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Neutron Diffraction— The Total Powder Pattern

T. M. Sabine

School of Physics and Materials, N.S.W. Institute of Technology, P.O. Box 123, Broadway, N.S.W. 2007.

Abstract

The value of the ordinate of a neutron powder pattern is expressed as the sum of Bragg scattering, due to the existence of an average lattice, and diffuse scattering, due to local deviations from the average lattice. In this form the calculated pattern can be refined by least squares methods against the observed pattern to give both average structural parameters and disorder parameters. Significant advantages over the use of only Bragg scattering for the determination of structural parameters are: (1) a powerful limit on the value of the temperature factor is imposed by the condition that neutrons removed from Bragg peaks must be accounted for in the diffuse scattering; (2) correlation between partially occupied sites can be found. The cross sections for Bragg and disorder scattering are given.

Introduction

Neutrons are of particular use in the study of solids, liquids and gases because of the following basic properties:

- (1) The thermal neutron wavelength is comparable with the interatomic spacing. Hence, there will be pronounced interference effects when neutrons are scattered by condensed atomic systems.
- (2) The change in neutron energy from inelastic processes involving the creation and annihilation of excitations in condensed matter is of the order of the incident neutron energy.
- (3) The neutron has a magnetic moment, which gives it a unique value in probing the magnetic structure and magnetic dynamics of atomic systems.
- (4) The neutron is a neutral particle, and can therefore penetrate deeply into matter.
- (5) Neutrons are a gentle wind, compared with the strong breeze of X-rays and the raging gale of electrons, in causing radiation damage in the systems under investigation.

As an experimental science, neutron diffraction started seriously in 1950 when neutron beam fluxes of about 10^{12} n cm⁻² s⁻¹ became available. The theoretical basis had been laid by Halpern and Johnson (1939), Weinstock (1944) and Cassels (1950).

The difficulty of obtaining quantitative information from single crystals, due to the breakdown of the kinematical approximation in crystals sufficiently large for appreciable scattering to occur, was noticed by the earliest workers (Fermi and Marshall 1947). To overcome these extinction effects Wollan and Shull (1948) constructed a powder diffractometer. Powder methods gave accurate data for simple compounds, but the problem of overlap between closely spaced reflections precluded study of materials with large unit cells or low symmetry. Many workers interested in the application of neutron diffraction to chemical compounds tried to reduce extinction effects or to correct for them. Early work was carried out by Bacon and Lowde (1948) and Peterson and Levy (1951). These studies showed that the effects of extinction could be reduced by destroying the perfection of the crystal. Quenching or irradiation damage were favoured techniques (Sanger 1969). The unfortunate result of these treatments is the introduction of dislocations, point defects and defect clusters, all of which produce appreciable diffraction effects and require explanation in a proper discussion of the structure.

Zachariasen (1967) treated extinction in terms of a crystal containing perfect crystal blocks of a certain size and separated by a certain degree of misorientation. His equations were soon incorporated into the least squares refinement procedure with provision for anisotropic block sizes and anisotropic mosaic distribution (Coppens and Hamilton 1970). Coppens and Sabine (1969) used these equations in a refinement of the structure of oxalic acid dihydrate; however, in a direct examination of the same material by Lang topography (Michell *et al.* 1969), the dislocation density was found to be orders of magnitude less than that predicted by the results of the Zachariasen treatment. While these discrepancies exist there must be doubt about this solution to the extinction problem.

The powder method continued to be developed slowly, but its use was largely limited to magnetic systems. Studies of the optics of powder diffractometers were made by Caglioti *et al.* (1958) and by Sabine and Browne (1963).

Rietveld (1969) made a significant improvement in methods of analysis by realizing that powder profiles closely followed a gaussian form. He calculated the ordinates of the Bragg profiles and refined them against the observed pattern. This method, particularly after the development of high resolution neutron diffractometers (Hewat 1975), led to the satisfactory refinement of data from a large number of inorganic compounds (Cheetham and Taylor 1977) with accuracies in positional parameters comparable with those found from single crystal work.

Agreement for thermal parameters was far less satisfactory (Andresen *et al.* 1980) and a treatment in which all the neutrons scattered by the specimen could be included in the refinement was given by Sabine and Clarke (1977).

Total Neutron Powder Pattern

Bragg Scattering

In this analysis it will be assumed that a conventional two-axis powder diffractometer is being used. The monochromatic neutron beam is of sufficient size to completely bathe the specimen. The pattern is scanned by a counter which is fitted with a narrow slit. Typically, this slit subtends 10-20' arc at the specimen position. The diffractometer arm moves in small steps of 2θ under the control of a monitor counter placed in the incident beam. The time spent at each 2θ position is t. The total number P of neutrons diffracted into a length h of the Debye–Scherrer ring (the height of the counter slit), under the above experimental conditions, is (Bacon 1955; Warren 1969)

$$P = \Phi_0 \lambda^3 h V \rho' j N_c^2 F^2 \exp(-2M) / 8\pi R \rho \sin \theta \sin 2\theta, \qquad (1)$$

where Φ_0 is the incident flux (neutrons m⁻² s⁻¹), λ the neutron wavelength, V the specimen volume, j the multiplicity, N_c the number of unit cells per unit volume, F the structure factor per unit cell, and exp(-2M) the Debye-Waller factor for inten-

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sities. Further, R is the specimen-to-counter distance, and ρ and ρ' are the theoretical and measured densities respectively.

To determine the ordinate of the profile at any point we will assume, following Rietveld (1969), that the profile of a reflection is obtained by convoluting equation (1) with a gaussian broadening function of unit area. Because of the Maxwellian distribution of neutron velocities in the reactor moderator and the gaussian distribution of mosaic blocks in the monochromator and the specimen, the profile is accurately gaussian. The full width at half maximum intensity B is given by (Caglioti *et al.* 1958)

$$B^2 = U\tan^2\theta + V\tan\theta + W,$$
(2)

where U, V and W are constants for a given experimental arrangement. The profile for Bragg scattering is then

$$I(2\theta) = \frac{\Phi_0 \lambda^3 h V \rho' j N_c^2 F^2 \exp(-2M)}{8\pi R \rho \sin \theta \sin 2\theta} \frac{2}{B} \left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}} \exp\left(-\frac{4\ln 2}{B^2} (2\theta_i - 2\theta)^2\right), \quad (3)$$

where $2\theta_i$ is the Bragg position for the *i*th reflection. It is assumed for the moment that there is no overlap between reflection profiles.

In an experiment the ordinate of the profile is measured by recording the number of neutrons received by the counter through a slit of width w in time t. Then, the Bragg component is given by

$$y_1(2\theta) = t \int_{2\theta - w/2R}^{2\theta + w/2R} I(2\theta) d(2\theta).$$
 (4)

Through the approximation

$$\int_{x-\frac{1}{2}\Delta x}^{x+\frac{1}{2}\Delta x} a \exp(-px^2) \, \mathrm{d}x \approx a \, \Delta x \exp(-px^2),$$

we obtain for equation (4)

$$y_1(2\theta) = \frac{\Phi_0 \lambda^3 h w V \rho' j N_c^2 F^2 \exp(-2M) a \exp(-px^2) t}{8\pi R^2 \rho \sin \theta \sin 2\theta},$$
(5)

where

$$a = 2B^{-1}(\pi^{-1}\ln 2)^{\frac{1}{2}}, \quad p = 4B^{-2}\ln 2, \quad x = 2(\theta_i - \theta).$$

Diffuse Scattering

If we assume Σ_D is the diffuse scattering cross section per unit cell, the number of neutrons received by the counter in time t will be

$$y_2(2\theta) = (\Phi_0 h w t N_c V \rho' / 4\pi R^2 \rho) \Sigma_D.$$
(6)

The total neutron count is then

$$y(2\theta) = \frac{\Phi_0 h w t N_c \rho' V}{4\pi R^2 \rho} \left(\frac{N_c \lambda^3 j F^2 \exp(-2M)}{2 \sin \theta \sin 2\theta} a \exp(-px^2) + \Sigma_D \right).$$
(7)

Superimposed on this count is the experimental background.

Measurement of all the quantities in front of the parentheses in equation (7) will enable the data to be put on an absolute scale. In general, we put

$$K = \Phi_0 h w t N_c \rho' V / 4\pi R^2 \rho .$$
(8)

Magnetic Bragg Scattering

Scattering from ordered magnetic ions in the crystal is included through the magnetic structure factor which is given by (Marshall and Lovesey 1971, p. 179)

$$F(\mathbf{k}) = \sum_{j} p_{j}(\mathbf{k}) \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_{j}) \{ \hat{\mathbf{\tau}} \times (\hat{\mathbf{n}}_{j} \times \hat{\mathbf{\tau}}) \}, \qquad (9)$$
$$p_{j}(\mathbf{k}) = (e^{2} \gamma / mc^{2}) \langle S_{j} \rangle f_{j}(\mathbf{k}),$$

where $\langle S_j \rangle$ is the average magnetic moment on the *j*th site, $f_j(\mathbf{k})$ is the magnetic form factor for this ion, $\hat{\mathbf{n}}_j$ is a unit vector parallel to the direction of the *j*th spin and $\hat{\mathbf{\tau}}$ is a unit vector parallel to the scattering vector. Implicit in this equation is isotropy in the distribution of unpaired electrons in the ion. A formalism allowing for anisotropy in this quantity can be developed, but is not warranted in the present discussion.

When unpolarized neutrons are used there are no cross terms between nuclear and magnetic scattering and the intensities add. For polarized neutrons the structure factors add.

Evaluation of $\Sigma_{\rm D}$

In a system exhibiting long range order, the diffuse scattering arises because of deviations from the average structure. These deviations can be compositional fluctuations (in both chemical and isotropic composition) or random displacements from lattice points, or both.

Atomic Short-range Order

The intensity scattered in the reciprocal lattice direction k ($k = 2\pi\lambda^{-1}\sin\theta$) is given by

$$I(\mathbf{k}) = \sum_{0}^{N-1} \sum_{0}^{N-1} b_j b_{j'}^* \exp\{2\pi i \mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})\}, \qquad (10)$$

where N is the total number of atoms in the crystal, and b_j , $b_{j'}^*$ are coherent scattering lengths. Following Wilson (1942) we put j' = j + m, and hence, equation (10) becomes

$$I(k) = \sum_{-(N-1)}^{N-1} N_m J_m \exp(2\pi i k \cdot r_m), \qquad (11)$$

where J_m is the average value of the product of the scattering lengths for sites separated by the vector \mathbf{r}_m , and N_m is the number of such vectors in the crystal.

To evaluate the average J_m we consider a disordered AB alloy with concentration C_A of A and C_B of B. Set P_m^{AA} as the probability that r_m joins two A sites, $P_m^{AB} (=P_m^{BA})$ the probability that it joins an A site and a B site, and P_m^{BB} the probability that it joins two B sites, then we have

$$J_m = b_A^2 P_m^{AA} + 2b_A b_B P_m^{AB} + b_B^2 P_m^{BB}.$$
 (12)

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In terms of the Cowley (1950) short-range order parameters α_m , these probabilities become

$$P_{m}^{AA} = C_{A}(C_{A} + \alpha_{m}C_{B}), \qquad P_{m}^{AB} = C_{A}C_{B}(1 - \alpha_{m}), \qquad P_{m}^{BB} = C_{B}(C_{B} + \alpha_{m}C_{A}), \quad (13)$$

and hence, equation (12) becomes

$$J_m = (C_A b_A + C_B b_B)^2 + C_A C_B (b_A - b_B)^2 \alpha_m.$$
(14)

Substitution into equation (11) then gives

$$I(\mathbf{k}) = (C_{\rm A} b_{\rm A} + C_{\rm B} b_{\rm B})^2 \sum_{-(N-1)}^{N-1} N_m \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_m) + C_{\rm A} C_{\rm B} (b_{\rm A} - b_{\rm B})^2 \sum_{-(N-1)}^{N-1} N_m \alpha_m \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_m).$$
(15)

For large values of N the first term in equation (15) represents Bragg scattering from the average lattice. As α_m will be nonzero only for small values of r_m , for which $N_m \approx N$, the second term represents diffuse scattering and can be written

$$I(\mathbf{k}) = NC_{\rm A} C_{\rm B} (b_{\rm A} - b_{\rm B})^2 \sum_m \alpha_m \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_m).$$
(16)

For a powder pattern we must average over all directions of k and obtain

$$I_{\rm D} = N C_{\rm A} C_{\rm B} (b_{\rm A} - b_{\rm B})^2 \sum_{m=0}^{\infty} c_m \alpha_m (\sin 2\pi k r_m) / 2\pi k r_m, \qquad (17)$$

where c_m is the number of atoms in the *m*th shell and r_m is its radius. Hence the short-range order cross section per unit cell is given by

$$\Sigma_{\rm SRO} = 4\pi I_{\rm D}/N', \qquad (18)$$

where N' is the number of unit cells in the crystal. The cross sections for several components of the pattern can be deduced from this expression.

Incoherent Scattering

If b_l is the scattering length associated with the *l*th isotope and spin state, then the contribution from incoherent scattering becomes ($\alpha_0 = 1$ and $\alpha_m = 0$ for m > 0)

$$\Sigma_{\rm INC} = 4\pi (\langle b_l^2 \rangle - \langle b_l \rangle^2). \tag{19}$$

Partial Site Occupancy

For systems with incomplete site occupancy, we have

$$C_{\rm A} = C_i b_{\rm A} = b$$
, $C_{\rm B} = 1 - C_i$, $b_{\rm B} = 0$,

where C_i is the site occupancy factor chosen so that for $C_i = 1$ all sites in all unit cells are occupied. Then, the disorder cross section is

$$\Sigma_{\rm DO} = 4\pi \sum_{i=1}^{n} C_i (1 - C_i) b_i^2, \qquad (20)$$

where n is the number of atoms in the unit cell. This expression assumes that there is no correlation between vacant sites. If there is clustering of either vacancies or occupied sites, modulated diffuse scattering of the form

$$\Sigma_{\rm DO} = 4\pi b^2 C(1-C) \sum_m \alpha_m c_m (\sin 2\pi k r_m)/2\pi k r_m$$
(21)

will appear for each atomic species. The cross sections will simply add if the ordering in each species is independent but, in general, cross terms could be expected.

Magnetic Diffuse Scattering

The treatment for systems in which the magnetic moment varies from site to site follows the treatment of composition fluctuations. Assuming that the magnetic system is collinear and parallel to the z axis, we have

$$I(k) = (1 - \tau_z^2) \sum_j \sum_{j'} p_j(k) p_{j'}(k) \exp\{2\pi i k \cdot (r_j - r_{j'})\}.$$
 (22)

Defining an AB alloy with C_A atoms of magnetic scattering factor p_A and C_B with scattering factor p_B , we obtain a Bragg term containing the average scattering factor, and the diffuse magnetic scattering is given by

$$\Sigma_{\rm DM} = 4\pi (1 - \tau_z^2) C_{\rm A} C_{\rm B} \{ p_{\rm A}(\mathbf{k}) - p_{\rm B}(\mathbf{k}) \}^2 \sum_m c_m \alpha_m (\sin 2\pi k r_m) / 2\pi k r_m.$$
(23)

The first term reduces to the expression used by Shull and Wilkinson (1955). Marshall (1968) has introduced short-range order parameters to describe the perturbation of the moments on B atoms which are close neighbours of type A atoms. These parameters are equivalent to α_m .

Paramagnetic Scattering

The appropriate cross section is (Marshall and Lovesey 1971, p. 112)

$$\Sigma_{\rm P} = \frac{8}{3}\pi (e^2 \gamma/mc^2)^2 \sum_{j=1}^n S_j(S_j+1)f_j^2(k), \qquad (24)$$

where *j* labels the magnetically active atoms in the unit cell.

Displacement Disorder

The formalism of this problem is similar to that of the composition fluctuation problem. An atom can be displaced from a lattice site by a defect in the unit cell or by a large discrepancy in atomic size. Detailed calculations have been given by Warren *et al.* (1951) and by Borie (1957, 1959). These calculations lead to the size effect cross section

$$\Sigma_{\rm SE} = 4\pi C_{\rm A} C_{\rm B} (b_{\rm A} - b_{\rm B})^2 \left\{ \sum_m \alpha_m c_m \frac{\sin 2\pi k r_m}{2\pi k r_m} - \sum_m c_m \beta_m \left(\frac{\sin 2\pi k r_m}{2\pi k r_m} - \cos 2\pi k r_m \right) \right\}, \quad (25)$$

where α_m is the short-range order coefficient and β_m the size effect coefficient.

Thermal Diffuse Scattering

At any temperature the intensity removed from the Bragg peaks by the Debye– Waller factor reappears as inelastic scattering in the diffuse background. The simplest Neutron Diffraction Powder Patterns

approximation to this term is based on the assumption that the atoms vibrate independently. With this assumption (Bacon 1955), the relevant cross section is

$$\Sigma_{\rm TDS} = \sum 4\pi b_i^2 \{1 - \exp(-2M_i)\},$$
(26)

where the summation is over the unit cell. For simple structures it is possible to find expressions which recognize the correlation between atomic vibrations. Treatments have been given of a correction to integrated intensities for the component of the thermal diffuse scattering which peaks at the position of the Bragg peak (Willis and Pryor 1975).

Marshall and Lovesey (1971, pp. 93–104) have given expressions in which the elastic and one-phonon terms are treated exactly and the multiphonon terms approximated. These are not, at present, convenient for calculation, but could form the basis for a detailed treatment of the thermal diffuse scattering contribution to the powder pattern.

Conclusions

Expressions have been given for scattering mechanisms which contribute to the total powder pattern. Inclusion of these removes the necessity for a subjective estimate of the background. Those quantities which are the result of local deviations from the average structure are included in the refinement process through their contributions to both the Bragg scattering and diffuse scattering. A constraint that the total scattering is conserved can then be applied.

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