crystal packing arrangements, each with a unique type of hydrogen bonding pattern within a two-dimensional hydrophilic layer [1]. When side chains are linear, as in aminobutyric acid (Abu), norvaline (Nva), norleucine (Nle) and methionine (Met), steric conflict is limited, and the inherently most favorable pattern can form, where the two hydrogen-bonded sheets constituting a hydrophilic layer contain amino acids of both chiralities (thus called LD-LD layers). The unique property of these four racemates is that they display reversible first-order solid-solid transitions between two monoclinic forms in space groups $P2_1/c$ ($\alpha$) and $C2/c$ ($\beta$). The crystal structures of two polymorphs of DL-Nva have now been determined [2], revealing details on the hydrogen bonding pattern, but also on side-chain conformations. In the low-temperature $\alpha$-form (data collected at -90 °C) the n-propyl side chain is disordered over two positions, while in the higher temperature $\beta$-form (-70 °C) it has three alternative positions with refined occupancies 0.509:0.345:0.146. From an analysis of steric conflict, where the conformation of one side chain affects its neighbours in a domino-like fashion, it is possible to construct an idealized, ordered pattern that rationalizes this odd distribution. The presence of such conformational cascades has implications for the understanding of the dynamics of proteins during enzymatic reactions.

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**Keywords: amino acids, phase transition, side-chain conformations**

## MS.74.1

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**Combined X-ray Diffraction and Absorption Measurements of Active Catalysts**

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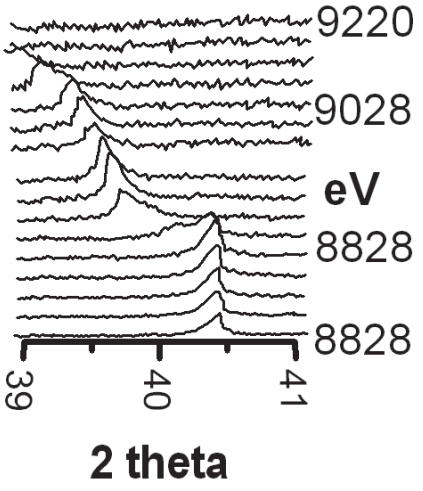
Combined X-ray diffraction (XRD) and X-ray absorption (XAS) has used effectively for 20 years [1]. At NSLS we have developed a new beam line for catalysis studies with combined XRD/XAS and *in situ* cells [2]. We have used the INEL curved linear detector as in the original experiments, but we have also used a Perkin Elmer amorphous silicon area detector and a silicon linear detector [3].

We will present expected and unexpected structural differences between the quantitatively analyzed XRD and XAS data. The most interesting was evidence for amorphous Cu metal in a CuO/Ceria catalyst. This is a remarkable demonstration between the measurement of long and short range order by the two techniques.

Experiments which combine two techniques can suffer from the compromises made to allow the combination. For instance, the XAS is measured at the most highly absorbing wavelength and consequently, the diffraction patters are difficult to correct for absorption. An obvious solution to this problem is moving away from the absorption edge when the diffraction is measured. However, this makes the time gap between XRD and XAS measurements larger.

On the other hand if there is sufficient flux and fast detectors, a diffraction pattern can be collected at each XAS point and the diffraction data can corrected for changing wavelength. The figure shows the raw time-resolved diffraction data at constant energy followed by measurement during a part of a single XAS scan of $CuFe_2O_4$ during CO reduction. Further analysis is in progress.

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## MS.74.2

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**Modulation Enhanced Diffraction: a new tool for solving crystal structures and study solid-state kinetics**

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When a system is perturbed by a periodic external stimulation, e.g. concentration, pH, light flux, pressure and temperature, for many materials the structural response is also periodic. Periodic perturbations are used frequently in spectroscopic investigations because they enhanced Sensitivity or Signal to Noise and introduce selectivity into experiments. This technique has been called Modulation Excitation Spectroscopy (MES) [1, 2].

We have adapted this methodology for diffraction and named it Modulation-Enhanced Diffraction (MED). First we present the theory that is developed to explain the kinematic diffraction response of a crystal when it is subjected to a periodically varying external perturbation [3]. We show that if a part the local electron density varies linearly with an external stimulus, the diffracted signal is not only a function of the stimulation frequency $\Omega$, but also of its double $2\Omega$. These frequency components can provide selective access to partial diffraction contributions that are normally summed up in the interference pattern. MED simulations and experiments will be presented where a phasing process applied to partial diffraction terms allow to recover *directly* the substructure actively responding to the stimulus.

Second we have also combined MED with its spectroscopic analogue, MES. Our experimental results using *in situ* MES-MED will be presented. These data contain both the information responsible for structural transformation in the long range from diffraction, while the spectroscopic techniques yield detailed insights into local chemical