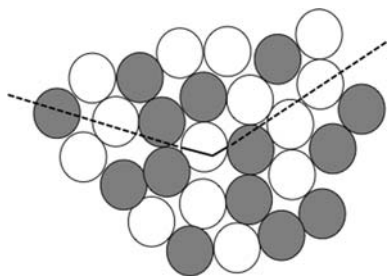


3.2. THE PHYSICS OF DIFFRACTION FROM POWDERS

**Figure 3.2.3**

Sketch illustrating an X-ray propagating through a mixture of two kinds of particles.

This leads to a weaker observed reflection from a phase a with larger absorption constant μ_a if the particle size is an appreciable fraction of $1/(\mu_a - \bar{\mu})$.

Averaging over the particle volume, we see that the observed intensity of phase a will be lowered from its value in a fine powder by a factor

$$\tau = V_a^{-1} \int \exp[-(\mu_a - \bar{\mu})x] dV_a,$$

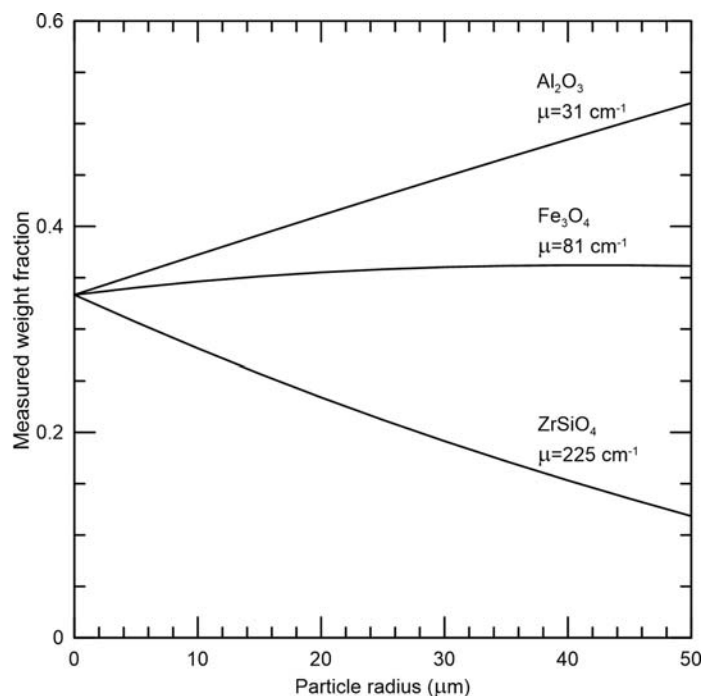
where the integral is taken over one representative grain of phase a . This is exactly the integral of equation (3.2.15), and if one assumes monodisperse spherical particles, it is tabulated in *International Tables for Crystallography*, Volume C, Section 6.3.3.2 and elsewhere, with $\mu_a - \bar{\mu}$ replacing μ . One hitch is that the tabulations are for $\mu > 0$, whereas $\mu_a - \bar{\mu} < 0$ for the less absorbing phases in a mixture. Brindley handles this with a series expansion and provides a table of τ versus $(\mu_a - \bar{\mu})R$.

By way of illustration, consider a mixture of equal weight fractions of corundum, magnetite and zircon powders, analysed with Cu $K\alpha$ radiation. Fig. 3.2.4 shows the weight fractions that would be measured from such a sample as a function of particle radius (assumed equal for all three phases). In this case, microabsorption biases the result by about 10% for particles of 10 μm diameter, and misses by a factor of two if the diameter is 70 μm .

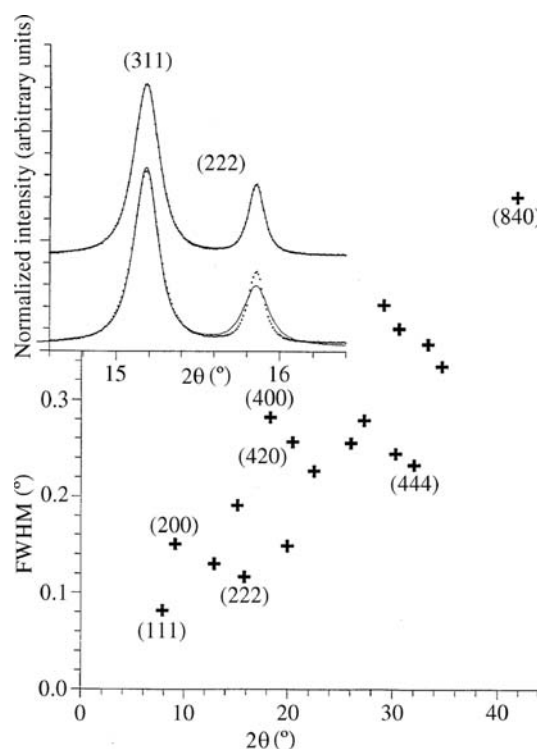
In considering microabsorption, there are several important points to note. This entire analysis is only valid for $\mu R \ll 1$, since otherwise the concept of an average absorption length becomes ill defined. That means that the Brindley analysis breaks down precisely when it becomes significant. Of course, the Brindley assumption of monodisperse spherical particles is unrealistic for most real samples. Both the surface roughness and Brindley corrections depend on diffraction angle as well as μR , but, as noted above, for moderate absorption, the angle dependence appears as an effective Debye–Waller factor. The parameter R is the radius of the grain of material, which is commonly very much larger than the size of a coherently diffracting region; a Scherrer analysis of particle size through line broadening does not provide a useful estimate of R . Most importantly, unless one has an accurate independent measurement of the size and shape of the grains, microabsorption corrections should be taken as a sign of impending trouble, not a quantitative correction.

3.2.3.4. Anisotropic strain broadening

Strain broadening is often observed not to be monotonically dependent on the magnitude of the d -spacing, but to have a more complicated dependence on the direction of the diffraction vector \mathbf{G} . An illustration of the effect in cubic Rb_3C_{60} is shown in Fig. 3.2.5 (Stephens, 1999). The lower part of the figure shows an apparently irregular trend of diffraction peak widths on diffraction angle 2θ .

**Figure 3.2.4**

Weight fractions that would be measured from a mixture of equal parts of three phases with Cu $K\alpha$ radiation.

**Figure 3.2.5**

Diffraction peak width versus diffraction angle from a powder pattern of face-centred cubic Rb_3C_{60} (Stephens, 1999). The inset at the top shows a limited range of the data, fitted by a model with two different peak widths (upper trace) and with the widths constrained to be equal (lower trace).

Whatever the nature of random internal stresses and strains, it can be argued on general grounds that strain broadening depends on a combination of fourth-rank tensors. On the assumption that the distribution of random strains is Gaussian, each diffraction peak has Gaussian shape, and the variance of the inverse d -spacing squared is a quartic form in the reflection indices (hkl) . This can be expressed as