Soft X-Ray Spectroscopies as Ideal Probes of the Electronic Structure of Transition Metal Compounds.

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Abstract. Transition metals form compounds with very interesting properties and a wide range of applications. On the other hand, x-ray spectroscopies are powerful tools that provide important information about the electronic structure of these strongly correlated compounds. In particular, soft x-ray absorption (XAS) and resonant inelastic x-ray scattering (RIXS) at the transition metal L₂,₃ edge can be used to selectively probe electronic states which in many cases determine the properties of the compound. Taking advantage of the element specificity and the electric-dipole selection rules, XAS gives a very complete picture of the transition metal unoccupied states, which contain information about the atomic multiplet, the crystal field and the chemical environment. RIXS spectra show details of site-projected valence states, and it also reveals the structure of d-excited states. In this talk two examples are presented that illustrate the use of these spectroscopies to study important transition metal compounds. In the first one XAS is used to track the oxidation state of the lithium ion battery electrode LiMn₂O₄ across the charge-discharge cycle. Comparison between the experimental spectra and the results of a charge transfer atomic multiplet calculation allows a direct determination of the manganese oxidation state in each stage. In the second example XAS is used to study the effect of the Cu ↔ Mn replacement in a family of <111> layered halide perovskites, which could be applied in solar cells. It is shown that the interpretation of copper XAS is hindered by the fact that soft x-rays may reduce Cu ions right at the surface of the compound. XAS and RIXS spectra, however, are in excellent agreement with the calculation, and show a Mn²⁺ ion in a close to perfect octahedral symmetry.

Key words: X-Ray Absorption and Emission; Electronic Structure; Transition Metal Perovskites.