Modeling nuclei quantum thermal fluctuations and core-hole effects in X-ray Raman scattering spectroscopy

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X-ray absorption spectroscopy (XAS) has recently been shown to be sensitive to nuclei quantum thermal vibration effects at the K edge of light elements like low-Z cations in oxides [1,2], with a main effect in the pre-edge of the spectra. The pre-edge peak is dominated by *s* empty states that are probed indirectly through electric dipole transitions thanks to vibration-induced hybridization between *s* and *p* empty states. X-ray Raman scattering spectroscopy (XRS), relying on non-resonant inelastic X-ray scattering, can provide both information equivalent to what is accessible by soft XAS, and information inaccessible to soft XAS. For low momentum transfer value q, the dipole electronic transitions dominate in the XRS spectra leading to a spectrum similar to a XAS spectrum. At high q value however, monopole electronic transitions that are forbidden in XAS become a significant part of the XRS spectrum. In this study, we focus on the Al *K* edge of α-Al_2O_3 measured in XRS and study the quantum nuclei quantum thermal vibrations effects on the electric dipole and monopole transitions.

The XRS spectra is calculated using the Xspectra module of Quantum-Espresso, using pseudopotentials, plane-wave basis sets and periodic boundary conditions, within a density functional theory framework [3,4,5,6]. The core-hole electron interaction is modelled using the final state rule in the FCH (Full Core-Hole) approach (1*s* core-hole taken into account during the pseudopotential generation, compensated by a background charge on all the cell). The nuclei quantum thermal vibrations effects are modelled in the Quasi-Harmonic Approximation (QHA), allowing the generation of temperature-dependent atomic configurations that are then used to compute an XRS spectrum with Xspectra. The theoretical spectrum is obtained by calculating the average of all the configuration spectra, and compared to experimental XRS spectra measured at the ID20 beam line of ESRF.

A good agreement between experience and calculation is achieved. Calculation allows the separation between contributions of electric dipole and monopole transitions. The Al *K* edge XRS spectrum of α-Al_2O_3 features an intense pre-edge peak due to direct and indirect 1*s*-3*s* transitions, indirect ones being caused by nuclei vibration-induced hybridization of 3*p* and 3*s* states, allowing to probe the 3*s* states of Al through the dipole transitions. This theoretical study shows thermal effects on XRS spectra at the Al K edge that could be of crucial importance in systems relevant for catalysis.

References

[1] - Nemausat et al., 2015 Phys. Rev. B 144310.
[2] - Nemausat et al., 2017 PCCP 19, 6246-6256.
[3] - Taillefumier et al., 2002 Phys Rev B 66, 195107.
[4] - Gougoussis et al., 2009 Phys. Rev. B 80, 075102.
[5] - Gianozzi et al., 2009 J. Phys.: Cond. Mat 21, 395502.
[6] - de Clermont Gallerande et al., 2018 Phys. Rev. B 98, 214104.