efficient of carbon of 4·17 cm^2 g^{-1}. This value was obtained from twenty-three measurements on thirteen different diamond crystals with a spread of results from 3·95 to 4·54 cm^2 g^{-1}.

Recently the tabulated value of the mass attenuation coefficient derived from smoothed functions of the mass attenuation coefficient against wavelength has been revised from 4·60 cm^2 gm^{-1} (*International Tables for X-ray Crystallography*, 1962) to 4·219 cm^2 gm^{-1} (*International Tables for X-ray Crystallography*, 1974): with this value is associated a $\pm \leq 2\%$ 'envelope of uncertainty' *i.e.* $\pm \leq 0{\cdot}084$ cm^2 g^{-1} and hence the outer limits of 4·219 cm^2 g^{-1} are $\leq 4{\cdot}303$ cm^2 g^{-1} and $\geq 4{\cdot}135$ cm^2 g^{-1}. If these limits are taken to imply $\sigma \leq 0{\cdot}028$ cm^2 g^{-1} then the difference between the *International Tables* value of 4·219 cm^2 g^{-1} and our derived value of 4·089(2) cm^2 g^{-1} (for Cu $K\bar{\alpha}$) is significant. Clearly, in the most accurate experimental work, it is still essential to determine the mass attenuation coefficient experimentally.

References

CALVERT, L. D., KILLEAN, R. C. G. & MATHIESON, A. McL. (1974*a*). *Abstracts, International Crystallography Conference. 'Diffraction Studies of Real Atoms and Real Crystals'*, pp. 88–89. Canberra: Australian Academy of Science.

CALVERT, L. D., KILLEAN, R. C. G. & MATHIESON, A. McL. (1974*b*). *J. Appl. Cryst.* **7**, 406.

CHIPMAN, D. R. (1955). *J. Appl. Phys.* **26**, 1387.

CHIPMAN, D. R. (1969). *Acta Cryst.* A**25**, 209–213.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 160–162. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 61. Birmingham: Kynoch Press.

MATHIESON, A. McL. (1968). *Rev. Sci. Instrum.* **39**, 1834–1837.

MOORE, A. W. (1973). *Chemistry and Physics of Carbon*, Vol. XI, pp. 87, 106, 107. New York: Marcel Dekker.

Acta Cryst. (1975). A**31**, 856

The information contained in neutron powder diagrams of magnetic materials.

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A reciprocal-space treatment is given of the effects of reflexion averaging on the information available from magnetic neutron powder diagrams. The results confirm those previously obtained by spin-density Patterson methods.

Introduction

Shirane (1959) has described the effects of reflexion overlap in powder patterns of magnetic materials which have a unique spin direction. The results have been extended to multi-spin axis structures by Wilkinson & Lisher (1973) using a spin density Patterson (real-space) treatment and subsequently verified by Litvin (1974) using group-theoretical methods. The present note reports the equivalent reciprocal-space treatment for multi-spin axis structures.

Theory

From the work of Halpern & Johnson (1939), the magnetic contribution to the *hkl* neutron diffraction line from a magnetically ordered material can be shown to be proportional to $I(\mathbf{k}) = |\mathbf{P}(\mathbf{k})|^2 - |\hat{\mathbf{k}} \, . \, \mathbf{P}(\mathbf{k})|^2$, where $\mathbf{P}(\mathbf{k})$ is a 'vector structure factor' defined by $\mathbf{P}(\mathbf{k}) = \sum_{i=1}^{n} \mathbf{S}_i f_i(\mathbf{k}) \times \exp 2\pi j \mathbf{k} \, . \, \mathbf{r}_i$ for a magnetic unit cell in which the atoms are in positions $\mathbf{r}_i$ and have spins $\mathbf{S}_i$ and form factors f_i. $\mathbf{k}$ is the scattering vector for the *hkl* reflexion and $\hat{\mathbf{k}}$ is a unit vector in the direction of $\mathbf{k}$.

Thus

$$\begin{aligned} I(\mathbf{k}) &= |\mathbf{P}(\mathbf{k})|^2 - |\hat{\mathbf{k}} \, . \, \mathbf{P}(\mathbf{k})|^2 \\ &= |\mathbf{P}(\mathbf{k})|^2 [1 - \hat{\mathbf{k}} \, . \, \hat{\mathbf{P}}(\mathbf{k})]^2 \\ &= |\mathbf{P}(\mathbf{k})|^2 \sin^2 \tau \end{aligned}$$

where τ is the angle between $\mathbf{k}$ and $\mathbf{P}(\mathbf{k})$.

Now

$$|\mathbf{P}(\mathbf{k})|^2 = \sum_{i=1}^{n} |\mathbf{S}_i|^2 f_i^2 + 2 \sum_{i \neq j}^{n} \mathbf{S}_i \, . \, \mathbf{S}_j f_i f_j \cos 2\pi \mathbf{k} \, . \, (\mathbf{r}_i - \mathbf{r}_j)$$

and the information contained in $|\mathbf{P}(\mathbf{k})|^2$ therefore concerns the magnitudes of the spins $\mathbf{S}_1 \ldots \mathbf{S}_n$ and the relative angles between them. There are no terms involving the orientation of the spins relative to the crystallographic axes of the material. This dependence is contained within the term $\sin^2 \tau$, and as shown by Shirane it is the averaging of this term over overlapped reflexions which results in a loss of information when the configurational symmetry is higher than orthorhombic.

In fact, it is easy to show that $\mathbf{P}(\mathbf{k})$ is identical for reflexions of the form $\{hkl\}$ related by the configurational symmetry axis. Consider, for example, a magnetic structure with tetragonal configurational symmetry. Atoms in positions x,y,z; $\bar{y},x,z$; $\bar{x},\bar{y},z$; $y,\bar{x},z$ related by the configurational tetrad have identical spins $\mathbf{S}$ and the expression for $\mathbf{P}(\mathbf{k})$ is

$$\begin{aligned} \mathbf{P}(hkl) = \sum_{i=1}^{n} \mathbf{S}_i f_i \{ & \exp [2\pi j(hx_i + ky_i + lz_i)] \\ & + \exp [2\pi j(h\bar{y}_i + kx_i + lz_i)] \\ & + \exp [2\pi j(h\bar{x}_i + k\bar{y}_i + lz_i)] \\ & + \exp [2\pi j(hy_i + k\bar{x}_i + lz_i)] \} \end{aligned}$$

where the symmation is taken over all groups related by the fourfold axis. The reflexion $\bar{k}hl$ has

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$$\begin{aligned}\mathbf{P}(\bar{k}hl)= \sum_{i=1}^{n} \mathbf{S}_i f_i\{&\exp\,[2\pi j(\bar{k}x_i+hy_i+lz_i)]\\ &+\exp\,[2\pi j(ky_i+hx_i+lz_i)]\\ &+\exp\,[2\pi j(kx_i+h\bar{y}_i+lz_i)]\\ &+\exp\,[2\pi j(\bar{k}y_i+\bar{h}x_i+lz_i)]\}\\ &=\mathbf{P}(hkl)\end{aligned}$$

and in general

$$\mathbf{P}(hkl)\equiv\mathbf{P}(\bar{k}hl)\equiv\mathbf{P}(\bar{h}\bar{k}l)\equiv\mathbf{P}(k\bar{h}l)\,.$$

The intensity resulting from the overlap of these reflexions in the powder pattern is

$$I(|\mathbf{k}|)=|\mathbf{P}\{hkl\}|^2(\sin^2\tau_{hkl}+\sin^2\tau_{\bar{k}hl}+\sin^2\tau_{\bar{h}\bar{k}l}+\sin^2\tau_{k\bar{h}l})$$

where $\tau_{\{hkl\}}$ are the angles between the scattering vectors of the form $\{hkl\}$ and the common direction of $\mathbf{P}\{hkl\}$. The averaging procedure is therefore identical to that described by Shirane for structures with a unique spin direction and thus the same rules apply to the different configurational symmetries.

Conclusions

It has been shown that the magnitudes of the spins associated with the magnetic atoms and the angles between them are contained within the modulus of the vector structure factor and are available for all configurational symmetries. The information concerning the angles between spin directions and the crystallographic axes is contained in the expression $\langle \sin^2\tau\rangle$ and as previously shown by Shirane these angles may be determined when the configurational symmetry is orthorhombic, monoclinic or triclinic. When the configurational symmetry is uniaxial the value of $\langle \sin^2\tau\rangle$ is dependent only on the angles between the spin directions and the unique axis, and when the configurational symmetry is cubic the value of $\langle \sin^2\tau\rangle$ is $\frac{2}{3}$ and no information is available concerning the relationship between the spin directions and the crystallographic axes.

The results obtained above could equally well be applied to multi-domain single crystals where the direction of **P** is rotated in different domains and the direction of **k** remains fixed.

The conclusions are in complete agreement with those previously reached by spin density Patterson methods.

References

Halpern, O. & Johnson, M. H. (1939). *Phys. Rev.* **55**, 898–923.
Litvin, D. B. (1974). *Acta Cryst.* **A30**, 785–791.
Shirane, G. (1959). *Acta Cryst.* **12**, 282–285.
Wilkinson, C. & Lisher, E. J. (1973). *Acta Cryst.* **A29**, 453–461.

Acta Cryst. (1975). **A31**, 857

Désordre structural et transformation de phase dans les fluosilicates de Fe, Mg, Mn.

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$FeSiF_6$ $6H_2O$ shows extra reflexions inconsistent with the space group $R\bar{3}m$. The same conclusion applies, for $T>300$K, to $MgSiF_6.6H_2O$ whose structure is similar to that of $MnSiF_6.6H_2O$. These three compounds undergo similar phase transformations with decreasing temperature.

Les fluosilicates de formule générale $MSiF_6.6H_2O$ (M= métal divalent) ont été décrits comme des déformations rhomboédriques de la structure CsCl. Certains d'entre eux (M = Ni, Co, Zn) présentent les éléments de symétrie du groupe $R\bar{3}$ alors que pour d'autres (M = Fe, Mg), le groupe $R\bar{3}m$ avait été retenu.

Concernant le fluosilicate de fer, à la température ambiante, les conclusions de Hamilton (1962) sont généralement admises. Selon Hamilton, il existe, pour les octaèdres de chaque type d'anions, deux orientations possibles symétriques par rapport aux plans {11.0}, (maille hexagonale: $Z=3$). Ces deux situations, également probables, sont intimement mêlées dans le cristal, ce qui laisse apparaître les miroirs.

Au cours de notre étude, il nous est apparu que les conclusions de Hamilton étaient erronées. A la température ambiante on observe bien des miroirs confondus avec les plans {11.0} de la maille hexagonale, mais il apparaît des réflexions supplémentaires très élargies à des positions approximatives correspondant à des indices tels que $-h+k+l=3n\pm1$, incompatibles avec le groupe $R\bar{3}m$ [Fig. 1(*a*)].

Par abaissement de la température jusqu'à 245K, ces taches s'affinent progressivement jusqu'à devenir aussi fines que les réflexions normales [Fig. 1(*b*)]. Les diagrammes de cristal tournant autour de l'axe ternaire révèlent alors que ces taches supplémentaires ne se situent pas exactement dans les strates de réflexions dites normales, mais de part et d'autre de ces strates. Le pseudo-hexagone de taches de surstructures (réflexions non indicées) centré sur 22.3, de la Fig. 1(*b*) est, en réalité, un octaèdre très aplati suivant c^*, les trois taches les plus intenses se situant au-dessous de la strate, les trois taches les plus faibles au-dessus. La distance entre ces deux groupes de taches, sensiblement égale à $c^*/7$ à 260K, évolue en fonction de la température: lorsque T décroît, les réflexions se rapprochent des strates sans jamais s'y localiser parfaitement. Ces taches supplémentaires accompagnent toutes les strates à l'exception de la strate équatoriale. Il s'agit là, de toute évidence, d'un nouvel exemple de structure modulée.

Dans le cas de $MgSiF_6.6H_2O$, pour $T>300$K, nous avons mis en évidence, un système de réflexions supplémentaires analogue mais, cette fois, elles sont toujours très fines et situées très exactement dans les strates norma-