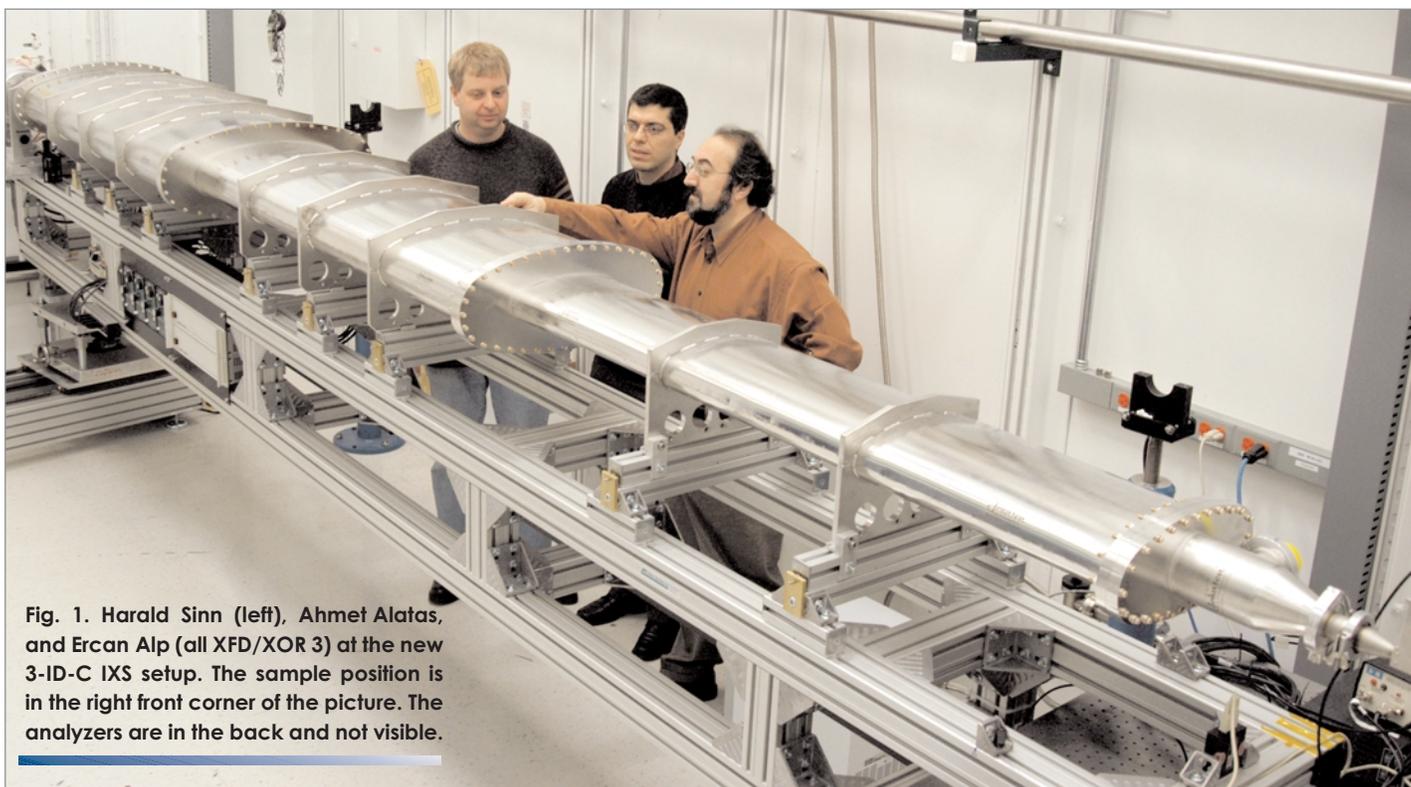


Fig. 1. Harald Sinn (left), Ahmet Alatas, and Ercan Alp (all XFD/XOR 3) at the new 3-ID-C IXS setup. The sample position is in the right front corner of the picture. The analyzers are in the back and not visible.

During the last decade, inelastic x-ray scattering (IXS) with an energy resolution of a few meV became a very successful spectroscopic method on third-generation synchrotron sources. At x-ray energies of about 20 keV, monochromatization of x-rays can be achieved either by multiple bounce in-line monochromators or—in the case of the analyzer—by high-order silicon reflections in backscattering geometry.

At the APS, an inelastic spectrometer with 2 meV resolution was built at XOR beamline 3-ID-C with, initially, one analyzer. However, with count rates often less than 0.1 Hz at the phonon position, many experiments would benefit from a multiple analyzer setup. Currently, the instrument is being upgraded to four analyzers, which will work simultaneously, enabling faster data collection for liquid and disordered samples.

UPGRADE DETAILS

The four analyzers are located 6 m from the sample. Each analyzer has an active diameter of 100 mm, and there is a lateral distance of 180 mm between two analyzers.

The four analyzers, and a 5.4-m-long vacuum chamber that connects to the backscattering detector, are on a common 2-theta arm, which can be moved in the horizontal plane (Fig. 1). The maximum angle of the 2-theta-arm is 17.6° and is limited only by the dimensions of the station.

The four analyzers were built as adjustable, two-dimensional bending devices (Fig. 2). Each analyzer is temperature controlled by Peltier elements stable to about 10 mK over nine days.

A four-element detector, developed in collaboration with AMPTEK, allows for collection of the radiation from the four analyzers individually. Each CdTe element is $3\text{ mm} \times 3\text{ mm}$ and is cooled by a peltier cooler. The center-to-center distance between elements is 6 mm. The quantum efficiency of the CdTe elements is close to 100%, while the noise rate is about 0.001 Hz per channel. (Contact E. Alp, eea@aps.anl.gov) ○

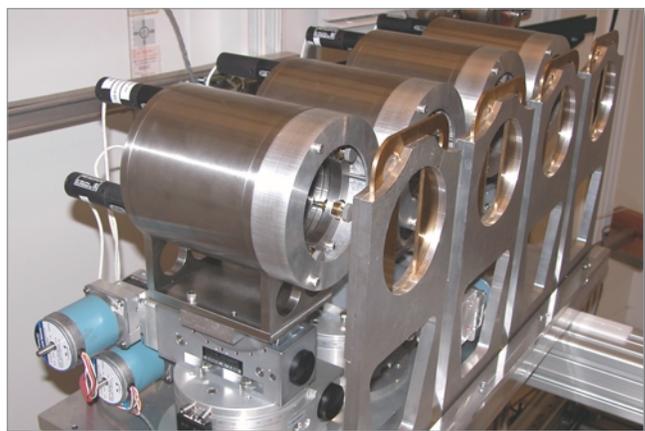


Fig. 2. Four-analyzer setup in the back of the 2-theta arm.