

## 8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

$$\langle \psi_{SM_S} | \hat{\mathbf{m}}_s | \psi_{SM_S} \rangle = \langle \psi_{SM_S} | \hat{\mathbf{S}} | \psi_{SM_S} \rangle f_S(\mathbf{r}), \quad (8.7.4.28)$$

where  $f_S(\mathbf{r})$  is a function that depends on  $S$ , but not on  $M_S$ . Comparison with (8.7.4.26) shows that  $f_S(\mathbf{r})$  is the normalized spin-density function  $s(\mathbf{r})$ , which therefore is an invariant for the  $S$  manifold [ $s(\mathbf{r})$  is calculated as the normalized spin density for any  $M_S$ ]. Expression (8.7.4.27) can thus be written as

$$\mathbf{m}_s(\mathbf{r}) = \langle \mathbf{S} \rangle s(\mathbf{r}), \quad (8.7.4.29)$$

where  $\langle \mathbf{S} \rangle$  is the expected value for the total spin, at a given temperature and under a given external field. As  $s(\mathbf{r})$  is normalized, the total moment of the system is

$$\boldsymbol{\mu}_S = \langle \mathbf{S} \rangle.$$

The behaviour of  $\langle \mathbf{S} \rangle$  is governed by the usual laws of magnetism: it can be measured by macroscopic techniques. In paramagnetic species, it will vary as  $T^{-1}$  to a first approximation; unless the system is studied at very low temperatures, the value of  $\langle \mathbf{S} \rangle$  will be very small. The dependence of  $\langle \mathbf{S} \rangle$  on temperature and orienting field is crucial.

Finally, (8.7.4.29) has to be averaged over vibrational modes. Except for the case where there is strong magneto-vibrational interaction, only  $s(\mathbf{r})$  is affected by thermal atomic motion. This effect can be described in terms similar to those used for the charge density (Subsection 8.7.3.7).

The expression (8.7.4.29) is very important and shows that the microscopic spin-magnetization density carries two types of information: the nature of spin ordering in the system, described by  $\langle \mathbf{S} \rangle$ , and the delocalized nature of the electronic ground state, represented by  $s(\mathbf{r})$ .

## 8.7.4.3.3. Spin density for an assembly of localized systems

A complex magnetic system can generally be described as an ensemble of well defined interacting open-shell subsystems (ions or radicals), where each subsystem has a spin  $\hat{\mathbf{S}}_n$ , and  $S_n^2$  is assumed to be a good quantum number. The magnetic interaction occurs essentially through exchange mechanisms that can be described by the Heisenberg Hamiltonian:

$$\mathcal{H} = - \sum_{n < m} J_{nm} \hat{\mathbf{S}}_n \cdot \hat{\mathbf{S}}_m - \sum_n \mathbf{B}_0 \cdot \mathbf{S}_n, \quad (8.7.4.30)$$

where  $J_{nm}$  is the exchange coupling between two subsystems, and  $\mathbf{B}_0$  an applied external field (magneto-crystalline anisotropic effects may have to be added). Expression (8.7.4.30) is the basis for the understanding of magnetic ordering and phase diagrams. The interactions lead to a local field  $\mathbf{B}_n$ , which is the effective orienting field for the spin  $\mathbf{S}_n$ .

The expression for the spin-magnetization density is

$$\mathbf{m}_s(\mathbf{r}) = \sum_n \langle \mathbf{S}_n \rangle s_n(\mathbf{r}). \quad (8.7.4.31)$$

The relative arrangement of  $\langle \mathbf{S}_n \rangle$  describes the magnetic structure;  $s_n(\mathbf{r})$  is the normalized spin density of the  $n$ th subsystem.

In some metallic systems, at least part of the unpaired electron system cannot be described within a localized model: a band-structure description has to be used (Lovesey, 1984). This is the case for transition metals like Ni, where the spin-magnetization density is written as the sum of a localized part [described by (8.7.4.31)] and a delocalized part [described by (8.7.4.29)].

## 8.7.4.3.4. Orbital magnetization density

We must now address the case where the orbital moment is not quenched. In that case, there is some spin-orbit coupling, and the

description of the magnetization density becomes less straightforward.

The magnetic moment due to the angular momentum  $\mathbf{l}_j$  of the electron is  $\frac{1}{2}\mathbf{l}_j$  (in units of  $2\mu_B$ ). As  $\mathbf{l}_j$  does not commute with the position  $\mathbf{r}_j$ , orbital magnetization density is defined as

$$\mathbf{m}_L(\mathbf{r}) = \frac{1}{4} \left\langle \sum_j \{ \mathbf{l}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \mathbf{l}_j \} \right\rangle. \quad (8.7.4.32)$$

If  $\mathbf{L}$  is the total orbital moment,

$$\mathbf{L} = \sum_j \mathbf{l}_j. \quad (8.7.4.33)$$

Only open shells contribute to the orbital moment. But, in general, neither  $\mathbf{L}^2$  nor  $\mathbf{L}_z$  are constants of motion. There is, however, an important exception, when open-shell electrons can be described as localized around atomic centres. This is the case for most rare-earth compounds, for which the  $4f$  electrons are too close to the nuclei to lead to a significant interatomic overlap. It can also be a first approximation for the  $d$  electrons in transition-metal ions. Spin-orbit coupling will be present, and thus only  $\mathbf{L}^2$  will be a constant of motion. One may define the total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (8.7.4.34)$$

and  $\{J^2, L^2, S^2, J_z\}$  become the four constants of motion.

Within the  $J$  manifold of the ground state,  $\mathbf{m}_s(\mathbf{r})$  and  $\mathbf{m}_L(\mathbf{r})$  do not, in general, fulfil the conditions for the Wigner-Eckart theorem (Condon & Shortley, 1935), which leads to a very complex description of  $\mathbf{m}(\mathbf{r})$  in practical cases.

However, the Wigner-Eckart theorem can be applied to the magnetic moments themselves, leading to

$$\mathbf{L} + 2\mathbf{S} = g\mathbf{J}, \quad (8.7.4.35)$$

with the Lande factor

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (8.7.4.36)$$

and, equivalently,

$$\begin{aligned} \mathbf{S} &= (g-1)\mathbf{J} \\ \mathbf{L} &= (2-g)\mathbf{J}. \end{aligned} \quad (8.7.4.37)$$

The influence of spin-orbit coupling on the scattering will be discussed in Subsection 8.7.4.5.

## 8.7.4.4. Probing spin densities by neutron elastic scattering

## 8.7.4.4.1. Introduction

The magnetic structure factor  $F_M(\mathbf{h})$  [equation (8.7.4.4)] depends on the spin state of the neutron. Let  $\boldsymbol{\lambda}$  be the unit vector defining a quantization axis for the neutron, which can be either parallel ( $\uparrow$ ) or antiparallel ( $\downarrow$ ) to  $\boldsymbol{\sigma}$ . If  $I_{\sigma\sigma'}$  stands for the cross section where the incident neutron has the polarization  $\sigma$  and the scattered neutron the polarization  $\sigma'$ , one obtains the following basic expressions:

$$\begin{aligned} I_{\uparrow\uparrow} &= |F_n + \boldsymbol{\lambda} \cdot \mathbf{Q}|^2 \\ I_{\downarrow\downarrow} &= |F_n - \boldsymbol{\lambda} \cdot \mathbf{Q}|^2 \\ I_{\uparrow\downarrow} &= I_{\downarrow\uparrow} = |\boldsymbol{\lambda} \times \mathbf{Q}|^2. \end{aligned} \quad (8.7.4.38)$$

If no analysis of the spin state of the scattered beam is made, the two measurable cross sections are

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

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,

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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  $M(\mathbf{h})$  is thus of crucial importance. The analysis of data must proceed through a least-squares routine fitting  $R_{\text{calc}}$  to  $R_{\text{obs}}$ , minimizing the error function

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

observed

where  $R_{\text{calc}}$  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

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

with

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

one obtains the result

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

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

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

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

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

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

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

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

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,

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

where  $T_j$  and  $\mathbf{R}_j$  are the Debye–Waller factor and the equilibrium position of the  $j$ th 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

$$f(h) = \int_0^\infty U^2(r) 4\pi r^2 dr j_0(2\pi hr) = \langle j_0 \rangle, \quad (8.7.4.56)$$

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 [ $\kappa$  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

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

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

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

the  $d$ -type charge density is

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

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

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

writing