

## 8. REFINEMENT OF STRUCTURAL PARAMETERS

$$\begin{aligned} I_{\uparrow} &= I_{\uparrow\uparrow} + I_{\uparrow\downarrow} \\ I_{\downarrow} &= I_{\downarrow\downarrow} + I_{\downarrow\uparrow}, \end{aligned} \quad (8.7.4.39)$$

which depend only on the polarization of the incident neutron.

## 8.7.4.4.2. Unpolarized neutron scattering

If the incident neutron beam is not polarized, the scattering cross section is given by

$$I = \frac{1}{2}[I_{\uparrow} + I_{\downarrow}] = |F_N|^2 + |\mathbf{Q}|^2. \quad (8.7.4.40)$$

Magnetic and nuclear contributions are simply additive. With  $x = Q/F_N$ , one obtains

$$I = |F_N|^2[1 + |x|^2]. \quad (8.7.4.41)$$

Owing to its definition,  $|x|$  can be of the order of 1 if and only if the atomic moments are ordered close to saturation (as in the ferro- or antiferromagnets). In many situations of structural and chemical interest,  $|x|$  is small.

If, for example,  $|x| \sim 0.05$ , the magnetic contribution in (8.7.4.41) is only 0.002 of the total intensity. Weak magnetic effects, such as occur for instance in paramagnets, are thus hardly detectable with unpolarized neutron scattering.

However, if the magnetic structure does not have the same periodicity as the crystalline structure, magnetic components in (8.7.4.40) occur at scattering vectors for which the nuclear contribution is zero. In this case, the unpolarized technique is of unique interest. Most phase diagrams involving antiferromagnetic or helimagnetic order and modulations of such ordering are obtained by this method.

## 8.7.4.4.3. Polarized neutron scattering

It is generally possible to polarize the incident beam by using as a monochromator a ferromagnetic alloy, for which at a given Bragg angle  $I_{\downarrow}(\text{monochromator}) = 0$ , because of a cancellation of nuclear and magnetic scattering components. The scattered-beam intensity is thus  $I_{\uparrow}$ . By using a radio-frequency (r.f.) coil tuned to the Larmor frequency of the neutron, the neutron spin can be flipped into the ( $\downarrow$ ) state for which the scattered beam intensity is  $I_{\downarrow}$ . This allows measurement of the 'flipping ratio'  $R(\mathbf{h})$ :

$$R(\mathbf{h}) = \frac{I_{\uparrow}(\mathbf{h})}{I_{\downarrow}(\mathbf{h})}. \quad (8.7.4.42)$$

As the two measurements are made under similar conditions, most systematic effects are eliminated by this technique, which is only applicable to cases where both  $F_N$  and  $F_M$  occur at the same scattering vectors. This excludes any antiferromagnetic type of ordering.

The experimental set-up is discussed by Forsyth (1980).

## 8.7.4.4.4. Polarized neutron scattering of centrosymmetric crystals

If  $\lambda$  is assumed to be in the vertical  $Oz$  direction,  $\mathbf{M}(\mathbf{h})$  will in most situations be aligned along  $Oz$  by an external orienting field. If  $\alpha$  is the angle between  $\mathbf{M}$  and  $\mathbf{h}$ , and

$$x = \frac{r_0 M(\mathbf{h})}{F_N(\mathbf{h})}, \quad (8.7.4.43)$$

with  $F_N$  expressed in the same units as  $r_0$ , one obtains, for centrosymmetric crystals,

$$R = \frac{1 + 2x \sin^2 \alpha + x^2 \sin^2 \alpha}{1 - 2x \sin^2 \alpha + x^2 \sin^2 \alpha}. \quad (8.7.4.44)$$

If  $x \ll 1$ ,

$$R \sim 1 + 4x \sin^2 \alpha. \quad (8.7.4.45)$$

For  $x \sim 0.05$  and  $\alpha = \pi/2$ ,  $R$  now departs from 1 by as much as 20%, which proves the enormous advantage of polarized neutron scattering in the case of low magnetism.

Equation (8.7.4.44) can be inverted, and  $x$  and its sign can be obtained directly from the observation. However, in order to obtain  $M(\mathbf{h})$ , the nuclear structure factor  $F_N(\mathbf{h})$  must be known, either from nuclear scattering or from a calculation. All systematic errors that affect  $F_N(\mathbf{h})$  are transferred to  $M(\mathbf{h})$ .

For two reasons, it is not in general feasible to access all reciprocal-lattice vectors. First, in order to have reasonable statistical accuracy, only reflections for which both  $I_{\uparrow}$  and  $I_{\downarrow}$  are large enough are measured; *i.e.* reflections having a strong nuclear structure factor. Secondly,  $\sin \alpha$  should be as close to 1 as possible, which may prevent one from accessing all directions in reciprocal space. If  $\mathbf{M}$  is oriented along the vertical axis, the simplest experiment consists of recording reflections with  $\mathbf{h}$  in the horizontal plane, which leads to a projection of  $\mathbf{m}(\mathbf{r})$  in real space. When possible, the sample is rotated so that other planes in the reciprocal space can be recorded.

Finally, if  $\alpha = \pi/2$ ,  $I_{\uparrow\downarrow}$  vanishes, and neutron spin is conserved in the experiment.

## 8.7.4.4.5. Polarized neutron scattering in the noncentrosymmetric case

If the space group is noncentrosymmetric, both  $F_N$  and  $M$  have a phase,  $\varphi_N$  and  $\varphi_M$ , respectively.

If for simplicity one assumes  $\alpha = \pi/2$ , and, defining  $\delta = \varphi_M - \varphi_N$ ,

$$R = \frac{1 + |x|^2 + 2|x| \cos \delta}{1 + |x|^2 - 2|x| \cos \delta}, \quad (8.7.4.46)$$

which shows that  $|x|$  and  $\delta$  cannot both be obtained from the experiment.

The noncentrosymmetric case can only be solved by a careful modelling of the magnetic structure factor as described in Subsection 8.7.4.5.

In practice, neither the polarization of the incident beam nor the efficiency of the r.f. flipping coil is perfect. This leads to a modification in the expression for the flipping ratios [see Section 6.1.3 or Forsyth (1980)].

## 8.7.4.4.6. Effect of extinction

Since most measurements correspond to strong nuclear structure factors, extinction severely affects the observed data. To a first approximation, one may assume that both  $I_{\uparrow\uparrow}$  and  $I_{\downarrow\downarrow}$  will be affected by this process, though the spin-flip processes  $I_{\uparrow\downarrow}$  and  $I_{\downarrow\uparrow}$  are not. If  $y_{\uparrow\uparrow}$  and  $y_{\downarrow\downarrow}$  are the associated extinction factors, the observed flipping ratio is

$$R_{\text{obs}} \sim \frac{I_{\uparrow\uparrow} y_{\uparrow\uparrow} + I_{\uparrow\downarrow}}{I_{\downarrow\downarrow} y_{\downarrow\downarrow} + I_{\downarrow\uparrow}}, \quad (8.7.4.47)$$

where the expressions for  $y_{\uparrow\uparrow, \downarrow\downarrow}$  are given elsewhere (Bonnet, Delapalme, Becker & Fuess, 1976).

It should be emphasized that, even in the case of small magnetic structure factors, extinction remains a serious problem since, even though  $y_{\uparrow\uparrow}$  and  $y_{\downarrow\downarrow}$  may be very close to each other,