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Combined Electron Spectroscopy and Imaging Associated with (S)TEM −Application of Multivariate Curve Resolution−

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Transmission electron microscopy (TEM) and its associated analytical instruments (*e,g*., electron energy-loss spectroscopy (EELS), energy- and wavelength-dispersive X-ray analysis (EDXA or WDXA), cathodoluminescence (CL)) are now indispensable for probing not only atomic scale structures but also chemical information of nano-size areas of functional materials. Recent development of digital technology has also enabled us to precisely control the electron beam, which facilitates to set the incident direction at the operator's disposal with respect to a specific symmetry axis of the crystalline materials of interest. At the same time by either utilizing the nano-probe or a position sensitive detector it is now also possible to visualize the projected spatial distributions of areas with different chemical properties, already known as a spectrum imaging (SI). Furthermore by applying statistical treatments based on the mathematical information theories to the raw SI datasets one can extract more information from them without reference spectra, embedded or hidden behind their apparent features. In the present talk, we present several effective application examples of a multivariate curve resolution (MCR) technique to EELS and WDX data sets; we adopted a fast, accurate and robust algorithm, called the modified alternating least-squares (MALS) method. It successfully separated different chemical states overlapping each other at the same energy region into pure constituent components.

1. Site specific electronic structure measurements by electron standing wave method [1]

ALCHEMI is well known as a site-specific elemental analysis by utilizing the standng wave (Bloch wave) propagating along a set of selected atomic planes in a crystalline material, and Taftø and Krivanek first applied a similar conditoin to EELS [2]. We revisited but further improved this method to obtain site-specific EELS (unoccupied states) and WDX (occupied states) spectra in the true sence of the words. The pure components, each corresponding to the separate atom sites, can be compared to the theoretical predicition to discuss the local chemical bonding states. In Fig. 1 are shown sets of experimental raw and resolved Al-K ELNES of $NiAl_2O_4$ reverse spinel and $Y_3Al_5O_{12}$ garnet structure (YAG) with the excitation error of opposite signs. In this example Al at the octahedral and tetrahedral sites are distinguished.

2. Chemical states mapping by EFTEM-SI [3] and STEM-SI [4]

A SI data cube (both in energy-filtering TEM (EFTEM) and STEM) can be treated by a set of a large number of spectra, which are supposed to be a linear combination of multiple ELNES features with different weights, each corresponding to a different chemical state depending on the position of the sample. MCR allows us to reconstruct the SI data into separate images of the resolved components, instead of extracting the energy-filtered images by selecting a part of the spectral features in a conventional manner. In Fig. 2 is shown an example for a $LiNiO_2$-based positive electrode of Li-ion batteries, in which the projected spatial distributions of two oxygen states and the corresponding resolved spectra are shown.

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References

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[4] S. Muto, et al, in preparation.

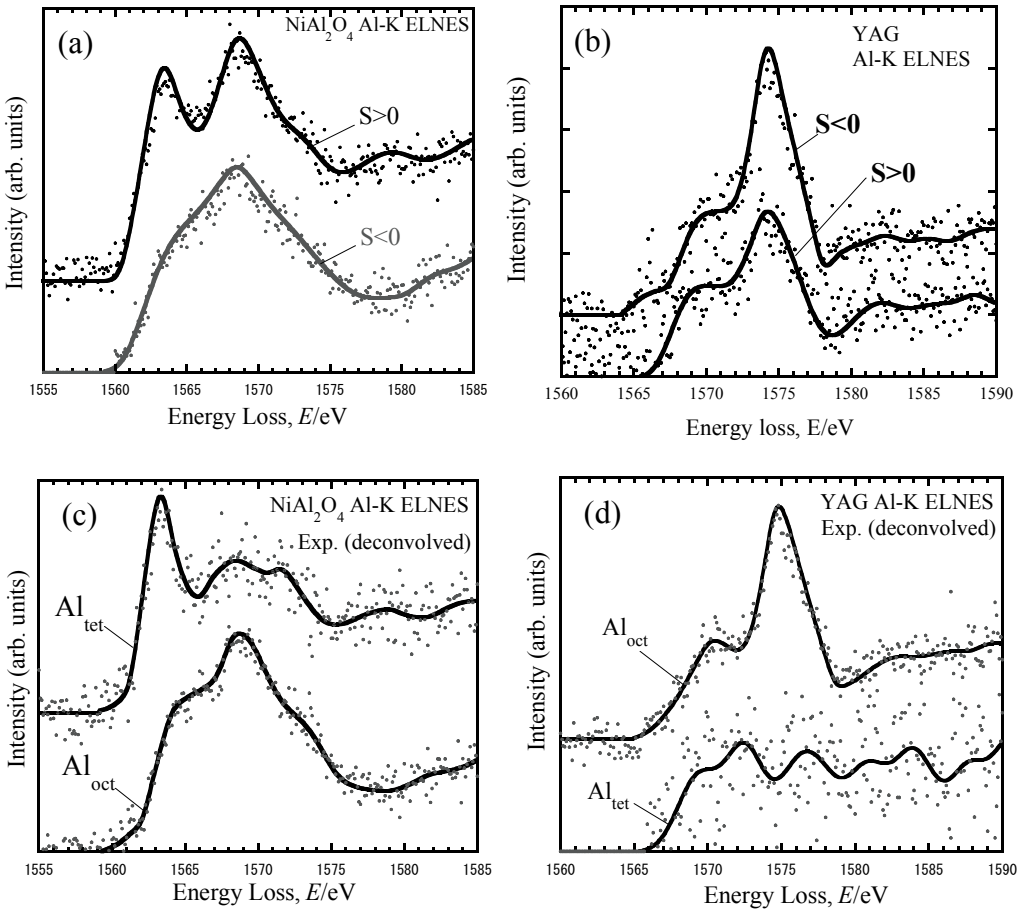

FIG. 1 Experimental Al-*K* ELNES (dots) of $NiAl_2O_4$ (a) and YAG (b). Solid lines represent noise-free line profiles after Pixon deconvolution. The pure component spectra are extracted as ELNES of tetrahedral and octahedral sites, using MALS algorithm, as shown in (c) and (d) for $NiAl_2O_4$ and YAG, respectively.

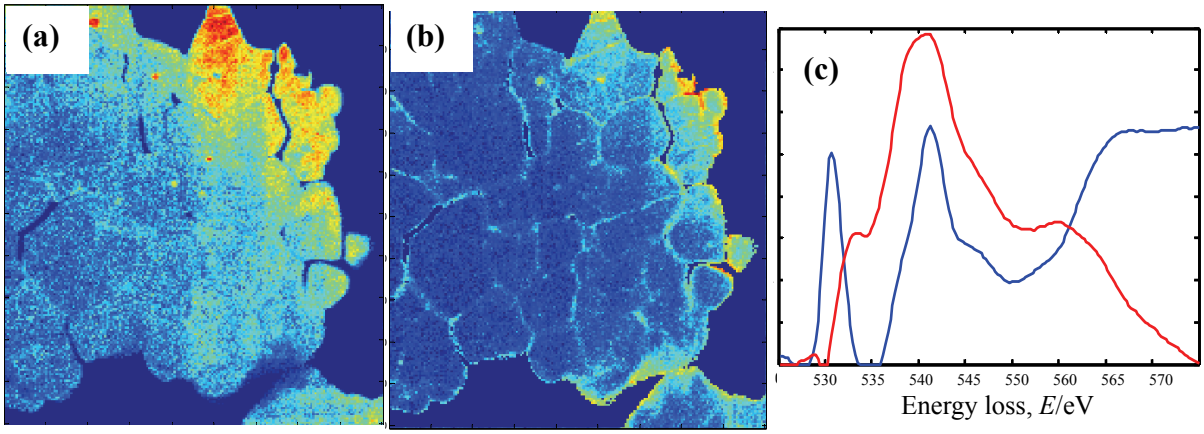

FIG. 2 Spatial distributions of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ phase (a) and NiO-like phase (b) in FIB-cross-sectioned sample, extracted from a STEM-SI image resolved by MALS algorithm. (c) Resolved spectra, blue line corresponding to (a) and red line to (b).