Fine structures of Fe L-emission examined by a new HR-SXES instrument

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L-emissions of 3d transition metal elements, which range from 400 to 1000 eV, gives us fruitful information about chemical states and/or charged sates of those elements in compounds [1]. L α , β emission profile and its intensity reflect the energy distribution and the amount of 3d electrons, respectively [2]. The energy position of it is affected by the charged state (chemical shift). The Ll, η emission energy, which is due to transitons between inner-shell levels, is changed by a relaxation energy in the final state with a core-hole in 3s level [3]. Furthermore, the Ll, η line profile of a 3d transition metal element can contain the information of the magnetic moment of 3d electrons via 3s3d exchange interaction with the spin of the singly occupied 3s level in the final state [2]. Unfortunately, the applied spectrometer did not have an enough energy resolution to analyze the magnetic information in Ll, η lines. Thus, a larger energy-dispersion spectrometer designed for TEM [4] was remade as a spectrometer for EPMA [5] and examined L-emission spectra of Fe and Mn.

Figure 1 shows a photo of the spectrometer attached to a EPMA. The distance from a specimen to a valied-line-specing (VLS) grating is the same with that of a commercial spectrometer (right-hand side in Fig.1), but the distance from the VLS grating to a detector is about two times larger than that of the usual one. This means that the two time larger energy-dispersion is expected for this larger spectrometer. Detector is composed of a MCP ($7.5 \square m$ pitch) optically coupled with a CMOS camera.

Figure 2(a) shows Fe-Lα, β emission spectra of metal-Fe and Fe2O3. As Lα, β emission is due to transitions between 3d valence states and 2p inner-shell levels, the intensity profile reflects bonding states of 3d electrons. Lα peak of Fe2O3 is not symmetric and has a larger width by about 1 eV than that of metal-Fe. It could be due to chemical bonding of Fe atom with surrounding O atoms. A small structure between Lα and Lβ is seen for metal-Fe as indicated by a vertical line but not for Fe2O3. A higher energy position of Lα of Fe2O3 may be due to a chemical shift of L3(2p3/2) binding energy reflecting the charged state of Fe3+ of Fe2O3. Figure 2(b) shows Ll, η emission peaks of metal-Fe and Fe2O3. As Ll, η emission is due to transitions between inner-shell levels of 3s and 2p, symmetric intensity profile is expected. However, Ll intensity profile of Fe2O3 shows a shoulder structure in the lower energy side of the peak as indicated by a vertical line unlike that of metal-Fe. This might be due to a 3s3d exchange interaction, an interaction between the magnetic moment of valence 3d electrons and the spin of 3s level with a hole in the final state. This type of interaction has been reported as a 3p3d exchange interaction for Kβ-emission spectra of high spin states of Mn ions [6].

Present high energy-resolution soft X-ray emission spectrometer attached to a EPMA clearly show a difference in intensity profile of Fe-L α emission of metal-Fe and Fe2O3, and also show a presence of structure in Ll line due to the 3s3d exchange interaction [7].



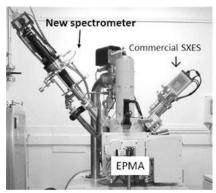


Figure 1. Photo of a newly constructed large-dispersion SXES spectrometer attached to EPMA.

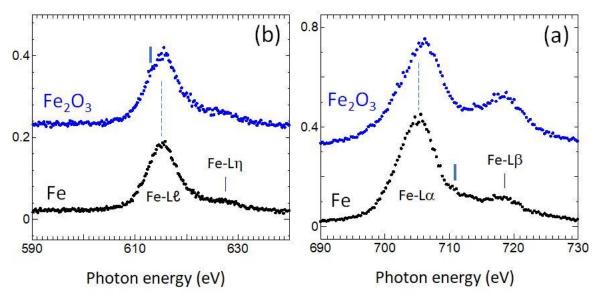


Figure 2. (a) Fe Lα,β-emission and (b) L ℓ ,η-emission spectra of meta-Fe and Fe2O3.

References

- 1. Terauchi, M., *Chap. 7 in "Transmission Electron Microscopy Characterization of Nanomaterials"* (ed. Kumar C S S R, Springer-Verlag Berlin Heidelberg, 2014)
- 2. Terauchi, M., *Microscopy* **68**, 330-337 (2019).
- 3. Terauchi, M., et al., IOP Conf. Series: Materials Science and Engineering 304, 012018 (2017).
- 4. Terauchi, M., et al., J. of Electron Microscopy **59**, 251-261 (2010).
- 5. Terauchi, M. et al., IOP Conf. Series: Materials Science and Engineering 891, 012022 (2020).
- 6. Peng G., et al., J. Am. Chem. Soc. 116, 2914-2920 (1994).
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