

## ANOMALOUS (RESONANCE) X-RAY SCATTERING FOR MATERIALS CHARACTERIZATION WITH SYNCHROTRON RADIATION

Yoshio Waseda

*Institute of Multidisciplinary Research for Advanced Materials (Tagen-ken), Tohoku University,  
Katahira- 2-chome 1-1, Aoba-ku, Sendai 980-8577, Japan ([waseda@tagen.tohoku.ac.jp](mailto:waseda@tagen.tohoku.ac.jp))*

Current progress in science and technology has let to the development of various functional materials such as fine ceramics, rare earth magnets, metallic glasses and semiconductors. The production of multi-layered thin films is also undoubtedly a key technology for the device fabrication in microelectronics. The properties of all these functional materials, usually consisting of multi-components, are well-known to heavily depend upon their atomic scale structure. Then, the determination of atomic arrangements or the atomic number density of constituent elements at the surface in materials is required with the highest priority in order to prepare an essential condition as inputs for discussing the relationships between the structure and the characteristic properties.

From both fundamental and engineering points of view, the use of anomalous (resonance) X-ray scattering (AXS) at energies near the absorption edge of constituent elements will provide answers for various questions unsolved by conventional X-ray or neutron diffraction methods by making available accurate partial structural functions for individual pairs of constituents or the environmental functions around a specific element in multi-component materials of both crystalline and non-crystalline systems. This is particularly true, because the AXS method enables us to reveal the structural

features of individual chemical constituents even for systems containing next neighbor elements in the periodic table, such as the distribution of cobalt in ferrite spinels or in amorphous ferrite glass.

**Figure 1** shows the anomalous dispersion factors of Fe, Co and Zn as a function of energy. At the higher energy side of the absorption edge, the theoretical values calculated by the relativistic Cromer-Liberman scheme do not coincide with the experimental data obtained from the absorption coefficient measurement for crystalline zinc ferrite, because of the presence of the fine structures such as EXAFS and XANES. On the other hand, it may be worth noting that the real component of the anomalous dispersion factors,  $f'$ , gives a drastic change at the lower energy side of the absorption edge and the absolute values of imaginary component of  $f''$  and their energy-variation are quite small. For these reasons, a large variation of  $f'$ , at the lower energy side of the absorption edge is convenient to the AXS measurement. The following point is also cited as one of the advantages of the AXS method. As easily seen in the results of **Fig. 1**, the characteristic absorption edge of any element is separated, at least by several hundred eV, so that a sufficient atomic sensitivity could be obtained even in a system containing next neighboring elements of the periodic table.

Figure 1.

Energy variations of anomalous dispersion terms for Fe, Co and Zn in the close vicinity of their respective K absorption edge, as calculated by the relativistic Cromer and Liberman method.

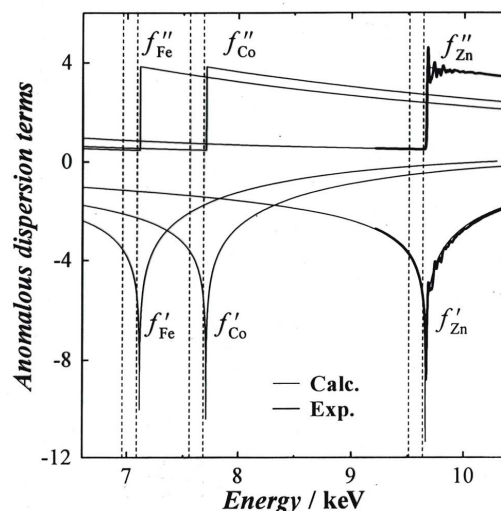


Figure 2.

Advantage of AXS method for measuring the X-ray scattering intensity of a solution sample in a cell or a film sample grown on a substrate.

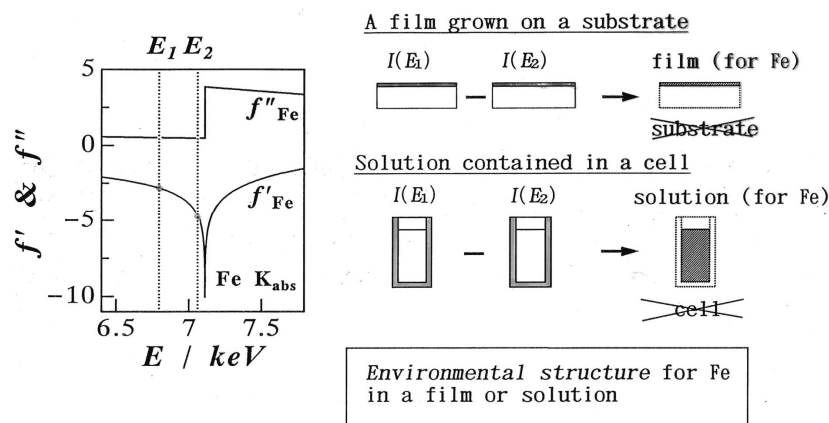
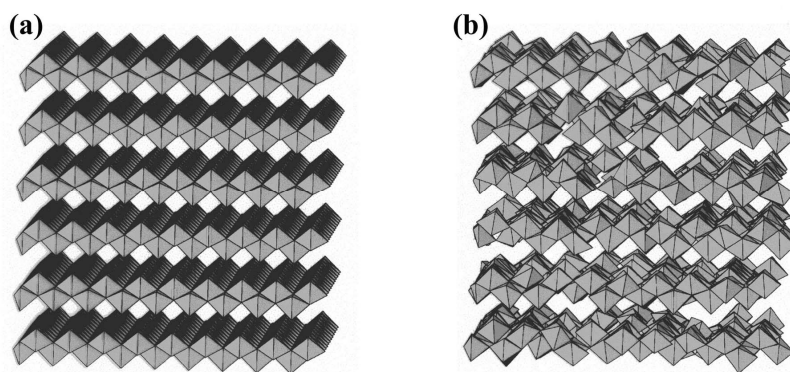


Figure 3.

Arrangements of the  $\text{FeO}_6$  octahedral units in (a) ideal  $\gamma\text{-FeOOH}$  and in (b)  $\gamma\text{-FeOOH}$  structure in corrosion products formed on the Fe-2%Cr alloy surface.



Another merit of the AXS method can also be stressed. In the AXS measurement, it is possible to change the weighting factors without the use of different samples. This contrasts with the situation of the isotopic substitution method requiring different samples where the structure is automatically assumed to remain identical upon substitution by the isotope. A solution sample is usually contained in a cell with windows transparent for X-rays. For quantitative structural analyses, the intensity from a solution sample alone should be obtained by accurately correcting the scattering intensity from the window materials measured. This is usually estimated from the total intensity data using the intensity only from the window materials corrected for absorption by the liquid sample. Sometimes it is extremely difficult to carry out two measurements (sample + cell and cell only) under the exactly same experimental conditions. As shown in the schematic diagram of **Fig. 2**, in the AXS measurements at the incident energies of  $E_1$  and  $E_2$  near the absorption edge  $E_{abs}$  of an element of  $A$ , each scattering intensity profile, of course, contains the contribution from the window materials as well as from the solution sample. However, when taking a difference between the two profiles at  $E_1$  and  $E_2$ , the contribution from the window materials as well as that from the none  $A$  pairs is automatically eliminated (see **Fig. 2**). In this

way, we can release from the tedious correction procedure for the window materials. This method was developed by analogy of the AXS measurement in amorphous thin films grown on a substrate, where the error in the subtraction process becomes more serious in a thinner film of sub-micron thickness.

The present paper will cover fundamentals of the anomalous dispersion effect, clearly appeared in the close vicinity of the absorption edge relevant to K- or L-shell electrons of a constituent, and the experimental apparatus suitable for structural studies by applying this interesting method. Then, the usefulness and validity of the AXS method are fully demonstrated using various examples; liquid alloys, solutions, amorphous thin films and ultra fine powders.

The AXS method coupled with reverse Monte Carlo (RMC) simulation is also found to be quite useful for providing the middle range (a few nm) ordering structure in crystalline and non-crystalline systems. This novel method enables us to provide a quantitative tool for describing imperfections in materials with complicated structure using polyhedral units. The usefulness of this method will be presented using the results of corrosion products formed on the steel surface as shown in **Fig. 3**, providing the Goethite ideal ( $\gamma\text{-FeOOH}$ ) case.