Local 3d electronic states of amorphous coordination polymers revealed by high-resolution soft X-ray absorption spectroscopy

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The two-dimensional amorphous coordination polymers : $[M\{Ni(CN)_4\}]$ (M = Mn^{2+}, Fe^{2+}, Co^{2+}, hereafter ***M*Ni**) has occlusion property for water molecules[1]. Our previous soft X-ray absorption spectroscopy (XAS) study, corresponding to $2p \rightarrow 3d$ absorption process, indicates that the N-coordinating M^{2+} ions have the T_d symmetry and the crystalline field effects are correlated with the degree of the occlusion property (Assignment No.S18005). In order to understand the electronic states of transition metal ions in detail, we performed high-resolution XAS for ***M*Ni**.

XAS measurements were carried out at BL-11 in SR Center of Ritsumeikan Univ. Thanks to optimize the X-ray optical system, the energy resolution was improved about twice better (from 500 meV to 250 meV according to our spectral calculations). The ***M*Ni** samples were treated under the glove box and transfer to chamber not to expose the air. XAS spectra were detected in the TEY, PEY, and PFY modes simultaneously. All measurements were measured at room temperature.

We have found that PEY mode is a better yield method for making quantitative discussions on XAS measurements on transition metal complexes so far. [2-4]. Figure shows the XAS spectra of Co, Fe, Mn ions of ***M*Ni** in PEY mode. Owing to the high-resolution measurements, we successfully observed the multiplet structures originating from the Coulomb interaction between $2p$ core holes and $3d$ electrons in the XAS final states. The spectral shape reflects that the Co, Fe, and Mn are in T_d symmetry, confirming the reproducibility of previous XAS results.

In order to discuss the contribution of the ligand field effects to the occlusion property, we have carried out the spectral simulations of cluster-model under T_d symmetry using Xtls ver.9.0 program[5]. As shown in the red solid line of Figure, the simulated spectra can reproduce the experimental spectra. We compared the value of the crystalline field splitting ($10Dq$) and the charge transfer energy between transition metal ions and ligand ions (Δ) (not shown here) and demonstrated that the charge transfer effects are also correlated with the occlusion property. This suggests that the ligand field effects have a key role of the occlusion effects within amorphous coordination polymers.

References

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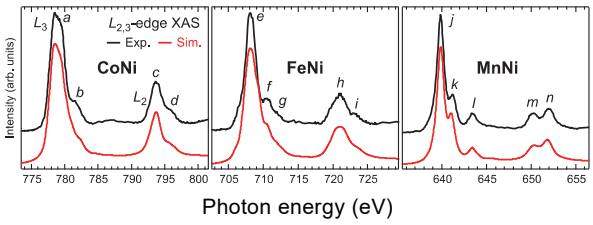

Figure The $L_{2,3}$-edge XAS spectra for M = Co, Fe, Mn of $[M\{Ni(CN)_4\}]$ and cluster model simulation. The spectral features are labeled as *a*-*n*.