International Tables for Crystallography (2006). Vol. C, Section 8.7.4.4.7, p. 729.

so are $I_{\uparrow\uparrow}$ and $I_{\downarrow\downarrow}$. An incorrect treatment of extinction may entirely bias the estimate of x.

8.7.4.4.7. *Error analysis*

In the most general case, it is not possible to obtain x, and thus $M(\mathbf{h})$ directly from R. Moreover, it is unlikely that all Bragg spots within the reflection sphere could be measured. Modelling of $\mathbf{M}(\mathbf{h})$ is thus of crucial importance. The analysis of data must proceed through a least-squares routine fitting $R_{\rm calc}$ to $R_{\rm obs}$, minimizing the error function

$$\varepsilon = \sum_{\substack{\mathbf{h}\\ \text{observed}}} \frac{1}{\sigma^2(R)}\,[R_{\rm obs}(\mathbf{h}) - R_{\rm calc}(\mathbf{h})]^2, \qquad (8.7.4.48)$$

where $R_{\rm calc}$ corresponds to a model and $\sigma^2(R)$ is the standard uncertainty for R.

If the same counting time for $I_\uparrow$ and for $I_\downarrow$ is assumed, only the counting statistical error may be considered important in the estimate of R, as most systematic effects cancel. In the simple case where $\alpha = \pi/2$, and the structure is centrosymmetric, a straightforward calculation leads to

$$\frac{\sigma^2(x)}{x^2} = \frac{\sigma^2(R)}{R^2}\,\frac{R}{(R-1)^2}; \qquad (8.7.4.49)$$

with

$$\frac{\sigma^2(R)}{R^2} \sim \frac{1}{I_\uparrow} + \frac{1}{I_\downarrow}, \qquad (8.7.4.50)$$

one obtains the result

$$\frac{\sigma^2(x)}{x^2} = \tfrac{1}{8}\,\frac{(F_N^2 + M^2)}{(F_N M)^2}. \qquad (8.7.4.51)$$

In the common case where $x \ll 1$, this reduces to

$$\frac{\sigma^2(x)}{x^2} \sim \tfrac{1}{8}\,\frac{1}{M^2} = \frac{1}{8F_N^2}\,\frac{1}{x^2}. \qquad (8.7.4.52)$$

In addition to this estimate, care should be taken of extinction effects.

The real interest is in $M(\mathbf{h})$, rather than x:

$$\frac{\sigma^2(M)}{M^2} = \frac{\sigma^2(x)}{x^2} + \frac{\sigma^2(F_N)}{F_N^2}. \qquad (8.7.4.53)$$

If F_N is obtained by a nuclear neutron scattering experiment,

$$\sigma^2(F_N) \sim a + bF_N^2,$$

where a accounts for counting statistics and b for systematic effects.

The first term in (8.7.4.53) is the leading one in many situations. Any systematic error in F_N can have a dramatic effect on the estimate of $M(\mathbf{h})$.

8.7.4.5. *Modelling the spin density*

In this subsection, the case of spin-only magnetization is considered. The modelling of $\mathbf{m}_s(\mathbf{r})$ is very similar to that of the charge density.

8.7.4.5.1. *Atom-centred expansion*

We first consider the case where spins are localized on atoms or ions, as it is to a first approximation for compounds involving transition-metal atoms. The magnetization density is expanded as

$$\mathbf{m}_S(\mathbf{r}) = \sum_j \langle \mathbf{S}_j\rangle\,\langle s_j(\mathbf{r} - \mathbf{R}_j)\rangle, \qquad (8.7.4.54)$$

where $\langle \mathbf{S}_j\rangle$ is the spin at site j, and $\langle s_j\rangle$ the thermally averaged normalized spin density $f_j(\mathbf{h})$, the Fourier transform of $s_j(\mathbf{r})$, is known as the 'magnetic form factor'. Thus,

$$\mathbf{M}(\mathbf{h}) = \sum_j \langle \mathbf{S}_j\rangle\, f_j(\mathbf{h})\, T_j \exp(2\pi \mathbf{h}\cdot\mathbf{R}_j), \qquad (8.7.4.55)$$

where T_j and $\mathbf{R}_j$ are the Debye–Waller factor and the equilibrium position of the jth site, respectively.

Most measurements are performed at temperatures low enough to ensure a fair description of T_j at the harmonic level (Coppens, 1992). T_j represents the vibrational relaxation of the open-shell electrons and may, in some situations, be different from the Debye–Waller factor of the total charge density, though at present no experimental evidence to this effect is available.

8.7.4.5.1.1. *Spherical-atom model*

In the crudest model, $s_j(\mathbf{r})$ is approximated by its spherical average. If the magnetic electrons have a wavefunction radial dependence represented by the radial function $U(r)$, the magnetic form factor is given by

$$f(h) = \int_0^\infty U^2(r) 4\pi r^2\,{\rm d}r\, j_0(2\pi h r) = \langle j_0\rangle, \qquad (8.7.4.56)$$

where j_0 is the zero-order spherical Bessel function. For free atoms and ions, these form factors can be found in *IT* IV (1974).

One of the important features of magnetic neutron scattering is the fact that, to a first approximation, closed shells do not contribute to the form factor. Thus, it is a unique probe of the electronic structure of heavy elements, for which theoretical calculations even at the atomic level are questionable. Relativistic effects are important. Theoretical relativistic form factors can be used (Freeman & Desclaux, 1972; Desclaux & Freeman, 1978). It is also possible to parametrize the radial behaviour of U. A single contraction-expansion model [κ refinement, expression (8.7.3.6)] is easy to incorporate.

8.7.4.5.1.2. *Crystal-field approximation*

Crystal-field effects are generally of major importance in spin magnetism and are responsible for the spin state of the ions, and thus for the ground-state configuration of the system. Thus, they have to be incorporated in the model.

Taking the case of a transition-metal compound, and neglecting small contributions that may arise from spin polarization in the closed shells (see Subsections 8.7.4.9 and 8.7.4.10), the normalized spin density can be written by analogy with (8.7.3.76) as

$$s(\mathbf{r}) = \sum_{i=1}^{5} \sum_{j\geq i}^{5} D_{ij}\, d_i(\mathbf{r})\, d_j(\mathbf{r}), \qquad (8.7.4.57)$$

where D_{ij} is the normalized spin population matrix. If $\rho_{d\uparrow}$ and $\rho_{d\downarrow}$ are the densities of a given spin,

$$s(\mathbf{r}) = \frac{\rho_{d\uparrow} - \rho_{d\downarrow}}{n_\uparrow - n_\downarrow}, \qquad (8.7.4.58)$$

the d-type charge density is

$$\rho_d(\mathbf{r}) = \rho_{d\uparrow} + \rho_{d\downarrow} \qquad (8.7.4.59)$$

and is expanded in a similar way to $s(\mathbf{r})$ [see (8.7.3.76)],

$$\rho_d(\mathbf{r}) = \sum_i \sum_{j\geq i} P_{ij}\, d_i d_j; \qquad (8.7.4.60)$$

writing

references