Quantum thermal effects of the Al *K*-edge X-ray Raman Spectrum in α-Al_2O_3

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X-ray absorption spectroscopy (XAS) was recently shown to be sensitive to quantum thermal effects at the *K* edge of low-Z cations in oxides, especially in the pre-edge region. The pre-edge peak is dominated by *s* empty states that are indirectly probed through electric dipole transitions thanks to vibrations. Relying on non-resonant inelastic X-ray scattering, X-ray Raman Spectroscopy (XRS) provides information equivalent to soft X-ray Absorption Spectroscopy (XAS), especially for low momentum transfer q values, i.e., when electronic transitions are dominated by dipole selection rules. For high q values, XAS-forbidden monopole electronic transitions significantly contribute to XRS spectra. In this study we focus on the Al *K* edge in α-Al_2O_3 as measured by XRS, and investigate the impact of quantum thermal fluctuations of nuclei on both monopole and dipole transitions.
The dynamic structure factors are calculated using the XSpectra module of Quantum-Espresso, using pseudopotentials, plane-wave basis sets and periodic boundary conditions, within a density functional theory framework. The electron-hole interaction is taken into account using the final state rule in the full core-hole approach. The quantum thermal effects are modelled in the Quasi-Harmonic Approximation (QHA) that allows the generation of temperature-dependent atomic configurations, used as input for XSpectra. The resulting theoretical spectra, obtained after an average of individual configurational spectra, are compared with temperature-dependent experimental XRS spectra carried out at the ID20 beam line of ESRF.
A good agreement between experimental and theoretical spectra is achieved. The calculation allows the separation between contributions of monopole and dipole transitions. The Al *K*-edge XRS spectrum of α-Al_2O_3 exhibits an intense pre-edge peak due to both pure and indirect 1*s*-3*s* transitions, whose respective contributions are quantified. The indirect ones are caused by vibrations, which permit to probe 3*s* states of aluminium through dipole transitions.
This theoretical study sheds thermal effects on XRS spectra at the Al *K* edge into light that could be on crucial importance in systems relevant for catalysis.