smooth nature of the modulation functions $f_\mu(x_4)$ or $u_i^\mu(\tau)$ from §5. As stated earlier, the continuity of these functions is an essential feature of modulated structures.

The author is greatly indebted to Dr Tuinstra (Delft) and to Professor Janner and Dr Janssen (Nijmegen) for reading and most helpfully criticising the manuscript.

References

AIZU, K. (1973). *J. Phys. Soc. Japan*, **34**, 1567–1574.

BERG, A. J. VAN DEN, TUINSTRA, F. & WARCZEWSKI, J. (1973). *Acta Cryst.* B**29**, 586–589.

DUBBELDAM, G. C. & DE WOLFF, P. M. (1969). *Acta Cryst.* B**25**, 2665–2667.

FAST, G. & JANSSEN, T. (1968). Technical Report 6–68, Katholieke Universiteit Nijmegen.

HOSHINO, H. & MOTEGI, H. (1967). *Jap. J. Appl. Phys.* **6**, 708–718.

JACOBI, H. (1972). *Z. Kristallogr.* **135**, 467–468.

JAMIESON, P. B., DE FONTAINE, D. & ABRAHAMS, S. C. (1969). *J. Appl. Cryst.* **2**, 24–30.

JANNER, A. (1972). *Acta Cryst.* A**28**, S111.

JANSSEN, T. (1969). *Physica*, **42**, 71–92.

KOREKAWA, M. & JAGODZINSKI, H. (1967). *Schweiz. Miner. Petrogr. Mitt.* **47**, 269–278.

TUINSTRA, F. (1967). Thesis, T. H. Delft.

TUINSTRA, F. & VAN ELDIK, H. (1973). Private communication.

WOLFF, P. M. DE & VAN AALST, W. (1972). *Acta Cryst.* A**28**, S101.

WONDRATSCHEK, H., BÜLOW, R. & NEUBÜSER, J. (1971). *Acta Cryst.* A**27**, 523–535.

Acta Cryst. (1974). A**30**, 785

The Symmetry of the Spin-Density Patterson Function

BY D. B. LITVIN

Department of Physics, University of British Columbia, Vancouver, Canada

(*Received* 23 *May* 1974; *accepted* 20 *June* 1974)

Generalized space groups are defined to describe the symmetry of a spin-density Patterson function due to the spin-group (generalized magnetic group) symmetry of a spin arrangement. The information on spin arrangements obtainable from the generalized space-group symmetry of a spin-density Patterson function is discussed. It is shown that one cannot infer from the symmetry of the spin-density Patterson function the characteristic spin-group symmetry of a spiral spin arrangement, and an alternate method of doing so is given.

1. Introduction

The Spin-Density Patterson Function, abbreviated by SDPF, is defined as the Fourier transform of the intensity of unpolarized neutrons elastically scattered from a magnetic crystal (Wilkinson, 1968, 1973). This function has been used in determining the spin arrangements of Mn_2P (Yessik, 1968) and vivianite (Forsyth, Johnson, & Wilkinson, 1970). Wilkinson & Lisher (1973) have discussed the symmetry properties of the SDPF due to the magnetic-group symmetry of the spin arrangement and the information on spin arrangements obtainable from the SDPF. They have shown that for multi-domain crystals one may be unable to determine the orientation of the spins from the SDPF.

Spin symmetry groups have been defined to describe the symmetry of spin arrangements in magnetic crystals (Litvin, 1973; Litvin & Opechowski, 1974). The theory of spin symmetry groups is briefly reviewed in § 2. In § 3 we determine the symmetry of the SDPF due to the spin symmetry group of a spin arrangement. We show that space groups are inadequate to describe these symmetries of the SDPF and define a generalization of the space groups to do so. We then discuss the information on spin arrangements obtainable from the generalized space-group symmetry of the SDPF. In §4 we discuss the information on spiral spin arrangements obtainable from the SDPF of single-domain magnetic crystals. We show that one cannot infer from the symmetry of the SDPF the characteristic spin symmetry of a spiral spin arrangement, and, as in the case of multi-domain crystals, one is unable to determine from the SDPF the orientation of the spins. An alternative method is given of determining the characteristic spin symmetry of a spiral spin arrangement from the SDPF. In § 5 we discuss the SDPF of multi-domain crystals and show that in general no symmetry information, neither magnetic space-group nor spin-group symmetry, on the spin arrangement can be inferred from the symmetry of the multi-domain SDPF.

2. Spin groups

Generalized magnetic groups called *spin groups* have been defined to describe the symmetry of spin arrangements in magnetic crystals (Litvin, 1973; Litvin &

Opechowski, 1974). An element of a spin group is denoted by $[R_1||R_2|\mathbf{V}]$ where R_1 and R_2 are proper or improper rotation matrices, and $\mathbf{V}$ is a column matrix. When applying an element of a spin group to a spin arrangement, the rotation R_1 to the left of the double verticle bar is defined to act only on the components of the spins, while the rotation and translation $(R_2|\mathbf{V})$ to the right are defined to act only on the coordinates of the magnetic atoms. Applying a spin-group element $[R_1||R_2|\mathbf{V}]$ to a spin arrangement $\mathbf{S}(\mathbf{r})$ therefore means replacing $\mathbf{S}(\mathbf{r})$ by the spin arrangement denoted by $[R_1||R_2|\mathbf{V}]\mathbf{S}(\mathbf{r})$ and defined by (Litvin & Opechowski, 1974)*

$$[R_1||R_2|\mathbf{V}]S^i(\mathbf{r})=\sum_{j=1}^{3}(R_1)_{ij}S^j[(R_2|\mathbf{V})^{-1}\mathbf{r}] \quad (1)$$

where $i=1,2,3$. A spin arrangement is said to be invariant under a spin-group element $[R_1||R_2|\mathbf{V}]$ if

$$[R_1||R_2|\mathbf{V}]\mathbf{S}(\mathbf{r})=\mathbf{S}(\mathbf{r}) \quad (2)$$

and the group of all such elements is called the *spin symmetry group* of the spin arrangement $\mathbf{S}(\mathbf{r})$.

Elements $[R_1||R_2|\mathbf{V}]$ of a spin group when applied to a spin arrangement are then defined to act both on the components of the spins and on the coordinates of the magnetic atoms. But, unlike elements of a magnetic group, the matrices, R_1, which is applied to the components of the spins, and R_2, which is applied to the coordinates of the magnetic atoms, need not necessarily be identical nor differ only by the matrix $\bar{E}=-E$, where E is the identity matrix.

Magnetic-group elements have been denoted by (F,A) where $F=(R|\mathbf{V})$ and A is either the identity E or time inversion E' (Opechowski & Dreyfus, 1971). Magnetic-group elements, in the notation used for spin-group elements, are of the form $[\varepsilon_A\delta_R R||R|\mathbf{V}]$ where $\delta_R=\det R$, $\varepsilon_A=+1$ if $A=E$ and $\varepsilon_A=-1$ if $A=E'$, that is, are a special case of spin-group elements $[R_1||R_2|\mathbf{V}]$ where $R_1=\delta_R\varepsilon_A R_2$. Consequently, the magnetic symmetry group of a specific spin arrangement is identical with or a subgroup of the spin symmetry group of the spin arrangement.

A spin group has been shown to be a direct product of a so-called *spin-only group* consisting of elements of the form $[R||E|\mathbf{0}]$, and a second group called a *non-trivial spin group* (Litvin & Opechowski, 1974). A non-trivial spin group contains elements of the form $[R_1||R_2|\mathbf{V}]$ but no elements of the form $[R||E|\mathbf{0}]$ with $R\neq E$.

The spin-only group of a spin arrangement is dependent only on whether the spin arrangement is a linear arrangement, where all spins are collinear, a planar arrangement, where all spins are coplanar, or a spatial arrangement, which includes all remaining possibilities. The set of all R of elements $[R||E|\mathbf{0}]$ of a spin-only group consitute a group b which for the three types of spin arrangements is as follows:

$$\begin{aligned} \mathsf{b}_l &= \mathsf{C}_\infty+\bar{C}_2\mathsf{C}_\infty \\ \mathsf{b}_p &= E, C_2 \\ \mathsf{b}_s &= \mathsf{E}\,. \end{aligned} \quad (3)$$

The indices l,p,s denote linear, planar, and spatial spin arrangements, respectively. C_∞ is the group of matrices representing all proper rotations about the direction of the spins, and C_2 is the matrix representing a rotation through angle π, which is about an axis perpendicular to that direction in the case of b_l, and to the plane of spins in the case of b_p. The matrix C_2 multiplied by -1 is denoted by $\bar{C}_2$.

A non-trivial spin group, consisting of elements $[R_1||R_2|\mathbf{V}]$ is called a non-trivial spin point group, translation group, or space group, according as the set of components $(R_2|\mathbf{V})$ to the right of the double verticle bar constitute, respectively, a point group, translation group, or space group. Non-trivial spin translation groups containing elements $[R||E|\mathbf{t}]$, where R is not $E,\bar{E},C_2$, or $\bar{C}_2$, are characteristic symmetry elements of spiral spin arrangements. The theory and derivation of all non-trivial spin translation groups have been given by Litvin (1973).

3. Symmetry of the single-crystal spin-density Patterson function

The single-crystal spin-density Patterson function will be denoted by $P(\mathbf{r})$. The SDPF consists of series of peaks centred at points $\mathbf{r}=\mathbf{u}$ where $\mathbf{u}$ is the distance between two magnetic atoms in the crystal. Wilkinson (1973) has shown that in the vicinity of the peak centred at $\mathbf{r}=\mathbf{u}$, $P(\mathbf{r})$ is given by

$$P(\mathbf{u}+\mathbf{x})=\int\{f_1(|\mathbf{x}|)\mathbf{S}(\mathbf{r})\,.\,\mathbf{S}(\mathbf{r}+\mathbf{u}) + f_2(|\mathbf{x}|)\,[\mathbf{S}(\mathbf{r})\,.\,\mathbf{x}]\,[\mathbf{S}(\mathbf{r}+\mathbf{u})\,.\,\mathbf{x}]\}d\mathbf{r} \quad (4)$$

where the integration is over the crystal volume, and $f_1(|\mathbf{x}|)$ and $f_2(|\mathbf{x}|)$ are functions of the distance $\mathbf{x}$ from the centre of the peak. The contribution of a pair of spins, whose magnetic atoms are separated by $\mathbf{u}$, to this peak is:

$$f_1(|\mathbf{x}|)\mathbf{S}(\mathbf{r})\,.\,\mathbf{S}(\mathbf{r}+\mathbf{u}) + f_2(|\mathbf{x}|)\,[\mathbf{S}(\mathbf{r})\,.\,\mathbf{x}]\,[\mathbf{S}(\mathbf{r}+\mathbf{u})\,.\,\mathbf{x}]\,. \quad (5)$$

The first term gives a spherically symmetric contribution to the peak, and the second a non-spherically symmetric contribution elongated along the bisector of directions of the spins $\mathbf{S}(\mathbf{r})$ and $\mathbf{S}(\mathbf{r}+\mathbf{u})$. The peak centred at $\mathbf{r}=\mathbf{u}$, see equation (4), is the superposition of contributions of the form (5) from all pairs of spins whose corresponding magnetic atom positions are separated by $\mathbf{u}$.

---

* It should be pointed out that definition (1) is somewhat different to that introduced by Litvin (1973). This modification does not require any changes in Tables 1 and 2 of Litvin (1973), except replacing primes by horizontal bars, *i.e.* Q' is replaced by $\bar{Q}$.

We will first determine the intrinsic symmetry of the SDPF, that is, the symmetry of the SDPF due to definition (4) and independent of the spin arrangement of the crystal. We will then determine the symmetry of the SDPF due to the spin-group symmetry of the spin arrangement of the crystal.

The intrinsic symmetry of the SDPF is found by considering equation (4) from which one finds:

$$P(\mathbf{u}+\mathbf{x})=P(\mathbf{u}-\mathbf{x}) \qquad (6a)$$

$$P(\mathbf{u}+\mathbf{x})=P(-\mathbf{u}+\mathbf{x}) \qquad (6b)$$

$$P(\mathbf{u}+\mathbf{x})=P(-\mathbf{u}-\mathbf{x})\,. \qquad (6c)$$

Equation (6*a*) means that each peak of the SDPF is centrosymmetric about its centre, equation (6*b*) that peaks whose centres are centrosymmetrically related with respect to the origin are identical, and equation (6*c*) that the SDPF is itself centrosymmetric.

The symmetry of the SDPF due to the spin-group symmetry of the spin arrangement is derived using equations (1), (2), and (4). If the spin arrangement $\mathbf{S}(\mathbf{r})$ is invariant under a spin-group element $[R_1||R_2|\mathbf{V}]$, then from equations (1) and (2) we have

$$S^i(\mathbf{r})=\sum_{j=1}^{3}(R_1)_{ij}S^j[(R_2|\mathbf{V})^{-1}\mathbf{r}]$$

where $i=1,2,3$. Substituting this relation into the integrand of equation (4) one derives:

$$P(\mathbf{u}+\mathbf{x})=P(R_2^{-1}\mathbf{u}+R_1^{-1}\mathbf{x})\,. \qquad (7)$$

Relation (7) means that the peak of the SDPF at $R_2^{-1}\mathbf{u}$ rotated by R_1 about its centre is identical with the peak of the SDPF at $\mathbf{u}$.

If a spin arrangement is invariant under a spin translation $[A||E|\mathbf{t}]$ where $A=E$ or $\bar{E}$ (corresponding to pure translations and translations coupled with time inversion respectively), using equations (1) and (2), and substituting into the integrand of equation (4), but replacing one of each pair of spins, one derives

$$P(\mathbf{u}+\mathbf{x})=\varepsilon_A P(\mathbf{u}-\mathbf{t}+\mathbf{x}) \qquad (8)$$

where $\varepsilon_A=+1$ if $A=E$ and $\varepsilon_A=-1$ if $A=\bar{E}$. The peak of the SDPF at $\mathbf{u}-\mathbf{t}$ is thus identical with the peak at $\mathbf{u}$ if $A=E$, or of opposite sign if $A=\bar{E}$.

The symmetry of the SDPF due to spin-only group elements $[R||E|\mathbf{0}]$, where R is an element of a group b given in equations (3), and non-trivial spin translation group elements $[R||E|\mathbf{t}]$, for any rotation R, can be derived as a special case of equation (7), and one finds that:

$$P(\mathbf{u}+\mathbf{x})=P(\mathbf{u}+R^{-1}\mathbf{x})\,. \qquad (9)$$

Every peak is thus invariant under the rotation R about the peak centre. The invariance of every peak under the rotation is, in the case of spin-only group elements, due to the fact that all spins are either collinear or coplanar. [In the case of spatial spin arrangements $\mathsf{b}_s=\mathsf{E}$ {see equation (3)}, and equation (9) becomes an identity.] In the case of non-trivial spin translation elements $[R||E|\mathbf{t}]$, equation (9) is due to relationships between overlapping contributions of pairs of spins to each peak.

If the spin arrangement is invariant under $[R||E|\mathbf{t}]$, then for every pair of spins $\mathbf{S}(\mathbf{r})$ and $\mathbf{S}(\mathbf{r}+\mathbf{u})$ which give a contribution (5) to the peak of the SDPF at $\mathbf{r}=\mathbf{u}$, there is a second pair of spins $R\mathbf{S}(\mathbf{r}-\mathbf{t})$ and $R\mathbf{S}(\mathbf{r}-\mathbf{t}+\mathbf{u})$ which also contribute to the same peak. Both pairs of spins contribute identical spherically symmetric contributions, but the non-spherically symmetric contributions of the former pair of spins is rotated by R about the centre of the peak at $\mathbf{r}=\mathbf{u}$ with respect to the non-spherically symmetric contribution of the latter pair of spins. Each peak of the SDPF is then a superposition of contributions of the form of equation (5) elongated in directions related by the rotation R, and consequently is invariant under this rotation.

We now will show that elements of space groups are in general inadequate to describe the symmetry of the SDPF given in equations (7), (8), and (9) due to the spin-group symmetry of the spin arrangement. We will then define a generalization of space groups which is capable of describing these symmetries of the SDPF.

The standard notation of elements of a space group is $(R|\mathbf{V})$. Applying a space-group element $(R|\mathbf{V})$ to a SDPF $P(\mathbf{u}+\mathbf{x})$ means replacing $P(\mathbf{u}+\mathbf{x})$ by the function denoted by $(R|\mathbf{V})P(\mathbf{u}+\mathbf{x})$ and defined by:

$$(R|\mathbf{V})P(\mathbf{u}+\mathbf{x})=P((R|\mathbf{V})^{-1}\mathbf{u}+R^{-1}\mathbf{x})\,. \qquad (10)$$

A SDPF is said to be invariant under a space-group element $(R|\mathbf{V})$ if:

$$(R|\mathbf{V})P(\mathbf{u}+\mathbf{x})=P(\mathbf{u}+\mathbf{x})\,. \qquad (11)$$

From equations (10) and (11), if the SDPF is invariant under the space-group element $(R|\mathbf{V})$ then:

$$P(\mathbf{u}+\mathbf{x})=P[(R|\mathbf{V})^{-1}\mathbf{u}+R^{-1}\mathbf{x}]\,.$$

Comparing this to equations (7), (8), and (9), one finds that space-group elements describe only those symmetries of the SDPF due to spin-group symmetries of the spin arrangement of the form $[R||R|\mathbf{V}]$ and $[E||E|\mathbf{t}]$; that is, describe only those symmetries of the SDPF due to those magnetic-group symmetries of the spin arrangement of the form $[\varepsilon_A\delta_R R||R|\mathbf{V}]$, $R\neq E$ when $\varepsilon_A\delta_R=1$, and due to 'non-magnetic' translations $[E||E|\mathbf{t}]$.

We therefore introduce generalized space-group elements of the SDPF which we shall denote by $\{R_1||R_2|\mathbf{V}\}$. Applying a generalized space-group element $\{R_1||R_2|\mathbf{V}\}$ to a SDPF $P(\mathbf{u}+\mathbf{x})$ shall be defined to mean replacing $P(\mathbf{u}+\mathbf{x})$ by a new function denoted by $\{R_1||R_2|\mathbf{V}\}P(\mathbf{u}+\mathbf{x})$ and defined by:

$$\{R_1||R_2|\mathbf{V}\}P(\mathbf{u}+\mathbf{x})=P((R_2|\mathbf{V})^{-1}\mathbf{u}+R_1^{-1}\mathbf{x})\,. \qquad (12a)$$

In addition we define elements $\{R_1||R_2|\mathbf{V}\}'$ such that:

$$\{R_1||R_2|\mathbf{V}\}'P(\mathbf{u}+\mathbf{x})=-\{R_1||R_2|\mathbf{V}\}P(\mathbf{u}+\mathbf{x})\,. \qquad (12b)$$

A SDPF is said to be invariant under $\{R_1\|R_2|\mathbf{V}\}$ and $\{R_1\|R_2|\mathbf{V}\}'$ if, respectively

$$\{R_1\|R_2|\mathbf{V}\}P(\mathbf{u}+\mathbf{x})=P(\mathbf{u}+\mathbf{x}) \qquad (13b)$$

$$\{R_1\|R_2|\mathbf{V}\}^1P(\mathbf{u}+\mathbf{x})=P(\mathbf{u}+\mathbf{x}) \qquad (13b)$$

and the set of all such elements constitute the generalized space group of the SDPF.

The symmetry of the SDPF due to the spin-group symmetry of the spin arrangement, see equations (7), (8), and (9), is expressed in terms of generalized space-group elements defined in equations (12*a*,*b*) as follows:

$$\begin{array}{ll} [R_1\|R_2|\mathbf{V}] & \{R_1\|R_2|\mathbf{0}\} \\ [R\|E|\mathbf{t}] & \{R\|E|\mathbf{0}\} \\ [R\|E|\mathbf{0}] & \{R\|E|\mathbf{0}\} \\ [E\|E|\mathbf{t}] & \{E\|E|\mathbf{t}\} \\ [\bar{E}\|E|\mathbf{t}] & \{E\|E|\mathbf{t}\}'. \end{array} \qquad (14)$$

In the left-hand column are listed spin-group symmetry elements of a spin arrangement, and the corresponding generalized space-group elements of the SDPF are listed in the right-hand column. From the intrinsic symmetry of the SDPF given in equation (6), every SDPF is invariant under the following generalized space-group elements:

$$\{\bar{E}\|E|\mathbf{0}\}\,, \quad \{E\|\bar{E}|\mathbf{0}\}\,, \quad \{\bar{E}\|\bar{E}|\mathbf{0}\}\,. \qquad (15)$$

Because of the intrinsic symmetry of the SDPF, one may not be able, from the generalized space-group symmetry of the SDPF, to determine uniquely the spin-group symmetry of the spin arrangement. For example, if the SDPF is invariant under $\{R_1\|R_2|\mathbf{0}\}$, then owing to the intrinsic symmetry, see equation (15), it is invariant under the four generalized space-group elements $\{\pm R_1\|\pm R_2|\mathbf{0}\}$. Using equation (14), these symmetries of the SDPF imply the spin-group symmetries $[\pm R_1\|\pm R_2|\mathbf{V}]$ of the spin arrangement. The ambiguity of the sign of R_2 can be resolved if the space group of the magnetic atom arrangement is known and does not contain inversion.

The use of generalized space groups to describe the symmetry of the SDPF enables one to determine from the symmetry of the SDPF information on the spin symmetry group of the spin arrangement. This in turn provides information on the orientation of the spins in the crystal. In general this will be more information on the orientation of the spins than one is able to obtain by considering the space-group symmetry of the SDPF and the magnetic-group symmetry of the spin arrangement, since the magnetic symmetry group of a spin arrangement is in general a subgroup of the spin arrangement's spin symmetry group.

Consider the hypothetical magnetic structure given by Wilkinson & Lisher [1973, Fig. 1(*a*)] and below in Fig. 1. The space group of the magnetic atom arrangement is $P4$ and the magnetic space group of the spin arrangement is $P2'$. The spin group of this spin arrangement is $\mathrm{b}_l\times P[E\|4|\mathbf{0}]$, the direct product of a spin-only group of a collinear spin arrangement, and a non-trivial spin group containing the group of translations $[E\|E|\mathbf{t}]$, denoted by P, and a non-trivial spin point-group of elements, $[E\|E|\mathbf{0}]$, $[E\|4|\mathbf{0}]$, $[E\|2|\mathbf{0}]$, and $[E\|4^{-1}|\mathbf{0}]$. The classification labels of this spin arrangement, using magnetic groups (Opechowski & Dreyfus, 1971), and using spin groups (Litvin & Opechowski, 1974), are respectively

$$[P4;\ P2',\ \mathbf{S}(\mathbf{r}_1)=\mathbf{S}(\mathbf{r}_2)=\boldsymbol{\sigma}]$$

$$(P4;\ \mathrm{b}_l\times P[E\|4|\mathbf{0}],\ \mathbf{S}(\mathbf{r}_1)=\boldsymbol{\sigma})$$

where $\mathbf{r}_1=(x,y,0)$ and $\mathbf{r}_2=4^{-1}r_1$.

The spin arrangement is generated from a single spin by the spin group, while it is generated from two spins by the magnetic group. Consequently, information on the relative orientation and magnitude of the spins $\mathbf{S}(\mathbf{r}_1)$ and $\mathbf{S}(\mathbf{r}_2)$ is not contained in the magnetic symmetry group of this spin arrangement, while the spin symmetry-group element $[E\|4|\mathbf{0}]$, determined by the generalized space-group symmetry $\{E\|4|\mathbf{0}\}$ of the SDPF, implies that $\mathbf{S}(\mathbf{r}_1)=\mathbf{S}(\mathbf{r}_2)$.

4. Spiral spin arrangements

Wilkinson & Lisher (1973) have shown that in the analysis of the SDPF of multi-domain magnetic crystals, one may be unable to obtain information concerning the orientation of the spins with respect to crystallographic directions. This was shown to be due to the superposition of contributions to each peak of the SDPF from each of the domains. We will show that similar information loss does occur in the SDPF of a single-domain magnetic crystal with a spiral spin arrangement.

The information on the orientation of the spins with respect to the crystallographic directions is contained in the second, non-spherically symmetric, term of the contribution, see equation (5), of pairs of spins to the peaks of the SDPF. In a SDPF all pairs of spins whose magnetic atoms are separated by $\mathbf{u}$ contribute to the peak of the SDPF at $\mathbf{r}=\mathbf{u}$. As we have seen in equation (14), if the spin arrangement is invariant under a spin-group translation $[R\|E|\mathbf{t}]$, the SDPF is invariant under the generalized space-group element $\{R\|E|\mathbf{0}\}$, *i.e.* overlapping contributions to each peak are related by the rotation R and each peak is invariant under the rotation R about the peak's centre. As we will show below, it is this invariance of the SDPF, under generalized space-group elements $\{R\|E|\mathbf{0}\}$ due to the non-trivial spin translation group elements $[R\|E|\mathbf{t}]$ which causes a loss of information on the orientation of the spins which can be obtained from the SDPF. Spin-group elements of a spin arrangement not of the form $[R\|E|\mathbf{t}]$ in general do not give relations between overlapping contributions to peaks in the SDPF, and consequently do not give rise to any information loss.

We calculate the form of the SDPF corresponding to spin arrangements which are invariant under a non-trivial spin translation group. To the group of elements $[R\|E|\mathbf{t}]$ of a non-trivial spin translation group there corresponds a group of generalized space-group elements $\{R\|E|\mathbf{0}\}$ of the SDPF. The set of rotations R of such elements constitutes a group R. Since $\{\bar{E}\|E|\mathbf{0}\}$ is an intrinsic symmetry element of the SDPF, see equation (15), we consider instead of the group of elements $\{R\|E|\mathbf{0}\}$, the group of elements $\{Q\|E|\mathbf{0}\}$ where the group of proper rotations Q is derived from R by replacing every improper rotation R by the proper rotation $\bar{R}$. All non-trivial spin translation groups have been derived (Litvin, 1973), and possible groups Q are $\mathsf{Q}=\mathsf{C}_2, \mathsf{D}_2$, and C_φ. The group C_2 contains a single rotation through an angle of π, and D_2 contains three mutually perpendicular rotations through an angle of π. C_φ denotes a group of rotations about a single axis generated by one, two, or three rotations through angles of $2\pi/M$ where the M are integers or irrational numbers.

We apply an element $\{Q\|E|\mathbf{0}\}$ to a SDPF $P(\mathbf{u}+\mathbf{x})$. Using equations (12*a*) and (13*a*), summing over all Q of Q, and dividing by the order N of the group Q, we obtain the following expression for the SDPF of a spin arrangement invariant under a non-trivial spin translation group:

$$P(\mathbf{u}+\mathbf{x})=\int f_1(|\mathbf{x}|)\mathbf{S}(\mathbf{r})\,.\,\mathbf{S}(\mathbf{r}+\mathbf{u})\mathrm{d}\mathbf{r}$$
$$+\frac{1}{N}\sum_{ijmn}\sum_{\mathsf{Q}} Q_{ij}Q_{mn}\int f_2(|\mathbf{x}|)S^i(\mathbf{r})S^m(\mathbf{r}+\mathbf{u})X_jX_n\mathrm{d}\mathbf{r}. \tag{16}$$

$S^i(\mathbf{r})$ denotes the ith component of $\mathbf{S}(\mathbf{r})$ and X_j the j th component of $\mathbf{x}$. The components of $\mathbf{S}(\mathbf{r})$ and $\mathbf{x}$ will be taken below in an orthogonal coordinate system, denoted by $\bar{x}$, $\bar{y}$, and $\bar{z}$, which will be dependent on the orientation of the rotation axes of the rotations of the group Q and not on the crystallographic axes of the crystal. In the case where $\mathsf{Q}=\mathsf{C}_2$ and C_φ, $\bar{z}$ denotes the direction of the rotation axis of the rotations of Q, and $\bar{y}$ and $\bar{z}$ denote two arbitrary perpendicular directions. In the case $\mathsf{Q}=\mathsf{D}_2$ $\bar{x}$, $\bar{y}$, and $\bar{z}$, denote the directions of the three mutually perpendicular rotation axes of Q.

In the case where $\mathsf{Q}=\mathsf{C}_2$, the second term of equation (16) becomes

$$\int f_2(|\mathbf{x}|)[\sum_i S^i(\mathbf{r})S^i(\mathbf{r}+\mathbf{u})X_i^2+\{S^{\bar{x}}(\mathbf{r})S^{\bar{y}}(\mathbf{r}+\mathbf{u})$$
$$+S^{\bar{y}}(\mathbf{r})S^{\bar{x}}(\mathbf{r}+\mathbf{u})\}X_{\bar{x}}X_{\bar{y}}]\mathrm{d}\mathbf{r}$$

and in the case where $\mathsf{Q}=\mathsf{D}_2$

$$\int f_2(|\mathbf{x}|)[\sum_i S^i(\mathbf{r})S^i(\mathbf{r}+\mathbf{u})X_i^2]\mathrm{d}\mathbf{r}$$

where $i=\bar{x},\bar{y},\bar{z}$. In these two cases there is no information loss concerning the orientation of the spins with respect to the crystallographic axes (Wilkinson & Lisher, 1973; Appendix I).

We define a spiral spin arrangement as a spin arrangement whose non-trivial spin translation group symmetry gives rise to the invariance of the corresponding SDPF under the group of generalized space-group elements $\{Q\|E|\mathbf{0}\}$ where $\mathsf{Q}=\mathsf{C}_\varphi$. In this case, the second term of equation (16) becomes:

$$\int f_2(|\mathbf{x}|)[\{S^{\bar{x}}(\mathbf{r})S^{\bar{x}}(\mathbf{r}+\mathbf{u})+S^{\bar{y}}(\mathbf{r})S^{\bar{y}}(\mathbf{r}+\mathbf{u})\}(X_{\bar{x}}^2+X_{\bar{y}}^2)$$
$$+S^{\bar{z}}(\mathbf{r})S^{\bar{z}}(\mathbf{r}+\mathbf{u})X_{\bar{z}}^2]\mathrm{d}\mathbf{r}\,. \tag{17}$$

In the case of spiral spin arrangements, as a consequence of equations (16) and (17), the SDPF is invariant not only under $\{Q\|E|\mathbf{0}\}$ for all Q of Q due to the non-trivial spin translation group symmetry of the spin arrangement, but is also invariant under $\{C_{\infty\bar{z}}\|E|\mathbf{0}\}$ where $C_{\infty\bar{z}}$ is an element of $\mathsf{C}_{\infty\bar{z}}$, the group of all rotations about the $\bar{z}$ axis. Therefore, one can not determine from the symmetry of the SDPF of a spiral spin arrangement the spiral spin arrangements characteristic non-trivial spin translation group symmetry.

A method to determine from a SDPF a spiral spin arrangement's non-trivial spin translation group symmetry is based on the comparison of peaks in the SDPF and is as follows: Let R denote a proper rotation through an angle of α degrees about the $\bar{z}$ axis. If $[R\|E|\mathbf{t}]$ is a symmetry element of the spiral spin arrangement, using equations (2), (16), and (17), one finds that

$$P(n\mathbf{t}+\mathbf{x})=\cos\,(n\alpha)\int[S^{\bar{x}}(\mathbf{r})^2+S^{\bar{y}}(\mathbf{r})^2]\,[f_1(|\mathbf{x}|)$$
$$+f_2(|\mathbf{x}|)\,(X_{\bar{x}}^2+X_{\bar{y}}^2)]\mathrm{d}\mathbf{r}+\int S^{\bar{z}}(\mathbf{r})[f_1(|\mathbf{x}|)$$
$$+f_2(|\mathbf{x}|)X_{\bar{z}}^2]\mathrm{d}\mathbf{r} \tag{18}$$

where n is an integer. If R is an improper rotation, a rotation through an angle α degrees about the $\bar{z}$ axis followed by a reflexion in the $\bar{x}\bar{y}$ plane, then the coefficient $(-1)^n$ must be inserted in equation (18) in front of the second integral. By comparing peaks of the SDPF one can then determine the characteristic non-trivial spin translation symmetry group of a spiral spin arrangement.*

From the SDPF of a spiral spin arrangement, see equations (17) and (18), one can determine the orientation of the $\bar{z}$ axis with respect to the crystallographic directions, the components of the spins parallel and perpendicular to the $\bar{z}$ axis, and the spiral spin arrangement's non-trivial spin translation group symmetry which determines the mutual orientation of the spins. But one cannot determine the orientation, with

---

* It has been pointed out by the referee of this paper that a relation similar to equation (18) has been derived by Lisher (1972).

respect to the crystallographic directions, of the components of the spins perpendicular to the $\bar{z}$ axis.

5. Multi-domain spin density Patterson function

In the previous sections we have discussed the SDPF of a magnetic single crystal, that is, the Fourier transform of the intensity $I(\mathbf{k})$ of unpolarized neutrons elastically scattered from a magnetic single crystal:

$$P(\mathbf{u}+\mathbf{x})=\int I(\mathbf{k})\exp\left[-i\mathbf{k}\,.\,(\mathbf{u}+\mathbf{x})\right]\mathrm{d}\mathbf{k}\,. \qquad (19)$$

In the case of a multi-domain sample of a magnetic crystal one measures not the intensity $I(\mathbf{k})$ but $\overline{I(\mathbf{k})}$ where

$$\overline{I(\mathbf{k})}=\frac{1}{N}\sum_{R} I(R\mathbf{k}) \qquad (20)$$

and where the sum is over all rotations of the point group R, of order N, associated with the space group F of the magnetic atom arrangement. The SDPF of a multi-domain sample will be called the *averaged* SDPF, denoted by $\overline{P(\mathbf{u}+\mathbf{x})}$, and is the Fourier transform of $\overline{I(\mathbf{k})}$:

$$\overline{P(\mathbf{u}+\mathbf{x})}=\int \overline{I(\mathbf{k})}\exp\left[-i\mathbf{k}\,.\,(\mathbf{u}+\mathbf{x})\right]\mathrm{d}\mathbf{k}\,. \qquad (21)$$

In this section we will discuss the symmetry of the averaged SDPF and will show that one can infer from the symmetry of the averaged SDPF neither the magnetic space-group symmetry nor the spin-group symmetry of the spin arrangement.

From equations (19), (20), and (21), one derives that the averaged SDPF can be written in the form:

$$\overline{P(\mathbf{u}+\mathbf{x})}=\frac{1}{N}\sum_{R} P(R\mathbf{u}+R\mathbf{x})\,. \qquad (22)$$

To compare the results below with the work of Wilkinson & Lisher (1973) we introduce the notation $P[\mathbf{u}+\mathbf{x};\mathbf{S}(\mathbf{r})]$ for the SDPF due to the spin arrangement $\mathbf{S}(\mathbf{r})$. In this notation equation (22) is written as:

$$\overline{P[\mathbf{u}+\mathbf{x};\,\mathbf{S}(\mathbf{r})]}=\frac{1}{N}\sum_{R} P[R\mathbf{u}+R\mathbf{x};\,\mathbf{S}(\mathbf{r})]\,. \qquad (23)$$

An alternative form of equation (23) can be derived by using equation (4):

$$\begin{aligned}\overline{P[\mathbf{u}+\mathbf{x};\,\mathbf{S}(\mathbf{r})]}&=\frac{1}{N}\sum_{R} P[R^{-1}\mathbf{u}+R^{-1};\,\mathbf{S}(\mathbf{r})]\\&=\frac{1}{N}\sum_{R}\int\{f_1(|\mathbf{x}|)\mathbf{S}(\mathbf{r})\,.\,\mathbf{S}(\mathbf{r}+R^{-1}\mathbf{u})\\&\quad+f_2(|\mathbf{x}|)[\mathbf{S}(\mathbf{r})\,.\,R^{-1}\mathbf{x}]\,[\mathbf{S}(\mathbf{r}+R^{-1}\mathbf{u})\,.\,R^{-1}\mathbf{x}]\}\mathrm{d}\mathbf{r}\\&=\frac{1}{N}\sum_{R}\int\{f_1(|\mathbf{x}|)R\mathbf{S}[(R|\mathbf{V}(R))^{-1}\mathbf{r}]\,.\\&\quad\times R\mathbf{S}[(R|\mathbf{V}(R)]^{-1}(\mathbf{r}+\mathbf{u})]\\&\quad+f_2(|\mathbf{x}|)[R\mathbf{S}[(R|\mathbf{V}(R)]^{-1}\mathbf{r})\,.\,\mathbf{x}]\,[R\mathbf{S}[(R|\mathbf{V}(R)]^{-1}\\&\quad\times(\mathbf{r}+\mathbf{u})\,.\,\mathbf{x}]\}\mathrm{d}\mathbf{r}\end{aligned}$$

where $[R|\mathbf{V}(R)]$ is an element of the space group F. Consequently:

$$\overline{P[\mathbf{u}+\mathbf{x};\,\mathbf{S}(\mathbf{r})]}=\frac{1}{N}\sum_{R} P\{\mathbf{u}+\mathbf{x};\,[R\|R|\mathbf{V}(R)]\mathbf{S}(\mathbf{r})\}\,. \qquad (24)$$

The averaged SDPF can then be interpreted, from equation (23), as a superposition of the SDPF $P[\mathbf{u}+\mathbf{x};\,\mathbf{S}(\mathbf{r})]$ and rotated images $P[R\mathbf{u}+R\mathbf{x};\,\mathbf{S}(\mathbf{r})]$ of the same SDPF; or from equation (24) as the superposition of several SDPF's $P[\mathbf{u}+\mathbf{x};\,[R\|R|\mathbf{V}(R)]\mathbf{S}(\mathbf{r})]$ associated with different spin arrangements.

The expressions for the averaged SDPF cannot in general be simplified; however in the following two cases, equations (23) and (24) do take on simpler forms. First consider a spin arrangement defined on a magnetic atom arrangement of space-group symmetry F, and such that for every rotation $[R|\mathbf{V}(R)]$ of F the spin arrangement is invariant under the spin group element $[E\|R|\mathbf{V}(R)]$ or $[-E\|R|\mathbf{V}(R)]$. Such spin arrangements include all ferromagnetic spin arrangements, see for example Fig. 1, where $[E\|R|\mathbf{V}(R)]$ is a symmetry element of the spin arrangement for every rotation $[R|\mathbf{V}(R)]$ of F; and many antiferromagnetic spin arrangements, *e.g.* the antiferromagnetic iron-group fluorides $\mathrm{MnF_2}$, $\mathrm{FeF_2}$, and $\mathrm{CoF_2}$ (Brinkman & Elliott, 1966). With equations (6*a*) and (14), equation (23) becomes in this case

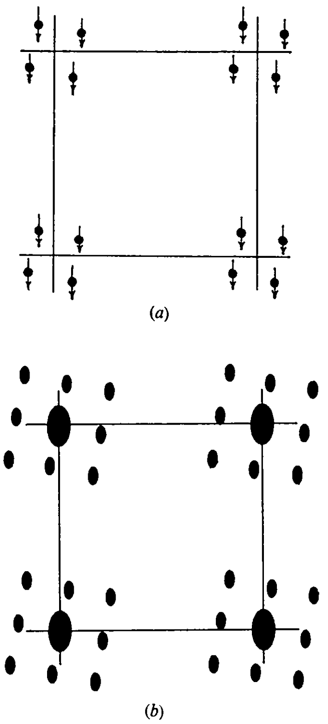

Fig. 1. A spin arrangement of magnetic space-group symmetry P2′ and spin space-group symmetry $\mathrm{b}_l \times \mathrm{P}[E\|4|\mathrm{O}]$ is given in (*a*) and its corresponding spin-density Patterson function in (*b*).

$$\overline{P[\mathbf{u}+\mathbf{x};\ \mathbf{S}(\mathbf{r})]}=\frac{1}{N}\sum_{R}P[\mathbf{u}+R\mathbf{x};\ \mathbf{S}(\mathbf{r})]$$

and equation (24), as $P[\mathbf{u}+\mathbf{x};\ -\mathbf{S}(\mathbf{r})]=P[\mathbf{u}+\mathbf{x};\ \mathbf{S}(\mathbf{r})]$:

$$\overline{P[\mathbf{u}+\mathbf{x};\ \mathbf{S}(\mathbf{r})]}=\frac{1}{N}\sum_{R}P[\mathbf{u}+\mathbf{x};\ R\mathbf{S}(\mathbf{r})]\,. \tag{25}$$

Equation (25) has been used by Wilkinson & Lisher (1973) to tabulate the form of the averaged SDPF for all possible point groups R. We stress, however, that while equation (25) is the expression for the averaged SDPF for all ferromagnetic and many antiferromagnetic spin arrangements, it is not valid for all spin arrangements.

A second case in which equations (23) and (24) take on a particularly simple form is when for every rotation $[R|\mathbf{V}(R)]$ of F the spin arrangement is invariant under the magnetic space-group element $[R\|R|\mathbf{V}(R)]$ or $[-R\|R|\mathbf{V}(R)]$. Such spin arrangements include that of $\mathrm{YMnO_3}$ (Bertaut, Pauthenet & Mercier, 1963) and the example of Fig. 1(*b*) of Wilkinson & Lisher (1973). In this case both equations (23) and (24) become

$$\overline{P[\mathbf{u}+\mathbf{x};\ \mathbf{S}(\mathbf{r})]}=P[\mathbf{u}+\mathbf{x};\ \mathbf{S}(\mathbf{r})]\,,$$

that is, the averaged SDPF is identical with the single-crystal SDPF.

As to the symmetry of the averaged SDPF, one finds that one cannot infer from the symmetry of the averaged SDPF the rotational magnetic space-group symmetry of the spin arrangement. This is due to the fact that from equations (6) and (22) one has, using the notation of equation (22),

$$\overline{P(\mathbf{u}+\mathbf{x})}=\overline{P(\pm R\mathbf{u}\pm R\mathbf{x})}$$

and the averaged SDPF is invariant under $\{\pm R\|\pm R|\mathbf{0}\}$ for every R belonging to the point group R of F. Consequently, one cannot infer from the symmetry of the averaged SDPF, using equation (14), the rotational magnetic space-group symmetry of the spin arrangement. There is also no guarantee that one can infer the translational symmetry $[E\|E|\mathbf{t}]$ of the spin arrangement from the symmetry of the averaged SDPF. From equation (22) we have

$$\overline{P(\mathbf{u}+\mathbf{t}+\mathbf{x})}=\frac{1}{N}\sum_{R}P(R\mathbf{u}+R\mathbf{t}+R\mathbf{x})$$

and this in general will not be equal to $\overline{P(\mathbf{u}+\mathbf{x})}$ since although the translational symmetry $[E\|E|\mathbf{t}]$ of the spin arrangement does imply that $P(\mathbf{u}+\mathbf{t}+\mathbf{x})=P(\mathbf{u}+\mathbf{x})$, it does not imply in general that $P(\mathbf{u}+R\mathbf{t}+\mathbf{x})=P(\mathbf{u}+\mathbf{x})$, for all rotations of R.

If the spin arrangement is invariant under the spin-group element $[R_1\|R_2|\mathbf{V}(R_2)+\mathbf{t}]$ then from equations (4), (14) and (22) one derives that

$$\overline{P(\mathbf{u}+\mathbf{x})}=\frac{1}{N}\sum_{R}P(R_2R\mathbf{u}+R_1R\mathbf{x})$$

and since R_2 belongs to the point group R, by changing the summation from over R to over R_2R, this relation takes on the form:

$$\overline{P(\mathbf{u}+\mathbf{x})}=\frac{1}{N}\sum_{R}P(R\mathbf{u}+R_1R_2^{-1}R\mathbf{x})\,. \tag{26}$$

While in principle one may be able to derive information from equation (26) on the product of rotations $R_1R_2^{-1}$, *e.g.* if $R_1R_2^{-1}$ commutes with all rotations of R, then $\overline{P(\mathbf{u}+\mathbf{x})}=\overline{P(\mathbf{u}+R_1R_2^{-1}\mathbf{x})}$, it is, however, doubtful that in general any information on the spin-group symmetry of the spin arrangement can in practice be obtained from equation (26).

We conclude then that one can obtain detailed information on the spin-group symmetry of a spin arrangement from the symmetry of a single-crystal SDPF, but in general no symmetry information can be obtained from the symmetry of the averaged SDPF. This however does not imply that no information at all is available on the spin arrangement from the averaged SDPF, as has been shown by Wilkinson & Lisher (1973) based on the use of equation (25).

This work was supported by a grant from the National Research Council of Canada.

References

Bertaut, E. F., Pauthenet, R. & Mercier, M. (1963). *Phys. Lett.* 7, 110–111.

Brinkman, W. & Elliott, R. J. (1966). *Proc. Roy. Soc.* A**294**, 343–358.

Forsyth, J. B., Johnson, C. E. & Wilkinson, C. (1970). *J. Phys. C*, 3, 1127–1139.

Lisher, E. J. (1972). Ph. D. Thesis. Univ of London.

Litvin, D. B. (1973). *Acta Cryst.* A**29**, 651–660.

Litvin, D. B. & Opechowski, W. (1974). *Physica*. In the press.

Opechowski, W. & Dreyfus, T. (1971). *Acta Cryst.* A**27**, 470–484.

Wilkinson, C. (1968). *Phil. Mag.* **17**, 609–621.

Wilkinson, C. (1973). *Acta Cryst.* A**29**, 449–452.

Wilkinson, C. & Lisher, E. J. (1973). *Acta Cryst.* A**29**, 453–461.

Yessik, M. (1968). *Phil. Mag.* **17**, 623–632.