

Site-specific transition metal valence state analysis by high angular resolution electron channeled electron energy-loss spectroscopy

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Electron channeling along lattice planes or atomic columns in crystalline materials is utilized in energy dispersive x-ray spectroscopy (EDX) called as a high angular resolution electron channeling x-ray spectroscopy (HARECXS) [1], while also in electron energy loss spectroscopy (EELS) to clarify site-specific electronic structures with the aid of *ab-initio* calculations [2]. Recently, Ruzs *et al.* have developed a rigorous computation code calculating EELS intensities taking dynamical diffraction effects into account with arbitrary incident beam convergence angle, direction and collection angle [3]. This theoretical scheme has enabled us to optimize the measurement conditions for the site-specific EELS.

In the conventional electron channeling EELS [2], the incident beam direction is tilted with respect to the atom planes of electron channeling and the exit beam direction is selected so as to keep the same boundary condition as the incident beam, as schematically shown in Fig.1-a. Here we propose an alternative scheme, on the basis of the theoretical prediction: the energy dispersive direction of EELS detector is set perpendicular to \mathbf{G} of the channeling plane, as shown in Fig. 1-b. The site-selectivity is expected to vary with the detector CCD positions which correspond to different exit beam directions.

As an attempt of the detector position sensitive electron channeling EELS, we placed the EELS detector aperture at three positions parallel to the systematic row (Fig. 2-a). Totally 243 spectra were collected and two embedded components and their weights were extracted by the multivariate curve resolution technique. The resolved spectra (Fig.2-b) and their weights with respect to the detector position are consistent with the theoretical prediction, confirming the validity of the proposed scheme.

We analyzed using the scheme in Fig.1-a the site-specific valence states in MnFe_2O_4 spinel whose inversion parameter was estimated to be 0.4 by HARECXS. Fig.3 shows the resolved site specific spectra and their concentrations at 11 different beam orientations. The Mn- L_3 peak of the octahedral site exhibits larger intensity around 645 eV than that of the tetrahedral site. The octahedral and tetrahedral Fe L_3 peaks show a chemical shift by 0.2 eV, which is smaller than 0.4 eV in the case of the tetrahedral and octahedral Fe^{3+} in NiFe_2O_4 [2]. By comparing the site-specific spectral profiles with the theoretical ones, a mixed valence state such as $[\text{Mn}^{2+}_{0.6}\text{Fe}^{3+}_{0.4}]_{\text{Tet}}[\text{Mn}^{2+}_{0.32}\text{Mn}^{3+}_{0.08}\text{Fe}^{3+}_{1.52}\text{Fe}^{2+}_{0.08}]_{\text{Oct}}\text{O}_4$ can explain the spectral differences between the two sites.

References

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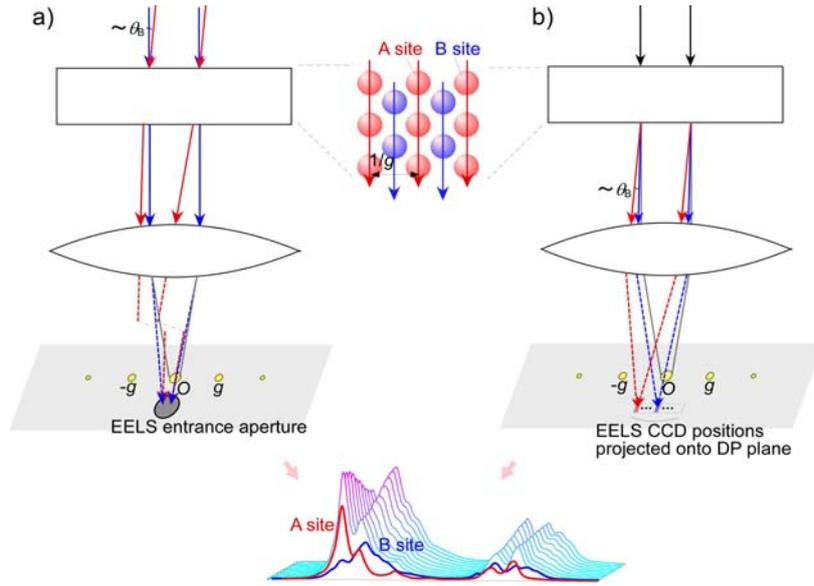


FIG. 1. Two methods detecting electron channeling EELS, incident beam rocking (a) and detector position sensitive scheme (b).

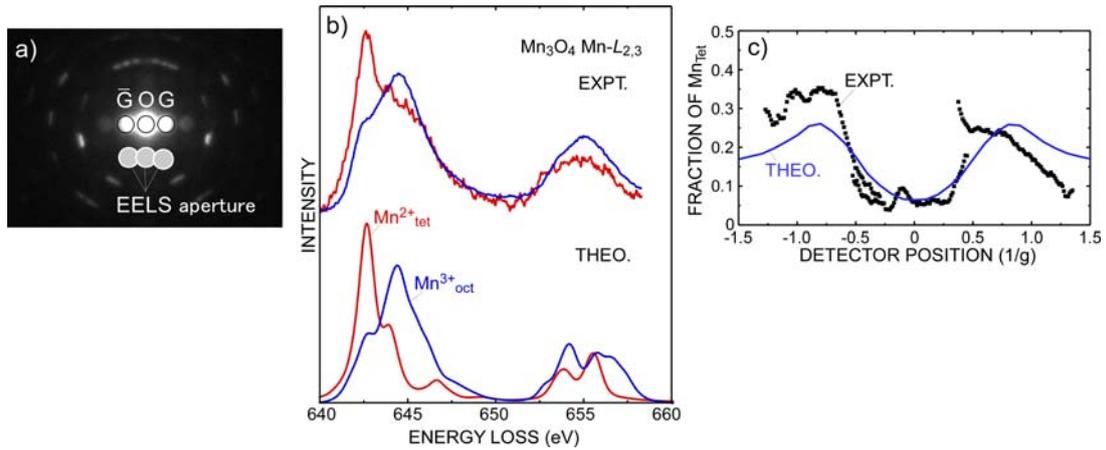


FIG. 2. Electron diffraction pattern with EELS aperture positions for the detector position sensitive measurement along the systematic row of $\mathbf{G}=400$ (a), resolved site-specific Mn- $L_{2,3}$ spectra of Mn_3O_4 (b), and tetrahedral site signal fractions with respect to detector positions (c). Theoretical spectra were calculated by the ab-initio code reported in ref. [4].

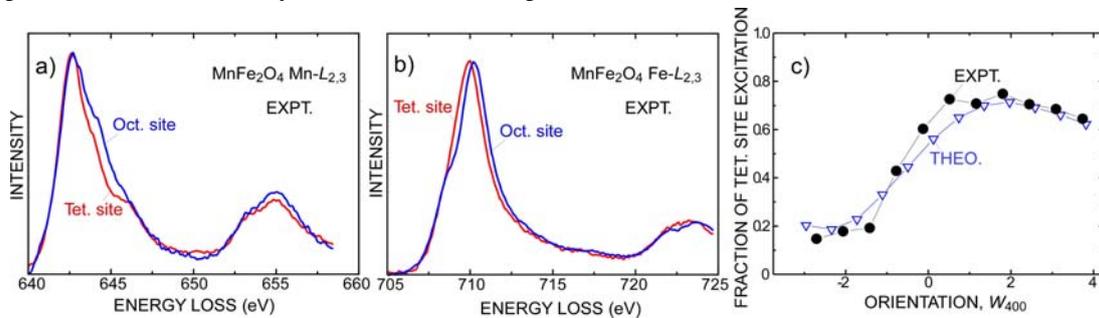


FIG. 3. Site-specific Mn, Fe- $L_{2,3}$ spectra resolved from the data with 11 different incident beam orientations (a,b) and tetrahedral site excitation fractions at these incident beam orientations (c).