Interpretation of the Cu K-edge EXAFS spectra of Cu_3N using *ab initio* molecular dynamics

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Copper nitride (Cu_3N) has a cubic anti-ReO_3-type structure composed of NCu_6 octahedra joined by corners. The dynamic properties of its lattice are determined by the anisotropic thermal vibrations of copper atoms, having stronger amplitude perpendicular to linear N-Cu-N atomic chains. As a result, Cu_3N has low decomposition temperature of about 300-470°C. Also its thermal displacement parameters suggest some degree of positional disorder at the Cu site, which can be responsible for the structural instability of Cu_3N under pressure. X-ray absorption spectroscopy is ideally suited to probe in-situ local atomic structure of Cu_3N as a function of external conditions [1, 2]. However, the analysis of total Cu K-edge EXAFS spectrum of Cu_3N is a challenging task due to outer shells overlap and multiple-scattering contributions.

Our preliminary attempts to use classical molecular dynamics to interpret EXAFS of Cu_3N, based on the approach suggested in [3], failed to describe accurately the lattice dynamics and, particularly, correlation effects already in the second coordination shell of copper. Therefore, in this study, we performed ab initio molecular dynamics (AIMD) simulations of Cu_3N in the temperature range from 300 K to 700 K in order to elucidate the details of lattice dynamics and anharmonicity of the Cu-N and Cu-Cu bonding. The AIMD simulations were done based on Kohn-Sham density functional theory (DFT) by the CP2K code using "Piz Daint" supercomputer at the Swiss National Supercomputing Centre.

To validate the obtained theoretical results, we performed a direct comparison with the Cu K-edge EXAFS using the MD-EXAFS approach developed in [3]. We demonstrate the efficiency of the MD-EXAFS approach in combination with AIMD method for theory validation and temperature dependent structural properties description in Cu_3N. The advantages and limitations of this approach are discussed.

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