

Role of iron in metal-metal charge transfer: a RIXS investigation of FeTiO₃

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From natural mineral dusts to artificial solar-cells, iron and titanium oxides are extensively investigated for their photocatalytical properties. Promising applications range from solar-driven water-splitting to air/water photo-remediation, and are motivated by the earth abundance of these materials. To improve the individual shortcomings of titanium oxide (TiO₂) and iron oxide (Fe₂O₃), numerous investigations have focused on mixed iron and titanium oxides, either as heterojunctions or doping such as Ti-doped hematite.^[1] While the increase of photocatalytical properties has been observed, the role of the Fe-Ti combination in the enhancement of the optical properties and charge carrier transport remains speculative. Photo-induced metal-metal charge transfer (MMCT) is expected to be the main mechanism that enables to harvest solar light energy. By analogy with Fe,Ti-doped blue sapphire (Al₂O₃), the MMCT has also been assigned in the isostructural ilmenite (FeTiO₃),^[2] as well as other binuclear complexes^[3] based on optical spectroscopy. Despite several experimental and theoretical studies, the relation between the atomic and electronic structures and the optical properties of compounds presenting MMCT is still not well understood. First-principal calculations of the electronic structures remain a challenge because of the complex electronic correlations, and result in controversial theoretical predictions of the Fe and Ti respective valence states.^[4]

This paper focuses on the investigation of FeTiO₃ as a model compound for Ti-doped hematite and MMCT using Resonant Inelastic X-ray Scattering (RIXS). RIXS is a photon-in photon-out process that relies on the transition upon x-ray absorption to an unstable excited intermediate state followed by the decay to the final state by x-ray emission. It provides an element selective probe of the speciation and of the low energy excitations complementary to the optical spectroscopy. The ability of RIXS to probe MMCT in FeTiO₃ was already suggested by the results from Agui et al.^[5]

We used RIXS at Fe K-edge (1s core-hole) to investigate the role of iron in the MMCT in FeTiO₃. Results from 1s2pRIXS measured at the beamline B6-2 (SSRL) enables to observe excitonic resonances at the Fe pre-edge peaks (1s → 3d) and unusual non-local transitions at the onset of the K edge. Comparison with ligand field multiplet and DFT calculations enabled to confirm the divalent speciation of Fe ions and to assign the non-local transitions to Ti 3d states hybridized with the Fe 3d states via the O 2p.^[6] Complementary RIXS investigations of the low energy excitations at the Fe K-edge were performed at the beamline ID20 (ESRF). The dispersion of the RIXS excitations measured at the pre-edge, at the non-local peaks and at the main edge enables to discuss the nature of the different charge-transfer channels. Interpretations in terms of electronic structure and optical properties of FeTiO₃ will be discussed. It would be appealing in the next steps to use these techniques to study the effect of Ti-doping in hematite in real photocatalyst systems. Furthermore the better understanding of the Fe K-edge provides

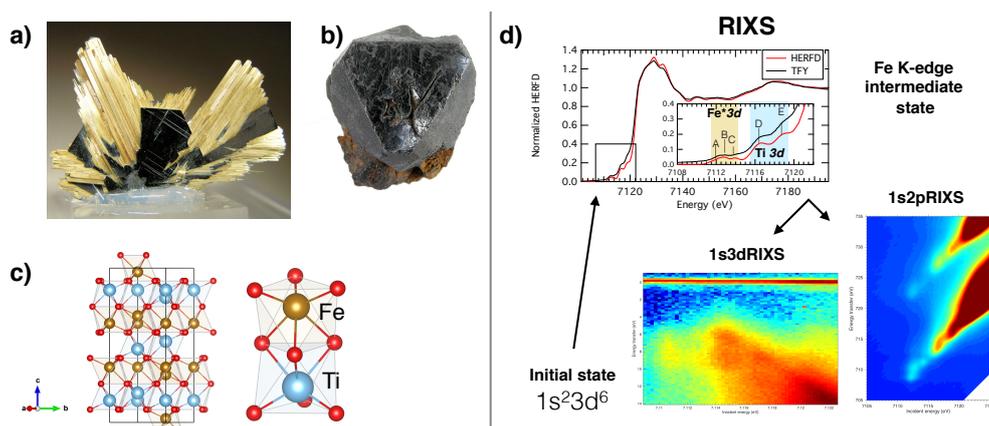


Figure 1: a) Natural epitaxial growth of rutile on hematite, b) natural ilmenite,^[7] c) ilmenite structure and zoom on the Fe-Ti face-sharing octahedrons, d) Fe K-edge RIXS process and the two different final states investigated.

the basis for future time-resolved spectroscopic investigations of the lifetime of MMCT excited states.

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