pressure, and it will be demonstrated that the guest-atom chains in the composite Rb-IV structure represent a realisation of the classic monatomic chain model. In modulated Te-III, a pronounced phonon anomaly is observed that will be discussed in the context of Fermi-surface nesting, Kohn anomalies and charge-density waves. This work was performed in collaboration with M. I. McMahon, L. F. Lundegaard, S. R. Evans (University of Edinburgh) and A. Bossak, M. Krisch (ESRF, Grenoble).

Keywords: incommensurate crystals, lattice dynamics, inelastic X-ray scattering

MS.56.5

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Phase transformations in silane — Hydrogen-dominant material

Mikhail Eremets, Ivan Trojan, Sergij Medvedev
Max Planck Institute fuer Chemie, Hochdruck, Postfach 3060, Mainz, 55020, Germany, E-mail: eremets@mpch-mainz.mpg.de

The metallization of hydrogen directly would require pressure of 400 GPa, out of the reach of present experimental techniques. The dense group IVA hydrides attract considerable attention because hydrogen in these compounds is chemically precompressed and a metallic state is expected to be achievable at experimentally accessible pressures(1). We report the transformation of insulating molecular silane to a metal at 50 GPa, becoming superconducting at a transition temperature of Tc = 17 K at 96 and 120 GPa(2). The metallic phase has a hexagonal close-packed structure with a high density of atomic hydrogen, creating a three-dimensional conducting network. These experimental findings support the idea of modeling metallic hydrogen in these compounds is chemically precompressed and a metallic state is expected to be achievable at experimentally accessible pressures(1). We report the transformation of insulating molecular silane to a metal at 50 GPa, becoming superconducting at a transition temperature of Tc = 17 K at 96 and 120 GPa(2). The metallic phase has a hexagonal close-packed structure with a high density of atomic hydrogen, creating a three-dimensional conducting network. These experimental findings support the idea of modeling metallic hydrogen in these compounds is chemically precompressed and a metallic state is expected to be achievable at experimentally accessible pressures(1).

Keywords: neutron diffraction, protein, structure

MS.57.2


Neutron crystallographic analysis of deuterated and selectively CH3-protonated deuterated rubredoxin

Flora Meilleur1,2, Kevin L Weiss1, Anna S Gardberg1, Matthew P Blakeley1, Dean A Myles1,2
1North Carolina State University & Oak Ridge National Laboratory, Structural and Molecular Biology, 1 Bethel Valley Road, Oak Ridge, TN, 37831, USA, 2Neutron Scattering Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge TN 37831, USA, 3Chemical Sciences Division, Center for Structural Molecular Biology, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge TN 37831, 4Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble, France, E-mail: meilleur@ornl.gov

Neutron crystallography is used to locate hydrogen atoms in biological materials and can distinguish between negatively scattering hydrogen and positively scattering deuterium substituted positions in isomorphous neutron structures. Recently, Hauptman and Lang (2003) have shown that neutron diffraction data can be used to solve macromolecular structures by direct methods and that solution is aided by the presence of negatively scattering hydrogen atoms in the structure. Selective labeling protocols allow the design and production of group or residue specific H/D-labeled macromolecular structures in which the ratio of hydrogen to deuterium atoms can be precisely controlled. We have applied labeling protocols to selectivity introduce protonated methyl groups into deuterated rubredoxin from Pyrococcus furiosus (PfRd). Perdeuterated and selectively CH3-protonated deuterated rubredoxin were crystallized. High quality neutron data sets extending to 1.75 Å resolution were collected on the new LADI-III instrument at the Institut Laue-Langevin. Of special importance, the 1.75 Å data from the perdeuterated crystal required just 14 hours of beam time, a record which heralds a new era in neutron protein crystallography. We will present the production, crystallization, and neutron analysis of the perdeuterated and selectively CH3-protonated PfRd. This research is sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy.
MS.57.3  


**Neutron macromolecular crystallography using the Laue diffractometer LADI-III**

Matthew P Blakeley
Institut Laue Langevin, Large Scale Structures, 6, rue Jules Horowitz, BP156, Cedex 9, Grenoble, Isere, 38042, France, E-mail : Blakeleym@ill.fr

At the Institut Laue-Langevin a new neutron Laue diffractometer (LADI-III) has been fully operational since March 2007. LADI-III is dedicated to neutron macromolecular crystallography at high-resolution (1.5 Å - 2.5 Å) and is used to study key hydrogen atoms and water structure in macromolecular structures. An improved detector design and readout system has been incorporated so that a miniaturized reading head located inside the drum scans the image-plate. From comparisons of neutron detection efficiency (DQE) with the original LADI-I instrument, the transferal of the image-plates and readout system internally provides a 2- to 3-fold gain in neutron detection, allowing data collection to higher resolution (~1.5 Å), using shorter exposure times and smaller crystal volumes. The improved neutron detector efficiency of LADI-III combined with the use of perdeuterated biological samples has enabled neutron macromolecular crystallography to become more accessible to the structural biology community, extending the size and complexity of systems that can be studied (~150 Å on cell edge) while lowering the sample volumes required (~0.1mm³). Current projects aim to address questions concerning enzymatic mechanism, ligand-binding interactions, solvent effects, structure dynamics and their implications. Examples of recent project highlights from LADI-III will be presented.

**Keywords:** neutron macromolecular crystallography, perdeuteration, Laue

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MS.57.5  


**Locating hydrogen atoms in enzymes: A neutron structure of D-xylulose isomerase with bound D-xylulose**

1. The Institute for Cancer Research, 333 Cottman Avenue, Philadelphia, Pennsylvania, 19111-2497, USA, 2. M888, Bioscience Division, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545, USA, 3. Chemistry Department, University of Toledo, Toledo, Ohio, 43606, USA, 4. Chemistry Department, University of Tennessee, Knoxville, Tennessee, 37996, USA, 5. The Institute for Cancer Research, Fox Chase Cancer Center, 333 Cottman Avenue, Philadelphia, Pennsylvania, 19111-2497, USA, E-mail: Jenny.Glusker@fccc.edu

The transfer of hydrogen is important in many enzyme reaction mechanisms, and yet hydrogen is difficult to visualize in proteins using X-ray crystallography because of its low X-ray scattering power. We have exploited the recently developed time-of-flight neutron Laue technique to determine the location of hydrogen atoms during the reaction of an enzyme of economic importance, D-xylulose isomerase (XI). Neutron diffraction studies of this deuterated enzyme with bound perdeuterated substrate show, unexpectedly, that the terminal $\text{O}5$ hydroxyl group of D-xylulose, the product, is not protonated but is H-bonded to doubly protonated His54 in a sugar hydroxyl-histidine-aspartate triad such as is found in trypsin. In addition, the metal ion-bound water molecule (which may be important in the enzyme mechanism) that was found in neutron diffraction studies of the native enzyme, is deprotonated in this XI-xylulose structure and exists as a hydroxyl group. Furthermore, lysine 289, which has only two protons on its terminal nitrogen atom (NZ) in the native enzyme neutron structure, has three in the XI-xylulose complex. This indicates that there is a positive charge on this amino group. These findings lead to further insight into the mode of action of this enzyme. Support from the National Institutes of Health (GM071939, CA06927, CA10925), the Office of Biological and Environmental Research of the Department of Energy, and Los Alamos National Laboratory (20070131ER and 20080001DR) is gratefully acknowledged.

**Keywords:** neutron structure analysis, enzyme structure function, isomerases

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MS.57.4  


**Seeing hydrogens: X-ray limitations and possibilities at 0.9 Å and synergy with neutron diffraction**

Svetlana Antonyuk, Robert R Eady, Samar S Hasnain
University of Liverpool, School of Biological Sciences, Crown Street, Liverpool, Merseyside, L69 7ZB, UK, E-mail: S.Antonyuk@dfl.ac.uk

Protons and proton transfer pathways play a critical role in many enzyme mechanisms. Direct information on proton (hydrogen) positions may be obtained from neutron crystallographic data. Despite advances in neutron sources and detectors, the application of neutron diffraction has remained limited to large crystals with small unit cell dimensions. This has resulted in general in a paucity of information about the proton delivery mechanisms that are central to our understanding of many enzyme mechanisms. In our attempt to understand the underlying mechanism of proton transfer, we have adopted the approach of obtaining X-ray data to subatomic (~1 Å) resolution. Electron density maps from structures determined to such resolution can reveal the positions of crucial hydrogens within the active sites and on proton pathways. Details of hydrogen location in green nitrite reductase from *Achromobacter cycloclastes* (0.90 Å) [1], human superoxide dismutase (0.88 Å) [2] and cytochrome c′ (CYPtcp) from *Alcaligenes xylosoxidans* will be presented. The last of these, CYPtcp is able to discriminate between CO and NO by binding them on opposite faces of the heme. Recently, we have determined the X-ray crystal structure of oxidised and reduced CYPtcp to 0.9 Å resolution and a detailed analysis of the structures is in progress. Crystals of CYPtcp have been grown to a size of 3000x500x500 microns and neutron diffraction studies are in progress. These data will allow us to explore the synergy between the two approaches for this important system.

**References**

**Keywords:** neutron crystallography, high-resolution X-ray crystallography, metalloproteins

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Microsymposia

**Keywords:** neutron macromolecule crystallography, specific labeling, proton