

Poster Sessions

Chem. **2010**, 6223-6225; T.C. Harrop, Z.J. Tonzetich, E. Reisner, S.J. Lippard *J. Am. Chem. Soc.* **2008**, 130, 15602-15610; Z.J. Tonzetich, H.L. Do, S.J. Lippard *J. Am. Chem. Soc.* **2009**, 131, 7964-7965.

Keywords: cluster, iron, spectroscopy

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Effects in the atomic structure of BaFe₂As₂ by pressure and chemical substitution

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The effects of K and Co substitutions and quasi-hydrostatic applied pressure ($P < 9$ GPa) in the local atomic structure of BaFe₂As₂, Ba(Fe_{0.937}Co_{0.063})₂As₂ and Ba_{0.85}K_{0.15}Fe₂As₂ superconductors were investigated by extended X-ray absorption fine structure (EXAFS) measurements in the As *K* absorption edge. The As-Fe bond length is found to be slightly reduced (d 0.01 Å) by both Co and K substitutions, without any observable increment in the corresponding Debye-Waller factor. Also, this bond is shown to be compressible ($\kappa = 3.3(3) \% 10^{-3}$ GPa⁻¹). The observed contractions of As-Fe bond under pressure and chemical substitutions are likely related with a reduction of the local Fe magnetic moments, and should be an important tuning parameter in the phase diagrams of the Fe-based superconductors.

Keywords: pnictides, superconductivity, EXAFS

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Anisotropy in Anomalous Scattering in TiO₂ and the influence of point defects

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Diffraction intensities near an absorption edge of one of the crystal's atoms show a considerable dependency on the polarization of the incident and scattered X-rays and also on the corresponding wave vectors called Anisotropy in Anomalous Scattering (AAS). The polarization is usually varied by rotating the crystal around the momentum transfer vector by an angle ψ . Based on the tensorial treatment of this dependency like described by Kirfel et. al. [1], we studied the forbidden reflection 001 and the allowed reflection 111 of rutile at the titanium K absorption edge. Furthermore we investigated the influence of diluted point defects, in particular oxygen vacancies, on the scattered intensity profiles. Point defects as one possible origin for polarization anisotropy were discussed by Dmitrienko et. al. [2] which formed the basis of our considerations. Variations of the AAS profiles with energy have been observed and theoretically been account for. For the allowed 111 reflection a clear change of these patterns with increasing number of oxygen vacancies has been measured at different beamlines of the light source DORIS at DESY.

[1] A. Kirfel, A. Petcov, K. Eichhorn, *Acta Cryst.* **1991**, *A47*, 180. [2] V.E. Dmitrienko, E.N. Ovchinnikova: *Acta Cryst.* **2000**, *A56*, 340.

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The Structure and X-ray Absorption Spectrum Studies of Mn and N Co-doped ZnO

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To grow ferromagnetic *P*-type Zn(Mn)O, nitrogen and manganese co-doped ZnO film with wurtzite structure were made by ion implantation method. The Mn *K*-edge and *L*_{3,2}-edge peaks of samples have same binding energy with peak of MnO. So the X-ray absorption spectrum show the valence of doped Mn ion is 2+. The ions substitution of Zn by Mn was proved. The X-ray diffraction show a extra peak about 1.3 degree lower than the ZnO(200) peak at 66.39 degree. The lattice length became longer after doping. The Curie temperature, coercive, and saturation moment were measured by SQUID. All of them were tuned by the controlling of nitrogen concentration. The effective magnetic moment and pinning force were enhanced but the Curie temperature was decrease upon the doped nitrogen concentration. The nitrogen substitution for oxygen can change not only carrier concentration but also the magnetic coupling strength between neighboring Mn ions.

Keywords: ZnO, X-ray absorption spectrum

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XRD and dual elemental XAFS analyses of inorganic solids

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Two inorganic solid solutions, γ -Fe_{2-x}Cr_xO₃ and LaFeNiTiO₃, were studied by X-ray absorption fine structure (XAFS) of K-absorption edge of two elements and by synchrotron radiation X-ray diffraction (XRD). Measurements were performed at the Stanford Synchrotron Radiation Lightsource at room temperature.

High-resolution XRD patterns were processed by means of the Rietveld method, using Fullprof [1]. In Rietveld refinements, the ordered/disordered degree of the considered solutions is indiscernible in cases of atoms being neighbors in the Periodic Table. Crystallographic interpretation of magnetic and ferroelectric phenomena is shortened by this limitation.

Double-element XAFS analysis was applied to clarify, via short-range structure characterization, the nature of investigated systems. In

each case, XAFS would confirm or reject the random character of the solution. Athena and Artemis codes as interfaces for IFEFFIT [2] and FEFF8.4 [3] codes were employed for XAFS spectra interpretation.

γ -Fe_{2-x}Cr_xO₃ maghemite for x=0.75, 1 and 1.25 was investigated by XAFS in both Fe and Cr K-edges. Pre-edge decomposition and theoretical modeling of XANES transitions were performed and interatomic distances were determined. Possible distortion of oxygen octahedra around both Fe(III) and Cr(III) cations was checked for potential ferroelectricity explanation, as well as possible vacancy superstructure.

LaFeNiTiO₃ has been confirmed to display magnetic behavior and was studied by its Fe and Ti K-edges. Interatomic distances were modeled for preferential occupation of sites by Fe or Ti atoms and for geometry of oxygen octahedra occupied by different cations.

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Keywords: X-ray diffraction, XANES, EXAFS

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NMR Crystallography applied to dicarboxylic acids

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A large number of active pharmaceutical ingredients (API) are developed as salts, generally for solubility reasons. Beside the common inorganic hydrochloride acid (by far the most represented) and sulphuric acid, others carbon-containing acids are widely used as counterions, e.g. fumaric and succinic acids. These organic dicarboxylic acids, having their carbon skeletons that differ only by an inner bond saturated or not, are usually highly difficult to be precisely localized in a ¹³C solid state NMR (ssNMR) spectrum. This is e.g. the case by comparison with liquid state ¹³C NMR data, since no more than two signals are expected in solution for such dicarboxylic acids; whatever the salt/base stoichiometry may be (for instance, salts of mono-, hemi- or sesqui-fumaric acid could be found in the Cambridge Structural Database). The NMR chemical shifts of the carbons belonging to the base may also vary in the liquid and solid state; which represent an additional difficulty for salt identification. However, using NMR crystallography, we were able to find the peak positions of fumaric and succinic acids mono complexed to a given API, notwithstanding the large number of carbons (35) displayed in their respective cross polarized magic angle spinning (CPMAS) spectrum. Crystallographic studies have been carried out for both salts; they crystallize in triclinic non centrosymmetrical structures, without organic solvent or water. The two crystal structures are remarkably isomorphous; this similarity even somewhat extends to the counterions, where the inner single bond for succinic acid is shorter than expected (both at room and low temperature). In contrast indeed to solution NMR data, four distinct signals are found by ssNMR both with fumaric and succinic salts, a consequence of salt bridges established in each case by only one carboxylic acid. Furthermore, this study allows the attribution without ambiguities of the carbons peak positions of each salt; they could readily be deduced from comparison of the two CPMAS spectra, since the chemical shifts characteristic of the base are found at same positions.

Keywords: ssNMR, structure elucidation

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Crystal structures of an enzyme duo involved in bacterial cell wall recycling

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Peptidoglycan in bacterial cell walls is synthesized by bacteria-specific enzymes by sequential addition of amino acids to UDP-N-acetylmuramic acid to form the peptidoglycan pentapeptide precursor, UDP-N-acetylmuramoyl-L-alanyl-γ-D-glutamyl-meso-diaminopimelyl-D-alanyl-D-alanine. In gram-negative bacteria, ~30–60% of the bacterial cell wall is recycled every generation in a complex process that involves ~18 proteins. LdcA catabolizes the bond between L- and D-amino acids in the degradation of the tetrapeptide L-alanyl-γ-D-glutamyl-meso-diaminopimelyl-D-alanine to form L-alanyl-γ-D-glutamyl-meso-diaminopimelate, which is the substrate for Mpl. Loss of LdcA or Mpl activity results in increased sensitivity to stationary phase lysis or antibiotic susceptibility, respectively. Crystal structures of a novel LdcA from *Novosphingobium aromaticivorans* (NaLdcA) and the Mpl from *Psychrobacter arcticum* (PaMpl) have been determined at 1.89 and 1.65 Å resolution, respectively. NaLdcA and the LdcA from *Pseudomonas aeruginosa* have similar overall structures and a conserved catalytic triad despite only a 20% sequence identity. Modeling a tetrapeptide substrate into the active site of the NaLdcA structure reveals residues that may be important in substrate recognition and how the catalytic triad is positioned for action. An unidentified ligand in the dimer interface might be involved in enzyme dimerization and indicates a possible site for inhibitor design. In PaMpl, ~30 residues are likely to be important for substrate recognition or may be involved in interdomain conformational changes on substrate binding. The PaMpl enzymatic activity has been characterized at different temperatures and with different peptide substrates. At 15 °C, PaMpl has almost twice the activity of Mpl from *E. coli*, consistent with *P. arcticum* adaptation at cold temperatures. These results expand the structural coverage of two important protagonists in bacterial cell wall peptidoglycan recycling and provide novel targets for anti-bacterial drug discovery.

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Structure Determination of HP0902, a Putative Secretory Protein from *H. pylori*

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As a structural genomics approach to the HP0902, a putative candidate for virulence factor of *Helicobacter pylori*, crystal structures were obtained from two different constructs and validated by nuclear