

# Multiway hyperspectral data analysis of trace element/valence-state in W-type ferrite magnet by concurrent high-angular resolution electron channeling X-ray/electron spectroscopy

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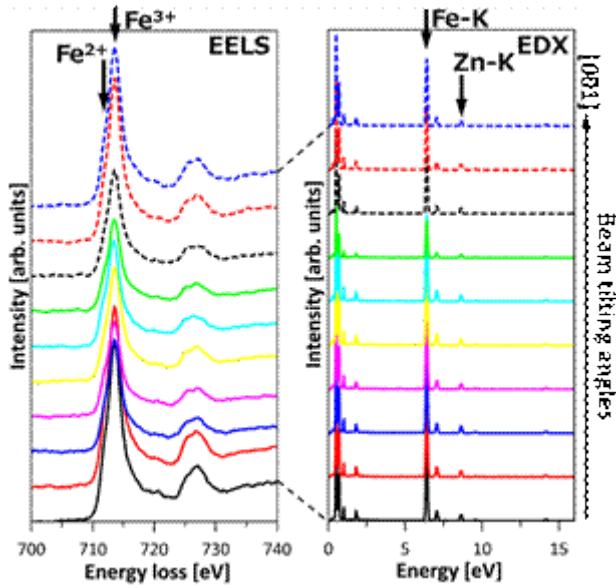
High angular resolution electron channeling X-ray/electron spectroscopy (HARECXs/HARECES) is a site-selective analysis technique based on electron channeling phenomena associated with the dynamical electron scattering effects [1]. As the incident electron beam is rocked with a pivot point fixed on the sample surface, the symmetry of the electron standing waves (i.e., Bloch waves) changes and site-selective spectroscopic signals can be collected as a function of the incident beam direction accordingly. Each site-specific spectrum can then be isolated from the obtained dataset, using a multivariate curve resolution (MCR) technique [2]. However, MCR does not provide a unique solution, and hence, additional constraint conditions should usually be imposed, particularly for extracting weak components. In the present study, we applied one of the blind source separation techniques, called the 'structured data fusion (SDF)' in tensor decomposition [3], a more generalized framework of MCR, to concurrently collect HARECXs/HARECES datasets; thereby the site-specific valence states (i.e., electron energy-loss spectral (EELS) components) associated with functional element doping were effectively extracted.

The sample used in this study was Zn-doped W-type ferrite,  $\text{SrZn}_2\text{Fe}_{16}\text{O}_{27}$ , which has seven inequivalent Fe sites, each contained in a lattice plane subsequently stacked along the *c*-axis of the unit cell. EELS and energy-dispersive X-ray (EDX) spectra were collected by consecutively tilting the incident beam along the [001] direction with the 00/systematic row of reflections excited. Figure 1 shows the variations of Fe-L<sub>2,3</sub> electron energy-loss near-edge structure (ELNES) and EDX spectra as functions of the incident-beam tilting angle. We have minimized the object function of SDF tensor form given by Eq. (1) shown in the inset of Fig. 2, where the experimental EEL and EDX spectra were moderately coupled [4] so that the sampling coordinates are moderately coupled through the correlation matrix **N** as an additional constraint, except the conventional non-negativity constraint. The decomposed result is shown in Figure 3. The divalent Fe-L<sub>2,3</sub> ELNES was successfully extracted as the first EELS spectral component (Fig. 3(a)), and the corresponding EDX spectral component includes the strong Zn-K peak (Fig. 3 (b)). This implies that Fe<sup>2+</sup> occupies the sites where Zn is partly substituted for, consistent with the expected model. The isolated abundance profiles shown in Figs. 3 (c) and 3(d) were confirmed to be consistent with the profiles calculated on the basis of the dynamical electron elastic/inelastic scattering theory as well, where Zn preferably occupies Fe 4e and 4f<sup>IV</sup> sites, separately determined by the extended statistical ALCHEMI method [1].

In conclusion, the SDF technique can simplify the data analysis to isolate a hidden small spectral component, utilizing correlated properties between different spectroscopic data concurrently obtained, where otherwise, a more tedious data analysis procedure is necessary.

## References

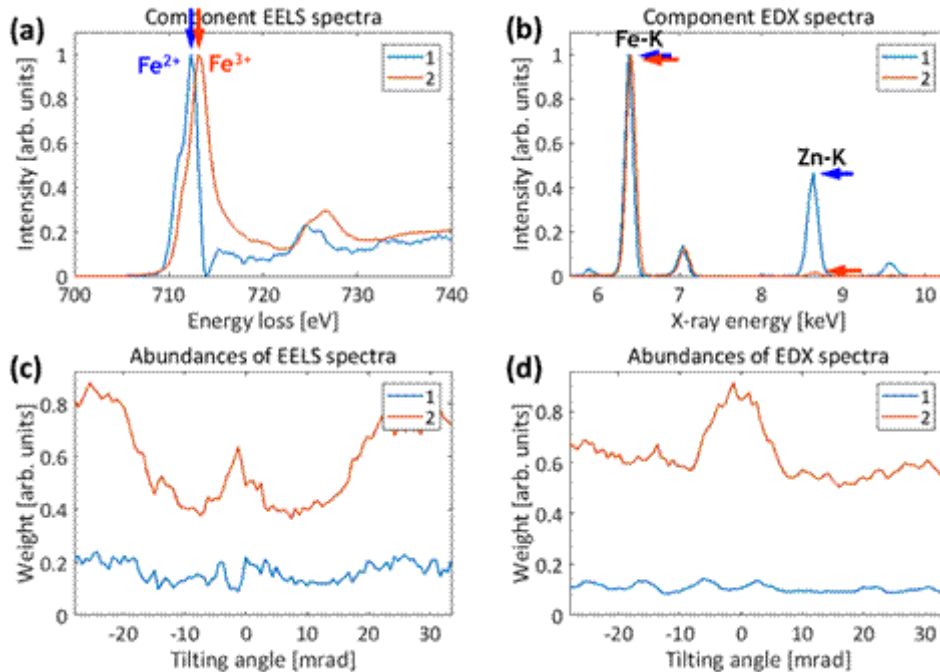
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**Figure 1:** Variations of EEL and EDX spectra as functions of incident-beam tilting angle.

$$\min_{\mathbf{C}, \mathbf{N}, \mathbf{S}_1, \mathbf{S}_2} [\lambda_1 \|\mathbf{X}_1 - (\mathbf{C} + \mathbf{N})\mathbf{S}_1^T\|^2 + \lambda_2 \|\mathbf{X}_2 - \mathbf{C}\mathbf{S}_2^T\|^2 + \lambda_N \|\mathbf{N}\|^2] \quad (1)$$

**Figure 2:** Equation referred to in the text. Objective function in SDF tensor form (i.e., coupled matrix decomposition) to be minimized.  $\mathbf{X}_1$ ,  $\mathbf{X}_2$ ,  $\mathbf{S}_1$ ,  $\mathbf{S}_2$ ,  $\mathbf{C}$ , and  $\mathbf{N}$  are matrices storing experimental EELS and EDX spectra, site-specific EELS and EDX component spectra, their abundances (weights of the components), and correlation between EELS and EDX, respectively.  $\lambda_i$  are weighting factors for individual terms, and  $\|\cdot\|$  stands for the Frobenius norm.



**Figure 3:** Extracted spectral component and corresponding abundance for EEL ((a), (b)) and EDX ((b), (d)), respectively.