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Coordination fingerprinting using EELS and XANES: experiments and *ab initio* multiplet calculations

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Both x-ray absorption near edge structure (XANES) and electron energy-loss near edge structure (ELNES) spectroscopy can be applied to determine coordination and valence state of the targeted ion in a specific compound [1]. Especially for transition-metal ions, crystal field splitting of the unoccupied 3d states probed by excitation of core-level electrons by either x-rays (XANES) or electrons (ELNES) can lead to drastic changes of spectral features [2].

While XANES, usually accomplished at synchrotron sources, possessing the benefit of a very good energy resolution (below 100 meV), is rather an integrating method, gaining information from typical sample volumes of some 10.000 μm^3 , ELNES can offer unsurpassed spatial resolution (just depending on the probe size of the electron beam in the Transmission Electron Microscope) with an energetic resolution on the range of typically 0,8 eV.

We show that *ab initio* charge-transfer multiplet calculations that take into account electronic configuration interactions [3] can be used to efficiently predict the spectral shape of transition-metal ions in different valencies and coordination states.

The variation of the Zr $L_{2,3}$ spectra for tetravalent Zr ions in different coordination states (six-, seven-, and eightfold coordinated), exemplified by different ZrO_2 polymorphs (monoclinic, cubic and tetragonal) and SrZrO_3 , is proven both experimentally and by calculation. Moreover, it will be shown that all zirconia polymorphs and in particular also cubic and tetragonal ZrO_2 , that both have eightfold coordination, can be differentiated using Zr $L_{2,3}$ edge XANES. It is shown that even ELNES at high energy electron losses (above 2,2 keV for the Zr $L_{2,3}$ edge) can be applied for a successful spectrum fingerprinting, in combination with the multiplet calculation thereof [4].

Concerning the interpretation of transition-metal white lines, three fersnoite-type vanadates ($\text{Ba}_2\text{VSi}_2\text{O}_8$ [BVS], $\text{K}_2\text{VV}_2\text{O}_8$ [KVV], and $\text{Rb}_2\text{VV}_2\text{O}_8$ [RVV]) were studied by XANES as model compounds. It is shown that not only the interaction of the target (V) ion with the anions of the first coordination sphere, but also with the cations of the second coordination sphere have to be taken into account in order to gain a good resemblance of the calculated V $L_{2,3}$ edge spectra with the experimental ones [5]. The importance of the latter finding is that simple experimental fingerprinting, i.e., the comparison with spectra obtained from known reference compounds used to interpret spectral features for decades, can result in misleading interpretations when interactions with second-nearest neighbouring cations are not taken into account.

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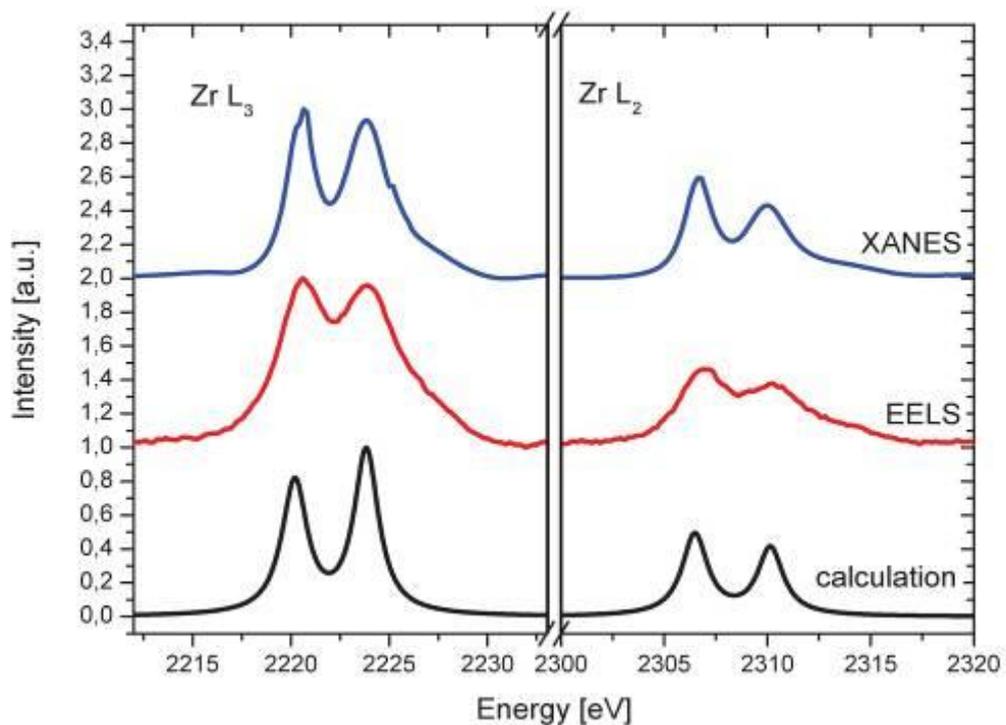


Figure 1. Zr L_{2,3} edge of SrZrO₃: XANES, EELS and multiplet calculation.

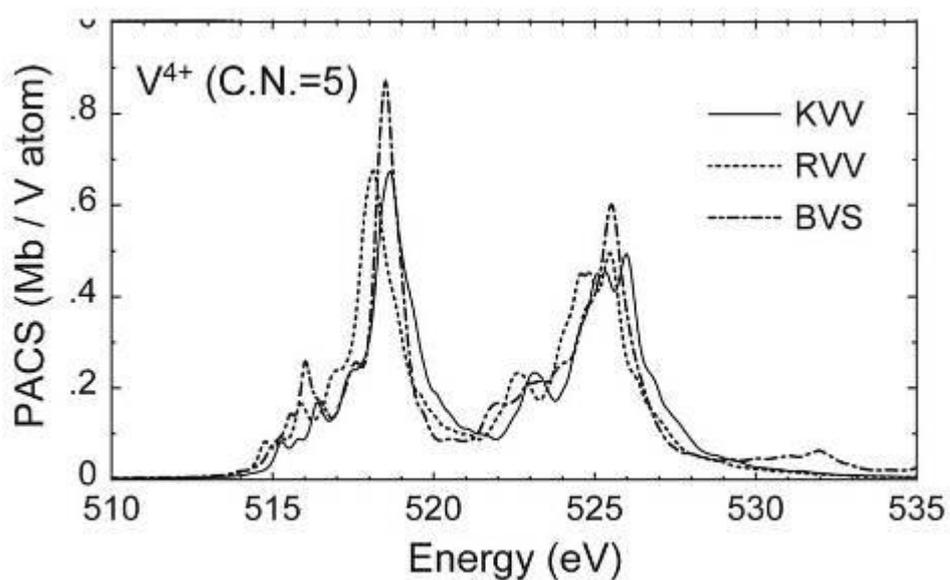


Figure 2. Juxtaposition of V⁴⁺ contributions to the theoretical V-L_{2,3} XANES in the three compounds BVS, KVV, and RVV.