Probing the quantum thermal fluctuations of nuclei at the Mg, Al and Si *K* Edges

R. Nemausat[1,2], D. Cabaret[1], et Ch. Gervais[2]

[1] IMPMC, Sorbonne Universités - UPMC Univ Paris 06, CNRS, MNHN, IRD, UMR 7590, case 115, 4 place Jussieu, 75005 - Paris - France. Email: ruidy.nemausat@impmc.upmc.fr
[2] LCMCP, Sorbonne Universités - UPMC Univ Paris 06, CNRS, UMR 7574, Collège de France, 11 place Marcelin Berthelot, 75005 - Paris - France.

X-ray Absorption Near Edge Structure (XANES) spectroscopy is a chemically selective local probe of the electronic environment of nuclei. XANES spectra are usually modeled within Density Functional Theory (DFT), considering the nuclei at their equilibrium positions. However, in the case of XANES, a pre-edge structure can be observed at the *K* edge of light cations in various minerals and oxides. It was shown, for α-Al_2O_3, at the Al *K* edge [1], that electronic transitions occurring in the pre-edge involve the 3*s* empty states of the Al absorbing atom. In the electric dipole approximation these $1s \rightarrow 3s$ transitions are forbidden. This symmetry violation is due to the nuclear motion [2] with a transition rate increasing with temperature. Considering the energy ranges involved (less than 2 keV), the same vibration effects can be observed using Electron Energy Loss Spectroscopy (EELS).

Using an experimental and theoretical coupled approach, the present work aims at studying the influence of the quantum thermal fluctuations on XANES spectroscopies, occurring especially in the *K* pre-edge structures.

We develop a DFT-based approach, that incorporates the quantum motion of nuclei in the harmonic approximation. Using the QUANTUM ESPRESSO suite of codes [3,4], we first compute phonon frequencies and harmonic dynamical matrices, and then, we generate various non-equilibrium structures for each temperature. Finally, we compute XANES spectra on these configurations and average the results. In parallel, we work on enforcing the theoretical background. From the experimental point of view, our aim is to obtain high quality temperature-dependent *K* edge XANES spectra of various oxides such as SiO_2 polymorphs, α-Al_2O_3, $AlPO_4$ and MgO.

Here are presented the results obtained on various structurally simple oxides: MgO, α-Al_2O_3, α-quartz and stishovite. Using our method, we computed temperature dependent XANES spectra. The results agree with experimental records. There is the emergence of the pre-edge from the white line, and both shift towards lower energies with temperature, but there are still some discrepancies. The achievements are quite promising. We will then integrate possible anharmonic effects in the procedure. This work provides both experimental and theoretical evidence of the impact of vibrations on the spectrometric data of minerals and oxides. Considering the impact of vibration in XANES, this effect can be also taken into account when analyzing EELS data.

This work has been done within the LABEX MATISSE project (under the reference ANR-10-LABX-67), and received financial state aid managed by the Agence Nationale de la Recherche, as part of the programme "Investissements d'avenir" under the reference ANR-11-IDEX-0004-02. It was granted access to the HPC resources of IDRIS under the allocation 2013- and 2014-100172 made by GENCI (Grand Equipement National de Calcul Intensif).

Références

D. Manuel, D. Cabaret, C. Brouder, et al. *Phys. Rev. B*, **85** (2012).
D. Cabaret, Ch. Brouder *J. Phys.: Conf. Series*, **190** (2009).
C. Gougoussis, M. Calandra, A.P. Seitsonen and F. Mauri *Phys. Rev. B*, **80** (2009).
P. Giannozzi et al *J. Phys.: Condens. Matter*, **21** (2009).