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ANOMALOUS SCATTERING AND DIFFRACTION ANOMALOUS FINE STRUCTURE

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Anomalous scattering and Diffraction Anomalous Fine Structure methods described herein are based on the variation with energy of the contribution of the atomic scattering factor to the structure factor of Bragg reflections. This *anomalous scattering* variation is important near the edge of a given atom *"A"* and induces a variation in the contribution of this specific atom to diffracted intensities. This property is used to extract directly the phase of the structure factor for complex crystallographic structures as in bio-crystallography in the so-called *MAD* analysis. It is also used for *contrast* analysis to perform element-selective diffraction experiments.

On the other hand, the *anomalous* (or *resonant*) *scattering* contribution which varies as a function of energy can be extracted from the diffracted intensities for a given atomic site or compound, so that diffraction and spectroscopy techniques can be combined to perform a site-selective spectroscopy by means of *Diffraction Anomalous Fine Structure*. Furthermore, this spectroscopy method can make use of *Anisotropy of Anomalous Scattering* to extract information on site symmetry or distortion.

It should be noted that this spectroscopic effect on diffraction intensity also yields an enhancement of the X-ray magnetic interaction by means of X-ray Resonant Magnetic Scattering. The latter effect, which is used to probe both the electronic structure and the magnetic properties, is not discussed in this chapter. In this contribution, after recalling the resonant scattering process and the properties of the resonant factors, we present a few examples of these applications and finally we focus on the Diffraction Anomalous Fine Structure method.

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1. ANOMALOUS SCATTERING, ABSORPTION AND REFRACTION

X-ray anomalous or resonant diffraction is related to the close relationship between scattering, absorption and refraction. It refers to the modification of the scattering intensity due to absorption processes. In this way, the long range structural information contained in diffraction peaks is combined with the chemical and local structure selectivity of X-ray absorption spectroscopy. Based on the anomalous scattering process, the Diffraction Anomalous Fine Structure (DAFS) method uses the variation of the diffracted intensities with photon energy and combines X-ray diffraction and X-ray absorption fine structure (XAFS) in the same experiment. Consequently, DAFS can provide site-selective and chemically selective structural information.

Elastic scattering from electrons or a nucleus of an atom *"A"* is proportional to the square of the modulus of the scattering length (b_A or f_A) of the atomic scatterer. For neutrons, b_A varies from nucleus to nucleus in a non-systematic way and can be negative. For X-rays scattered from electrons in an atom, f_A is defined as the ratio of the amplitude of the wave scattered by the atom to the amplitude of the wave scattered by a free electron. This term f_A is complex ($f_A = f_{0A} + f'_A + i\,.f''_A$) and varies with the scattering vector $\boldsymbol{Q}$ and the photon energy E [$|\boldsymbol{Q}| = (4\pi/\lambda)\sin\theta$, $E = \hbar\omega$, $\lambda = 2\pi c/\omega$)]. The Thomson scattering factor $f_{0A}(\boldsymbol{Q})$ is frequency or energy independent and is the Fourier transform of the electronic density in the atom, $\rho_A(r)$. This real form factor f_{0A} decreases with increasing $\boldsymbol{Q}$ and, in the forward scattering limit, tends to the atomic number Z_A in electron units (e.u.). A fraction of the X-rays is absorbed by the photoelectric effect and therefore the atomic scattering factor contains a complex quantity [$f'_A(\omega,\boldsymbol{Q}) + i\,.f'_A(\omega,\boldsymbol{Q})$], named anomalous or resonant contribution. When the photon frequency ω is close to an atomic resonance, this photon can interact with the corresponding bound inner electron and be absorbed. This complex term depends on the chemical nature of the scatterer and becomes substantial near absorption edges. Anomalous effects are more important near absorption edges occurring in the soft X-ray energy range.

Basics on the origin of X-ray anomalous scattering are reported by James (1965). In the forward scattering limit, the refraction index $n(\omega)$ is related to the scattering factor $f_A(\omega,0)$ of the N_A atoms *"A"* [1-3] by

$$n = 1 - \delta = 1 - (2\pi e^2/m\omega^2)[\,\Sigma_A N_A f_A(\omega,0)] \qquad \{1\}$$