International Tables for Crystallography (2018). Vol. H, Figure 3.9.15, p. 363.

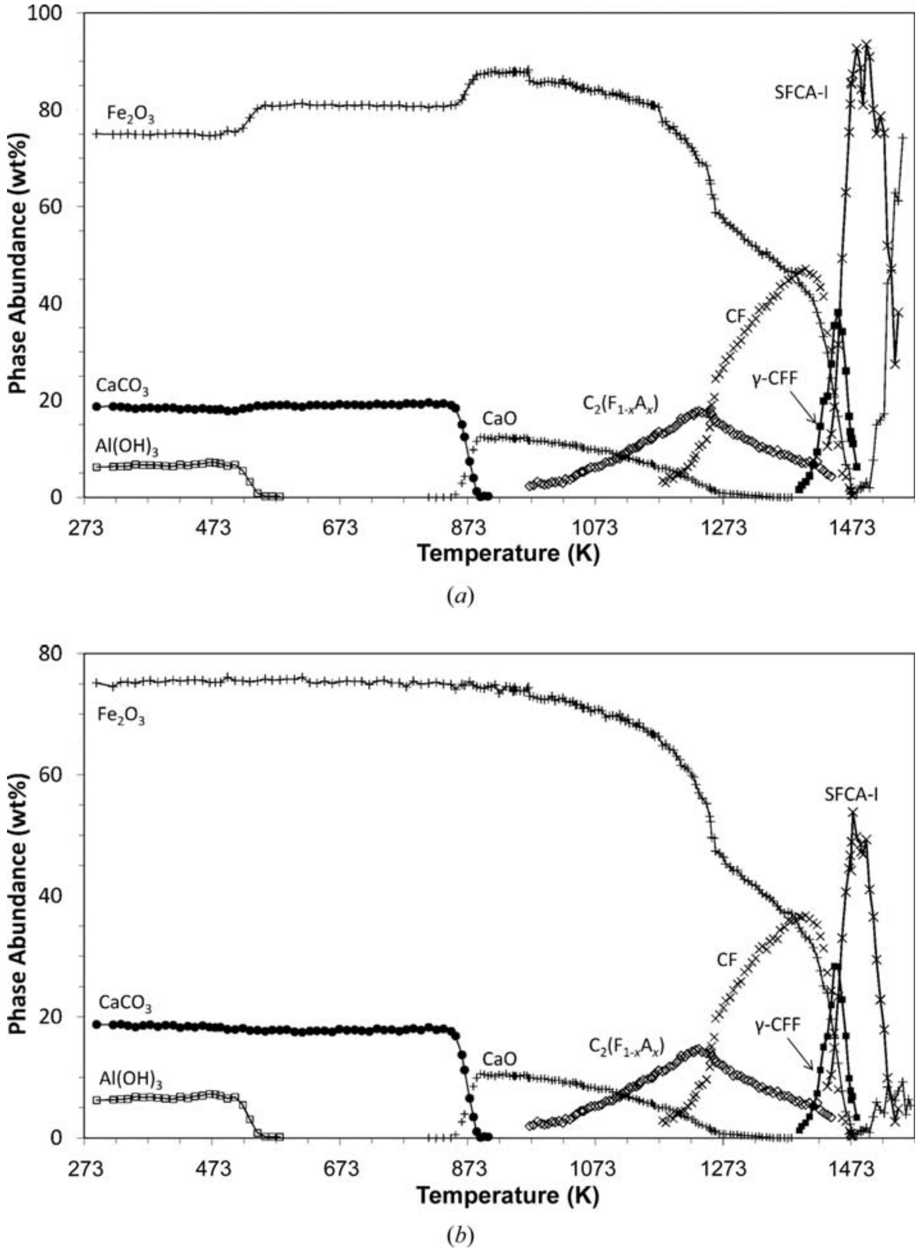

Figure 3.9.15

Results of Rietveld-based QPA of the *in situ* data sequence shown in Fig. 3.9.14 (Webster *et al.*, 2013). The relative phase abundances (upper) are derived using the Hill/Howard algorithm (Hill & Howard, 1987) in equation (3.9.26), while the absolute phase abundances (lower) have been derived from the external-standard approach (O'Connor & Raven, 1988) embodied in equation (3.9.21).

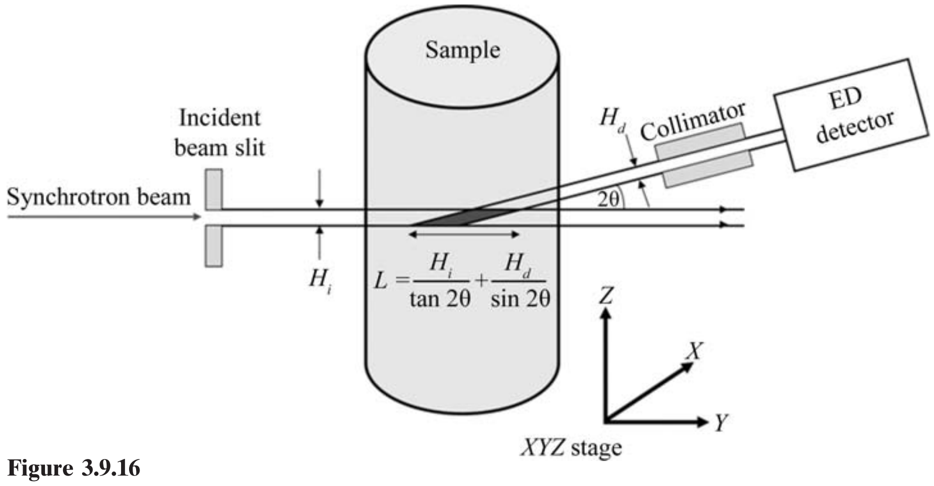

Figure 3.9.16

Basic experimental arrangement for energy-dispersive diffraction. The length of the active area or lozenge (dark grey region), L, is given by the function relating the incident- and diffracted-beam heights (H_i and H_d, respectively) and the angle of diffraction (2θ).

tors producing a spectrum of diffracted intensity as a function of energy.

Traditional angle-dispersive diffraction (ADD) satisfies Bragg's law by using a fixed wavelength and varying 2θ to map the d-spacings. In contrast, EDD data are collected directly on an energy scale at a constant 2θ and the energy is measured to map the d-spacings. This impinges upon the use of Rietveld methodology for QPA since, in contrast to ADD, the structure factors now vary as a function of energy. Energy is related to wavelength *via*

$$E\ (\mathrm{keV}) = \frac{hc}{\lambda} \simeq \frac{12.395}{\lambda}, \qquad (3.9.46)$$

where E is the energy of the incident radiation in keV, h is Planck's constant, c is the speed of light and λ is the wavelength associated with that energy in ångstroms. Rearrangement of equation (3.9.46) and substitution for λ in Bragg's law enables the mapping of the measured energy scale to d-spacings:

$$E\ (\mathrm{keV}) = \frac{6.197}{d \sin\theta}, \qquad (3.9.47)$$

where 2θ is the angle between the incident beam and the detector slit.

EDD data can be analysed using structureless profile-fitting methods such as those of Le Bail *et al.* (see Chapter 3.5) once the energy scale has been converted to a d-spacing scale (Frost & Fei, 1999; Larson & Von Dreele, 2004; Zhao *et al.*, 1997). If the distribution of intensities in the incident spectrum can be measured, it is possible to normalize the EDD data, correct for absorption and convert the pattern to an ADD form using a 'dummy' wavelength (Ballirano & Caminiti, 2001). Access to the incident spectrum, however, is not always possible, especially at synchrotron-radiation sources where the highly intense incident beam could damage the detector.

An alternative approach is to model the pattern directly on the energy scale *via* equation (3.9.47) (Rowles *et al.*, 2012; Scarlett *et al.*, 2009) and extract phase abundances using the methodologies described earlier in this chapter.

However, the major impediment to achieving this is the nonlinearity of the intensity distribution in the incident spectrum. This is due to (i) the nonlinear distribution of intensity as a function of energy in the incident beam, (ii) nonlinear detector responses (Bordas *et al.*, 1977) and (iii) absorption along the beam path (by the sample and air), which skews the energy distribution to the higher energies. This overall nonlinearity can be modelled empirically by functions such a lognormal