

The 64th Annual Pittsburgh Diffraction Conference

Fisher Conference Center Duquesne University Pittsburgh, PA 15282

October 26-28, 2006

Program and Abstracts

Symposia:

Frontiers in Electron Diffraction In-Situ and Time-Resolved Diffraction Studies Challenges of Crystal Twinning Diffraction and Scattering of Amorphous Materials



The 64th Annual Pittsburgh Diffraction Conference

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Poster Chair

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Sidhu Award

This award is made in memory of Professor Surhain Sidhu, who was a founding member of the Pittsburgh Diffraction Conference. At the time (1942), he was Professor of Physics and Director of the X-ray Laboratory at the University of Pittsburgh. Later, he moved to Argonne National Laboratory, where he pioneered the use of the null matrix in neutron diffraction. This involves choosing isotopes of an element in the proportion that gives a zero net coherent scattering factor. The procedure has been widely used for studying biological materials in which the isotopic ratio of H to D is appropriately adjusted.

The Sidhu Award is made to a scientist within five years of the PhD who has made an outstanding contribution to crystallography or diffraction. The previous Awardees are listed below:

1967	A. I. Bienenstock	1989	M. Luo
1968	R. M. Nicklow	1990	L. Brammer
1969	T. O. Baldwin	1992	R. C. Stevens
1970	SH. Kim	1993	M. Pressprich & T. Yeates
1971	L. K. Walford	1994	A. Vrielink & J. Wang
1972	D. E. Sayers	1995	M. Georgiadis
1974	B. C. Larson & N. C. Seeman	1996	M. J. Regan
1975	P. Argos	1999	C. Ban & M. Wahl
1978	K. Hodgson & G. DeTitta	2000	W. R. Wikoff
1980	G. Petsko	2001	L. Shapiro
1985	D. C. Rees	2002	Y. Lee
1986	D. Agard & J. M. Newsam	2003	E. O. Saphire
1988	Q. Shen	2004	Y. Xiong
		2005	CY. Ruan

Chung Soo Yoo Award

Dr. Chung Soo Yoo, Adjunct Associate Professor in the Department of Medicinal Chemistry and Research Associate in the Department of Crystallography of the University of Pittsburgh, was killed in the Korean Airlines Flight 007 disaster of August 31, 1983. Dr. Yoo came to the U.S. from Korea in 1965, obtained his M.S. degree in Chemistry at Rice University in 1967, his PhD in Crystallography at the University of Pittsburgh in 1971, and became a U.S. citizen. He was a member of the Biocrystallography Laboratory of the Veterans Administration Medical Center in Pittsburgh.

Dr. Yoo was one of the most likeable crystallographers among students and colleagues in Pittsburgh, and was always very enthusiastic about the Pittsburgh Diffraction Conference.

The Chung Soo Yoo Award, established by the Pittsburgh Diffraction Society in his honor, is given to a graduate student presenting the best poster at the annual Conference.



Pittsburgh Diffraction Society Life-Time Members

Wade Adams	Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University
Robert H. Blessing	Hauptman-Woodward Medical Research Institute and Department of Structural Biology, SUNY Buffalo
Bryan Craven	Department of Chemistry, Indiana University of Pennsylvania
George DeTitta	Hauptman-Woodward Medical Research Institute and Department of Chemistry and Department of Structural Biology, SUNY Buffalo
Thomas Emge	Department of Chemistry and Chemical Biology, Rutgers The State University of New Jersey
P. Lynne Howell	Department of Biochemistry, University of Toronto and The Hospital for Sick Children
Laura-Lee Kelley	Department of Biochemistry and Molecular Biology, the University of Georgia
Jeanette Krause	Department of Chemistry, University of Cincinnati
Charles Lake	Chemistry Department, Indiana University of Pennsylvania
David Langs	Hauptman-Woodward Medical Research Institute and Biochemical Pharmacology Department and Department of Structural Biology, SUNY Buffalo
Allen Oliver	University of California, Santa Cruz
John Ricci	Department of Biomaterials and Biomimetics, New York University
Nadrian Seeman	Department of Chemistry, New York University
G. David Smith	The Hospital for Sick Children
John Woolcock	Chemistry Department, Indiana University of Pennsylvania

Life-time membership can be obtained for a tax deductible donation of \$100 to the Society. This is the first time that a list of the life-time members is appearing in the conference program. If anyone has been accidentally left off of this list or if any of this information is not correct, please let Jen Aitken know, so that the information can be corrected for next year's program.



The 64th Annual Pittsburgh Diffraction Conference Program Schedule

Thursday, October 26

Fisher 324

8:45 AM *Welcoming Remarks and Announcements* **Thomas Koetzle** Argonne National Laboratory President, Pittsburgh Diffraction Society

Symposium A Frontiers in Electron Diffraction Chairs: Kenneth Downing and Jennifer Aitken

Opening Remarks 8:55 AM Jennifer Aitken **Duquesne University** 9:00 AM "Femtosecond Electron Diffraction: Making the Molecular Movie" A1. R. J. Dwayne Miller University of Toronto A2. "Precession Electron Diffraction" 9:30 AM Laurence Marks Northwestern University Coffee Break. 10:00 AM 10:30 AM A3. "Electron Backscattering Diffraction (EBSD): Crystallography in the Scanning Electron Microscope" **Alwyn Eades** Lehigh University

Thursday, October 26

Fisher 324

11:00 AM	A4.	"Atomic Structure of Nanotubes and Nano-Clusters" Jim Zuo University of Illinois, Urbana-Champaign
11:30 AM	S1.	"A Charge Density Study of Dienestrol" Eric Yearley University of Toledo
12:00 PM		Lunch Break
1:30 PM	A5.	"Studies of Ligand Binding to Tubulin by Electron Crystallography" Kenneth Downing Lawrence Berkeley National Laboratory
2:00 PM	A6.	"Electron Crystallography of the Ca ²⁺ -ATPase and Phospholamban Inhibitory Complex" Howard Young University of Alberta
2:30 PM	A7.	"Commensurate and Incommensurate Superstructures in Polytelluride Compounds with Square Nets: Are they "Everywhere"?" Mercouri Kanatzidis Northwestern University
3:00 PM		Coffee Break
3:30 PM	A8.	"Fluctuation Electron Microscopy: Mixing Real and Reciprocal Space to Reveal Nanoscale Order in Amorphous Materials" Paul Voyles University of Wisconsin, Madison
4:30 PM	D1.	"X-ray Amorphous and Disordered Crystalline Pharmaceutical Materials: Characterization Using X-Ray Powder Diffraction" Simon Bates SSCI-Inc
5:00 PM	S2.	<i>"In Situ</i> Neutron Diffraction Studies on the Polymorphs of Sodium Monothiophosphate" Nathan Takas Duquesne University
5:30 PM		Adjournment

POSTER SESSION AND CONFERENCE MIXER Poster Chair: Thomas Emge Rutgers University

7:00 PM Poster Session and Mixer – Open Bar, Appetizers Will Be Served

7:30 PM Formal Poster Session and Judging

Posters should be mounted on Thursday morning or afternoon and left on display throughout the conference. The formal poster session, including the judging for the Chung Soo Yoo Award, will begin at 7:30 p.m. Thursday evening. The Chung Soo Yoo Award is made to the graduate student who presents the best poster. Candidates must be present to meet with the judges. The Award, consisting of a cash prize of \$200, will be made at the Conference Dinner on Friday evening. All conference attendees are welcome to the mixer.

Poster Session Poster Titles and Presenters

- P1. "Crystallization of Pollucite (CsAlSi₂O₆) from Cs-based Geopolymer Precursor"
 Jonathan Bell University of Illinois at Urbana-Champaign
- P2. "Pair Distribution Function Studies of Functional Framework Materials"
 Karena Chapman Argonne National Laboratory
- P3. "Precession Diffraction Investigation of Kinematical Extinctions in Andalusite" James Ciston Northwestern University
- P4. "Development of a Powder X-ray Diffraction Laboratory Module for use in Honors General Chemistry: Identification of Unknown Household Solids Using Powder X-ray Diffraction"
 Molly Gahan Duquesne University
- P5. "The Capabilities and Limitation of Powder X-ray Diffraction in the Characterization of A₂M₃O₁₂ Compounds"
 Stacy Gates
 University Toledo
- P6. "Crystallization Studies of MgZrW₃O₁₂" Amy Gindhart University of Toledo
- P7. "Characterisation of Femtosecond Electron Pulses" Christoph Hebeisen University of Toronto
- P8. "Controlling Particle Size of Negative Thermal Expansion Oxides"
 Leah Kozy
 University of Toledo

Poster Session

Poster Titles and Presenters Continued...

- P9. "Synthesis and Characterization of Diamond-Like Semiconductors" Jonathan Lekse Duquesne University
- P10. "Controlled-Temperature Diffraction Measurements on Samples in Glass Capillaries"
 Brian Litteer PANalytical Inc.
- P11. "Non-hydrolytic" Sol-gel Processing of Transition Metal Sulfides" Nathalie Pedousssaut University of Toledo
- P12. "Steric and Electrostatic Accessibility of H-bond Donor and Acceptor Sites in H-bonding Quaternary Imine Salts" Thomas Emge Rutgers, The State University of New Jersey
- P13. "Light When YOU Need it: SER-CAT's Beamlines at the Advanced Photon Source"
 John Rose Argonne National Laboratory
- P14. "New Generation of Dithiolene Ligands" Barbara Serli Mitasev Duquesne University
- P15. "Monitoring an Unusual Phase Transition in Sodium Monothiophosphate"
 Nathan Takas Duquesne University
- P16. "Crystallography for Undergrads: How Computer Software and Collaborations Can Make it Happen at a Small College" Jason Vohs St. Vincent University

Poster Session

Poster Titles and Presenters Continued...

- P17. "Synthesis of Mixed Substituted Acetylacetonate Complexes: New Single-Source Precursors for Metal Oxide Thin Film Growth"
 Jason Vohs
 St. Vincent University
- P18. "A Charge Density Study of Dienestrol" Eric Yearley University of Toledo
- P19. "Microstructure Evolution of Polycrystalline Mullite System A High Temperature Synchrotron X-ray Diffraction Study" Wonki Yoon University of Illinois at Urbana-Champaign
- P20. "Consensus Policy Statement on Crystallography Education and Training"
 Victor Young United States National Committee for Crystallography
- P21. "Ultra-fast Framing X-ray Detector for Time-Resolved Synchrotron Experiments"
 Guy Barbagelata Bruker AXS

Symposium B In-Situ and Time-Resolved Diffraction Studies Chairs: Robert Von Dreele and Jennifer Aitken

8:55 AM	Opening Remarks
	Jennifer Aitken
	Duquesne University

- 9:00 AM **B1.** "Picosecond Time-Resolved X-ray Crystallography: Watching Proteins Function in Real Time" **Philip Anfinrud** National Institutes of Health
- 9:30 AM **B2.** "In Situ Time-Resolved X-ray Diffraction (TR-XRD) as a Tool for Characterizing Catalysts and Active Sites" Jonathan Hanson Brookhaven National Laboratory
- 10:00 AM Coffee Break
- 10:30 AM **B3.** "Allosteric Action in Real Time: Time-Resolved Crystallographic Studies of a Cooperative Dimeric Hemoglobin" **William Royer** University of Massachusetts Medical School
- 11:00 AM **B4.** "A Double-Lever Mechanism Driving Structural Transitions in Crystalline Silicotitinates Revealed by Combined Time-Resolved X-ray and Neutron Powder Diffraction" John Parise Stony Brook University
- 11:30 AM S3. "In-Situ X-ray Powder Diffraction Analysis of the Reaction System, 2SrCO₃-Fe₂O₃ in Atmospheres of CO₂, Air and Argon"
 I. N. Lokuhewa Ohio State University
- 12:00 PM *Lunch Break*

Friday, October 27

1:30 PM	B5.	"X-ray Powder Diffractometry in High Magnetic Fields" V. K. Pecharsky Ames Laboratory and Iowa State University
2:00 PM	B6.	"Cryopreservation of Protein Crystals: From Art to Science" Robert Thorne Cornell University and Mitegen, LLC
2:30 PM	B7.	"In-Situ, High-Temperature Synchrotron Powder Diffraction Studies of Oxide Systems in Air Using a Thermal-Image Furnace" Waltraud Kriven University of Illinois at Urbana-Champaign
3:00 PM		Coffee Break
3:30 PM	B8.	"Effect of Radiation Damage on Polycrystalline Proteins" Robert Von Dreele Argonne National Laboratory
4:00 PM	B9.	<i>"In Situ</i> Neutron Diffraction Studies of Single Crystals and Powders During Microwave Irradiation" Gavin Whittaker The University of Edinburgh
4:30 PM	S4.	"Using In-Situ High-Temperature Synchrotron Diffraction to Study Dynamic Phenomena in Polycrystalline Material Systems" Ryan Haggerty University of Illinois at Urbana-Champaign
5:00 PM		Adjournment

CONFERENCE DINNER Pittsburgh Marriot City Center Marquis Ballroom C, Second Floor 7:00 – 8:00 PM Social Hour - Drink Tickets and Cash Bar 8:00 PM Banquet, President's Address and Awards Presentations

		Symposium C Challenges of Crystal Twinning Chairs: Victor Young and Jennifer Aitken
8:55 AM		<i>Opening Remarks</i> Victor Young University of Minnesota
9:00 AM	C1.	"Non-Merohedral Twinning in Small Molecule and Protein Crystallography" Regine Herbst-Irmer University of Göttingen
9:30 AM	C2.	"Twinning in Protein Crystals" Zbigniew Dauter Argonne National Laboratory
10:00 AM		Coffee Break
10:30 AM	C3.	"Low-Melting Organic Salts: Phase Transitions, Twinning and Disorder" Victor Young University of Minnesota
11:00 AM	C4.	"The Diagnosis and Treatment of Merohedral and Pseudo- Merohedral Twins: Examples from Chemical Crystallography" Charles Campana Bruker AXS Inc.
11:30 AM	C5.	"Twinned and Modulated Lattices; Strategies for Success" Lee Daniels Rigaku Americas Corp.
12:00 PM		PDS General Membership Meeting
12:05 PM		Lunch Break

Saturday, October 28

SIDHU AWARD LECTURE Peter Chupas Argonne National Laboratory

1:30 PM Opening Remarks and Sidhu Award Thomas Koetzle Argonne National Laboratory

1:35 PM Sidhu Award Lecture "Application of the Pair Distribution Function Method to In-Situ, Time-Resolved and Spatially-Resolved Measurements" Peter Chupas Argonne National Laboratory

> Symposium D Diffraction and Scattering of Amorphous Materials Chair: Peter Wildfong

- 2:25 PM Opening Remarks Peter Wildfong Duquesne University
- 2:30 PM **D2.** "Determination of Fully Hydrated, Fluid Phase Lipid Bilayer Structures and Elastic Properties Using Synchrotron X-Radiation and Diffuse Scattering Analysis" **Stephanie Tristram-Nagle** Carnegie Mellon University

3:00 PM Coffee Break.

3:30 PM **D3.** "Atomic-Scale Structure of Amorphous Materials Using High-Energy X-ray Diffraction **Valeri Petkov** Central Michigan University Saturday, October 28

- 4:00 PM A9. "Structure and Function of Icosahedral Pyruvate Dehydrogenase Complexes" Jacqueline Milne National Institutes of Health
 4:30 PM D4. "Snapshot of the High Throughput Search Lab: Precipitates Rule Our Macromolecular Crystallization World George DeTitta Hauptman-Woodward Institute
- 5:00 PM *Adjournment*



The 64th Annual Pittsburgh Diffraction Conference

ABSTRACTS

OF

PRESENTATIONS

2006 Sidhu Award Lecture – Peter J. Chupas

Application of the Pair Distribution Function Method to In-situ, Time Resolved and Spatially Resolved Measurements

Peter J. Chupas X-ray Science Division Argonne National Laboratory Argonne, IL 60563

Rapid advances in experimental techniques are moving the frontiers of materials characterization into understanding how local atomic structure on the sub-nanometer to nanometer length scales can underpin materials properties. Correlations over these medium-range distances are historically difficult to quantify. Over the last three decades, pair distribution functions (PDFs), obtained by the Fourier transform of scattering data, have been increasingly used to study the nature of local-, intermediate- and extended-range order in glasses, nano-crystalline solids, and liquids. Typically these types of measurements are very time consuming requiring on average 8-12 hours for a single data set to be recorded to the accuracy necessary for Fourier transformation. Recent advances in experimental methodology, combining high energy X-rays (>60 keV) and large area detectors have driven a significant decrease in measurement times from hours to as short as 50 milliseconds. These advances have opened up the possibility of new types of measurements, from studying materials in-situ at high pressures/temperatures, to studying solid state reactions in a time-resolved manner. Furthermore, when focused X-ray beams are combined with sensitive detection, spatially resolved studies of materials with structural variability on the micron scale are feasible. Example of recent types of these measurements will be discussed as well as development of dedicated facilities.

S1. Student Speaker/Travel Award Winner – Eric J. Yearley

A Charge Density Study of Dienestrol

Eric J. Yearley, Elizabeth A. Zhurova, Vladimir V. Zhurov, and A. Alan Pinkerton Department of Chemistry University of Toledo Toledo, OH 43606, USA

In an effort to determine a relationship between the biological function and the electronic properties of steroidal and nonsteroidal estrogens, a charge density study has been pursued on the non-steroidal, synthetic estrogen, dienestrol. Crystals of dienestrol were crystallized from methanol by slow evaporation (Doyle *et al.*, 1975) and x-ray diffraction data then obtained using a Rigaku R-Axis Rapid high-power rotating anode diffractometer with a curved image plate detector at 20.0(1) K. In order to obtain a high amount of redundancy, five runs were collected at 240 sec. with 4^0 images. Adjacent images that overlapped by 2^0 were collected to ensure correct scaling between the images for a total of 89 images per run. The data collection lasted less than two days.

This data collection technique gave a completeness of 99.8% (data up to 0.7Å^{-1}) to a maximum resolution of 1.30Å^{-1} with a redundancy of 8.1 for all data. The data was indexed with the program HKL2000 (Otwinowski & Minor, 1997) and the predicted positions of the reflections were then used for data integration with the program VIIPP (Zhurov *et al.*, 2005; Zhurova *et al.*, 1999). The program SORTAV (Blessing, 1987) was then implemented to scale each run and average equivalent measurements. The use of the program SORTAV (Blessing, 1987) gave R_{int} = 0.0229 for all data and the scales between the runs did not differ more than 4%.

A preliminary refinement has been completed on dienestrol with the Hansen-Coppens multipole model (Hansen & Coppens, 1978) using the program XD (Koritsanszky *et al.*, 1995). A preliminary $R(F^2)$ value of 0.0330 has been obtained. Experimental residual and deformation maps along with a preliminary topological analysis of dienestrol will be reported.

References

Blessing, R.H. (1987). Cryst. Rev., 1, 3-58.

Doyle, T., Stewart, J. M., Filipescu, N., Benson, W. R. (1975). J. Pharm. Sci. 64, 1525-1528.

Hansen, N. & Coppens, P. (1978) Acta Cryst. A34, 909-921.

Koritsanszky, T., Howard, S., Mallison, P.R., Su, Z., Ritcher, T., & Hansen, N.K. (1995). XD. A Computer

Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data. User's Manual. University of Berlin, Germany.

Otwinowski, Z. & Minor, W. (1997) *Methods Enzymol. Macromol. Crystallogr. A*, **276**, 307-326. Zhurov, V.V., Zhurova, E.A., Chen, Y.S., Pinkerton, A.A. (2005) *J. Appl. Cryst.* **38**, 827-829. Zhurova, E.A., Zhurov, V.V. & Tanaka, K. (1999) *Acta Cryst.* **B55**, 917-922.

S2. Student Speaker/Travel Award Winner – Nathan J. Takas

In Situ Neutron Diffraction Studies on the Polymorphs of Sodium Monothiophosphate

Nathan J. Takas and Jennifer A. Aitken Department of Chemistry and Biochemistry Duquesne University Pittsburgh, PA 15282

Oxythiophosphates are a class of chemically interesting compounds which bridge the gap between the technologically useful phosphate and tetrathiophosphate families. Sodium monothiophosphate, Na₃PO₃S, was among the first of these inorganic materials to be discovered, however new and interesting discoveries are still being made regarding the properties of this material.

We report observation of a γ -phase in addition to the α - and β -phases previously confirmed by diffraction techniques. We also report that anhydrous β -Na₃PO₃S can convert to anhydrous α -Na₃PO₃S at room temperature by exposure to atmospheric water. Under vacuum in a differential thermal analyzer, this transition occurs at approximately 300°C. Data acquired at the Intense Pulsed Neutron Source (IPNS) regarding the rate and nature of this humidity-catalyzed transition will be presented. Spectroscopic studies and reactivity of Na₃PO₃S will also be discussed.

In-Situ X-ray Powder Diffraction Analysis of the Reaction System, 2SrCO₃-Fe₂O₃ in Atmospheres of CO₂, Air and Argon

I. N. Lokuhewa¹, P. M. Woodward¹, P. K. Gallagher² and J. P. Sanders³

¹Dept. of Chemistry, The Ohio State University, Columbus, OH 43210, USA

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In-situ X-ray powder diffraction studies have been performed on the system $2SrCO_3$ -Fe₂O₃ in CO₂, air and in Ar atmospheres from room temperature to 1175 ^oC. The study reveals a complex reaction pathway that is markedly different in carbon dioxide and air. The complexity is due to the variable oxidation state of iron, the atmosphere dependent stability of SrCO₃, the presence of transient phases, and the observation of several different types of oxygen vacancy ordering in SrFeO_{3-x} phases. The dominant product at high temperature in all atmospheres is the cubic perovskite SrFeO_{3-x}. However, upon cooling back to room temperature in an atmosphere of either carbon dioxide or argon, SrFeO_{3-x} transforms to the end member of the family that has lowest oxygen content, Sr₂Fe₂O₅ which adopts the Brownmillerite structure. Orthorhombic SrCO₃ that has *Pmcn* symmetry transforms to *R-3m* at 900 ^oC in both CO₂ and air, but the reaction with Fe₂O₃ begins at a lower temperature in air. In contrast, in Argon, SrCO₃ transforms to the highly reactive SrO before transforming to the rhomobohedral phase. This speeds the reaction with Fe₂O₃. Another difference with the CO₂ atmosphere is the formation of an oxycarbonate phase Sr₄Fe_{2.6}O_{8.2}(CO₃)_{0.4} at high temperature. This phase has *I4/mmm* symmetry and a structure that is related to the *n*=3 Ruddlesden-Popper structure.

Using In-situ High-Temperature Synchrotron Diffraction to Study Dynamic Phenomena in Polycrystalline Material Systems

R.P. Haggerty, P. Sarin, W. Yoon, J.L. Bell, M. Gordon and W.M. Kriven Department of Materials Science and Engineering University of Illinois at Urbana-Champaign, IL 61801

Time resolved x-ray diffraction experiments on polycrystalline samples impose stringent requirements on a detector system. While brief exposure times are possible using synchrotron radiation without compromising the S/N ratio in diffraction data, a shorter data readout time can also enhance temporal resolution. In addition wide angular (2) range and large dynamic range are other desirable attributes for a detector which enable recording of diffraction data for several peaks of different intensities. Angular resolution is also critical for distinguishing peaks and for gaining information from the peak shapes (e.g. grain size or dislocation density). A fast 1-D curved image plate (CIP) detector has been configured and together with a quadrupole lamp furnace (QLF) was used to study dynamic behavior of powder samples, in-situ at high temperatures. The CIP detector has an angular coverage of $\sim 40^{\circ}$ 2 , a fast readout time (~ 20 s) and high angular resolution (FWHM $< 0.006^{\circ} 2$). The CIP detector was used in conjunction with the QLF to study oxidation behavior of borides (TiB₂ and ZrB₂) as well as the kinetics of amorphous to crystalline transition of a geopolymer powder to pollucite (Al₂O₃·Cs₂O·4SiO₂) to examine the time resolution and phase identification capabilities of this detector. Furthermore, the high resolution afforded by the CIP detector was suitably used to study the microstructural evolution of sintered polycrystalline mullite (3Al₂O₃·2SiO₂) samples under isothermal conditions up to 1700°C in air. The anisotropic grain growth of templated mullite samples was studied insitu at high temperatures along various crystallographic directions and was characterized by the rate of change in the corresponding peak width. These examples underscore the potential applications of the QLF + CIP detector combination, and demonstrate the usefulness of in-situ diffraction in developing fundamental understanding of mechanisms as well as quantifying the kinetics of such phenomena.

A1. Femtosecond Electron Diffraction: "Making the Molecular Movie"

R. J. Dwayne Miller Departments of Chemistry and Physics Institute for Optical Sciences University of Toronto Toronto, Ontario, Canada, M5S 3H6 dmiller@lphys.chem.utoronto.ca

The picosecond barrier to high brightness electron pulses has been broken.

Femtosecond Electron Diffraction harbours great potential for providing atomic resolution to structural changes as they occur, essentially watching atoms move in real time – directly observe transition states. This experiment has been referred to as "making the molecular movie" and has been previously discussed in the context of a gedanken experiment. With the recent development of femtosecond electron pulses with sufficient number density to execute nearly single shot structure determinations, this experiment has been finally realized. A new concept in electron pulse generation was developed based on a solution to the N-body electron propagation problem involving up to 10,000 interacting electrons. This study determined the conditions for a new generation of extremely bright electron pulsed sources that minimizes space charge broadening effects, specifically for high time resolution applications in molecular imaging. This development represents a significant advance that has taken a gedanken experiment to reality. It is now possible to atomically resolve transition state processes. In this context, an atomic level view of melting has been obtained under strongly driven conditions for Al in which the process can be described within a thermally accessed barrier crossing. Subsequent studies of Au have helped further elucidate the mechanism for the melt zone propagation. In addition to this line of study, applications to specific molecular systems will be discussed in the context of directly imaging reaction dynamics at the atomic level of inspection.

A2. Precession Electron Diffraction

L. D. Marks Department of Materials Science and Engineering Northwestern University Evanston, IL 60201

An electron diffraction technique that has recently garnered considerable interest, precession electron diffraction, has been a promising development in diffraction-based crystallographic methods because it reduces the severity of the dynamical diffraction problem in the TEM. The method involves conically rocking the illuminating electron beam, sequentially tracing out a path of tilts that avoid exciting the zone axis condition. The diffracted intensities are then de-scanned in a complementary fashion to bring the deflected beams to the location on the collection medium where the equivalent on-zone (non-tilted) spots would be. This talk will focus on describing both some of the practical elements of precession diffraction, for instance the improvement in the quality of the qualitative diffraction data, as well as understanding it in terms of systematic row conditions.

A3. Electron Backscattering Diffraction - EBSD: Crystallography in the Scanning Electron Microscope

Alwyn Eades Department of Materials Science and Engineering Lehigh University

The scanning electron microscope (SEM) has been a powerful instrument for materials characterization because of the way it can combine high-resolution imaging with compositional analysis through energy dispersive x-ray analysis (EDS). In recent years the value of the scanning electron microscope has been further increased by the addition of crystallographic analysis to the techniques available. Electron backscattering diffraction (EBSD) is a powerful and valuable addition to the methods available for materials characterization. The talk will cover the fundamentals of the technique, examples of applications, and future prospects.

A4. Atomic Structure of Nanotubes and Nano-Clusters

Jian-Min (Jim) Zuo Department of Materials Science and Engineering and F. Seitz Materials Research Laboratory University of Illinois, Urbana-Champaign jianzuo@uiuc.edu



(left) A single double wall nanotube is illuminated with a narrow beam of electrons. (right) The diffraction pattern of the tube

This talk will introduce the new science of atomic structure of nanomaterials and their significance to our new understanding about properties and growth of these materials. Nanotubes and metallic nanoclusters will be used as examples of study. Nanotubes, in particular of single wall carbon nanotubes, have been one of major focus areas of nanoscience and nanotechnology research because of their remarkable electrical and mechanic properties. However, the electric properties of carbon nanotubes (CNT) are very sensitive to small structural differences. Metallic nanoclusters are important catalyst for energy and environmental applications. The atomic structure of metal clusters can be very different from bulk crystals. Information mostly comes from HREM. Consequently, our understanding of these structures is subjected to the limitations of atomic resolution imaging.

Recently, we have developed a new electron diffraction technique, nanoarea electron diffraction (NED), which is capable of structure determination of individual nanotubes and clusters using a nanometer-sized, coherent, parallel electron beam. We will illustrate the potential of this technique for atomic structure determination. The talk is divided into three parts. The first part will cover structure determination of single and double wall carbon and multiwall boron nitride nanotubes. The second part will focus on our efforts to obtain atomic resolution images from coherent diffraction patterns and its potential to image defects in individual nanoclusters. The last part of this talk highlights other materials science problems that can be addressed by NED.

A5. Studies of Ligand Binding to Tubulin by Electron Crystallography

Kenneth H. Downing Life Sciences Division Lawrence Berkeley National Lab Berkeley, CA 94720

The electron crystallographic structure of tubulin bound to the anti-cancer drug Taxol (1,2) revealed both the structure of the tubulin dimer and the nature of the Taxol binding site on tubulin. A number of other compounds with widely differing structures are now known that, like Taxol, stabilize microtubules. We are studying several of these, including epothilone, eleutherobin and discodermolide, and have collected 3-D electron diffraction data sets of each to around 2.8 A. Competitive binding measurements indicate that these compounds hare a common binding site on tubulin, and indeed our difference maps show that they all bind in the same area as Taxol. However, the limited resolution of the tubulin-Taxol crystal structure, 3.5 Å, has required development of refinement and modeling procedures in order dock the drugs accurately enough to make chemical sense of the interactions. Many candidate ligand structures are tested for their fit to the experimental data by docking in orientations compatible with the density map. followed by structure refinement against the diffraction data. This approach converged to a stable solution for the epothilone-tubulin structure (3) that is consistent with a wealth of SAR data.

(1) E. Nogales et al., Nature **391** 199 (1998)

- (2) J. Löwe et al., J. Mol. Biol.. 313 1045 (2001)
- (3) J.H. Nettles et al., Science **305** 866 (2004)

A6. Electron Crystallography of the Ca²⁺-ATPase and Phospholamban Inhibitory Complex

Howard Young Department of Biochemistry University of Alberta

Phospholamban (PLB) physically interacts with Ca²⁺-ATPase and regulates contractility of the heart. We have studied this interaction using electron microscopy of large two-dimensional cocrystals of Ca²⁺-ATPase and the I40A mutant of PLB. Crystallization conditions were derived from those previously used for thin, helical crystals, but the addition of a 10-fold higher concentration of magnesium had a dramatic effect on the crystal morphology and packing. Two types of crystals were observed, and were characterized both by standard crystallographic methods and by electron tomography. The two crystal types had the same underlying lattice, which comprised antiparallel dimer ribbons of Ca²⁺-ATPase molecules previously seen in thin, helical crystals, but packed into a novel lattice with $p22_12_1$ symmetry. One crystal type was single-layered, whereas the other was a flattened tube and therefore double-layered. Additional features were observed between the dimer ribbons, which were substantially farther apart than in previous helical crystals. We attributed these additional densities to PLB, and built a threedimensional model to show potential interactions with Ca²⁺-ATPase. These densities are most consistent with the pentameric form of PLB, despite the use of the presumed monomeric I40A mutant. Furthermore, our results indicate that this pentameric form of PLB is capable of a direct interaction with Ca²⁺-ATPase.

Stokes, D., Pomfret, A., Rice, W., Glaves, J., and Young, H. (2006) Interactions between Ca²⁺-ATPase and the pentameric form of phospholamban in two-dimensional co-crystals. *Biophysical Journal* **90**:4213-23.

A7. Commensurate and Incommensurate Superstructures in Polytelluride Compounds with Square Nets: Are they "Everywhere"?

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Many low-dimensional metal polytelluride compounds contain layers made of square lattice networks composed of Te atoms. The properties of these materials are largely influenced by the behavior of these square nets, and by their interaction with the remaining part of the structure. A fair number of examples are known for tellurium, e.g. $RETe_2$, RE_2Te_5 , and $RETe_3$, as well as more complex compounds such as $K_{0.33}Ba_{0.67}AgTe_2$. These square Te nets have unstable electronic structures that can lead to structural distortions or charge density wave (CDW) phenomena. The CDWs are often incommensurate and the crystallography of these phases can be rather challenging requiring a combination of electron diffraction and superspace approaches. In fact, the correct structure resolution of these compounds is such a complex issue that even superspace approaches can be inadequate in giving the correct picture. These studies need to be complemented with pair distribution function analysis and possibly other experimental techniques. The crystallographic details of observed modulations in these polytelluride compounds will be reviewed and discussed.

A8. Fluctuation Electron Microscopy: Mixing Real and Reciprocal Space to Reveal Nanoscale Order in Amorphous Materials

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In fluctuation electron microscopy, we use electron nanodiffraction in a TEM to study nanoscale structural order in amorphous materials. A single nanodiffraction pattern encodes two-body correlations, but the statistical distribution of intensities from many such patterns acquired from different volumes of the sample encodes three- and four-body correlations. Fluctuation microscopy reveals structures at two lengths scales: an atomic pair spacing set in reciprocal space by the momentum transfer, and a cluster size of correlated atomic pairs set in real space by the size of the probe. Fluctuation microscopy has revealed new structure in amorphous semiconductors, oxides, and metals. This talk will highlight recent work on structural order in amorphous metals which controls nucleation and recrystallization.

A9. Structure and Function of Icosahedral Pyruvate Dehydrogenase Complexes

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Understanding how multi-component molecular machines function and mapping their location within the dynamic and fluid architecture of cells are emerging frontiers in cell biology. Combining atomic structural information of individual proteins with high resolution electron microscopy is increasing powerful given advances in the latter in imaging large and dynamic complexes not amenable by NMR or X-ray crystallographic techniques, in obtaining three-dimensional reconstructions with resolutions better than 10 Å resolution and the development of more powerful algorithms to dock X-ray structures into density maps obtained by electron micrographic analysis of individual molecular complexes *in vitro*, or *in vivo* by tomographic analysis.

We have used cryo-electron microscopy to study the architecture of the multifunctional pyruvate dehydrogenase complex, which couples the activity of three component enzymes (E1, E2, and E3) in the oxidative decarboxylation of pyruvate to generate acetyl CoA, a key metabolic intermediate. We have determined the three-dimensional structures at ~ 27 Å resolution for two giant icosahedral pyruvate dehydrogenase complexes from *B. stearothermophilus* using electron cryo-microscopy: one is an 11 MDa complex composed of 60 copies of E1 and E2 enzymes, and the other is a 9 MDa complex composed of 60 copies of E2 and E3 enzymes. By positioning the previously determined structures of E1, E3 and the three domains of E2 into the model, we have arrived at atomic interpretations for the entire E1E2 and E2E3 complexes. These are among the largest non-viral protein complexes for which such atomic models are available, and they provide unique insights into the functional mechanism of a fascinating cellular machine that remains inaccessible to structural analysis by X-ray crystallography. The inner linkers of E2 appear to serve a critical role in maintaining the size and shape of the complex. Related work on obtaining a high resolution map of the E2 catalytic core using computional sorting to identify the best individual molecular images will also be presented.

B1. Picosecond Time-Resolved X-ray Crystallography: Watching Proteins Function in Real Time

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Proteins execute their designed function with exquisite selectivity and efficiency. Understanding how a particular protein functions requires knowledge not only of its static structure, but also of its conformational evolution as it executes its function. Myoglobin (Mb), a ligand-binding heme protein found in our muscle tissue, has long served as a model system for investigating the relations between protein structure, dynamics, and function. Flash photolysis of the carbon monoxide adduct (MbCO) liberates CO from the heme binding site, promptly producing a welldefined reactive state. We have used time-resolved X-ray crystallography to probe the structural changes that ensue after photolysis. Three-dimensional electron density maps, reconstructed from time-resolved X-ray diffraction "snapshots," have been stitched together into movies that unveil, with < 2-Å spatial resolution and 150-ps time-resolution, the correlated protein motions that accompany and/or mediate ligand migration within the hydrophobic interior of the protein. The structural dynamics of wild-type and several engineered mutants of myoglobin (Mb) have been compared, and their differences provide a structural explanation for their markedly different ligand binding dynamics. The ability to witness correlated protein motion in real time with nearatomic resolution deepens significantly our understanding of the relationships between protein structure, dynamics, and function.

B2. In Situ Time-Resolved X-Ray Diffraction (TR-XRD) as a Tool for Characterizing Catalysts and Active Sites

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The development of techniques for characterizing the structural properties of catalysts under the high-pressure conditions of industrial processes is widely recognized as a top priority in the area of heterogeneous catalysis. At the NSLS beam line X7B, we have put together a facility capable of conducting *in situ*, sub-minute TR-XRD experiments under a wide variety of temperature and pressure conditions (80 K <, T < 1250 K; 1 Torr <P< 150 atm)[1] Current measurements also include control of gas flow and measurement of gas composition of the products with mass spectrometry. This important advance results from combining the high intensity of synchrotron radiation with new parallel data-collection devices.

Using TR-XRD, one can obtain information about structural details, phase composition, kinetics of transformation, intermediate phases and crystal characteristics. Examples of problems studied to date with TR-XRD include: (1) Substrate binding of zeolites[2]; (2) reduction/oxidation of oxide catalysts[3]; (3) Water Gas Shift reaction with Copper[4] and Gold [5]supported on cerium oxide; (4) Synthesis of Manganese oxide catalysts[6].

The work at BNL was supported through contract DE-AC02-98CH10086 with the US DOE, Office of Basic Energy Sciences. The work at the APS was supported by the US DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

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B3. Allosteric Action in Real Time: Time-resolved Crystallographic Studies of a Cooperative Dimeric Hemoglobin

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The ability of allosteric protein molecules to alter their structures in response to ligand binding provides an important regulatory mechanism. Despite the availability of static structures of different states in a number of allosteric proteins, information about the kinetic pathway between such alternate states is limited. Time-resolved crystallographic analysis provides tools to obtain direct time-dependent structural information at high resolution on the entire protein molecule. We have carried out nanosecond time-resolved diffraction experiments on single crystals of Scapharca dimeric hemoglobin, a protein whose alternate states show strong functional differences, despite relatively localized transitions that are compatible with the crystal lattice. Our results provide an unprecedented view of global allosteric protein transitions as they proceed from 5ns to 80 s. Within 5ns of the photolytic release of ligands, an intermediate forms as Rstate protein subunits respond to the presence of unliganded heme groups. Transition to this intermediate involves structural changes in the heme groups, neighboring residues and interface water molecules. The intermediate changes very little during the ns time-domain and lays a foundation for apparently concerted tertiary and quaternary structural changes that occur on a microsecond time scale and are associated with the transition to a low affinity T-state structure. Persistence of a T-state structure even after ligands rebind suggests a slow T to R transition that may result from the greater dimeric stability in the T-state.

B4. A Double-Lever Mechanism Driving Structural Transitions in Crystalline Silicotitinates Revealed by Combined Time-Resolved X-Ray and Neutron Powder Diffraction

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The crystal structure of the selective Cs^+ ion exchanger $H_2Ti_2SiO_7$ · 1.5H₂O, known as crystalline silicotitanate or CST, has been determined in situ in both native (D-CST) and in the Csexchanged forms (Cs,D-CST) from angular dispersive (AD) X-ray and neutron powder diffraction and from time-of-flight neutron diffraction studies. After Cs⁺ exchange to the maximum capacity allowed by the structure, D-CST transformed from one configuration with unit cell parameters a=11.0704(3)Å c=11.8917(5)Å and space group $P4_2/mbc$, to one with a=7.8902(1)Å c=11.9051(4)Å and space group $P4_2/mcm$. Rietveld structure refinements of both D-CST and Cs,D-CST suggest the transition, and ultimately the selectivity, is driven by changes in the positions of water molecules, in response to the initial introduction of Cs⁺. The changes in water position disrupt the near linearity of the D-O-O-D torsion angle associated with the CST framework in space group P_{4}/mbc that ultimately leads to the structural transition. The new geometric arrangement of the water-deuteroxyl network in Cs,D-CST suggests that D_{water}- $D_{deuteroxyl}$ repulsion forced by Cs⁺ exchange drive the structural transformation. The experimentally determined mechanism, supported by independent molecular dynamics simulations, therefore involves a "double-lever" (see figure below). Initial introduction of Cs causes rearrangement of a water molecule (the first "lever" indicated by the curved arrow) and subsequent repulsion of a proton attached to the titinate framework. Displacement of this second "lever", indicated by the straight arrow, causes a structural phase transition in the framework, which makes available another site for Cs-exchange.



Illustration of the dynamic interactions of Cs2 with water and hydroxyl derived from use XN powder diffraction and calculated from MD. The results of the MD simulation are shown here. Upon Cs+ exchange, water is forced to rotate close to the framework, and as a result the hydroxyl bends away from the approaching water. Grev atoms and bonds are the before H+ positions, blue atoms and bonds are the after H+ positions. The neutron diffraction investigations carried were out using deuterated samples to minimize incoherent scattering.
B5. X-ray Powder Diffractometry in High Magnetic Fields

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Temperature and/or pressure induced polymorphism is common compared to structural rearrangements triggered by a magnetic field. While the former is routinely probed in-situ by temperature and pressure dependent powder diffraction, the most common tools employed in detecting magnetic field induced polymorphic transformations are bulk field-dependent measurements of the physical properties, such as strain, electrical resistance and magnetization. On one hand, discontinuities in the behavior of these macroscopic properties serve as suitable evidence of a crystallographic phase transition, but on the other hand, they provide no clues about the atomic-scale mechanism. By successfully coupling a rotating anode powder diffractometer with a continuous-flow cryostat and a split-coil superconducting magnet we are now capable of obtaining excellent, Rietveld-quality powder diffraction data between 2.5 and 320 K in 0 to 4 T magnetic fields. A typical experiment can be carried out in ~10 minutes (usually sufficient to quantify phase content and determine changes in unit cell parameters) or in a few hours (if detailed information about individual atomic parameters is required). Both subtle and massive magnetic field-induced structural changes can be detected, providing much needed structural data in order to develop a better understanding of structure-property relationships of solids.

This research was supported by the Division of Materials Science of the Office of Basic Energy Sciences of the US DOE under contract No. W-7405-ENG-82.

B6. Cryopreservation of Protein Crystals: From Art to Science

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There are two limiting approaches to cryopreservation. One is to cool slowly in the presence of large cryoprotectant concentrations, allowing full relaxation and equilibration of sample constituents so as to achieve a homogeneous low-temperature state. The other is to cool so quickly that the high temperature state is frozen in [1]. Previous studies have shown that cooling rates achieved in cryopreservation of protein crystals are 10^3 K/s or less [2], in neither of these favorable limits. This produces inhomogeneities within the crystal that correlate with degradation of mosaicity and resolution [3]. We describe experiments showing that, for plunge cooling in liquid nitrogen and propane and for sample volumes less than 0.1 ml — i.e., for the sample volume range of interest in protein crystallography — most cooling occurs in the cold gas layer above the liquid cryogen, before the sample ever reaches the liquid [6]. By removing this cold gas layer, cooling rates are increased to $>1.5 \times 10^4$ K/s, with even larger cooling rates possible with smaller samples. Glycerol concentrations required to eliminate ice crystallization in protein-free aqueous mixtures drop from $\sim 28\%$ [4,5] to less than 5%. These results will allow many crystals to go from crystallization tray to liquid cryogen to X-ray beam with no intervening cryoprotectant screening, and should yield consistent increases in the maximum achievable resolution. By reducing or eliminating the need for cryoprotectants in growth solutions, they may also simplify the search for crystallization conditions and for optimal screens. Our results resolve many puzzles, such as why plunge cooling in liquid nitrogen or propane has — until now — not yielded significantly better diffraction quality than gas stream cooling.

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B7. In-situ, High-temperature Synchrotron Powder Diffraction Studies of Oxide Systems In Air Using A Thermal-image Furnace

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Ceramics are the materials of choice for use in extremely demanding high temperature applications. It is important to understand the behavior and performance of ceramic materials in their anticipated working environment. In this talk a novel methodology for high temperature X-ray diffraction (XRD) using a quadrupole lamp furnace and synchrotron radiation will be presented. This apparatus allows experiments to be conducted *in air* up to 2000°C. The reliability, accuracy and the reproducibility of the method will be demonstrated using standard materials. Examples will be presented to illustrate the advantages of this technique over other methods in understanding structural phase transformations in materials, as well as in the development of advanced materials with customized properties.

A new Curved Image Plate Detector (CIPD) has been designed for x-ray diffraction investigations of ceramics using synchrotron radiation. It has been configured primarily for use with the Quadrupole Lamp Furnace (QLF). The CIPD in conjunction with QLF has enabled rapid acquisition of high resolution x-ray diffraction (XRD) patterns for studying in situ, advanced materials at ultra-high temperatures in air. Various in-situ high temperature XRD investigations that are now possible include (a) structural phase transformations e.g. martensitic or reconstructive, (b) crystallographic thermal expansion behavior, (c) microstructural evolution with temperature, (d) chemical reaction kinetics e.g. of binary and ternary mixtures of ceramic materials, oxidation studies of non-oxide ceramics such as borides, and (e) phase equilibria and phase diagrams based upon them. Selected results will also be presented on the above listed applications. We anticipate that the advantages of the CIPD + QLF setup along with the intense parallel x-ray beam available at synchrotron sources will revolutionize the way in which in situ, ultra-high temperature XRD studies are performed.

B8. Effect of Radiation Damage on Polycrystalline Proteins

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The effect of radiation exposure on proteins is an inherent problem for structural studies by x-ray diffraction. Powder diffraction provides a possible means for study of this phenomenon because the entire diffraction pattern can be collected in a single exposure, thus facilitating exploration of the time series effect of radiation. Although it is generally recognized that radiation exposure induces lattice expansion, detailed effects can be more complex particularly at low doses. We will explore these effects for hen egg white lysozyme where the low dose lattice variations may arise from shifts in solvent chemistry rather than inherent crystal damage effects.

B9. In Situ Neutron Diffraction Studies of Single Crystals and Powders During Microwave Irradiation

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Microwave dielectric heating has become an important method in chemical synthesis and materials processing over the past 15 years, and in the case of the reactions in solutions, there is a well-developed understanding of heating mechanisms and their influence on reaction rate. In the solid-state there is much less clarity, despite the advantages to be gained from better insight into the way in which such electromagnetic radiation may couple directly to charge carriers, accelerating reactions in good conductors. The related issue of the influence of microwave irradiation on biological systems, in particular proteins, and the way in which this may pose hazards to health is similarly poorly understood despite the obvious relevance this may have to the current debate on the influence of electromagnetic radiation - in particular microwave transmission – on human health. One reason for the paucity of fundamental insight in both fields is because most work has been performed with microwave equipment whose design is derived from that of a domestic oven, and which is not ideal for *in situ* studies of microwave driven processes. A second reason is that there are few analytical methods that allow insight into the motions of atoms or ions within bulk materials. In an effort to address this, we have been developing new methods of irradiating a variety of solid samples, whilst measuring structural parameters through a range of diffraction techniques. We here describe apparatus that will enable X-ray or neutron scattering measurements to be performed on powders or single crystals under microwave irradiation with controlled power level. We also describe preliminary studies of a single crystal of the molecular solid Aspirin, a powder of the microwave-susceptible ionic material BaTiO₃, and of model MoS₂-Alumina supported catalysts during microwave irradiation.

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C1. Non-merohedral Twinning in Small Molecule and Protein Crystallography

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In contrast to twinning by merohedry the reciprocal lattices of the different domains of nonmerohedral twins do not overlap exactly. So only part of the reflections are affected by the twinning. This will often become apparent during data collection. If both twin domains are similar in size, there are often problems with the cell determinations and usual automatic indexing programs fail. But nowadays there are several programs that can deal with such kinds of problems [1], [2], [3]. With these programs it is possible to find two (or even more) orientation matrices that lead to the same cell constants.

In principle two different integration procedures are possible. The simpler one would be to integrate with all orientation matrices separately in different runs. This leads to three kinds of reflections: the reflections with no overlap, the reflections with an exact overlap, and the reflection with a partial overlap of a reflection of a second domain. A better way of integration is to use all orientation matrices in one step. Then the whole intensity of every reflection is integrated and we only have non- or exactly overlapped reflections [4], [5].

A special program for scaling and absorption correction is necessary to handle such data sets [6].

Small molecule and protein structures refined with data sets generated by this integration process will be presented. Taking non-merohedral twinning into account is only possible using a special data file that distinguishes between non-overlapped and exactly overlapped reflections [7].

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C2. Twinning in Protein Crystals

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Merohedral or pseudomerohedral twinning, very well known in small-structure crystallography, for long time has been treated by macromolecular crystallographers as a sort of incurable disease and only relatively recently more papers dealing with this phenomenon appeared in the literature. Although the underlying principles of twinning in the small and large structures are identical, the methods of its practical identification and treatment differ to some extent, related in part to the different methods of structure solution. Taking into account that most of protein structures are currently solved by the Single- or Multiwavelength Anomalous Diffraction methods (SAD or MAD), of particular importance is the influence of twinning on the measurability of the naturally rather weak anomalous signal. It appears that in some cases the structures of even highly twinned crystals can be solved by Molecular Replacement or anomalous methods. The Isomorphous Replacement methods may be even more challenging, since (in contrast to previous techniques) they rely on diffraction data measured from several crystals with potentially different twinning fractions. Various aspects of twinning of protein crystals will be discussed and illustrated by practical examples.

C3. Low-Melting Organic Salts: Phase Transitions, Twinning, and Disorder

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Low-melting organic salts often exhibit complex temperature-dependent properties. Below melting temperatures these are best described as crystalline materials with liquid-like properties where some or all of the cations and/or anions are disordered. At yet lower temperatures, as monitored by DSC, these undergo stepwise phase transitions to ordered systems where some are twinned by non-merohedry and have high Z' structures. Many of these have intermediate phases with both ordered and/or disordered species. For example,¹ the salt PYR₁₂TFSI undergoes four known solid-solid phase transitions before melting at 91°C. At -120°C, the crystal structure consists of ordered ions (Phase IV). This crystal structure is found in space group P2₁/n with Z'=2 as a non-merohedral twin. Above the phase transition at -85°C all of the PYR₁₂⁺ and TFSI ions become disordered forming a plastic crystalline phase (Phase III). This crystal structure is found in space group P₁ with Z'=1 as a non-merohedral twin. The crystal structures of both Phase II and Phase I have not been determined due to their inherent liquid-like properties. The structures and phase behavior of several new low-melting organic salts will be presented in this paper.

¹ Wesley A. Henderson, Victor G. Young, Jr., Stefano Passerini, Paul C. Trulove, and Hugh C. DeLong, Chem. Mater. (2006) **18**, 934.

C4. The Diagnosis and Treatment of Merohedral and Pseudo-Merohedral Twins: Examples from Chemical Crystallography

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Within the last 15 years, advances in X-ray crystallographic instrumentation and software have made single crystal structure determination one of the most important physical characterization techniques available to chemists. With current commercial instrumentation and software, publication quality crystal structures may now be routinely carried out in a few hours on a large majority of chemical compounds, using default parameters and/or automatic software.

However, there still remain a relatively small portion of non-routine structures which require crystallographic knowledge and the use special techniques in order to successfully complete the analysis. The application of these advanced data analysis techniques allows many of types of previously intractable crystallographic problems (e.g., twinned and disordered structures) may now be routinely solved with commonly available software [1-5].

This presentation will use a diagnostic approach to solution and refinement of problem structures, with special emphasis on the analysis of merohedrally and pseudo-merohedrally twinned datasets. This approach will be illustrated with numerous examples taken from the field of chemical crystallography.

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C5. Twinned and Modulated Lattices: Strategies for Success

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In the days of serial detectors, perhaps only the cleverest could hope to index a unit cell from a twinned crystal. The rest of us solved the problem by throwing the crystal away and moving to another sample! Today we're blessed to have marvelous hardware and software tools that allow twin handling with relative ease. We can "detwin" – but what considerations are important? What strategies should be applied to increase the chance of success? Tips and techniques will be offered for discussion.

An entirely different challenge is offered by crystals that exhibit packing characteristics that go beyond the 230 ways that we know and love. But some of the strategies for twins are applicable to the handling of modulated structures, including indexing the main lattice and the determining the q-vectors followed by integrating the intensities of these samples. A straightforward approach will be described.

D1. X-ray Amorphous and Disordered Crystalline Pharmaceutical Materials: Characterization Using X-ray Powder Diffraction

Simon Bates SSCI-Inc

Amorphous and disordered pharmaceutical materials pose a significant challenge to the development of acceptable products. In general, they may have some attractive properties like increased solubility, but these properties are highly dependent on processing, and in addition physical and chemical stability is usually a concern. X-ray powder diffraction (XRPD) measurements taken during cryo-grinding experiments performed on pharmaceutical API material have revealed two very different disordering processes. The first is a discreet thermodynamic disordering process that occurs when a crystalline material looses symmetry operators (translation, orientation, conformation) to become a mesophase or thermodynamic amorphous material into defected crystalline material eventually producing short range order and a kinetic glassy state. Under continued disordering, the kinetic glassy material may transform into the thermodynamic amorphous state. Examples will be presented from cryo-grinding and dehydration studies that demonstrate modeling of XRPD data, pair wise distribution functions (PDF) and a new disordered material characterization scheme.

D2. Determination of Fully Hydrated, Fluid Phase Lipid Bilayer Structures and Elastic Properties Using Synchrotron X-Radiation and Diffuse Scattering Analysis

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All living membranes contain an underlying lipid bilayer in the fully hydrated, fluid phase. Since these samples are fully hydrated, they exhibit thermal fluctuations which diminish the long-range order that occurs with dehvdrated lipid bilavers. Instead of discrete Bragg reflections, we observe cloud-like diffuse data resulting from disorder between bilayers and bending of individual bilayers. The Nagle lab uses synchrotron x-radiation at 10.4 keV at the Cornell High Energy Synchrotron Source (CHESS) and two sample preparations to determine structures of pure lipid bilayers and inclusions, yielding areas/lipid at a precision level of ± 0.5 $Å^2$. X-ray diffuse scattering from unilamellar vesicles (ULV) occurs at q values from 0.05 to 0.2 Å^{-1} , and from 0.1 to .9 Å⁻¹ for oriented stacks. This guasi-long range order is analyzed using liquid crystal theory modified for oriented samples (Lyatskaya et al., 2001) that contains the height-height pair correlation function in the structure factor. As part of the structure factor calculation the membrane bending modulus, Kc, and the compression modulus, B, are determined, i.e., there is more information in the diffuse scatter than in the peaks! We have now determined the structures of 11 fluid phase lipids, (DOPC with cholesterol) and 8 gel phase lipids, which are of interest to molecular dynamics simulators to check their potentials. Results showing the relation of structure and elastic properties to water permeability, and to peptide interactions with membranes will be shown. (Lvatskava et al., 2001, Phys. Rev. E 63:011907:1-9). Supported by NIH grant GM44976.

D3. Atomic-Scale Structure of Amorphous Materials Using High-Energy X-ray Diffraction

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Knowledge of the three-dimensional (3D) atomic structure is an important prerequisite to understanding and predicting properties of materials. It is usually obtained by diffraction experiments and, in the case of amorphous materials, described in terms of the so-called atomic pair distribution functions (PDF). The PDF peaks at real space distances where interatomic distances occur thus enabling convenient testing and refinement of 3D structural models. Hence, the better the quality of the experimental PDF data, the more accurate the structure knowledge/model is. Recently, a real progress has been made in deriving high quality, high-resolution PDFs using high-energy x-ray diffraction (XRD). The high flux of high energy (~ 100 keV) x-rays delivered by third generation synchrotron sources and improved detectors made it possible to resolve structural features that are only 0.15 Å apart. In the talk, the great potential of high-energy XRD in studying amorphous materials will be discussed and illustrated with examples from recent experiments on inorganic glasses such as SiO₂ [1] and GeSe₂ [2]. Results from high-energy XRD studies on a new class of heavily disordered materials, the so-called "nanocrystals", such as (Polyaniline)xV₂O₅.nH₂O nanocomposites [3], PAMAM polymeric macromolecules [4] and metallic nanoparticles [5] will be shown as well.

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D4. A Snapshot of the High Throughput Search Lab: Precipitates Rule Our Macromolecular Crystallization World

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Over the last six years we have received over 7500 proteins from the structural biology and structural genomics communities. For each protein we have conducted 1536 chemically distinct crystallization experiments using the microbatch-under-oil method. After setup, each experiment is recorded by digital videomicroscopy, yielding six images captured from the time of setup until four weeks after setup.

Due to the high work load we have actually examined only a small percentage of the nearly 70 million images recorded in the lab. Recently we randomly selected 96 proteins for careful analysis. The proteins were submitted by 94 structural biology investigators in 2005; they span a molecular weight range of 10 - 2000 kDa. The 1536 images for each protein, recorded either 1,2,3 OR 4 weeks after setup, were classified in one (or more) of seven simple categories: clear drops, phase separation, precipitate, skin formation, crystals, garbage, and unsure. Each image was classified by three observers. Of the 147, 456 images examined, 70,465 images were identically classified by all three observers; an additional 64,674 images were identically classified by two of the three observers.

The following observations were made for those images scored identically by three observers. Three simple categories (clear drops, phase separations, precipitates) and one compound category (precipitate AND skin formation) account for 97% of the outcomes. By far, precipitates (41.7%) and clear drops (41.2%) account for the lion's share of outcomes. In contrast, crystals (alone or in combination with other categories) account for just 0.38% of all outcomes. In our hands, crystallization is by any measure a rare event. Fortunately, crystals appear in one or more of the 1536 chemical cocktails in 51 of the 96 proteins, meaning that for 51% of the proteins examined we were able to return a crystallization lead for optimization to the structural biologist. At first blush it appears that examination two weeks after setup has the best chance of revealing crystals (16 of 24) while examination three weeks after setup has the worst chance (10 of 24).

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P1. Crystallization of Pollucite (CsAlSi₂O₆) from Cs-based Geopolymer Precursor

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Geopolymers are a new class of ceramic materials which are best understood as rigid, inorganic, aluminosilicate, hydrated gels, charge-balanced by cations such as Na^{+1} , K^{+1} , or Cs^{+1} . These materials are x-ray amorphous and convert to crystalline ceramic phases upon heating. In this study, the crystallization behavior of $4SiO_2 \cdot Al_2O_3 \cdot Cs_2O \cdot 11H_2O$ geopolymer into pollucite (CsAlSi₂O₆) was studied using high temperature x-ray diffraction (HTXRD), differential scanning calorimetry (DSC), and pair distribution function (PDF) x-ray analysis.

Pollucite was formed on heating to approximately 1000 $^{\circ}$ C and was confirmed using X-ray diffraction (XRD). Additionally, the structure evolution of Cs-based geopolymer to CsAlSi₂O₆ phase was studied ex-situ using pair distribution function (PDF) analysis. The Cs-based geopolymer prior to heating had short range structural ordering up to 8 Å similar to as in crystalline pollucite as revealed by PDF. After heating above 1000 $^{\circ}$ C, long range order was established due to pollucite crystallization.

The kinetics of crystallization of Cs-based geopolymer was observed in-situ, as a function of temperature under both isothermal (by HTXRD) and non-isothermal conditions (by DSC). The HTXRD experiments were conducted using a quadrupole lamp furnace and a curved image plate (CIP) detector at the Advanced Photon Source, Argonne National Laboratory, Argonne, IL. Diffraction patterns were acquired under isothermal conditions at five different temperatures between 840C to 900 C. Using this setup, samples were heated at very fast rates (> 400 °C/min) such that the desired temperatures were reached in ≤ 2 minutes. Individual diffraction patterns were subsequently acquired with a time resolution of approximately 90 seconds for over 30 minutes. The amorphous and crystalline phase content was quantitatively determined from the HTXRD patterns using whole pattern fitting methods. The evolution of crystalline phase content was compared with crystallization behavior studied using DSC experiments. Quantitative results will be presented together with activation energies for crystallization. The suitability of different kinetic models will be discussed to explain the structural changes, observed under both isothermal and non-thermal experiments.

P2. Pair Distribution Function Studies of Functional Framework Materials

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The evolving demands of our modern society fuel a perpetual drive to develop innovative materials for advanced technological and industrial applications. Pivotal to the rational design of next generation materials optimized for real world applications, is the fundamental understanding of the key structural features underlying functional behavior. While conventional Bragg crystallographic techniques are routinely applied for determination of *average* structures, translational symmetry is assumed and therefore limited insight is provided into disordered features which underlie the bulk properties of many complex materials including sorption in nanoporous host-guest systems, negative thermal expansion (NTE) behavior and pressureinduced structural transitions. Such disordered features may only be probed by also considering the total scattering including the diffuse component from atomic correlations that deviate from the average structure. Consequently, there is a growing interest in the application of techniques such as pair distribution function (PDF) methods to the study of complex materials. Here we present recent applications of high-energy X-ray total scattering methods to study cyanidebridged molecular framework materials which exhibit NTE behavior and reversible hydrogen uptake.

P3. Precession Diffraction Investigation of Kinematical Extinctions in Andalusite

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Precession electron diffraction is an innovative data collection technique for bulk crystallography. In a precession diffraction experiment, the electron beam is conically scanned above the sample and subsequently descanned below the specimen. This avoids the strong dynamical scattering of a zone axis condition and allows for instantaneous collection and integration of hundreds of off-zone diffraction experiments. The acquired intensities from a precession experiment are of higher quality, meaning one is more likely to find the true structure.

We investigate the effect of cone semiangle (φ) on the intensity of the forbidden (001) reflection of Andalusite in a [110] zone axis pattern using multislice calculations which incorporate structure factors computed from DFT calculated full charge density, and also from conventional isolated atom structures. These results are compared to experiments in which the cone semiangle was varied from 0-32 mrad in 5 discrete steps. From both theory and experiment, the kinematically forbidden (001) reflection has a larger intensity than the allowed (002) reflection in the on-zone condition, but decreases in a near-exponential (e^{-A φ}, A=0.1-0.2) fashion as cone angle increases. Electron direct methods analysis was used for phase recovery of both precessed and non-precessed zone axis patterns and, as expected, the recovered projected potential from the more kinematical precession data set is a much better approximation to the actual potential.

P4. Development of a Powder X-ray Diffraction Laboratory Module for use in Honors General Chemistry: Identification of Unknown Household Solids Using Powder X-ray Diffraction

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Many of the items that we encounter in our homes on a daily basis are crystalline in nature. Xray diffraction is a common method used to identify crystalline materials and mixtures, since each crystalline solid produces a unique powder pattern, like a fingerprint. In this research project, a powder X-ray diffraction (PXRD) module is being developed for use in Honors General Chemistry at Duquesne University. Students will be supplied with a white, unknown, powdered crystalline solid that they will identify using PXRD. This module will reinforce the concepts of basic crystalline solids covered in lecture.

A number of household items have been studied as potential unknowns. Once a pattern has been obtained from the ground solid, it is analyzed using a software package and compared with patterns in the Powder Diffraction File. Several household items have already been identified as appropriate unknowns. Cosmetics and toothpaste have been excluded as potential unknowns due to their pattern complexity.

P5. The Capabilities and Limitation of Powder X-ray Diffraction in the Characterization of A₂M₃O₁₂ Compounds

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Negative thermal expansion (NTE) is a concept that describes materials that shrink when they are heated. The growing interest in these materials can be attributed to the discovery that NTE materials incorporated into composites can be used to reduce thermal expansion, and tailor expansion coefficients to desired values for metallic, ceramic, and polymeric applications. Preparation of composite materials containing NTE oxides should allow control over thermal expansion behavior, and ideally circumvent application limitations due to thermal expansion problems. Currently, zirconium tungstate (ZrW_2O_8) is the best-known material that displays NTE; it exhibits a significant reduction in size when heated. However, its properties are almost unaffected by cation substitution (AM_2O_8 ; A = Zr, Hf; M = Mo, W), which limits the uses of these materials if tailored properties are needed. In contrast, there are several other oxide families that also display NTE characteristics, such as the $A_2M_3O_{12}$ family (A = trivalent metal; M = W, Mo), which show a more extended range of properties. These materials can crystallize in either a monoclinic (low temperatures, positive expansion), or orthorhombic unit cell (high temperatures, negative expansion), and are known to commonly undergo a phase transition from one phase to the other as a function of temperature. Their expansion coefficient (α) and phase transition behavior are highly dependent on the identity of the cations (A^{3+} and M^{6+}). Literature suggests that the magnitude of NTE is affected by cation size, and the crystal structure and phase transition temperatures are influenced by the electronegativity of the trivalent cation. Thus, the $A_2M_3O_{12}$ family has the greatest potential for tunable NTE materials. Use of these compounds will allow for custom-made composites.

In our group, $A_2M_3O_{12}$ materials are synthesized using a non-hydrolytic sol-gel (NHSG) method, which allows for preparation of metastable compounds at low temperatures. The NHSG process enables cation substitution without sacrificing the homogeneity of the mixed metal oxides. The expansion, and phase transition behavior of the materials are characterized using powder X-ray diffraction (PXRD). Various crystallographic details can be determined from diffractograms including the phase(s) present in the sample (crystal structure), and the sample composition. Performing variable temperature powder X-ray diffraction (VT-PXRD) provides information on phase transition behavior as a function of temperature. Refinement of the diffraction data gives lattice parameters, which can be used to calculate expansion as a function of temperature. In addition, high pressure diffraction studies are performed to characterize phase behavior as a function of pressure. The stability of the NTE materials under pressure is important due to the possibility of irreversible pressure induced phase transitions. These transitions usually result in loss of NTE character, making the incorporation of $A_2M_3O_{12}$ compounds into composites futile.

Although PXRD has proven is an indispensable technique for characterizing the various properties of the $A_2M_3O_{12}$ family, there are several factors that can limit the usefulness of diffraction data. The quality and reproducibility of the data are greatly affected by temperature calibration offsets during VT-PXRD experiments. An offset was discovered between the temperature calibrations of two powder diffractometers, which resulted in discrepancies in the diffraction data. The high pressure experiments were performed in a diamond anvil cell where

data resolution can be compromised. The poor data quality during some high pressure experiments made characterization of the materials' behavior difficult. This can be attributed to variations in the hydrostaticity of the cell, and detector calibration problems. In this poster, ideas to circumvent some of these limitations will be addressed.

P6. Crystallization Studies of MgZrW₃O₁₂

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There has been interest in negative thermal expansion (NTE) materials because of the effects seen when they are incorporated into composites. The incorporation of such materials could reduce the overall thermal expansion of their respective composites. Previous work done in the $A_2(WO_4)_3$ system has shown that the thermal expansion is dependent on the identity of the A^{3+} cation. Suzuki and associates have substituted the A site by a mixture of Hf⁴⁺ and Mg²⁺. There have not been any other reports of different M^{II}M^{IV} cation mixtures occupying the A site in the $A_2(WO_4)_3$ system.

The cations of interest in this paper are Mg^{2+} and Zr^{4+} , which can combine to form a previously unknown NTE compound in this family. There were several possible pathways explored for the preparation of this material. These included solid state routes, dissolution and evaporation of water soluble precursors, hydrothermal treatment, and the heating of preformed binary and ternary compounds. The formation of unreactive MgWO₄ was observed in several approaches, which interferes with some traditional solid-state methods. The desired phase, MgZr(WO₄)₃, was crystallized by ball-milling and subsequent calcination of the samples. Crystallization studies were then performed on the samples to establish what phases were preferentially formed, and to investigate the material's thermal expansion properties. Variable temperature X-ray diffraction on MgZr(WO₄)₃ suggests that the material adopts the monoclinic structure at room temperature, and transforms to an orthorhombic phase at temperatures greater than 100 °C.

P7. Characterisation of Femtosecond Electron Pulses

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Femtosecond Electron Diffraction (FED) has been developed to directly observe structural transitions on the atomic scale [1]. These transitions happen on the time-scale of hundred femtoseconds. To resolve them, the temporal resolution of FED has to match this critical timescale. FED is a pump-probe technique: a laser pulse induces a structural transition in the sample and an electron pulse acts as the probe by diffracting off the excited sample after a variable time delay. The temporal resolution of such an experiment is intrinsically limited by the durations of the pump and probe pulses. While femtosecond laser systems have been available for many years, generating femtosecond electron pulses for use in FED still poses significant challenges. Traditionally, electron pulse durations have been measured by streak camera setups [2,3]. In these measurements, a voltage ramp is applied to a pair of streaking plates to produce a timedependent deflection of the electron pulse. Limitations of the streaking speed combined with the size of the beam used for FED experiments essentially limit this method to pulses longer than a picosecond [4]. The geometry of a streak camera produces another, even more severe problem: The length of the streaking plates along the propagation direction is on the order of several centimetres. Since high density electron pulses change their duration while propagating, the pulse duration as measured by a streak camera is ill-defined. To avoid the problems associated with streak cameras, a strongly time-dependent interaction has to take place over a short section of the propagation path around the sample position. The transient scattering of an electron pulse by the ponderomotive potential of an intense femtosecond laser pulse encodes timing information into the electron pulse over the size of the laser focus and hence it can be applied exactly at the position where a sample would be placed in a diffraction experiment [5]. Since the timing of the photoelectron gun and the laser pulse generating the scattering potential originate from the same laser, the measurement is also inherently jitter free and the signal can be integrated over many electron pulses.

The ponderomotive force arises from the cycle-averaged Lorentz force of the laser field and acts to expel electrons from regions of high light intensity. It can be described in terms of a potential that is proportional to the intensity of the light:

$$U_P(\vec{r},t) = \frac{e^2 \lambda^2}{8\pi^2 m_e \varepsilon_0 c^3} I(\vec{r},t)$$
(1)

where Up is the ponderomotive potential and λ and I are the wavelength and the intensity of the applied laser light, respectively. By scanning the delay between the electron and the laser pulse and recording the lateral electron pulse profile using a detector downstream from the beam crossing, we obtained a time trace of the laser-electron interaction [6]. After deconvolution, an electron pulse duration of 410 ± 30 fs is obtained from the trace shown in Fig. 1. These experiments were performed at a fluence of 4×10^7 electrons/cm².



Fig. 1. The scattering signal vs. delay time (sample electron beam profiles shown as insets). The dashed line is a Gaussian fit to the data with a FWHM of 438 fs.

Since the ponderomotive interaction takes place in vacuum, there is no material response involved in this measurement, eliminating the possibility of a potentially time-dependent response. The signal therefore faithfully reflects the actual overlap of the electron and laser pulses. Hence, this method can also serve as a very accurate albeit involved method to determine the temporal overlap of pump and probe pulses in FED experiments.

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P8. Controlling Particle Size of Negative Thermal Expansion Oxides

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Materials that contract upon heating instead of expanding are called negative thermal expansion (NTE) materials. A variety of applications for these materials have been explored including their incorporation into composites. This allows the control of overall expansion to positive or negative values and therefore tailoring for a specific use. The particle size of the filler influences the dispersion of the material inside the matrix and the homogeneity of the composite. It is expected that particles of the NTE materials cubic zirconium tungstate and cubic zirconium molybdate below 100 nanometers are sufficient for the preparation of high quality polyimide composites. Zirconium tungstate hydroxide hydrate and zirconium molybdate hydroxide hydrate, the precursors for the cubic oxides, were prepared using hydrothermal and reflux methods, respectively. The particle size has been reduced significantly from micron-scale to between 100 and 200 nm for both materials by optimizing the reaction variables. These include the concentration of the starting materials, the concentration of the acid, heating and reflux times, as well as temperature.

P9. Synthesis and Characterization of Diamond-Like Semiconductors

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Diamond-like semiconductors (DLS) are a special class of semiconductors that crystallize in structures related to that of diamond. In order to be diamond-like, a material must obey a set of rules. The first rule is that the average number of valence electrons must equal four. The second rule states that the number of valence electrons per anion must be eight. From these two rules it follows that the number of cations must equal the number of anions. The compound should also obey Pauling's rules. Pauling's first rule is the radius-ratio rule, which predicts a tetrahedral coordination sphere only when the ratio of the cation to the anion is between 0.2 and 0.4. In DLS all atoms must be coordinated tetrahedrally. The second of Pauling's rules states that each anion in the structure must receive enough electrons from the cations in its first coordination shell to satisfy the octet rule.

DLS can possess a number of technologically useful properties, such as second harmonic generation, that are derived from their structure. In addition, the properties of DLS can be fine tuned because of their remarkable compositional flexibility. DLS can also be doped to yield dilute magnetic semiconductors (DMS) with possible applications in spin-based electronics (spintronics). A large volume of work has been performed on binary DLS, such as CdS and GaN; however, ternary and quaternary DLS are not as well studied. We have synthesized a number of ternary and quaternary DLS using high temperature solid-state synthesis. Diffraction data and diffuse reflectance spectroscopy of these materials will be presented.

P10. Controlled-Temperature Diffraction Measurements on Samples in Glass Capillaries

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The measurement of samples in glass capillaries has advantages for certain types of materials, for instance samples with anisotropic crystallite shapes or crystallites in liquids. With the introduction of multi-purpose X-ray powder diffractometers, the capillary technique has become a standard addition to the conventional Bragg-Brentano reflection geometry. For controlled temperature experiments, however, the reflection geometry is still mostly used, especially in the case of low-temperature measurements.

In order to obtain a controlled-temperature device for capillary powder diffraction, a Cryostream (an established product in the single crystal community) has been modified, in close collaboration between Oxford Cryosystems and PANalytical. Key question in this integration is of course the accuracy of the sample temperature along the capillary length. In this study, we determined the temperature accuracy of the Oxford Cryostream for this powder diffraction application and show an example of what can be done with this capillary heater-cooler.

P11. "Non-hydrolytic" Sol-gel Processing of Transition Metal Sulfides

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Sol-gel techniques have been successfully applied to the synthesis of metal oxides. They can also be used to prepare metal sulfides. The advantages of sol-gel techniques are their moderate temperatures and their enhanced control over stoichiometry and shape of the particles. As some metal sulfides are oxophilic, non-hydrolytic sol-gel techniques are attractive. This process produces transition metal sulfides by a reaction between an organic sulfur source, like *tert*-butylsulfide, and a transition metal halide. The synthesis is carried out in a glove box under argon to avoid any contact with air or moisture. The reagents are mixed in a glass ampoule, with dry chloroform as a solvent. The ampoule is then sealed and heated. The obtained products were powders. They were characterized by thermogravimetric analysis to determine the sulfur to metal ratio, powder X-ray diffraction to check the crystallinity and identify phases, and scanning electron microscopy to measure the size of the particles. This process usually leads to amorphous products, which crystallize after heating under inert atmosphere. Using this procedure, a new phase was discovered in the WS_x system.

P12. Steric and Electrostatic Accessibility of H-bond Donor and Acceptor Sites in H-bonding Quaternary Imine Salts

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While studying the H-bonding motifs of just two different imine salts recently synthesized in our department, we have found a wealth of features describing the H-bond geometry. The specific characteristics can be illustrated quite simply and include comparisons based upon: chemical composition (quaternary *vs* protonated ternary imines; organic *vs* halide anions); chemical potential (weak *vs* strong H-bonds qualified simply with H...X distances and X-H donor atom types, or more rigorously with a map of the electrostatic potential); bond geometry (distances and direct or oblique angles of the Y-H...X interaction); and steric considerations (the accessibility of the H-bond donor and acceptor sites);. Also, the use of low-resolution *vs* high-resolution x-ray data yielded some surprises in H-bond geometry! In summary, a rather complete description of the H-bonding in crystal structures, especially those with protonated organic ions, can be readily made, and there is no good reason not to have such a description in even the most concise crystal structure communication.

P13. Light When YOU Need it: SER-CAT's Beamlines at the Advanced Photon Source.

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SER-CAT, Sector 22 APS, provides an insertion device (22ID) and a bending magnet (22BM) beamline for macromolecular crystallography. 22ID ($5x10^{11}$ photons/sec over 100x100 mm) hosts a MAR 300 CCD detector. 22BM ($2-3x10^{11}$ photons/sec over 80x80 mm) hosts a MAR 225 CCD detector, a highly modified ALS - style automounter and has remote user capabilities. Both beamlines are MAD/SAD capable with an experimental envelope ranging from 0.5Å to 2Å.

SER-CAT's goal is to provide its members with immediate access to one of the best synchrotron data collection facilities in the world. This is done by the continued integration of new technologies and methodologies, and by providing its users with outstanding user support.

Since October 2003, 22ID has hosted more than 500 investigators. Over 10000 data sets have been collected that contributed to 334 PDB deposits and 267 published papers. SER-CAT's is hosting General Users on 22ID and will begin hosting General Users on 22BM in January 2007.



P14. New Generation of Dithiolene Ligands

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Molybdenum is present in the enzyme nitrogenase as part of a multinuclear cluster with seven iron atoms, and in a mononuclear center in other molybdoenzymes.^{1,2,3} In the active site of molybdenum mononuclear enzymes the metal is coordinated to one or two equivalents of the pyranopterin (or molybdopterin) cofactor. Mononuclear molybdenum enzymes catalyze a variety of reactions that are important in the metabolism of nitrogen and sulfur-containing compounds. With the exception of membrane bound respiratory nitrate reductase (Nar), in all cases the tricyclic ring remains intact. In Nar, however, a ring opened form has been observed. The key features of pyranopterin cofactor are: *a) pyran ring can undergo ring scission which may influence the reactivity; b) dithiolene moiety as well as the pterin unit are redox noninnocent and can influence the redox chemistry, c) high degree of metal-sulfur covalency present in the Moditholene can be modulated by distortion at the pyran ring as well as the pyrazine ring of the cofactor.*

In recent years a large number of molybdenum complexes have been synthesized and investigated as models for molybdenum enzymes. In the majority of the systems, the metal is coordinated to simple unfunctionalized dithiolene.^{2,3} Very recently two reports outlined the synthesis of molybdenum complexes with dithiolene ligands that contain the pyran feature of the cofactor: $[MoO(fdt)]^{2-}$ (fdt= flavanyl-1,3-dithiolate)⁴ and $[MoO(LO)]^{2-}$ (LO= 2,3-dihydr-2H-pyran-4,5-dithiolate)⁵. We developed a new strategy for the synthesis of a new generation of ligands in which the dithiolene moiety is synthesized before the pyran-ring closure.



Molybdenum cofactor

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P15. Monitoring an Unusual Phase Transition in Sodium Monothiophosphate

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Oxythiophosphates are a class of chemically interesting compounds which bridge the gap between the technologically useful phosphate and tetrathiophosphate families. Our investigations into the properties of sodium monothiophosphate have revealed an unusual transition between two of the three known polymorphs.

We report observation of the third polymorph, the γ -phase, in addition to the α - and β -phases previously confirmed by diffraction techniques. We also report that anhydrous β -Na₃PO₃S can convert to anhydrous α -Na₃PO₃S at room temperature by exposure to atmospheric water/humidity, but no hydrated intermediate is observed during the transition. Under vacuum in a differential thermal analyzer, this transition occurs at approximately 300°C, indicating that atmospheric water is able to suppress the transition temperature by ~275°C. Data acquired at the Intense Pulsed Neutron Source (IPNS) regarding the rate and nature of this humidity-catalyzed transition will be presented.

P16. Crystallography for Undergrads: How Computer Software and Collaborations Can Make it Happen at a Small College

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Single crystal x-ray diffraction is essentially a required component to most synthetic endeavors in inorganic and materials chemistry. As such, undergraduate students should be exposed to this method both in terms of the theory behind it and in practical experience with data collection and structural solutions. To this end, the theory and practice of X-ray crystallography was presented to junior and senior undergraduate students in a 10 week special topics course at Saint Vincent College. Principles of x-ray generation and safety, lattice types, and crystallographic symmetry and space groups were presented along with hands-on data collection and structural solution experience made possible by collaboration with nearby Duquesne University. Herein is presented a summary of the course content, student hands-on activities, media resources, and a description of the collaborative activities that took place at Duquesne University.

P17. Synthesis of Mixed Substituted Acetylacetonate Complexes: New Single-Source Precursors for Metal Oxide Thin Film Growth

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Metal acetylacetonates have long been used as precursors for the chemical vapor deposition (CVD) of metal and metal oxide thin films. Upon substitution of $-CH_3$ groups with $-CF_3$ (i.e., from acetylacetonate, acac - trifluoroacetylacetonate, tfac – hexafluoroacetylacetonate, hfac), the volatility drastically increases due to enhancement of intermolecular interaction. To date, there have been no reported syntheses of metal acetylacetonate complexes that contain more than one type of acac/tfac/hfac ligand. Herein, we report the synthesis and characterization of Group 13 complexes that feature a mixed ligand field of fluorinated acetylacetonates.

P18. A Charge Density Study of Dienestrol

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In an effort to determine a relationship between the biological function and the electronic properties of steroidal and nonsteroidal estrogens, a charge density study has been pursued on the non-steroidal, synthetic estrogen, dienestrol. Crystals of dienestrol were crystallized from methanol by slow evaporation (Doyle *et al.*, 1975) and x-ray diffraction data then obtained using a Rigaku R-Axis Rapid high-power rotating anode diffractometer with a curved image plate detector at 20.0(1) K. In order to obtain a high amount of redundancy, five runs were collected at 240 sec. with 4⁰ images. Adjacent images that overlapped by 2⁰ were collected to ensure correct scaling between the images for a total of 89 images per run. The data collection lasted less than two days.

This data collection technique gave a completeness of 99.8% (data up to 0.7Å^{-1}) to a maximum resolution of 1.30Å^{-1} with a redundancy of 8.1 for all data. The data was indexed with the program HKL2000 (Otwinowski & Minor, 1997) and the predicted positions of the reflections were then used for data integration with the program VIIPP (Zhurov *et al.*, 2005; Zhurova *et al.*, 1999). The program SORTAV (Blessing, 1987) was then implemented to scale each run and average equivalent measurements. The use of the program SORTAV (Blessing, 1987) gave R_{int} = 0.0229 for all data and the scales between the runs did not differ more than 4%.

A preliminary refinement has been completed on dienestrol with the Hansen-Coppens multipole model (Hansen & Coppens, 1978) using the program XD (Koritsanszky *et al.*, 1995). A preliminary $R(F^2)$ value of 0.0330 has been obtained. Experimental residual and deformation maps along with a preliminary topological analysis of dienestrol will be reported.

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P19. Microstructure Evolution of Polycrystalline Mullite System – A High Temperature Synchrotron X-ray Diffraction Study

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Mullite $(Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x})$ is one of the most important minerals and materials in crystallography and in ceramic science and technology. It is a strong candidate material for advanced structural applications at high temperatures, because it has good chemical stability, creep resistance, mechanical strength and displays low thermal expansion. Several studies in the past have focused on understanding the impact of processing conditions and compositional variations on the microstructure and properties of this material system. Many of these studies were conducted ex-situ, or else were limited in evaluating this material system under true conditions of its applications. To the best of our knowledge, this investigation is the first ever effort aimed at studying the kinetics of microstructural evolution of this very important material system at temperatures within 200 to 300 °C of its melting point ($T_{melt} = 1828$ °C) in air atmosphere.

In this study high temperature X-ray diffraction (HTXRD) experiments were conducted using synchrotron radiation to evaluate the effect of time, temperature and composition on microstructure evolution of polycrystalline mullite. For this purpose, sample powders of mullite with the composition $3Al_2O_3 \cdot 2SiO_2$ (i.e. 3:2 mullite) and mullite doped with 5 mol% of titania (TiO₂) were synthesized by the sol-gel method. Pre-sintered flat plate specimen were prepared at 1400°C, cut and polished to 250 µm thickness and coated with platinum, which served as an internal thermometer. HTXRD experiments were conducted in transmission geometry in the temperature range from 1500 °C to 1750 °C in air for ≤ 2 hrs using a quadrupole lamp furnace and a curved image plate (CIP) detector. All experiments were conducted under isothermal conditions and HTXRD patterns were acquired with a time resolution of < 2 minutes and spatial resolution of 0.008° in 20. The diffraction patterns were analyzed using whole pattern fitting (Rietveld method) to extract sample temperature and lattice expansion. Individual peaks were fitted with pseudo-voigt function and Willamson-Hall plots were constructed to assess crystallite size growth along different crystallographic orientations.

Our studies highlight the anisotropic nature of crystallite size growth along different crystallographic directions in the mullite systems. TiO_2 doping was found to promote crystallite growth preferentially along the c-axis, which is consistent with earlier reports in the literature. Quantitative results on crystallite growth rates together with activation energies for growth along different crystallographic axis will also be presented. Suitable models will be discussed to explain the microstructural changes, observed in situ at high temperatures.

P20. Consensus Policy Statement on Crystallography Education and Training

Victor G. Young, Jr. and Katherine Kantardjieff United States National Committee for Crystallography

In 2001 and 2003, the USNC/Cr conducted two surveys to determine the content and extent of coverage of crystallography in university curricula, as well as the views of the broader crystallographic community on the status of crystallography education and training in the US, in both the physical and the life sciences. These surveys suggested that, perhaps as a result of rapid technological advances in the field of modern crystallography, there appears to be a declining number of practicing crystallographers, as well as a lack of sufficient education and training in crystallography for individuals who wish to understand and/or use crystallography as a tool in their hypothesis-driven research. Recognizing the opportunity to communicate to the broader scientific community the research opportunities afforded by crystallography, as well as the value of crystallographic information, the ACA and USNC/Cr organized an education summit in 2005, the outcome of which is a consensus policy statement on crystallography education and training. This document makes recommendations for a comprehensive re-evaluation of crystallography education and suggests ways to develop in the broader scientific community an appreciation for the value of crystallographic information. The ACA and the USNC/Cr intend that the document, which stands as the white paper on crystallography education and training, provides guidelines to professional societies and academic departments for crafting future crystallography curricula that adequately address the needs of the scientific community. The ACA and the USNC/Cr will provide guidance and support to interested colleagues and policy makers who wish to put these recommendations into practice.
P21. Ultra-fast Framing X-ray Detector for Time-Resolved Synchrotron Experiments

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A new fast photon-counting X-ray imaging detector is described. The detector is based on the VANTEC and AXIOM MikroGapTM detectors and is capable of frame rates of up to 1 million frames per second. This detector is thus capable of studying fast kinetic processes such as chemical reactions, phase transitions, reactions of materials to pulsed magnetic fields, photo-excited processes, etc. with unprecedented time resolution.