

X-ray absorption near-edge and pre-edge structure: the contributions of ab initio plane-wave pseudopotential calculations and of multiplet theory.

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X-ray absorption near-edge structure (XANES) and electron energy-loss structure (ELNES) spectroscopies are powerful techniques to probe electronic and structural information of materials [1,2]. However the interpretation of spectra is not straightforward and often requires sophisticated simulation tools. The basic principle for any ELNES or XANES calculation is given by the Fermi Golden rule: one considers a sum of probabilities per unit of time of making a transition from an initial state to an unoccupied final state through an interaction Hamiltonian, usually expressed within the electric dipole approximation [3]. Most calculation methods assume that this process can be described as a single-electron excitation. Among single-electron methods one distinguishes the real-space (cluster) approaches from the band-structure (using periodic boundary conditions) approaches. The real-space multiple scattering approach has been extensively used in the past twenty years [4,5,6]. However, multiple scattering theory has traditionally suffered from the muffin-tin approximation used to build the electronic potential. Here, we will present a non-muffin-tin scheme for calculating XANES spectra [7]. The method uses periodic boundary conditions, a plane-wave basis set and pseudopotentials. All-electron wave-functions are reconstructed within the projector augmented wave (PAW) method of Blochl [8]. The use of a Lanczos basis and of the continued fraction [9] permits the calculation of spectra for large supercells (hundreds of atoms), so that the core-hole-electron interaction as well as complicated materials can be easily treated [7].

The use of single-electron methods is justified in the case of all K -edges, for which electron-electron interaction in the final state is weak. In this case, XANES or ELNES spectra reflect the density of empty p -states projected on the excited atom (containing a $1s$ core-hole). When electron-electron interaction is strong, as in the case of $L_{2,3}$ -edges of metal transition elements, single-electron approaches fail to reproduce experiment [10]. Indeed in this case, experimental spectra do not represent the local density of empty d -states. We then use a parameterized method based on multiplet theory [11].

We will show several examples that illustrate the efficiency of both approaches (single-electron pseudopotential method and multiplet theory). In particular, core-hole effects will be investigated at the Si and O K -edges in α -quartz. For instance, Fig. 1 displays experimental XANES spectra compared with calculated spectra performed for a 72 atom supercell including a core-hole on the $1s$ level on the absorbing atom. We will also present a study of the environment of chromium impurities in α - Al_2O_3 (i.e., ruby) at the chromium K and $L_{2,3}$ -edges. On the one hand, the calculation of the Cr K -edge permits the validation of a structural model of ruby, obtained by structural and electronic relaxation ab initio calculations performed within the Car-Parrinello framework [12,13] (cf Fig. 2 left). On the other hand, the interpretation of the $L_{2,3}$ -edges of chromium permits the determination of electronic parameters, directly correlated to the beautiful red color of ruby (cf Fig.2 right). In addition,

we will present a detailed analysis of the pre- K -edge of chromium, where both electric dipole (E1) and quadrupole (E2) transitions are observed (i.e., both empty p and d states are probed). The E2 transitions are indeed evaluated within the two frameworks cited above.

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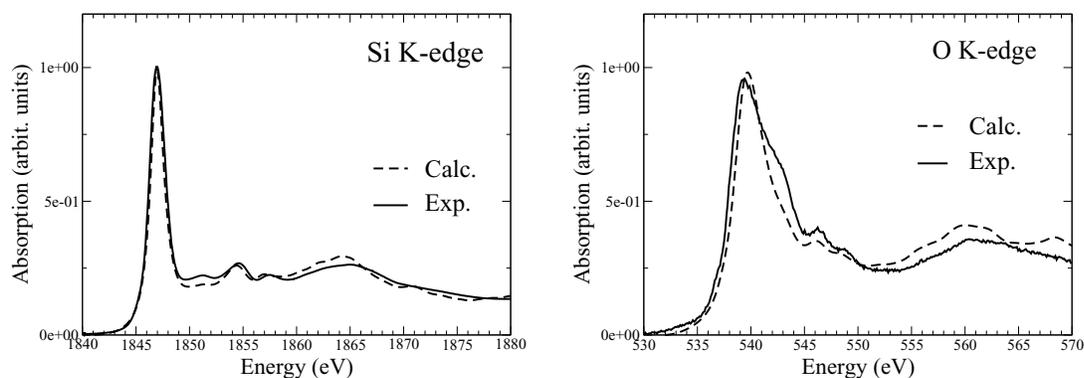


FIG. 1. Si (left) and O (right) K -edges in α -quartz. Comparison between XANES experiments and single-electron pseudopotential calculations.

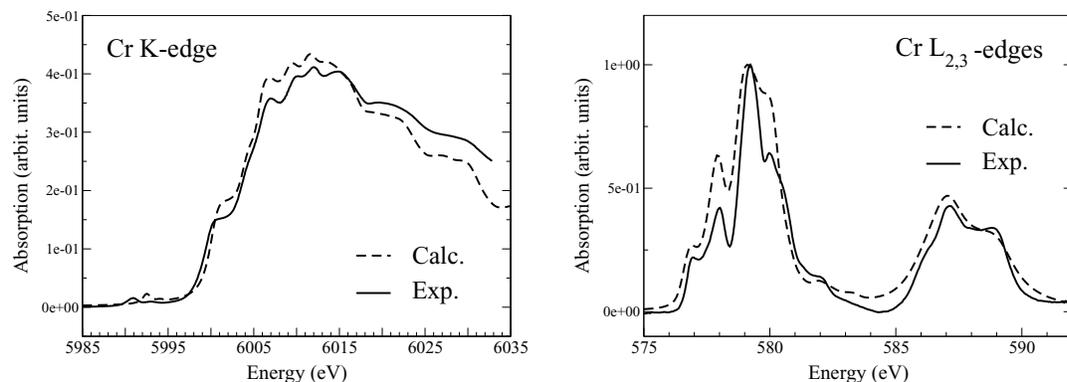


FIG. 2. XANES experimental and calculated spectra in ruby. Left: Cr K -edge (single-electron calculation). Right: Cr $L_{2,3}$ -edges (multiplet calculation).