3d-, 3s-Partial Fluorescence yield XAS and RIXS electronic structure characterization – some insights on the $L_{2,3}$-edge of 3d-metal materials

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Synchrotron-based x-ray absorption and emission methods for electronic structure determination have become a common option for scientists in physics, chemistry and materials science [1]. In order to have the best chemical (energy) resolution in x-ray absorption spectroscopy (XAS) as well as in resonant inelastic x-ray scattering (RIXS), Himpsel has shown that for all elements in the Periodic Table, the sharpest core levels are in the soft x-ray regime [2]. However, the soft x-ray regime has the disadvantage that the penetration depth is rather small [1], which requires vacuum for the experiment. As well, for XAS, normally performed in transmission-mode, alternative probing methods, like electron-yield and (partial) fluorescence yield are required. However these secondary decay yield methods might not reproduce the "true" XAS, especially for the fluorescence yield decay methods [3]–[5].

At the XAFS2015 conference, the presenting author has shown that for the soft x-ray $L_{2,3}$-edge of 3d-materials, 3d-PFY is different from the XAS in transmission mode due to the local core-hole exchange interaction [5]. In this contribution, some progress concerning simulation studies on 3s-PFY as an alternative decay method for XAS will be discussed, where in this 3s fluorescence process one circumvents the core-hole exchange interaction interference in the fluorescence. Although 3s-PFY is better than 3d-PFY in reproducing the $L_3/(L_2+L_3)$ branching ratio as observed for simulations on XAS in transmission mode, it still does not completely resemble XAS in transmission mode when common experimental constraints are taken into account.

In connection with the 3d-PFY-XAS and electronic structure characterization we also would like to discuss our findings on $L_{2,3}$-edge RIXS on Al_2O_3:Ti^{3+} and $LiCaAlF_6$:Cr^{3+} measured with the SolidFlexRIXS setup [6] at BESSY-II in Berlin, in terms of the electronic structure and the insights concerning the main crystal field parameter 10Dq in these systems [7], which we found to be different for the $L_{2,3}$-edge 3d-PFY-XAS and the $L_{2,3}$-edge RIXS and we have quantified the ratio between these different obtained values of 10Dq.

References

[1] F. de Groot and A. Kotani, *Core Level Spectroscopy of Solids*. 2008.
[2] F. J. Himpsel, "Photon-in photon-out soft x-ray spectroscopy for materials science," *Phys. Status Solidi* 248 (2011) 292.
[3] F. M. F. de Groot, *et al.*, "Fluorescence yield detection: why it does not measure the x-ray absorption cross section," *Solid State Commun.* 92 (1994) 991.
[4] R. Kurian, *et al.*, "Intrinsic deviations in fluorescence yield detected x-ray absorption spectroscopy: the case of the transition metal $L_{2,3}$ edges," *J. Phys. Condens. Matter* 24 (2012) 452201.
[5] P.S. Miedema, *et al.*, "State-dependent fluorescence yields through the core-valence Coulomb exchange parameter," *PRA* 89 (2014) 52507.
[6] M. Beye and P.S. Miedema, "Solid flexRIXS : A RIXS endstation for solid systems at BESSY II," *J. large-scale res. fac.* 3 (2017) A124.
[7] P. S. Miedema, *et al.*, "X-ray spectroscopy on the active ion in laser crystals," *PCCP* 19 (2017) 218000.