Charge Transfer in FeOCl Intercalation Compounds and Its Pressure Dependence

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For the last two decades, FeOCl has been considered as a well-suited host matrix to grow oriented conductive polymers, owing to its quasi two-dimensional crystallographic structure. We measured as a function of pressure the Fe K (3p→1s) emission and the absorption at the Fe K edge in the partial fluorescence yield (PFY-XAS) for FeOCl and polyaniline (designated hereafter as PANI) and Na intercalated FeOCl. At ambient pressure, measurements were performed at both 10 and 298 K.

As shown in (a), both absorption spectra for PANI and Na intercalated FeOCl present significant differences compared with the non-intercalated FeOCl. These differences have supposedly an electronic origin. Indeed, about 10-13% of the Fe sites are reduced into Fe(II) in the case of the intercalated compounds, while the crystal structure is supposed almost identical within the FeOCl layers with or without intercalate. In (b), the presence of a K ' satellite in the emission spectra of both FeOCl and Na-FeOCl suggests that Fe is in a high-spin state in these compounds. Interestingly, this satellite vanishes in the case of PANI-FeOCl, signifying a magnetic collapse. No difference was observed either in the absorption or in the emission spectra between 10 and 298 K.

When applying a pressure as low as 0.4 GPa in the case of FeOCl and 1 GPa in the case of PANI-FeOCl, the center of mass of the K emission is shifted towards lower photon energies, as seen in (e,f). This change appears more pronounced in the case of PANI-FeOCl than FeOCl. The origin of this shift has yet to be understood, either in terms of charge transfer or spin transition. The absorption spectra obtained on FeOCl (c) show a gradual decrease of the intensity for both structures at 7124 and 7129 eV when increasing the pressure. The absorption spectra obtained on PANI-FeOCl have their edge shifted by 0.5 eV towards lower photon energies when the pressure is increased up to 6.5 GPa, suggesting a partial reduction of the Fe sites.

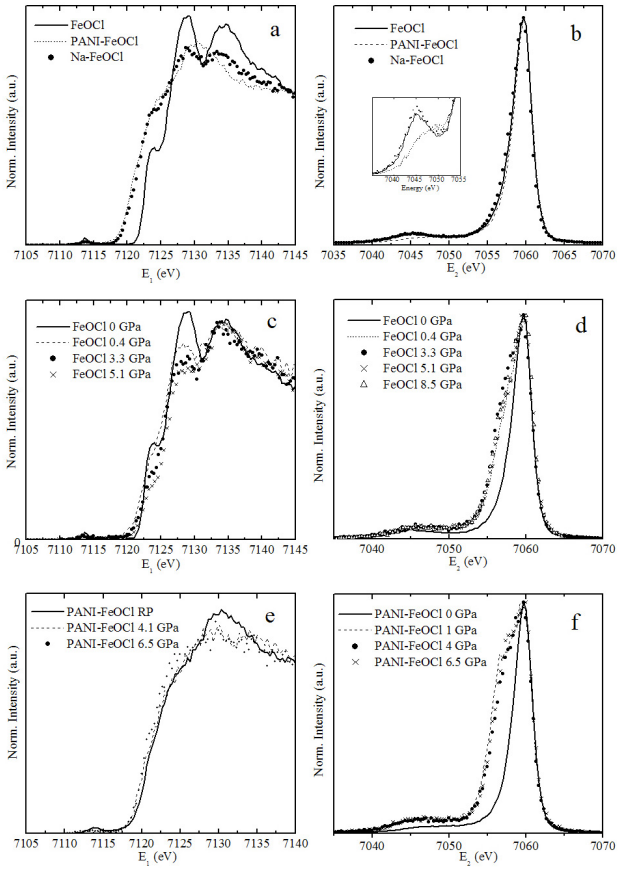

Figure: PFY-XAS (a) and emission (b) at ambient conditions; PFY-XAS (c) and emission (d) as a function of pressure for FeOCl; PFY-XAS (e) and emission (f) as a function of pressure for PANI-FeOCl.