

Letter of Intent (Category A)

**Three-Dimensional Atomic Resolution Imaging
of Nanoscale Materials by Using the LCLS**

Jianwei (John) Miao

SSRL, SLAC, Menlo Park, CA 94025

Ph: 650 926-5168 Fax: 650 926-4100 Email: miao@slac.stanford.edu

*Address after 8/2004: Department of Physics and Astronomy and the
California Nanosystems Institute, University of California, Los Angeles, CA 90095*

Sunil Sinha

Department of Physics, University of California, San Diego, CA 92093

Ph: 858 822-5537 Fax 858 534-0173 Email: ssinha@physics.ucsd.edu

Tetsuya Ishikawa

SPring-8/RIKEN, 1-1-1, Kouto, Mikazuki, Sayo-gun, Hyogo 679-5198, Japan

Ph: 81 791 58 2805 Fax: 81 791 58 2807 Email: ishikawa@sp8sun.spring8.or.jp

Paul Fuoss and Brian Stephenson

Materials Science Division, Argonne National Laboratory, Argonne IL 60439

Ph: 630 252-3289 Fax: 630 252-9595 Email: fuoss@anl.gov

Ph: 630 252-3214 Fax: 630 252-9595 Email: stephenson@anl.gov

Subhash Risbud

Department of Chemical Engineering & Materials Science

University of California, Davis, CA 95616

Ph: 530 752-0474 Fax: 530 752-1031 Email: shrisbud@ucdavis.edu

Keith Nugent

School of Physics, University of Melbourne, Victoria 3010, Australia

Ph: 61 3 8344 5420 Fax: 61 3 9349 4912 Email: k.nugent@physics.unimelb.edu.au

Claudio Pellegrini and James Rosenzweig

Department of Physics and Astronomy

University of California, Los Angeles, CA 90095

Ph: 310 825-3440 Fax 310 206-5668 Email: pellegrini@physics.ucla.edu

Ph: 310 206-4541 Fax 310 825-4057 Email: rosenzweig@physics.ucla.edu

James Amonette and Donald Baer

Pacific Northwest National Laboratory, Richland, Washington 99352.

Ph: 509 376-5565 Fax: 509 376-3650 Email: jim.amonette@pnl.gov

Ph: 509 376-1609 Fax: 509 376-5106 Email: don.baer@pnl.gov

Summary

Visualizing the arrangement of atoms has played a crucial role in understanding the microscopic world. There are already a few ways of imaging atomic structures, but each has its limitations. Scanning probe microscopes are limited to imaging atomic structures at surface. Transmission electron microscopes can resolve individual atoms but only for samples thinner than ~ 30 nm. Crystallography can reveal the globally averaged 3D atomic structures based on the diffraction phenomenon, but requires crystals. These limitations can in principle be overcome by coherent diffraction imaging that is based upon the principle of using coherent x-ray scattering in combination with a method of direct phase recovery called oversampling. Coherent diffraction imaging has been successfully applied to 2D and 3D imaging of nanoscale materials and biological samples, and a highest resolution of 7 nm has been achieved. The imaging resolution is currently limited by coherent X-ray flux and the low dynamic range of CCD, while the ultimate resolution is only limited by the X-ray wavelengths. By using the 3rd generation synchrotron radiation sources, we expect to continue to improve the resolution to the 1 nm level within the next few years. In a combination of the LCLS with pixel array detectors, we propose to improve the 3D imaging resolution to the atomic level. Such an approach for 3D structure characterization of nanoscale materials at atomic resolution, coupled with computer modeling, would have an important impact in a wide range of scientific and technological programs including: 1) development of self-assembled molecular clusters (e.g. the structure of fuzzy clusters), 2) materials for nanotechnology, 3) microstructure research (e.g. making experimental contact with the mesoscale dynamics simulations), and 4) medical research (e.g. drug delivery systems). While this proposal focuses on the application of coherent diffraction imaging to nanoscience and technology, with the LCLS pulse length improved to be shorter than 10 fs in the future, it can be potentially applied to imaging single protein molecules that are difficult to crystallize,

Background and Prior Results

The discovery of X-ray diffraction from crystals by von Laue and Bragg nearly 100 years ago marked the beginning of a new era for visualizing the 3D atomic structures inside crystals. Indeed, X-ray crystallography has since made a tremendous impact in materials sciences, chemistry, structural biology, and other areas. It has now reached a point where it can determine almost any structures, as long as good-quality crystals are obtained. Many samples, however, such as amorphous and disordered materials including glasses, polymers, strains and defects in crystals, quantum dots and wires, dislocation and deformation structures, and some inorganic nanostructures, cannot be accessed by this approach. In biology, structures such as whole cells, organelles, viruses and many important protein molecules cannot or are difficult to crystallize and are hence not currently accessible by X-ray crystallography.

These limitations can potentially be overcome by using coherent diffraction imaging (or X-ray crystallography without crystals) [1,2]. When a coherent beam of x-rays illuminates a noncrystalline specimen, the far-field diffraction intensities are continuous and weak. This continuous diffraction pattern can be sampled at a spacing finer than the Nyquist frequency (*i.e.* the inverse of the specimen size), which corresponds to surrounding the electron density of the specimen with a no-density region [3]. The higher the sampling frequency, the larger the no-density region. When the no-density region is larger than the electron density region, it has been shown that the phase information is uniquely

encoded inside the diffraction pattern [4] and can be recovered directly by an iterative process that takes advantage of information such as the fact that electron density outside the object is zero and within the object is positive [5].

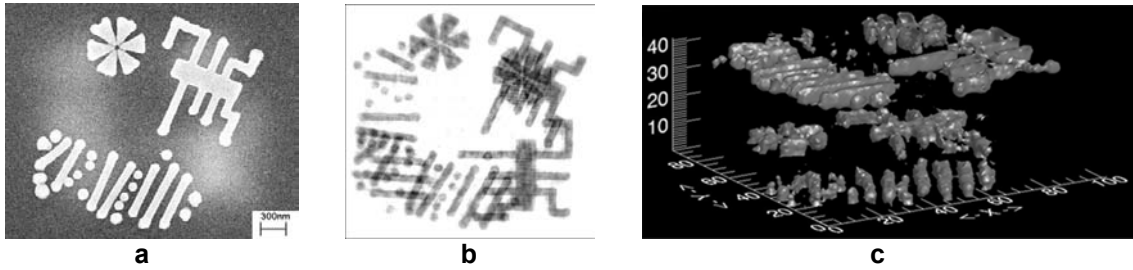


Fig. 1 (a) A SEM image of a buried nanostructure, showing the pattern in the top layer, but not the pattern in the bottom layer. (b) An image reconstructed from a coherent X-ray diffraction pattern at a resolution of 8 nm ($\lambda = 2 \text{ \AA}$) where both the top and bottom layered patterns are clearly seen as overlapped in this 2D image projection. (c) An iso-surface rendering of a reconstructed 3D image. (See ref. 9 for details)

The first successful experimental demonstration of coherent diffraction imaging was carried out in 1999 [6]. Since then, it has been successfully applied to imaging a variety of samples ranging from nanocrystals to *E. Coli.* bacteria in both two and three dimensions by using coherent X-rays from 3rd generation synchrotron radiation sources [1,2,7-19]. Fig. 1 shows a 3D image of a nanostructured material reconstructed from thirty-one 2D diffraction patterns that were recorded by rotating the specimen around one axis [9]. More recently, by using coherent X-rays from the SPring-8, currently the brightest X-ray source in the world, we have imaged a single GaN quantum dot shown in Fig. 2. A 3D reconstruction of the quantum dot is under way which will reveal both the 3D morphology and the internal structure. In the study, we improved our experimental instrument to record high quality diffraction patterns so that the image (Fig. 2c) was reconstructed directly from the diffraction pattern (Fig. 2b) without using any other information such as a low-resolution image of the specimen. To check the reproducibility of the reconstruction, we have carried out four more trials with different initial seeds and the results were very consistent.

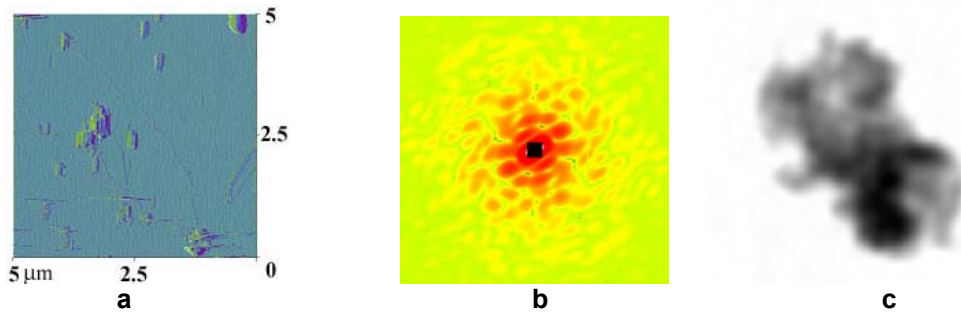


Fig. 2 (a) An AFM Image of GaN quantum dots provided by Risbud. (b) A coherent X-ray diffraction pattern recorded from a single GaN quantum dot ($\lambda = 2 \text{ \AA}$). (c) An image directly reconstructed from the diffraction pattern without using a low-resolution image of the specimen, which shows more detailed structure information than the AFM image.

Proposed Research

Science Cases. GaN and the related wide band gap III-V nitride semiconductors are at the heart of dramatic advances in electronic and optical device applications such as blue/green lasers, flat panel displays and other high-tech devices [20,21]. Nanocrystals, thin films, and bulk single crystals of GaN (and alloys of GaN with other nitrides) have all been synthesized leading to a wealth of literature in recent years. Despite these synthetic advances, characterization of the morphology, chemistry and structure at the nanometer level has been mainly done in the customary two-dimensions by a host of standard methods like TEM, AFM, or routine x-ray diffraction [22]. To our knowledge, no work has been reported that shows the 3D morphology of GaN and its alloys in nanocrystal form. This deficiency is particularly alarming given the well-documented realization that nanoparticle shape anisotropy and nanoparticle interaction with the matrix in which they are formed profoundly affect light emission and other optical properties. Thus, 3D coherent diffraction imaging will be a powerful new technique for characterization of GaN and other III-nitride alloys (like Ga-In-N).

The recent explosive growth in methods for the production of nano- and meso-porous materials promises a range of new materials whose controllable pore sizes make them ideal for applications from catalysis to molecular sorting, thus greatly expanding the range of existing materials such as zeolites [23-25]. To date, the structure of these nanoscale materials have been inferred from either absorption isotherm measurements or X-ray scattering where a model was first assumed. For extremely small crystals, a direct 3D imaging technique has recently been developed by using high-resolution electron microscopy (HREM) [26]. However, if the specimen is thicker than 30 nm, multiple scattering becomes a serious issue for HREM. Also, the HREM imaging technique only provides an averaged 3D structure from a large number of unit cells. By using coherent X-rays from 3rd generation synchrotron radiation, we have recently imaged a disordered porous silica particle at a resolution better than 10 nm [19]. With the LCLS, we propose to characterize the local 3D structures of nano and meso-porous materials at atomic resolution. The ability to image the internal pore structures in three dimensions, coupled with computational methods such as molecular dynamics, and *ab initio* calculations, will profoundly expand our understanding of the critical structural and morphological features required to make a superior catalyst, adsorbent, or electrode.

The study of magnetic thin films and superlattices has been driven by the variety of novel physics and phenomena that can be studied in such structures. In general, much of the new physics comes from combining materials (e.g. ferromagnetic, antiferromagnetic, paramagnetic, and nonmagnetic) on nanometer length scales. With reduced layer thicknesses, the interfaces increasingly dominate the magnetic response of the system [27,28]. The interfaces can perturb the system in a variety of important ways including interfacial strains that alter the atomic structure within the layer, reduced coordination of the atoms at the interface producing unique properties of the interfacial atoms compared to the bulk and coupling of the layers either directly across the interface or indirectly via an interlayer. The details of the interface roughness, spacing of steps, existence of dislocations, etc. are important in understanding the variations of magnetic anisotropy, exchange bias and domain structure that determine the properties of these films in device applications. Since these structures are typically made by sputtering or vapor deposition and are not in thermodynamic equilibrium, structural characterization of the atomic and interfacial structure is a prerequisite for a complete understanding of the magnetic properties. The structural features referred to above have relevant length scales ranging from several hundred nanometers down to 1 or 2 nanometers, and cannot be probed with the usual surface imaging microscopes such as AFM or STM,

since the interfaces are buried. Direct imaging with coherent X-rays of the nature of the defects at these buried interfaces would thus provide unique information relevant to the physics of these materials. This can be done in principle by an adaptation of the oversampling method to grazing incidence scattering from such films [29].

3D structure characterization of nanoscale materials at atomic resolution would have a great and broad impact in nanoscience and technology, which would be analogous with the impact of X-ray crystallography in materials science in the early days. The science examples given above are just the tip of the iceberg of the applications of coherent diffraction imaging to nanoscience and technology. In the long run, we will also explore the properties of the ultra-short pulse duration of the LCLS, which could open up an even more interesting horizon of atomic resolution imaging of nanostructured materials in a sub-picosecond time scale.

Effect of Radiation Damage. Because the LCLS will provide coherent X-rays with 10 orders in peak brightness and 3 orders in averaged brightness higher than any existing X-ray sources in the world [30], it will even impose radiation damage to materials science samples. We propose to mitigate the radiation damage problem by using the distance from the undulator source to the sample and also controlling the size of the focal spot. For example, at the upstream experimental hutch (~ 100 m from the source), the LCLS beam size will be around $150 \times 150 \mu\text{m}^2$. By using X-ray optics, the beam can be focused down to a spot of $0.1 \times 0.1 \mu\text{m}^2$. This will enable us to control the coherent X-ray flux in a range of 6 orders between unfocused and focused beam. If the downstream hutch (~ 250 m from the source) is used, it will give us another order of flexibility. Furthermore, our sample size is typically around 100 nm or smaller and the absorption of 8 keV X-rays is very low. For example, for an unfocused LCLS beam, a 100 nm silicon particle will absorb ~ 70 photons per pulse where we assume that a crystal monochromator will be used with 10% efficiency. We will hence be able to use multiple shots to record diffraction patterns from a single nanoparticle.

Coherence Measurement for the LCLS. The acceleration and compression process of the electron beam in the LCLS could produce an electron phase space distribution at the undulator entrance that would amplify more than one optical mode. In this case the angular distribution and coherence properties of the X-ray beam at the undulator exit might be more complicated than that expected in a simple model. Since coherence of the X-ray beam is crucial to our experiment, we propose to measure the coherence of the LCLS as our first experiment and study the coherence properties as a function of the angular aperture accepted in the experiment.

The most powerful method to acquire full coherence information is that of phase-space tomography. This approach can measure the full phase-space portrait of the beam. However this method relies on the acquisition of multiple sets of data and so cannot be directly applied to beams that show significant shot-to-shot variation. The first step in a full characterization therefore is to understand the shot to shot variation in the broad beam properties. For most experimental purposes, it is sufficient to provide a simple characterization of the beam via the coherence length. Coherence has now been extensively measured for third generation synchrotron sources and a number of methods exist. The properties of partially coherent diffraction are well understood and in this project we will observe the diffraction of the beam from a well-characterized structure and use this to deduce a coherence length [31]. The structure used in earlier work has been a lithographically produced aperture and this will be difficult to

meaningfully apply to very high coherence beams. Instead, we will measure the diffraction of the beam from a thin crystal. The properties of the diffraction pattern from such structure will allow the coherence properties to be broadly characterized as a function of experimental parameters. Once the beam parameters and variation are understood, we will apply phase-space tomography to provide a complete characterization of the beam.

Instrumentation and Phasing Algorithm. We propose to use the upstream hutch for our imaging experiment. Fig. 3 shows a schematic layout of the experimental instrument. We will use a crystal monochromator to achieve an energy resolution of better than 10^{-4} . The monochromatic X-rays will be focused by using a pair of super-polished mirrors. We will control the size of the focal spot so that the X-ray flux will be below the radiation damage threshold to the samples. At a distance of ~ 5 m downstream of the mirrors is a $10 \mu\text{m}$ pinhole that is used to make a small beam and remove the unnecessary X-ray flux. A guard slit, placed ~ 1 m downstream of the pinhole, is used to eliminate the scattering from the edge of the pinhole. Immediately following the guard slit is a sample holder that will be mounted on a goniometer and can be rotated around two axis to record diffraction patterns at different orientations. The samples, with size of ~ 100 nm or smaller, will be supported on silicon nitride membranes with 10 nm in thickness. A pixel array detector (PAD), with a small hole ($< 50 \mu\text{m}$) at the center allowing the direct beam to go through, will be placed a few centimeters downstream of the sample. The PAD, which will likely be developed between SSRL and Cornell University for the LCLS experiments, will be able to measure diffraction patterns to a few tenths of percent accuracy anywhere over an intensity variation that can span 7 – 8 orders of magnitude [32].

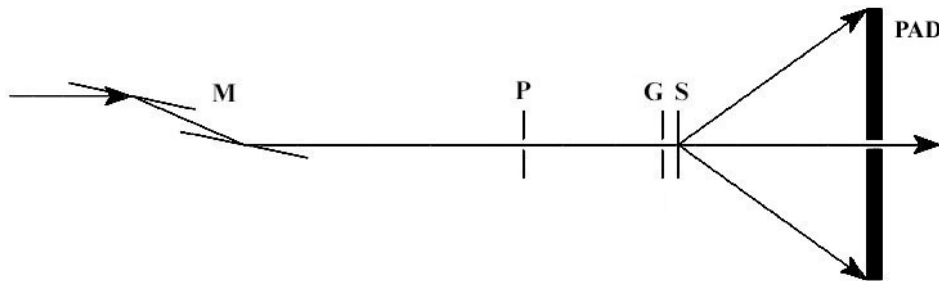


Fig. 3 Schematic layout of the experimental instrument where M: mirrors, P: pinhole, G: guard slit and S: sample.

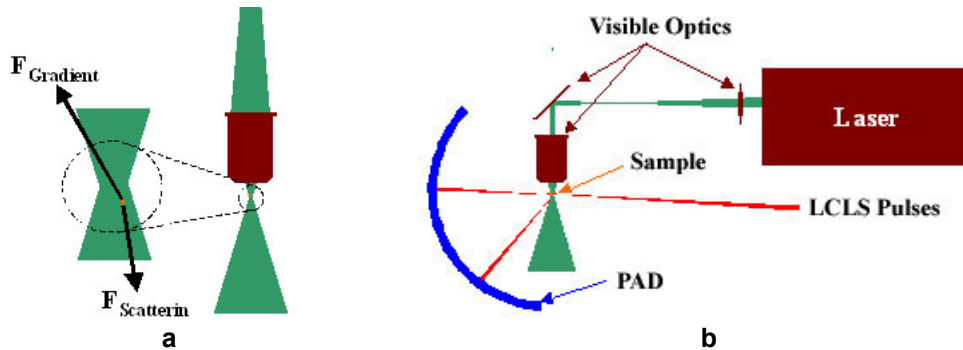


Fig. 4 (a) A diagram of a laser “optical tweezers” trap. **(b)** Schematic layout of the overall system.

To further reduce the background scattering, we will explore the use of optical tweezers to manipulate samples [33]. The general approach is shown in Figure 4. The light from a ~100 mW laser is brought through an optical system (typically a modified microscope) to a sharp focus. The waist of the focus has strong gradients in the electric field intensity both along the beam and radially away from the focus. In a polarizable material, this field will induce a significant electric dipole in the particle that reduces the total energy of the system and, since the field is greater at the focus, creates a force on the particle towards the focus. This gradient force is countered by a scattering force in the direction of the laser beam but, typically, the gradient force can be made larger than the scattering force. Thus, a highly focused laser can be used to create a potential well, which traps particles.

By using the instruments described above, we expect to record coherent X-ray diffraction patterns at a resolution of 2.5 Å or higher from nanoscale materials. The oversampled diffraction patterns will be assembled to a 3D diffraction pattern in Cartesian coordinates by using an interpolation algorithm that we have already developed [9]. The 3D diffraction pattern can then be directly phased by using the oversampling method with an iterative algorithm. The reconstructed 3D structure will be further refined by using constraints such as atomicity and bond information. Our experience has indicated that, with high quality oversampled diffraction patterns, the phasing algorithm is very robust.

Roles and Responsibilities for Each Team Member

John Miao has been working on coherent diffraction imaging for over seven years. He proposed a theoretical explanation to the oversampling phasing method in 1998 and conducted a seminal experiment of X-ray crystallography without crystals in 1999. He has since been applying coherent diffraction imaging to 2D and 3D structure determination of both nanoscale materials and biological samples. In 2000, he carried out a computer simulation on the potential of imaging single protein molecules in a combination of the oversampling method with X-ray free electron lasers. He will be acting as a coordinator for the proposed LCLS imaging experiment. His group will contribute to build the experimental instrument, and participate in data acquisition and 3D imaging reconstruction.

Sunil Sinha has extensive experience in neutron and X-ray scattering. He will bring to the experiments samples made by Prof. Ivan Shuller's group at UCSD who are experts in the fabrication of magnetic thin films and bilayers (*e.g.* ferromagnetic thin films deposited on antiferromagnetic substrates), patterned structures, nanodots, *etc.* Sinha's group has experience in grazing incidence scattering from such systems and will develop the cell and goniometer to orient the samples in the X-ray beam. His group will also develop the software to analyze the data.

Tetsuya Ishikawa is director of Coherent X-ray Optics Laboratory, RIKEN and has been working on ultra-high-resolution x-ray optics since the early 1980s. He measured the coherence length of hard x-rays by using dynamical diffraction effect in 1985 and developed a couple of x-ray interferometers to measure x-ray coherence, including Hambury-Brown-Twiss type intensity interferometer in 2001. He has been leading the beamline development at the SPring-8 since 1994, and constructed a 1000 m beamline and a 27 m undulator beamline which have been widely utilized for a variety of coherence-related investigations including coherent scattering imaging. These

beamlines, although not as bright as the LCLS, provide a sufficiently high degree of coherence to develop and characterize optical elements for coherence experiments. By using these beamlines, he has been developing atomic flat x-ray mirrors, speckle-free x-ray filters, windows, slits and pinholes, and perfect synthetic diamond crystals for XFELs. These beamlines will be used to test the instruments and optical elements developed for the proposed experiments. In addition, he will supply well-proven optical elements for the experiments at the LCLS.

Paul Fuoss and Brian Stephenson will take a lead role in the development of manipulation techniques for the nanoparticles, particularly "optical tweezers" trapping and guiding techniques. They will participate in measurements of nanoparticle structure at LCLS and will involve collaborators from Argonne National Laboratory who have active programs in synthesizing, characterizing and modeling novel nanoparticles. Paul Fuoss and Brian Stephenson each have extensive experience in developing synchrotron sources and techniques. Brian is director of the nanoprobe beamline at ANL and is developing techniques to image nanoscale materials using coherent x-rays. Paul has played a key role in the commissioning and operation of the SPPS facility.

Subhash Risbud will continue to provide the expertise and experience of nearly 15 years in the synthesis and processing of nanocrystals of a range of semiconductors and organic-inorganic nanocomposites. Risbud has been at the forefront of establishing state-of-the-art Materials Science Central Facilities that benefits all materials research on the UC Davis campus. His laboratory has standard heat treatment and materials processing facilities (powder mixing, ball milling, melting and casting of glasses, sintering furnaces) and access to a broad spectrum of spectroscopic techniques. In the previous work on quantum dots in Risbud's group, for example, his students have used Varian Mercury 300 Mhz Spectrometers, 2 QE-300 NMR spectrometers with multinuclear and variable temperature capabilities and a host of other characterization techniques (UV-visible, fluorescence, atomic absorption, GC-MS, EPR, FT-IR, Raman).

Keith Nugent and his group at the University of Melbourne will take responsibility for the characterization of the coherence properties of the LCLS beam. The aims will be to first model and then develop a coherence diagnostic based on diffraction from the thin crystal. This diagnostic will allow an overall measurement of the coherence properties (*i.e.* a coherence length) of the beam. The variation of the diffraction pattern will allow an assessment of the shot-to-shot variation of the beam properties. Once this is understood, a method to measure the complete wavefield properties will be developed using phase-space tomography. The design of this diagnostic will depend on the extent and nature of the beam stability.

Claudio Pellegrini and James Rosenzweig have been working on the physics of free-electron lasers (FELs) for many years. Their group was the first to demonstrate high gain in a SASE FEL, and to show how a complex electron beam phase space distribution can produce complicated angular distribution of the amplified radiation. They will mainly participate in the preparation and analysis of the measurements of the coherence properties of the X-ray radiation,

Jim Amonette has 25 years of experience in the areas of aqueous geochemistry and soil mineralogy. He has a strong interest in the structure and chemistry of minerals and in the application of spectroscopic techniques, such as laser photoacoustic, Mössbauer (conventional and synchrotron), electron paramagnetic, infrared, and x-ray

absorption/scattering, to characterize the solid phases and to predict and monitor the reactions associated with the disposal of hazardous wastes in soil environments. He is a charter member of the PNC-CAT at the Advanced Photon Source and has used synchrotron radiation for variety of spectroscopic, chemical imaging, and kinetic studies. Dr. Amonette has particular interest and experience in heterogeneous redox chemistry, and, more recently, in the roles played by nanoporous materials and minerals in contaminant retention and carbon fixation by soils and sediments. He will coordinate the preparation of nano- and meso-porous materials for the project and help devise and participate in key experiments that demonstrate the progress made in coherent diffraction imaging.

Donald Baer has 25 years of experience in the study of the impact of interfaces and surfaces on the properties of materials. His research has involved developing new ways to apply a variety of surface and interface sensitive tools to understand how different environments and surface contaminants alter materials structure and chemical or mechanical properties. His research includes study of x-ray and electron damage of material and the influence of elemental segregation on materials properties. As materials structures approach the nano-scale, contamination, component segregation, and environmental effects are increasingly important and the atomic scale understanding of these properties is critically important. He will work with the team to identify key materials and topic to explore questions of particle stability, impurity and contaminant effects, and the role of the environment on the structure of nanoparticles.

Budget

A. Personnel (including fringe benefits and indirect cost)

Four postdoctoral associates and five graduate students will participate in instrumentation design and commissioning, sample preparation, coherence measurement, software development, data acquisition and analysis, imaging reconstruction, and computer modeling. $\$500K/yr \times 5\text{ yrs} = \$2,500K$

B. Permanent Equipment

Years 1, 2 & 3: We will build an instrument for coherent diffraction imaging. We assume that a pixel array detector and a crystal monochromator will be funded separately by DOE. Detailed specifications and costs are:

- An alpha server for 3D imaging reconstruction. \$100K
- A motorized JEOL goniometer. \$60K
- A MDC vacuum chamber. \$80K
- A high resolution Nikon optical microscope. \$20K
- Vacuum motors and a motor control system \$55K
- Superpolished mirrors with a liquid nitrogen cooling system, pinholes and guard slits. \$100K
- Equipment for a laser trap. \$200K

Years 4 & 5: Commissioning and early experiment.

- Equipment maintenance costs. \$100K

C. Materials and Supplies

Sample preparation supplies, computer supplies, small tools laptops and PCs for the postdoctoral associates and the graduate students.

\$30K/yr x 5 yrs = \$150K

D. Travel

\$25K/yr x 5 yrs = \$125K

Total cost (5 years): \$3,490K

References

1. J. Miao, H. N. Chapman, J. Kirz, D. Sayre, and K. O. Hodgson, *Annu. Rev. Biophys. Biomol. Struct.* **33**, 157 (2004).
2. I. K. Robinson and J. Miao, *MRS Bulletin* **29**, 177 (2004).
3. J. Miao and D. Sayre, *Acta Cryst. A* **56**, 596 (2000).
4. J. Miao, D. Sayre, and H.N. Chapman, *J. Opt. Soc. Am. A* **15**,1662 (1998).
5. J.R. Fienup, *Opt. Lett.* **3**, 27 (1978).
6. J. Miao, P. Charalambous, J. Kirz, and D. Sayre, *Nature* **400**, 342 (1999).
7. I.K. Robinson, et al., *Phys. Rev. Lett.* **87**, 195505 (2001).
8. U. Weierstall et al., *Ultramicroscopy* **90**, 171 (2001).
9. J. Miao et al., *Phys. Rev. Lett.*, **89**, 088303 (2002).
10. G.J. Williams, M.A. Pfeifer, I.A. Vartanyants, and I.K. Robinson, *Phys. Rev. Lett.* **90**, 175501 (2003).
11. H. He et al., *Phys. Rev. B* **67**, 174114 (2003).
12. H. He et al., *Acta Cryst. A* **59**, 143 (2003).
13. J. Miao, T. Ishikawa, E.H. Anderson, and K.O. Hodgson, *Phys. Rev. B* **67**, 174104 (2003).
14. J. Miao, K.O. Hodgson, T. Ishikawa, C.A. Larabell, M.A. LeGros, and Y. Nishino, *Proc. Natl. Acad. Sci. USA* **100**, 110 (2003).
15. Y. Nishino, J. Miao and T. Ishikawa, *Phys. Rev. B (Rapid Commun.)* **68**, 220101 (2003).
16. S. Marchesini et al., *Phys Rev. B* **68**, 140101 (2003).
17. S. Marchesini et al., *Opt. Express* **11**, 2344 (2003).
18. I.K. Robinson, F. Pfeiffer, I.A. Vartanyants, Y. Sun, and Y. Xia, *Opt. Express* **11**, 2329 (2003).
19. J. Miao, J. Amonette, Y. Nishino, T. Ishikawa and K. O. Hodgson, *Phys. Rev. B* **68**, 012201 (2003).
20. S. Nakamura, *Science* **281**,956 (1998).
21. S.J. Pearton and C. Kuo, *MRS Bulletin* **22**, 17 (1998).
22. M. Hajra et al., *J. Vac. Sci. Technol.* **21B**, 458 (2003).
23. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* **359**, 710 (1992).
24. Q. Huo, R. Leon, P. M. Petroff, and G. D. Stucky, *Science* **268**, 1324 (1995).
25. D. Zhao et al., *Science* **279**, 548 (1998).
26. Y. Sakamoto et al., *Nature* **408**, 449 (2000).
27. L.M. Falicov et al., *J. Mater. Res.* **5**,1299 (1990).
28. J.B. Kortright et al., *J. Mag. Magnetic Matls.* **207**,7 (1999).
29. I.A. Vartanyants et al., *Phys. Rev.B* **55**, 13193 (1997).
30. C. Pellegrini, "A 4 to 0.1 FEL Based on the SLAC Linac," in *Proceedings of the Workshop on 4th Generation Light Sources*, ed. M. Cornacchia, H. Winick, pp. 376-84. SLAC, Stanford, 1992.
31. J. Lin et al., *Phys. Rev. Letts.* **90**, 074801 (2003).
32. Sol Gruner, private communication.
33. A. Ashkin, J.M. Dziedzic, J.E. Bjorkholm, and S. Chu, *Opt. Lett.* **11**, 288 (1986).