William R. Wiley
EMSL
Environmental Molecular Sciences Laboratory

EMSL Monthly Report

April 2003

The W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) is a U.S. Department of Energy (DOE) national scientific user facility located at Pacific Northwest National Laboratory (PNNL) in Richland, Washington. EMSL is operated by PNNL for the DOE Office of Biological and Environmental Research. At one location, EMSL offers a comprehensive array of leading-edge resources in six research facilities.

Access to the capabilities and instrumentation in EMSL facilities is obtained on a peer-reviewed proposal basis. Users are participants on accepted proposals. Staff members work with users to expedite access to the facilities and scientific expertise. The Monthly Report documents research and activities of EMSL staff and users.

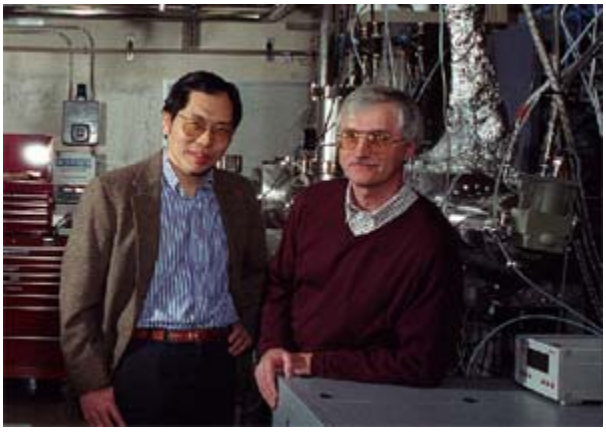
Research Highlights

All-Metal Antiaromatic Molecule: Rectangular Al_4^{4-} in the $Li_3Al_4^-$ Anion

AE Kuznetsov,[(a)] KA Birch,[(a)] AI Boldyrev,[(a)] X Li [(b,c)] HJ Zhai,[(b,c)] and LS Wang[(b,c)]

(a) Utah State University, Logan
(b) Washington State University, Richland
(c) W.R. Wiley Environmental Molecular Sciences Laboratory

Chemical Physics of Complex Systems Facility users Lai-Sheng Wang of Washington State University and Alexander Boldyrev of Utah State University have recently reported the discovery of a new class of antiaromatic inorganic cyclic compounds. The work was published in *Science* 300, 622 (2003) and featured in the "News of the Week" section of the April 28th, 2003 issue of *Chemical and Engineering News*.



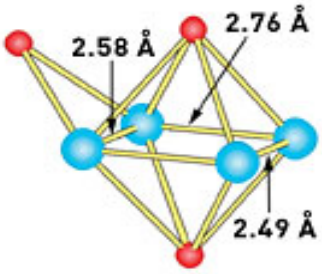


Figure 1: (left) Lai-Sheng Wang and Alexander Boldyrev. (right) Optimized structure for $Li_3Al_4^-$; bond lengths in angstroms.

The paper reports on the experimental and theoretical characterization of antiaromaticity in an all-metal system, $Li_3Al_4^-$, which is produced by laser vaporization and studied with the use of photoelectron spectroscopy and ab initio calculations. The most stable structure of $Li_3Al_4^-$ is found to theoretically contain a rectangular Al_4^{4-} tetraanion stabilized by the three Li^+ ions in a capped octahedral arrangement. Molecular orbital analyses reveal that the rectangular Al_4^{4-} tetraanion has four π electrons, consistent with the $4n$ Hückel rule for antiaromaticity.

The introduction of antiaromaticity helps to explain and characterize the structure and chemical bonding of $Li_3Al_4^-$ and completes the extension of two important chemical concepts, aromaticity and antiaromaticity, into the realm of all-metal systems. The work should contribute to the further advancement of the aromaticity and antiaromaticity concepts into metal territory and will be of value in understanding not only the properties of metal clusters but also those of bulk metallic and alloy systems.

Rhodobacter sphaerodies

MS Lipton[(a)] and T Donahue[(b)]

(a) Pacific Northwest National Laboratory

(b) University of Wisconsin-Madison

Rhodobacter sphaerodies 2.4.1 is a purple nonsulfur eubacterium with an extensive metabolic repertoire. Under anaerobic conditions, it is able to grow by photosynthesis, respiration and fermentation. Characterizing the proteome of *R. sphaerodies* cultured under specific growth conditions will flag proteins involved in each of the different metabolic pathways. The generation of a protein mass tag database from tryptic digestions of global lysates, cytoplasmic fractions, and membrane preparations of *R. sphaerodies* grown under specific conditions is the focus of the fiscal year 2003 effort. The analysis of tryptic digests of proteins from *R. sphaerodies* cultures by LC-IT tandem MS has resulted in the following ORF coverage (Table 1).

Table 1. Total open reading frames (ORFs) used for Search: 3980

***R sphaerodies*: Aerobic growth**		
Total	Chromosome 1	Chromosome 2
809	671	138
***R sphaerodies*: Photosynthetic growth**		
Total	Chromosome 1	Chromosome 2
797	676	121

Fourier Transform Infrared Characterization of Chelsea Soil Humic Acid

MS Diallo[(a)] and P Gassman[(b)]
(a) California Institute of Technology, Pasadena
(b) W.R. Wiley Environmental Molecular Sciences Laboratory

Humic substances are the most abundant reservoir of carbon on earth. Humic acids are operationally defined as the fraction of humic substances that is insoluble in water at low pH (<2) and soluble at higher pH (>2). They significantly impact a variety of biogeochemical and environmental processes. For example, they act as (i) soil stabilizers, (ii) nutrient and water reservoirs for plants, (iii) sorbents for toxic metal ions, radionuclides, and organic pollutants and (iv) chemical buffers with catalytic activity. Because humic acids are operationally defined through their solubility in aqueous solutions, the development of 2-D and 3-D structural models for these compounds has remained an outstanding challenge in environmental chemistry, soil chemistry, and organic geochemistry.

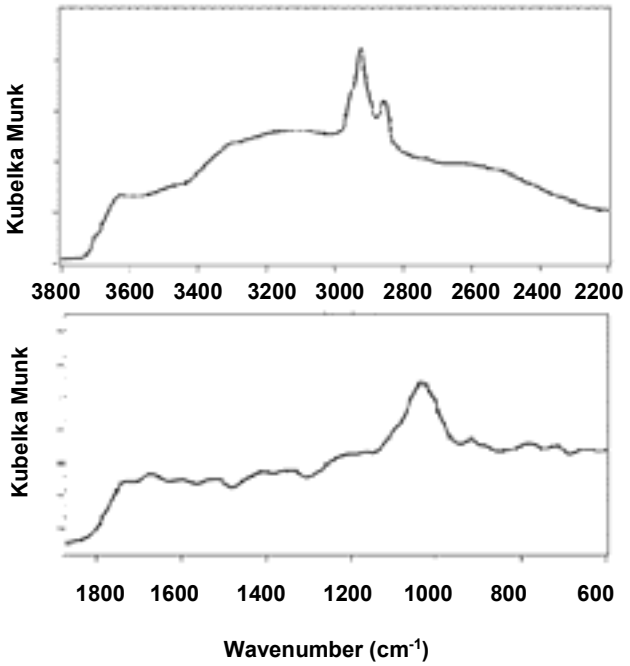


Figure 2. Diffuse reflectance FT-IR spectrum for Chelsea soil humic acid.

The overall goal of Diallo's research is to describe an integrated experimental and computational framework for developing 3-D structural models for humic acids. This approach combines experimental characterization, computer-assisted structure elucidation (CASE), and atomistic simulations to generate all 3-D structural models or a representative sample of these models consistent with the analytical data and bulk thermodynamic/structural properties of humic acids. To illustrate this methodology, Diallo et al. (2003) used structural data derived from elemental analysis, diffuse reflectance FT-IR (DRIFT) spectroscopy, 1-D/2-D ^{1}H and ^{13}C solution nuclear magnetic resonance spectroscopy, and electrospray ionization quadrupole time-of-flight mass spectrometry as input to the CASE program SIGNATURE to generate all 3-D structural models for Chelsea soil humic acid.

Diallo obtained the DRIFT spectroscopy data at EMSL in collaboration with Paul Gassman. The organic normalized weight fractions for carbon (51.31%), hydrogen (4.00%), oxygen (39.67%), nitrogen (4.12%), and sulfur (0.93%) along with the oxygen/carbon atomic

ratio (0.58) of Chelsea soil humic acid are typical of soil humic acids. Its DRIFT spectrum (Fig. 2) exhibits typical broad bands and shoulders found in the infrared spectra of many soil humic acids. The region between 3800 and 2200 cm^{-1} exhibits very broad bands with four distinct frequency ranges. The high-frequency modes above 3500 cm^{-1} are assigned to nonbonded OH stretches. Most of these occur as broad shoulders of poorly resolved aromatic C-H stretches in the 3400 to 3000 cm^{-1} region. The 3000 to 2800 cm^{-1} region exhibits high-intensity bands characteristic of symmetric and asymmetric aliphatic CH_2 and CH_3 stretches. Conversely, the weak bands in the 2800 to 2400 cm^{-1} region are assigned to OH stretches from COOH groups. In the 1800 to 1300 cm^{-1} region, Diallo observed several peaks including the following: (i) C=O stretches from COOH groups, (ii) aromatic C=C stretches, (iii) CH deformation of CH3 groups, and (iv) CH bending of CH2 groups. In the 1270 to 760 cm^{-1} region, Diallo observed several peaks including the following: (i) aromatic C-H and C-OH stretches and (ii) out-of-plane C-H bends. These are assigned to mono-, di-, and tri-hydroxyl substituted aromatics. Characteristic aliphatic C-O and C-OH stretches of carbohydrates are also observed in the 1270 to 760 cm^{-1} region. Overall, the results of the DRIFT spectroscopic experiments were consistent with the hypothesis that the condensation of plant and microbial degradation products (e.g., lignin degradation products, polyphenols, sugars, amino acids, etc.) was a major formation pathway for Chelsea soil humic acid.

This work was recently published in *Environmental Science and Technology* 37(9):1783-1793.

Quasiharmonic Vibrations of Water, Water Dimer, and Liquid Water from Principal Component Analysis of Quantum or QM/MM Trajectories

RA Wheeler,[(a)] H Dong,[(a)] and SE Boesch[(a)]
(a) University of Oklahoma, Norman

Computational approaches for examining vibrational modes in solution phase have generally fallen behind the experimental capabilities. Often the computational simulations have relied on harmonic approximations based on the use of Wilson FG matrix eigenvalue problems. In this work, quantum molecular dynamics simulations are analyzed using multivariate statistics with principal mode analysis to determine vibrational frequencies for an isolated water molecule, water dimer and liquid water. This method includes some anharmonic effects and time-averaged information, which brings the frequencies into better agreement with experimental results. Importantly, it is also possible to assign realistic estimations of errors associated with these calculated frequencies.

^{31}P-NMR Spectroscopic Investigations of Phosphate Speciation on Soil Minerals and Waste Products

S Hunger,[(a)] DL Sparks,[(a)] SD Burton,[(b)] and H Cho[(c)]

(a) University of Delaware, Newark
(b) W.R. Wiley Environmental Molecular Sciences Laboratory
(c) Pacific Northwest National Laboratory

Phosphorus contamination of surface water from agricultural solids can lead to eutrophication and disruption of aquatic ecosystems. Information on phosphorus speciation in animal wastes and in soils is needed to determine the fate of phosphorus in the environment to predict its mobility towards surface water bodies. Structural solid-state experiments performed in the High-Field Magnetic Resonance Facility were run to examine the connectivity of phosphate on soil minerals (aluminum hydroxide, calcium carbonate) and the phosphorus speciation in animal wastes.

Standard solid-state nuclear magnetic resonance (NMR) techniques were employed, namely high-speed spinning of the sample about the magic angle, a single pulse excitation sequence under proton decoupling, and ^{31}P{^{1}H} CP-MAS. Additionally, a ^{31}P{^{27}Al} TRAPDOR (Transfer of Population by Double Resonance) pulse-sequence was optimized and used to directly probe the connectivity of phosphorus and aluminum. The combination of these techniques should allow for the unambiguous identification of phosphorus species in heterogeneous systems.

The TRAPDOR pulse sequence (Schaller et al. 1999) collects two echo spectra, of which the first spectrum serves as a reference. During the evolution of the second spectrum, a radio frequency is applied to the ^{27}Al-channel. The difference spectrum will show the peaks of phosphorus nuclei in close proximity to aluminum nuclei. A central parameter is the dephasing time, during which radio frequency is applied to the ^{27}Al-channel. We found that employing dephasing times of 2 to 3 ms is most effective, but the signal intensity is also lost during this time due to relaxation via pathways other than dipolar coupling. A dephasing time of 1.6 ms showed the best TRAPDOR effect while retaining maximum signal intensity.

EMSL's High-Field Magnetic Resonance Facility was invaluable in conducting these investigations, due to the availability of dedicated NMR spectrometers and the state-of-the-art equipment, particularly the triple-resonance probe necessary for the TRAPDOR sequence.

This work was recently published in *Journal of Non-Crystalline Solids* 248(1):19-27.

Investigation of Exchange Bias in MnPd/Fe Bilayers

P Blomqvist,[(a)] X Ji,[(a)] KM Krishnan,[(a)] and DE McCready[(b)]

(a) University of Washington, Seattle

(b) W.R. Wiley Environmental Molecular Sciences Laboratory

The magnetic exchange coupling in nanoscale MnPd/Fe(Co) heterostructures was studied to gain fundamental understanding of the relationship between structure and magnetic properties in structures that have a strong impact on a variety of technologies. All of the samples in this study have been deposited in ultra-high vacuum on single-crystalline MgO (001) substrates using the ion-beam sputtering technique. MnPd and Fe can be grown epitaxially on top of each other yielding bilayer structures with high crystalline quality. The structural and magnetic properties of the samples are investigated by means of a combination of techniques available at EMSL and the University of Washington, including X-ray diffraction (XRD), transmission electron microscopy, Rutherford backscattering, vibrating sample magnetometry, magnetic torque magnetometry and spin polarized neutron reflectivity. A very thorough XRD investigation shows MnPd/Fe bilayers with high crystalline quality and well-defined interfaces. The magnetization measurements show systematic variations in exchange bias behavior as a function of crystallography. This data has been successfully interpreted using a very simple analytical model. As an example of the measurements conducted in EMSL, Fig. 3a, shows a high-angle XRD scan from a sample deposited at 375°C, which is found to be the optimum growth temperature. At higher temperatures, inter-diffusion between the MnPd and the Fe layer is initiated. As seen in the figure, only the Fe (002) Bragg peak at 65.25° is detected, which indicates that the Fe film is single-crystalline. This was verified by an XRD texture scan which showed four (220) reflections with a four-fold symmetry as expected for a body-centered cubic unit cell (Fig. 3b).

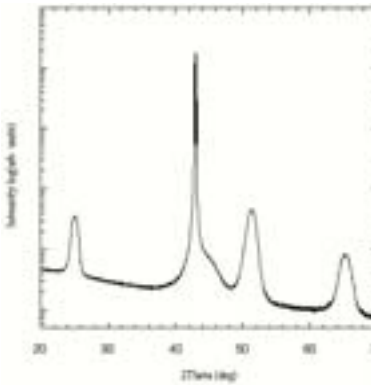


Figure 3a. 2Theta-Omega scan.

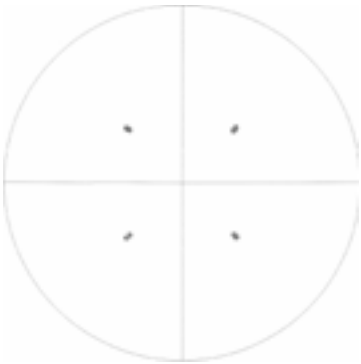


Figure 3b. Fe (220) pole figure.

Temperature-Induced Phase Separation in Chromium Films

LV Saraf,[(a)] CM Wang,[(a)] MH Engelhard,[(a)] and DR Baer[(b)]
(a) W.R. Wiley Environmental Molecular Sciences Laboratory
(b) Pacific Northwest National Laboratory

Chromium metal is known to change its phase upon size reduction. In this study, the possibility of controlled phase separation in chromium has been obtained using the knowledge that nanophase chromium exists in a δ-A15 type structure—apart from a recently observed fcc (Huh et al. 2000) phase. The δ-A15 structure is stable up to 428° to 450°C, where significant grain growth and phase transformation to the bcc structure occur. Also, nanophase chromium suppresses the nonmagnetic antiferromagnetic phase transition and gives rise to a surface ferromagnetic phase. Thus, selective phase transformation or controlled phase separation in chromium can be useful for technological applications due to the changed physical properties as a result of different electronic structures with the same base material.

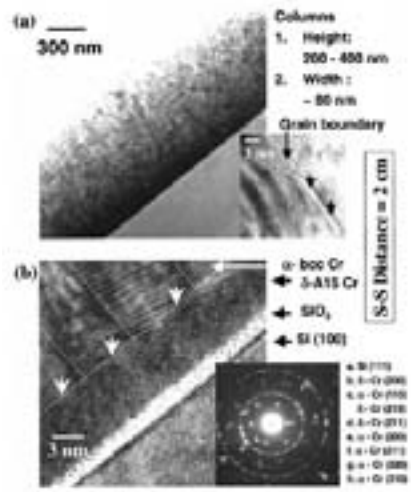


Figure 4. Cross-sectional TEM micrographs of chromium film deposited at a SS distance of 2 cm. (a) Low magnification image across the interface. Inset: high-resolution cross section of a grain boundary region near the surface. (b) High-resolution cross section across the interface indicating phase separation. Inset: electron diffraction pattern.

In this study, films were deposited with rapid evaporation of chromium and characterized using high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), and X-ray diffraction (XRD). Vacuum evaporations of chromium on Si(100) were carried out at 3×10^{-5} Pa at SS (source to sample) distances of 2 and 32 cm. The evaporation rate was maintained at ~3 μm/min, the fastest possible in this system. The tungsten filament of the evaporator also served as the heating source. During evaporation, no additional heating was provided to the substrate. *In situ* thickness measurements were done using a quartz crystal thickness monitor. The thicknesses of the films grown at SS distances of 2 nm and 32 cm were measured as 800 nm and 20 nm, respectively. The samples were exposed to atmospheric pressure 15 min after closing the filament current to ensure no additional sample heating due to source filament, especially for the short distance depositions.

A cross-section TEM micrograph of chromium film deposited at a SS distance of 2 cm is shown in Fig. 4a. A columnar-type α structure is observed in the topmost part of the film. Growth of these columns is observed perpendicular to the substrate with the height ranging from 200 nm to 400 nm and an average width of 80 nm. In order to verify the compactness of these grains, the density variation in the region between the columns was analyzed using

HRTEM of a grain boundary region, as seen as an inset of Fig. 4a. No significant density variation is observed. HRTEM across the interface of chromium and silicon in the film deposited at a SS distance of 2 cm is shown in Fig. 4b. A 70-Å -thick layer of chromium nanograins is observed near the interface with a very sharp interface between Si and SiO_2. Markers in Fig. 4b show approximate vertical grain separations and a nanophase layer. Existence of a δ-A15 phase of chromium was verified by a cross-section electron diffraction pattern (Fig. 4b inset). Bright reflection circles corresponding to reflections in α-bcc chromium, such as (110), (200), (211), and (220), are clearly visible. Reflections denoted by b, c, and d correspond to (200), (210), and (211) of the δ-A15 phase of chromium.

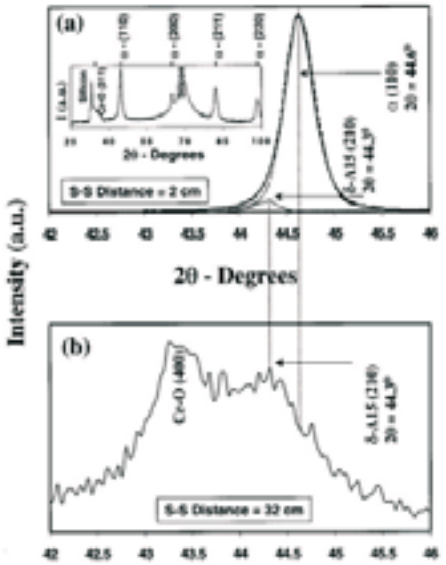


Figure 5. Strongest hkl region XRD spectra of chromium films deposited at SS distances of (a) 2 cm (Inset: complete scan); (b) 32 cm.

Structural properties of films grown at SS distances of 2 and 32 cm were analyzed by XRD. Scans in the strongest *hkl* reflection 2θ regions of Cr α-bcc and δ-A15 phases are represented in Fig. 5. The chromium α-bcc (110) reflection is observed at 44.6° for growth at a SS distance of 2 cm (Fig. 5a). The peak fitting profile indicates the presence of a weak peak of the δ-A15 phase at 44.3°. The complete XRD scan of the film deposited at a SS distance of 2 cm is shown as an inset in Fig. 5a. The film deposited at a SS distance of 32 cm (Fig. 5b) shows a strong (210) reflection at 44.3° attributed to the δ-A15 phase with Cr–O (400) reflection. Dotted lines in Fig. 5(b) represent the distinct nature of α and δ-A15 reflections. From the peak broadening in the case of growth at 32 cm, the average grain size is estimated to be ~7 nm at and below 7 nm.

In conclusion, a sharp phase separation between δ-A15 and α-bcc chromium has been obtained using a close distance rapid evaporation where the temperature gradient as well as interfacial stress combined to achieve separation between nanophase chromium and bulk columnar grains. The observed suppression of the antiferromagnetic order and the rise in surface magnetization in nanophase chromium can be used to create layered phase separated structures with varying magnetic properties, where a single element system with changed properties can be used to replace multicomponent systems.

This work was published in *Physical Review B* 62(4):2937-2943.

Awards and Recognition

PNNL was a finalist in this year's Computerworld Honors Program in the Environment, Energy & Agriculture category for the EMSL high-performance computer project. The Laureate presentation was held April 6, 2003 in San Francisco. Scott Studham, leader of the EMSL Molecular Science Computing Facility Operations group, accepted the medal on behalf of the laboratory (Fig. 6).

Figure 6. Computerworld Honors Program medal.

High-Field Magnetic Resonance Facility user David Bryce – formerly of the University of Alberta in Rod Wasylishen's group – was among four winners of the Natural Sciences and Engineering Research Council of Canada (NSERC) prizes for top doctoral research in science or engineering. Using nuclear magnetic resonance, Bryce characterized for the first time some of the 3-dimensional interactions specific to elements such as boron, chlorine and chromium. This information is important to materials scientists who are trying to understand the fundamental properties of molecules that contain these elements. This innovative NMR work with solid-state samples was further complicated by the fact that most of the elements Bryce was studying are "quadrupolar." Rather than having straightforward up and down magnetic poles, they also have lateral poles. Bryce credits resources at the High-Field Magnetic Resource Facility in EMSL as required for his work. For a full-length feature on his work, go to: http://www.nserc.ca/news/2003/p030328_b1.htm. Bryce is presently continuing his work in developing new NMR techniques as an NSERC postdoctoral fellow at the U.S. National Institutes of Health Laboratory of Chemical Physics in Bethesda, Maryland.

Major Facility Upgrades

The new EMSL storage system reached full operational status this month and started to accept production workload from EMSL instruments. The new filesystem is called NWfs and is designed to provide high performance, fault tolerant disk storage for a cost that is comparable to tape. The current filesystem is 17 Terabytes. The filesystem is backed up to a remote location to ensure data protection. Data that are in the existing SAM Archive will be migrated to NWfs in May.

News Coverage

An April 1, 2003 story by the *New York Times* on biodetectors featured an image of technology developed at EMSL: The Biodetection-Enabling Analyte Delivery System (BEADS).

An article in nanotechweb.org on April 17, 2003 highlighted research being carried out at EMSL by Lai-Sheng Wang and Hai-Feng Zhang of Washington State University, and Chong-Min Wang, Pacific Northwest National Laboratory, and their discovery of a procedure to make helical silicon nanosprings. The article can be found at http://nanotechweb.org/articles/news/2/4/12/1. This research is reported in the May 2003 issue of *Nano Letters*.

Research on antiaromatics by Wang and Boldyrev (see EMSL Monthly Report – April Research Highlights) was featured in the "News of the Week" section of the April 28th, 2003 issue of *Chemical and Engineering News*.

An image (Fig. 7, graphic art by Mike Perkins) created with resources in the MSCF Graphics and Visualization Lab was featured in the Viewpoint section of an April 11, 2003 article in *Science* (300:290-293). The image is an artist's conception of a cutaway view of an immobilized enzyme within a functionalized nanoporous silica pore. The enzyme is shown as green with positively charged regions shown in red. The blue structures inside the pores represent the negatively charged functional groups added to the mesoporous silica to create a favorable chemical environment for the enzyme.

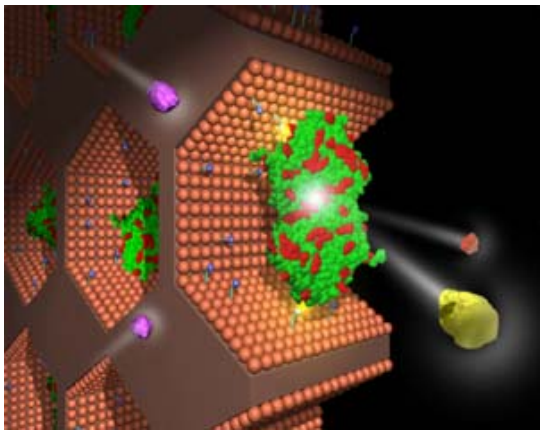


Figure 7. Enzyme within a functionalized nanoporous silica pore.

Visitors and Users

Chemistry & Physics of Complex Systems

- Linda Brown, NASA Jet Propulsion Laboratory, Pasadena, California, visited EMSL to obtain high resolution spectra of methane using the 100 meter White cell and the Bruker IFS 120 FTIR. She calibrated the intensities of the rotationally resolved methane transmission in the far infrared portion of the spectrum. These lab measurements are used by planetary astronomers at NASA to determine the atmospheric temperatures of the outer planets. (See http://www.hitran.com).
- Kristin Hermann and Krishnamoorthy Kuppannan, University of Arizona, Tucson, studied the implementation of Surface-Induced Dissociation into FT-MS. The research involves low-energy collisions of ions with well-ordered surfaces such as self-assembled monolayers of alkanethiols on gold or Langmuir-Blodgett films. The process of fragmentation (surface-induced dissociation) is the major experimental variable that is used in the determination of peptide dissociation mechanisms for potential use in high-throughput identification of proteins.
- George Nieman, Monmouth College, Monmouth, Illinois, is a visiting professor on sabbatical working with Jim Cowin and Alex Laskin studying aerosol particles. They plan to install a mass spectrometer on the ESEM (environmental scanning electron microscope) to get molecular information in addition to the atomic composition data already obtained.

Environmental Spectroscopy & Biogeochemistry Facility

- Barry Bickmore, Brigham Young University, Provo, Utah, in collaboration with Kevin Rosso, EMSL, performed density functional theory structure optimizations of surfaces of gibbsite (001) and cristobalite (100) for use in a new surface reactivity model being developed that accounts for relaxation of atomic positions at interfaces. The model will allow surface-specific charging behavior to be predicted and compared with direct measurements based on atomic force microscopy.
- Chris Tadanier, Virginia Polytechnic Institute, Blacksburg, in collaboration with Kevin Rosso, EMSL, performed *ab initio* structure optimizations of periodic bond chains in the goethite (alpha-FeOOH) crystal structure. The calculations are intended to provide high-accuracy, internally consistent bond length data for incorporation into a next-generation surface complexation model. The model will link structure to acidity constants and provide a predictive tool for the charging behavior of oxide mineral surfaces.
- Kiril Tsemekhman, University of Washington, Seattle, in collaboration with Eric Bylaska, Pacific Northwest National Laboratory, implemented and tested an algorithm for generating virtual orbital energies into the Density Functional Theory with Self Interaction corrections (DFT-SIC) program that they have developed. This development significantly improves the calculation of band gaps for semi-conducting and insulating materials. The DFT-SIC program is contained in the EMSL molecular modeling program, NWChem.

High-Field Magnetic Resonance Facility

- Cheryl Arrowsmith, University of Toronto (University Health Network), Ontario, Canada, recently sent samples to analyze using the 600-MHz spectrometer for studies of "Structural Proteomics: Annotating the Genome Using 3D Structure."
- Hanne Bertram, Danish Institute of Agricultural Sciences, Tjele, Denmark, recently worked on the 300-MHz spectrometer for the examination of "Post Mortem Energy Metabolism and Water Characteristics in Rabbit *M. longissimus* Studied by Dynamic Slow-Speed MAS NMR Spectroscopy and Relaxometry."
- Ann Campbell, University of Washington Cell Systems Initiative, Seattle, and her graduate student Jeffrey Grinstead worked remotely on the 500a- and 750-MHz spectrometer for studies of "MUC1 Humoral Immune Recognition: Mapping Antibody-Tumor Associated Antigen Interactions."
- Colin Fyfe, University of British Columbia, Vancouver, Canada, recently sent Darren Henry Brouwer to work on the 750-MHz spectrometer for "Structural Investigations of Solid Materials by High Resolution Solid State NMR at Very High Field."
- Robert Mantz, Air Force Research Laboratory, Wright Patterson Air Force Base, Ohio, recently used the 500-MHz spectrometer for studies of "NMR Characterization of Spider Silk Proteins and the Effect of Processing on Spider Silk Films."
- Gaetano Montelione and James Mario Aramini, Rutgers University, Piscataway, New Jersey, recently sent samples to analyze using the 600-MHz spectrometer for the studies of "Structural Genomics of Eukaryotic Model Organisms."
- Louis Silks, Los Alamos National Laboratory, Los Alamos, New Mexico, recently worked remotely on the 500-MHz spectrometer for studies of "Ultra-High Field NMR Studies of Stable Isotope Applications."
- Susan S. Wallace, University of Vermont, Burlington, recently worked remotely on the 500-MHz spectrometer for studies of the "Interaction of *Escherichia coli* Formamidopyrimidine-DNA Glycosylase (Fpg) with Damaged DNA."
- Jianjun Wang, Southern Illinois University, Carbondale, Illinois, recently worked remotely on the 600-MHz spectrometer for the studies of "Structural Determination of Apolipoprotein/HDL Particles."

High Performance Mass Spectrometry Facility

- Michael Daly, Uniformed Services University of Health Sciences, Bethesda, Maryland, provided samples that were analyzed on the 11.4 tesla FTICR to gather data for a "Comparative Display of *D. radiodurans* Proteome after Exposure to Ionizing Radiation."
- Ronald W. Davis, Stanford University, Stanford, California, sent samples that were analyzed on the 11.4 tesla FTICR to gather data on the "Functional Genomics and Proteomics of Mitochondria."
- Timothy Donohue, University of Wisconsin-Madison, sent samples of "*Rhodobacter sphaerodies*" that were analyzed to determine which proteins were expressed. This information will be used to identify which are important in the different metabolic pathways.
- Mary Lipton, Pacific Northwest National Laboratory, analyzed samples from *Shewanella oneidensis* on the LCQ spectrometers to gather data to access the effects of "Low Dose" radiation on the formation of complexes.

- Anil J. Patwardhan, University of California-San Francisco, brought 6 mg of protein from MCF-7 and other breast cell cancer lines for analysis. Nearly 70 runs of the SCX fractionated samples were completed on the LCQ. Presently, these runs are being analyzed for the presence of receptor tyrosine kinase proteins and data analysis is continuing but incomplete. The information will be used in the "Identification and Relative Expression of Membrane Proteins in Breast Cancer Cell Lines."
- Amy K. Schmid, University of Washington, Seattle, sent samples that were analyzed on the LCQ spectrometers to gather data for the "Identification of Heat Shock Proteins in the Radioresistant Bacterium *Deinococcus radiodurans*."

Interfacial & Nanoscale Science Facility

- Venugopal Arjunan and Josh Lamb, University of Nevada, Reno, visited to use the Quantum 2000 X-ray photoelectron spectrometer to characterize some of the passive film/corrosion products formed on a carbon steel and Ni-base alloy in the Yucca Mountain repository environment.
- Fereydoon Namavar, University of Nebraska Medial Center, Omaha, visited EMSL to explore the possibilities for collaborative user activities. Namavar presented a seminar entitled, "Engineering Nanocrystalline, Superhard Ceramic and Metallic Films for Orthopedic Prostheses and Geothermal Applications."
- Brad Pate, Washington State University, visited EMSL to use the Quantum 2000 X-ray photoelectron spectrometer with Mark Engelhard to understand some issues associated with his system at the university.
- Ambrosio Rouse, eV Products Inc., Saxonburg, Rhode Island, visited EMSL to continue to work on the investigation related to the understanding of chemistry on cadmium zinc telluride surfaces after processing. Ambrosio worked with the Quantum 2000 X-ray photoelectron spectrometer for some characterization and the accelerator facility for ion implantation.
- Richard Smith, Montana State University, Bozeman, visited EMSL to work with Shuttha Shutthanandan and Theva Thevuthasan on developing low-cost, high-temperature corrosion (oxidation) resistant coatings for bipolar interconnect plates in solid oxide fuel cell stacks. He investigated the performance of steel plates with multilayer coatings consisting of CrN for electrical conductivity and CrAlN for oxidation resistance. The coatings were deposited using large area filtered arc deposition technology, and subsequently annealed in air for up to 25 hours at 800°C. The composition, structure and morphology of the coated plates were characterized using Rutherford backscattering, nuclear reaction analysis, X-ray photoelectron spectrometry and atomic force microscopy techniques. By altering the architecture of the layers within the coatings, the rate of oxidation was reduced by more than an order of magnitude.

Figure 8. Richard Smith from Montana State University.

Molecular Science Computing Facility

- Bethany Little and Mary McBride, Office of U.S. Senator Patty Murray, visited the MSCF to discuss educational programs available at the Laboratory.
- James Vollmer, Knolls Atomic Power Laboratory, Schenectady, New York, visited with the MSCF Consultants about our capabilities and our research.
- Many young daughters and sons toured the facility during the National Take Our Daughter and Sons to Work Day.

Molecular Sciences Software - New user agreements with NWChem/Ecce:

- Arizona State University, Tempe
- Australian National University, Canberra
- Bull Worldwide Systems, Echirolles, France
- CATON Sistemas Alternativos, Santiago de Compostela, Spain
- Korea Advanced Institute of Science, Taejon, Korea
- Ludwig-Maximilians-Universitaet Muenchen, Muenchen, Germany
- MSIT Bioinformatics, Andhra Pradesh, India
- NIST, Gaithersburg, Maryland
- Octigabay Systems Corporation, Burnaby, BC, Canada
- Pittsburgh Supercomputing Center, Pittsburgh, Pennsylvania
- Pliva Inc., Croatia
- Rhode Island College, Providence, Rhode Island
- Silicon Graphics, Mexico
- Sun Microsystems, Hillsboro, Oregon
- The Chinese University of Hong Kong
- University of Bonn, Germany
- University of Metroploitana, Cupey, US Minor
- University of Puerto Rico at Bayamon
- University of Spain, Sevilla
- University of Tokyo, Japan
- Vrije Universiteit, Amsterdam, Netherlands
- Western Michigan University, Kalamazoo, Michigan

New Facility Staff

Kenny Schmidt, Senior Technician I, joined the Molecular Science Computing Facility Operations group.

Publications

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Presentations

El-Azab A, HE Trease, and JR Rustad. 2003. "Generalized Quasicontinua: An Approach to Atomistic-Continuum Modeling of Complex Oxides." Presented by Anter El-Azab (Invited Speaker) at MRS 2003 Spring Meeting, Symposium U: Mechanical Properties Derived from Nanostructuring Materials, San Francisco, CA on April 22, 2003.

Experimental Nuclear Magnetic Resonance Conference. 3 staff members from PNNL , David Hoyt and Sarah Burton of EMSL and Paul Ellis of MS&D attended the 44th Experimental Nuclear Magnetic Resonance Conference (ENC) held at the Convention center in Savannah, GA March 30th – April 4th. Two posters were presented including one research poster in the area of solid-state NMR of metallo-proteins. In addition to the research poster, an invited facility poster was presented that highlighted the capabilities of the NMR User Facility including several user research highlights, the arrival of the 900-MHz NMR and how to access the HFMRF facility. Brochures were distributed highlighting all the facilities within EMSL. The invited NMR facility poster was entitled "High Field Magnetic Resonance Facility (HFMRF): Capabilities, Highlights and Access to our National NMR User Facility" and was authored by Nancy G. Isern, Sarah D. Burton, Joseph J. Ford, Donald N. Rommereim, Jesse A. Sears, David W. Hoyt, and Paul D. Ellis. This international meeting had 900 registrants.

Perrine KA and DR Jones. 2003. "Gigapixel-size Real-time Interactive Image Processing with Parallel Computers." Presented by Donald R. Jones at the Workshop on Parallel and Distributed Image Processing, Video Processing, and Multimedia at the International Parallel and Distributed Processing Symposium, Nice, France on April 26, 2003.

Perrine KA, and DR Jones. 2003. "Interactive Imaging Science on Parallel Computers: Getting Immediate Results." Presented by Donald R. Jones at the International Parallel and Distributed Processing Symposium, Nice, France on April 23, 2003.

Witteveen T, S Studham, G Skouson. 2003. "Pacific Northwest National Laboratories-Home of HPCS2 1400 Processor HP Supercluster." Presented by Tim Witteveen (invited speaker) at the High Performance Cluster Computing Symposium in Houston, TX on April 22, 2003.