and with $a_0 = 3{\cdot}74$ Å, the diffuse scattering in the vicinity of $h_1h_2h_3 = 100$ ($hkl = 200$) in the h_1h_20 plane was computed by means of equation (8) and the size effect function of Fig. 1. It is compared with the experimentally measured distribution in Fig. 2. The experimental data are those shown in Fig. 4 of Part I.

4. Discussion

By a rearrangement of the expression for the diffuse intensity associated with the atomic size effect, it has been shown that Huang's integral approximation is unnecessary and that the diffuse scattering may be expressed in a very simple form. In spite of the fact that the Cu_3Au specimen used contained a significant degree of short-range order, agreement between observed and calculated intensity distributions in the vicinity of the Bragg maxima is quite good. It is interesting that the Laue monotonic diffuse scattering, the second term of equation (4), here completes a square, while in the case of short-range order with no size effect, it is the leading term of a Fourier series.

Equation (8) has been arranged so that the size effect function of Fig. 1 is quite general and may be used to compute the diffuse scattering for any close-packed cubic solid solution.

References

Borie, B. (1957). *Acta Cryst.* **10**, 89.

Huang, K. (1947). *Proc. Roy. Soc.* A, **190**, 102.

Warren, B. E., Averbach, B. L. & Roberts, B. W. (1951). *J. Appl. Phys.* **22**, 1493.

Acta Cryst. (1959). **12**, 282

A Note on the Magnetic Intensities of Powder Neutron Diffraction

By Gen Shirane

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, U.S.A.

(*Received* 12 *September* 1958)

General intensity formulae of powder neutron diffraction lines are given for magnetic structures with a single-spin-axis as a function of the spin direction with respect to the crystallographic axes. If we disregard the vector properties of spins and assign a positive or negative scattering amplitude to the magnetic atoms, these scalar scatterers constitute a 'configurational symmetry' of the magnetic structure. When this symmetry is tetragonal, rhombohedral or hexagonal, the powder intensities cannot provide more information than the angle between the spin direction and the unique axis of the structure. The ambiguity of spin directions in α Fe_2O_3, NiAs and MnO type structures is discussed.

1. Introduction

Neutron intensities of magnetic origin at a Bragg reflection can be obtained by straightforward calculations based upon the fundamental formula of Halpern & Johnson (1939). If suitable single domain crystals are available for neutron diffraction studies of magnetic compounds, the interpretation of the magnetic intensities gives a unique solution for the spin arrangements. However, if one must depend upon the powder data alone, some ambiguities arise because of the superposition of several non-identical reflections with the same Bragg angle θ.

It has been known that the spin direction cannot be deduced from the powder data of cubic ferromagnetics, such as Fe, because any spin direction with respect to the crystallographic axis gives the same magnetic intensities if the domains are oriented randomly. The ambiguity of spin structures in cubic antiferromagnetics of the MnO-type has been discussed in detail by Li (1955) and by Keffer & O'Sullivan (1957) considering the possibility of multi-spin-axis orientations.

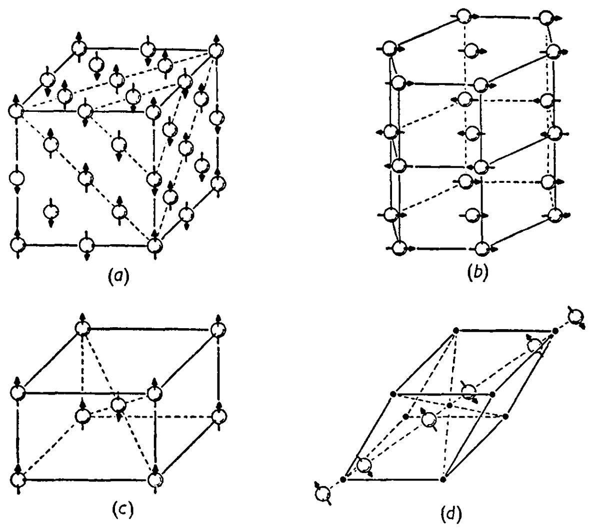

Fig. 1. Examples of antiferromagnetic spin arrangements, (*a*) MnO type, (*b*) NiAs type, (*c*) Rutile type, (*d*) Fe_2O_3 type—after Shull & Wollan (1956).

Table 1. *Crystal symmetry and configurational symmetry of magnetic structures shown in Fig.* 1

		Crystal structure	Magnetic structure
(*a*)	MnO-type	Cubic, $Fm3m$ NaCl-type with a_0	Rhombohedral, $R\bar{3}$, $a = 2a_0$ $+p$ at $(0, 0, 0)$ $(0, \frac{1}{2}, \frac{1}{2})$ ↻ $\pm(0, \frac{1}{4}, \frac{3}{4})$ ↻ $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ ↻
(*b*)	NiAs-type	Hexagonal, $P6_3mc$ Ni at $(0, 0, 0)$, $(0, 0, \frac{1}{2})$	Hexagonal, $P6mm$ $+p$ at $(0, 0, 0)$ $-p$ at $(0, 0, \frac{1}{2})$
(*c*)	MnF_2-type	Tetragonal $P4_2/mmm$ Rutile-type Mn at $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	Tetragonal $P4/mm$ $+p$ at $(0, 0, 0)$ $-p$ at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
(*d*)	Fe_2O_3-type	Rhombohedral $R\bar{3}c$ Fe at $\pm(u, u, u)$ $\pm(\frac{1}{2}+u, \frac{1}{2}+u, \frac{1}{2}+u)$	Rhombohedral, $R3c$ for Cr_2O_3 ($R\bar{3}$ for Fe_2O_3) $+p$ at (u, u, u), $(u+\frac{1}{2}, u+\frac{1}{2}, u+\frac{1}{2})$ $-p$ at $(-u, -u, -u)$, $(\frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-u)$

It is the purpose of this note to demonstrate that a similar ambiguity may occur in other crystallographic systems with high symmetries. For example, the spin directions within the plane perpendicular to the unique axis of the crystal, as shown in Fig. 1(*b*) and (*d*), cannot be determined by the powder data alone. The conditions under which the ambiguities occur will be described and a convenient formula for the intensity calculations will be given for the tetragonal, rhombohedral and hexagonal systems.

2. Powder intensities of magnetic scattering

The magnetic structure factor F_{hkl} for a (hkl) reflection can be written as (see, for example, Bacon, 1955).

$$\bar{\mathbf{F}}_{hkl} = \sum_i p_i \bar{\mathbf{q}}_i \exp\,[2\pi j(hx_i+ky_i+lz_i)]\,, \tag{1}$$

with

$$p = (e^2/mc^2).\gamma.S.f\,, \tag{2}$$

$$\mathbf{q} = \mathbf{e}(\mathbf{e}.\mathbf{k})-\mathbf{k}\,, \tag{3}$$

where **e** is the unit scattering vector and **k** is the unit vector parallel to the magnetic moment of the scattering atom. Denoting the angle between **e** and **k** as η, we obtain from equation (3)

$$q^2 = \sin^2\eta\,. \tag{4}$$

If we consider the case where all the q_i's are parallel or antiparallel to each other

$$F^2 = q^2[\sum_i \pm p_i \exp\,[2\pi j(hx_i+ky_i+lz_i)]]^2\,. \tag{5}$$

The sign of p_i is determined by the direction of $\mathbf{q}_i$. For convenience we consider that p_i can assume positive or negative values and drop the signs ±. Now, the intensities of the powder lines can be written

$$\begin{aligned} I &= K\cdot\sum_{hkl} F^2_{hkl} \\ &= K.\sum_{hkl} q^2_{hkl}[\sum_i p_i \exp\,[2\pi j(hx_i+ky_i+lz_i)]]^2\,, \end{aligned} \tag{6}$$

where K is a constant at a given angle θ and the summation should be carried out over all possible combinations of h, k and l, which result in the same Bragg angle.

For the present discussion, it will be convenient to visualize the magnetic structure as consisting of atoms with a scalar scattering amplitude p_i, which may be either positive or negative, while the spin direction is represented in the intensity formula by q^2 only. We put

$$F(m)_{hkl} = \sum_i p_i \exp\,[2\pi j(hx_i+ky_i+lz_i)]\,. \tag{7}$$

This $F(m)_{hkl}$ is thus computed formally in the same way as the normal structure factor of nuclear scatterers. The only difference is that equivalent atoms may possess values of the scattering amplitude p_i which are different not only in magnitude, because of the spin state of the atoms, but also in sign, because of the spin direction.

Let us consider the symmetry of the p_i's of the magnetic structure. This may be called 'configurational symmetry' of the magnetic structure. This symmetry may not be equal to the 'chemical symmetry' of the crystal, because $F(m)$ is concerned with magnetic atoms only. This situation is illustrated in Table 1. The configurational symmetry allows several $F(m)_{hkl}$ to assume the same absolute value for different combinations of $\pm h$, $\pm k$ and $\pm l$, but each $F(m)_{hkl}$ may be associated with a different value of q^2. For example, (hkl), (klh) and (lhk) planes are equivalent if the symmetry is rhombohedral. This group of equivalent hkl reflections may be represented by $\{hkl\}$.

We obtain from equations (6) and (7)

$$I = K\sum_{\{hkl\}} j_{\{hkl\}}\langle q^2\rangle.F(m)^2_{\{hkl\}}\,, \tag{8}$$

where $j_{\{hkl\}}$ is the multiplicity of $F(m)_{\{hkl\}}$ and $\langle q^2\rangle$ is the average value of q^2 for the j equivalent $F(m)$'s. The summation $\{hkl\}$ must be carried out if there is more than one non-equivalent $F(m)$'s at the same Bragg angle. An uncertainty in the magnetic structure may arise if the equal intensities are obtained with different sets of $F(m)^2$ and $\langle q^2 \rangle$, as was demonstrated in the case of antiferromagnetics of the MnO-type. In this note, however, we shall limit ourselves to the case where equivalence of the intensities is a result of equivalent $\langle q^2 \rangle$ with different spin directions.

This picture is, of course, correct only for the single-spin-axis solutions. The triangular spin configuration given by Yafet & Kittel (1952) and the multi-spin-directions discussed by Keffer & O'Sullivan (1957) are exceptional cases where equation (6) cannot be used.

3. Calculations of $\langle q^2 \rangle$

The value of q^2 can be expressed as a function of the direction cosines of $\mathbf{e}$ and $\mathbf{k}$ using equation (3). However, this straightforward method is rather lengthy when we must deal with systems with oblique axes. A more convenient formula for the general case may be obtained if we assume that the spin direction is the normal to a plane $(h_0k_0l_0)$. The angle between the normals of the planes (hkl) and $(h_0k_0l_0)$ can be written as (see, for example, James, 1954).

$$\cos\eta = (h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*)(h_0\mathbf{a}^*+k_0\mathbf{b}^*+l_0\mathbf{c}^*)dd_0\,, \quad (9)$$

or multiplying out

$$\begin{aligned}\cos\eta = \{&hh_0a^{*2}+kk_0b^{*2}+ll_0c^{*2}\\ &+(hk_0+h_0k)a^*b^*\cos\gamma^*+(kl_0+k_0l)b^*c^*\cos\alpha^*\\ &+(lh_0+l_0h)c^*a^*\cos\beta^*\}dd_0\,,\end{aligned} \quad (10)$$

where a^*, b^*, $c^*\cos\alpha^*$, $\cos\beta^*$ and $\cos\gamma^*$ refer to reciprocal space and $d(hkl)$ and $d_0(h_0k_0l_0)$ are the spacing of the planes (hkl) and $(h_0k_0l_0)$ in the real space.

From equation (4)

$$\langle q^2 \rangle = 1-\langle\cos^2\eta\rangle\,.$$

In order to obtain $\langle q^2 \rangle$, $\cos\eta$ of equation (10) must be first squared and summed over equivalent (hkl). A table of general multiplicity factors and equivalent reflections in various systems is given in a concise form in *The International Tables* (1952). The final formula of $\langle q^2 \rangle$ should be expressed as a function of the angles, φ_a, φ_b, and φ_c, between the spin direction and the crystallographic axes. This can be done by utilizing the same equation (10), which gives $\cos\varphi$ as a function of h_0, k_0 and l_0, if we put (hkl) as (100), (010) and (001).

(A) *Cubic*

$$\begin{aligned}\cos\eta &= (hh_0+kk_0+ll_0)a^{*2}dd_0\\ \langle\cos^2\eta\rangle &= \tfrac{1}{3}(h^2+k^2+l^2)(h_0^2+k_0^2+l_0^2)a^{*4}d^2d_0^2 = \tfrac{1}{3}\,.\end{aligned}$$

(B) *Tetragonal*

$$\cos\eta = \{(hh_0+kk_0)a^{*2}+ll_0c^{*2}\}dd_0\,.$$

Summing up for the equivalent reflections (hkl), $(hk\bar{l})$, $(k\bar{h}l)$ and $(k\bar{h}\bar{l})$

$$\begin{aligned}\langle\cos^2\eta\rangle &= \{\tfrac{1}{2}(h^2+k^2)(h_0^2+k_0^2)a^{*4}+l^2l_0^2c^{*4}\}d^2d_0^2\\ &= \{\tfrac{1}{2}(h^2+k^2)a^{*2}\sin^2\varphi+l^2c^{*2}\cos^2\varphi\}d^2\,,\end{aligned} \quad (11)$$

where φ is the angle between the spin direction and the c axis.

(C) *Hexagonal*

$$\cos\eta = [\{(hh_0+kk_0)+\tfrac{1}{2}(hk_0+h_0k)\}a^{*2}+ll_0c^{*2}]dd_0\,.$$

Summing up for the equivalent reflections, $(hkil)$, $(hki\bar{l})$, $(kihl)$, $(kih\bar{l})$, $(ihkl)$, and $(ihk\bar{l})$, where $i = -(h+k)$

$$\begin{aligned}\langle\cos^2\eta\rangle &= \{\tfrac{1}{2}(h^2+k^2+hk)(h_0^2+k_0^2+h_0k_0)a^{*4}+l^2l_0^2c^{*4}\}d^2d_0^2\\ &= \{\tfrac{1}{2}(h^2+k^2+hk)a^{*2}\sin^2\varphi+l^2c^{*2}\cos^2\varphi\}d^2\,,\end{aligned} \quad (12)$$

where φ is the angle between the spin direction and the [0001] axis.

(D) *Rhombohedral*

$$\begin{aligned}\cos\eta = \{&(hh_0+kk_0+ll_0)\\ &+\cos\alpha^*(hk_0+h_0k+kl_0+k_0l+lh_0+l_0h)\}a^{*2}dd_0\,.\end{aligned}$$

Summing up for the equivalent reflections (hkl), (klh) and (lhk)

$$\begin{aligned}\langle\cos^2\eta\rangle &= \{2(n-r)(n_0-r_0)(1-\cos\alpha^*)^2\\ &\quad+(n+2r)(n_0+2r_0)(1+2\cos\alpha^*)^2\}\tfrac{1}{9}a^{*4}d_0^2d^2\\ &= \{(n-r)(1-\cos\alpha^*)\sin^2\varphi\\ &\quad+(n+2r)(1+2\cos\alpha^*)\cos^2\varphi\}\tfrac{1}{3}a^{*2}d^2\,,\end{aligned} \quad (13)$$

with

$$n = h^2+k^2+l^2,\quad r = hk+kl+lh\,,$$

where φ is the angle between the spin direction and the [111] axis.

(E) *Orthorhombic*

$$\cos\eta = (hh_0a^{*2}+kk_0a^{*2}+ll_0c^{*2})dd_0\,.$$

Summing up for the equivalent reflections (hkl), $(hk\bar{l})$, $(h\bar{k}l)$ and $(\bar{h}kl)$

$$\begin{aligned}\langle\cos^2\eta\rangle &= (h^2h_0^2a^{*4}+k^2k_0^2b^{*4}+l^2l_0^2c^{*4})d^2d_0^2\\ &= (h^2a^{*2}\cos^2\varphi_a+k^2b^{*2}\cos^2\varphi_b+l^2c^{*2}\cos^2\varphi_c)d^2,\end{aligned} \quad (14)$$

where φ_a, φ_b, and φ_c are angles between the spin direction and a, b, and c axes, respectively.

4. Discussion

From the general formulae for $\langle q^2 \rangle$ we can arrive at the following conclusions as to the limitations of the powder technique to determine the spin direction of magnetic structures. No information is obtained about the spin direction if the configurational symmetry is cubic. When the symmetry is uniaxial, that is, either tetragonal, hexagonal or rhombohedral, the spin direction cannot be defined except for its angle with the unique axis of the magnetic structure.

This is not an unexpected result, especially if we realize the fact that q^2 is a function of second order terms of the direction cosines of **e** and **k**, and the summation over equivalent reflections may cancel the cross terms and leave only the terms referring to the unique axis. It may be pointed out here that considerable similarity exists between the expression for $1/d^2$ and $\langle \cos^2 \eta \rangle$, especially in the cases of tetragonal, hexagonal and orthorhombic symmetries. We may examine some of the known magnetic structures (see, for example, Bacon, 1955, and Shull & Wollan, 1956), in the light of the present results (see Fig. 1).

In most of the cases of uniaxial crystals the spin lies in a direction parallel or perpendicular to the unique axis. When it coincides with the unique axis ($\varphi = 0$), the spin direction can be given by the powder data unambiguously. This is not true, however, when it is perpendicular to the unique axis ($\varphi = 90°$). Although in some cases special directions were assumed within the plane, it must be recognized that any other direction within this plane satisfies the powder data equally well.

One known case with φ not equal to 0° or 90° is tetragonal NiF_2, in which the spin direction was found to be 10° off the tetragonal axis (Erickson, 1953). In this case, Erickson stated clearly that the data could not be interpreted to give more information than the inclination of the moment with respect to the tetragonal axis.

The spin configuration of the MnO-type antiferromagnetics shown in Fig. 1(*a*) presents an interesting example. In this case, the configurational symmetry is rhombohedral although the chemical symmetry is cubic. It can thus be concluded that the spin direction cannot be defined except for its angle with the [111] direction. The spin directions of this group of compounds were first studied by Shull, Strauser & Wollan (1951) and recently reexamined by Roth (1958). Although the uncertainty of the spin direction within the (111) plane was recognized, the general uncertainty associated with rhombohedral symmetry was overlooked and the spin directions were obtained by a trial-and-error method. A simple formula for $\langle q^2 \rangle$ can be obtained from equation (13) by assuming $\cos \alpha^* = 0$

$$\langle \cos^2 \eta \rangle = \{(n-r) \sin^2 \varphi + (n+2r) \cos^2 \varphi\} \frac{a^{*2}d^2}{3} .$$

Then the problem becomes a one parameter problem to determine φ from the observed intensities.

The author is very grateful to Drs F. Jona, W. J. Takei, and T. Oguchi for helpful discussions.

References

Bacon, G. E. (1955). *Neutron Diffraction*. Oxford: Clarendon Press.

Erickson, R. A. (1953). *Phys. Rev.* **90**, 779.

Halpern, O. & Johnson, M. H. (1939). *Phys. Rev.* **55**, 898.

International Tables for X-ray Crystallography (1952), p. 32. Birmingham: Kynoch Press.

James, R. W. (1954). *The Optical Principles of the Diffraction of X-Rays*, p. 604. London: Bell.

Keffer, F. & O'Sullivan, W. (1957). *Phys. Rev.* **108**, 637.

Li, Y. Y. (1955). *Phys. Rev.* **100**, 627.

Roth, W. L. (1958). *Phys. Rev.* **110**, 1333.

Shull, C. G. & Wollan, E. O. (1956). '*Application of Neutron Diffraction to Solid State Problems*', *Solid State Physics*, vol. 2, p. 137. New York: Academic Press.

Shull, C. G., Strauser, W. A. & Wollan, E. O. (1951). *Phys. Rev.* **83**, 333.

Yafet, Y. & Kittel, C. (1952). *Phys. Rev.* **87**, 290.

Acta Cryst. (1959). **12**, 285

X-ray Scattering by Bundles of Cylinders

By R. E. Burge

Wheatstone Physics Laboratory, University of London King's College, Strand, London, W. C. 2, England

(*Received* 18 *September* 1958)

The effects of interparticle interference on the low-angle scattering by a bundle of parallel cylinders in close-packed hexagonal array are calculated. The application of the results to the elucidation of the sizes of coherent hexagonal aggregates from X-ray scattering measurements obtained from both solid samples and solutions of long chain molecules is discussed; the calculations may also be of value in the interpretation of light-scattering results from similar solutions.

Introduction

Interference effects in X-ray scattering at small angles are well known and theoretical and experimental discussions have been published both for scattering by spheres (e.g. Lund & Vineyard, 1949; Oster & Riley, 1952*a*; Guinier, Fournet, Walker & Yudowitch,