

# Chemical sensitivity of $K\beta$ and $K\alpha$ X-ray emission spectroscopy: insights from a systematic investigation on iron compounds

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K fluorescence X-ray emission spectroscopy (XES) is increasingly used in all branches of natural sciences to investigate the spin moment in  $3d$  transition metal compounds. Unlike the valence-to-core emission lines, the core-to-core transitions in  $K\beta$  ( $3p$  to  $1s$ ) and  $K\alpha$  ( $2p$  to  $1s$ ) do not probe the valence shell directly and the chemical sensitivity is thus indirect. In  $K\beta$  and  $K\alpha$  emission the chemical sensitivity arises from intra-atomic electron-electron interactions. In particular, the local spin sensitivity stems from the exchange interaction between the  $3p$  ( $K\beta$ ) or  $2p$  ( $K\alpha$ ) core-hole and the  $3d$  valence shell spin of the transition metal ion, which is larger for  $K\beta$  than  $K\alpha$  [1]. The magnitude of the exchange interaction depends for a given element on the valence shell spin, which, within an ionic picture, is defined by the metal atom oxidation and spin state. This is a very crude description of the electronic structure and the influence of covalence in  $K\beta$  has been pointed out by several authors [1,2].

Herein, we present a thorough investigation of  $K\beta$  and  $K\alpha$  XES spectra measured on a wide range of Fe compounds with the aim to get further insights into the spectral sensitivity beyond an ionic model. More than 30 samples with different oxidation state (+2, +3, +4 and mixed-valence), spin (high spin, low spin and mixed-spin), ligands (fluorides, oxides, sulfides, etc.) or local coordination (octahedral, tetrahedral) were measured at beamline ID26 of the ESRF. We analysed the experimental spectra in terms of commonly used quantitative parameters ( $K\beta_{1,3}$ -first moment,  $K\alpha_1$ -full width half maximum, and integrated absolute difference –IAD- [3]) and we examined the fine structure in the difference spectra. Semi-empirical multiplet calculations were also performed to interpret the experimental trends.

Our results provide evidence that covalency strongly influences both  $K\beta$  and  $K\alpha$  lines. We establish a reliable local spin sensitivity of  $K\beta$  XES as it is dominated by the exchange interaction whose variations can be quantified by either  $K\beta_{1,3}$ -first moment or  $K\beta$ -IAD and result in a systematic difference signal lineshape. For  $K\alpha$  XES, the smaller exchange interaction together with the influence of other electron-electron interactions make it difficult to extract a quantity that directly relates to the spin.

## References

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