CRYSTALLOGRAPHIC SYMMETRY OF THE MAGNETICALLY ORDERED STATE

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Krishna Kumari Yallabandi
1969

This is to certify that the

thesis entitled

CRYSTALLOGRAPHIC SYMMETRY IN THE

MAGNETICALLY ORDERED STATE

presented by

Krishna Kumari Yallabandi

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Physics

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Date January 16, 1969

O-169

ABSTRACT

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By

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For a crystal in a magnetically ordered state, the general symmetry behavior of its internal magnetic field - considered as a time-averaged classical axial vector field - and the general symmetry behavior of the Fourier components of the field in reciprocal lattice space are properties of interest in nuclear magnetic resonance and neutron diffraction experiments. In this thesis, general procedures based on the theory of finite groups are developed which allow the behavior of the internal field and of its Fourier components to be deduced from the magnetic space group (Shubnikov group) of the crystal. The procedures are illustrated through application to seven particular magnetic space groups belonging to the tetragonal system.

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

1969

956227
6-25-69

TO MY PARENTS

TABLE OF CONTENTS

LIST OF TABLES

Page

CHAPTER I

INTRODUCTION

It is an experimental fact that at sufficiently low temperatures most paramagnetic crystals become magnetically ordered.[1, 2]

Under an interaction which tends to make the ionic or atomic magnetic moments line up parallel, the paramagnetic substance becomes ferromagnetic at a temperature characteristic of the material, called the Curie temperature. Such an interaction may be discussed in terms of an effective uniform internal magnetic field, called the Weiss field[2] or the exchange field, and the interaction energy of a spin magnetic moment with the Weiss field must be of the order of magnitude of the thermal energy of the magnetic ion at the Curie point. Below the Curie point, the exchange field interaction is able to overcome the disorder due to thermal energy of the ions, and neighboring spins will tend to align in parallel even in the absence of an external magnetic field. In this way a cooperative process is set up which results in spontaneous magnetization of the material.

The exchange coupling mechanism has no classical analog. It is a quantum mechanical effect which has its origin in the Pauli exclusion principle. It is very sensitive to relative spin alignment and it is only for a very small range of spin separation that the energy is a minimum when the neighboring spins are parallel. In most cases the exchange energy turns out to be smallest when neighboring spins are antiparallel. The alignment of the spins in an antiparallel array is also a cooperative effect which spontaneously sets in at a definite temperature known as the Néel temperature, and this phenomenon is known as antiferromagnetism.

Whereas many substances are magnetically ordered at room temperature or above, there is also considerable low-temperature interest in this phenomenon. The reason for this is that if one has a system of magnetic ions, then, however small the exchange interaction may be, there must exist some temperature low enough for a cooperative alignment to take place.

Above the transition temperature the crystal structure is invariant under a group H of unitary spatial operators which is the space group of the crystal. In the paramagnetic state the crystal is also invariant under the time reversal operation T, and the products of T with the elements of H since we assume that in this state the crystal possesses a vanishing time-averaged magnetic moment density. Below the transition temperature, however, the crystal exhibits a non-vanishing magnetic moment density which reverses direction under the time reversal operation. Although such crystals cannot therefore then be invariant with respect to time inversion, they may be invariant with respect to a product of time inversion and a particular set of spatial symmetry operations. The full symmetry of such crystals must therefore be investigated by considering the proper combinations of time inversion and space group operations. As will be discussed in Chapter II, introduction of the time-reversal operator leads to a generalization of the 32 ordinary crystallographic point groups to 122 magnetic crystallographic point groups, and to a corresponding generalization of the 230 ordinary crystallographic space groups to 1651 magnetic crystallographic space groups.

In this dissertation we shall investigate the following problems: (a) what is the symmetry of the most general time-averaged classical internal magnetic field $\underline{B}(\underline{r})$ allowed by a given magnetic space group, and (b) what is the character of neutron scattering from such a field $\underline{B}(\underline{r})$.

CHAPTER II

MAGNETIC CRYSTAL GROUPS

Classical crystallography allocates all possible crystal morphologies to one of 32 crystal classes (point groups), the symmetry being characterized by the existence of planes, axes, and centers of symmetry. If the crystalline lattice is considered to be of infinite extent, then the crystal also possesses translational symmetry. The inclusion of this translational symmetry increases the number of distinguishable geometrical forms to 230. These 230 ordinary space groups or Fedorov groups are appropriate for the characterization of the charge density $\rho(\underline{r})$ in a crystal which is of interest in the analysis of x-ray diffraction data.[3] However, to characterize, in addition, the symmetries of distribution of internal current densities $\underline{j}(\underline{r})$, internal magnetic fields $\underline{B}(\underline{r})$, or magnetization densities $\underline{M}(\underline{r})$, a still more general system of symmetry operations is required, because the time-averaged non-vanishing $\underline{j}(\underline{r})$, $\underline{B}(\underline{r})$, or $\underline{M}(\underline{r})$ are not invariant under time reversal. Hence for these cases, the time reversal operation has non-trivial consequences, and inclusion of the time-inversion operator produces a generalization of the 230 ordinary space groups to the magnetic space groups (Shubnikov[4] groups) which are 1651 in number.

In 1930, Heesch[5] broadened the concept of symmetry by introducing non-spatial double-valued attributes such as sign, color, or even more general qualities. In 1951, Shubnikov[4] developed the theory of symmetry groups in which an operation interchanging black and white colors is considered in addition to the usual spatial operators. This color change can be identified as the time reversal operation and can therefore be interpreted as producing a reversal in the direction of the internal current, magnetic field, and magnetic density. By adding this non-spatial operation in the 32 ordinary point groups, one obtains 122 magnetic point groups (Heesch[5, 6] groups).

In the magnetic groups there exist two types of elements: "uncolored" elements g_i which do not include time reversal, and "colored" elements $Tg_k = g_k'$ which do include time reversal. The latter are referred to as antioperators as they are antiunitary[7] operators. The time reversal operator T commutes with all spatial operators and it is of order two, i.e., $T^2 = E$, where E is the identity operator. Hence, the product of two colored or two uncolored operators is uncolored, and the product of a colored with an uncolored operator is colored. Thus suppose that $(g_i, g_j, \ldots)$ is a set of uncolored elements and $(g_k', g_l', \ldots)$ a colored set.

Then,

$$g_i g_k' = g_i' g_k = g_l'; \qquad g_i g_k = g_i' g_k' = g_l. \tag{2.1}$$

One distiguishes three types of magnetic point groups.[8] The first type is the set of 32 ordinary point groups with no anti-unitary operators. These are called uncolored point groups.

The second type of point group is the set of 32 formed from an uncolored group by adding to the uncolored elements those which are formed by adjoining the time reversal operator to each of these elements, i.e., for all g_i in a group G, g_i' is also in the group which leads to the fact that T itself is an element of the group, since TE = T. These groups are called grey groups and they are denoted by G1' in the international notation. It is clear that T cannot be a symmetry operation in a magnetically ordered crystal, since it would reverse the sign of all magnetic moments in the crystal. Hence the grey space groups are applicable only to dia-magnetic or paramagnetic crystals which have no time-averaged non-zero magnetic moments. However, T is a possible point group operation in an antiferromagnetic crystal if it always appears in combination with a translation connecting two antiparallel spins in identical chemical environments.

The third type of magnetic point group is that which contains T only in combination with a spatial rotation or reflection. These groups, 58 in number, cannot include elements of the type $g_k' = Tg_k$ if g_k is of odd order n, since that would give $(g_k')^n = T$.

The following properties of $G = \{g_i, g_k'\}$, with G one of the 58 colored groups, can be proved[9] with ease: (a) no element g_i occurs both with and without T, i.e., the set $\{g_i\}$ is always distinct from the set $\{g_k\}$; (b) if T is replaced by E in the colored group G, i.e., if the set $\mathcal{G} = \{g_i, g_k\}$ is formed, then $\mathcal{G}$ is one of the 32 ordinary point groups; (c) if we consider the group $G = \{g_i, g_k'\}$, then all the uncolored elements $H = \{g_i\}$ of G form an invariant unitary subgroup of G which again is one of the 32 ordinary point groups; (d) the number of uncolored elements of G is equal to the number of colored elements of G, i.e., H is an invariant subgroup of index two.

Considering the above properties of G, one can devise a simple method for constructing all 122 magnetic point groups starting with the 32 ordinary point groups. The procedure is as follows. After choosing an ordinary point group G, one finds all its invariant subgroups H_i of index two. For each H_i one then constructs the corresponding magnetic group $G_i = H_i + T(G-H_i)$. By successively considering all 32 groups one finds all 58 colored groups G_i, and adjoining T to <u>all</u> elements of G, one obtains the 32 grey groups. Thus, with the addition of the 32 colorless point groups, the total number of magnetic point groups is $58 + 32 + 32 = 122$.

For example, let us construct all magnetic point groups that derive from the ordinary point group mm2 (in international notation). This is an abelian group[10] of order four, containing the identity element E, a two-fold z-axis of rotation 2_z, and the two perpendicular reflection planes containing the z-axis, m_x and m_y. These elements form a group as can be seen from the group multiplication table, Table I.

Now let us consider the colored groups. One is mm'2' and the other is m'm'2. Their group multiplication tables are given as Tables II and III, respectively. From these tables it is seen that these two groups are also abelian which is not, however, generally true for colored groups. The grey group is mm21' which consists of eight elements four of which are colored and four are uncolored. It is also an abelian group which follows from the fact that T commutes with all spatial operators and mm2 itself is an abelian group. Specifically we have that, e.g.,

$$m_x'm_y' = m_y'm_x' = 2_z, \tag{2.2}$$

$$m_x'm_y = m_y m_x' = m_y'm_x = m_x m_y' = 2_z', \text{ etc.} \tag{2.3}$$

In order to construct all possible magnetic space groups, it is necessary to derive the appropriate Bravais lattices.[11] This can be done[4, 9, 12] by starting with the Bravais lattices of the Fedorov groups and by adding colored translations along the edges, diagonals of the faces, and spatial diagonals of the unit cell. In addition to the fourteen uncolored Bravais lattices, one obtains 22 colored translational lattices for the Shubnikov groups. Joining these lattices in all possible combinations of uncolored and colored elements of symmetry, one arrives at the 1651 Shubnikov groups. If S stands for a Shubnikov group $S = \{F + D'\}$, then the uncolored

Table I. Group Multiplication Table for Point Group mm2

mm2	E	2_z	m_x	m_y
E	E	2_z	m_x	m_y
2_z	2_z	E	m_y	m_x
m_x	m_x	m_y	E	2_z
m_y	m_y	m_x	2_z	E

Table II. Group Multiplication Table for Point Group mm'2'

mm'2'	E	$2_z'$	m_x'	m_y
E	E	$2_z'$	m_x'	m_y
$2_z'$	$2_z'$	E	m_y	m_x'
m_x'	m_x'	m_y	E	$2_z'$
m_y	m_y	m_x'	$2_z'$	E

Table III. Group Multiplication Table for Point Group m'm'2

m'm'2	E	2_z	m_x'	m_y'
E	E	2_z	m_x'	m_y'
2_z	2_z	E	m_y'	m_x'
m_x'	m_x'	m_y'	E	2_z
m_y'	m_y'	m_x'	2_z	E

elements F of S always form one of the 230 ordinary space groups, and also constitute an invariant subgroup of index two. In fact for any space group, the set of all its pure translational symmetry operations is an invariant subgroup of index two. If in S one replaces T by E, forming the set $\mathcal{S} = \{F + D\}$, then $\mathcal{S}$ is also one of the 230 ordinary space groups. Thus the algorithm for constructing the magnetic space groups is similar to that for the magnetic point groups. As an example, magnetic space groups derivable from the uncolored space group $P4_222$ will be discussed in Chapter III.

Table IV lists the way in which the number of point and space groups allocates among the seven crystal systems.

Table IV. The Number of Ordinary and Magnetic Point and Space Groups for the Seven Crystal Systems

Crystal System	Number of Ordinary Groups		Number of Magnetic Groups	
	Point	Space	Point	Space
Cubic	5	36	16	149
Hexagonal	7	27	31	164
Trigonal	5	25	16	108
Tetragonal	7	68	31	570
Orthorhombic	3	59	12	562
Monoclinic	3	13	11	91
Triclinic	2	2	5	7
Total	32	230	122	1651

An axial vector such as, for example, the magnetic field vector $\underline{B}(\underline{r})$ at two positions $\underline{r}_i$ and $\underline{r}_o$ in the magnetic crystal which are related by the equation

$$\underline{r}_i = \phi_i \cdot \underline{r}_o + \underline{\tau}_i \tag{2.4}$$

is given by[13]

$$\underline{B}(\underline{r}_i) = \theta_i \cdot \underline{B}(\underline{r}_o), \tag{2.5}$$

where the rotation matrix ϕ_i acts on the components of the polar vector $\underline{r}$, and the rotation matrix θ_i acts on the components of the axial vector $\underline{B}$. The translation $\underline{\tau}_i$ is the vector sum of translational components (as in glide planes and screw axes) and the location of the element in the magnetic unit cell. The relationship between ϕ_i, θ_i, and $\underline{\tau}_i$ on the one hand, and the elements $(s_i|\underline{\tau}_i)$ of the magnetic space group of the crystal on the other hand was first studied by Donnay and Donnay.[14] From their work it is possible to develop the results summarized in Table V in which n stands for n-fold rotation, n' stands for n-fold antirotation, $\overline{n}$ stands for n-fold reflection-rotation, and $\overline{n}'$ stands for n-fold antireflection-rotation. Thus, for a particular choice of a Shubnikov operation $(s_i|\underline{\tau}_i)$, Table V gives the corresponding operations ϕ_i, θ_i, and $\underline{\tau}_i$ which with the aid of (2.4) and (2.5) specify the behavior of $\underline{B}$ under that Shubnikov operation.

The set of elements $\{\phi_i|\underline{\tau}_i\}$ generated by a given Shubnikov group constitutes an ordinary space group $G(\phi_i|\underline{\tau}_i)$ which is often

Table V. Relation between the Operations $(s_i|\underline{\tau}_i)$, $(\phi_i|\underline{\tau}_i)$, and θ_i

Description of the Operations s_i	Operation s_i	Operation ϕ_i	Operation θ_i
n-fold rotation	n	n	n
n-fold antirotation	n'	n	$\bar{n}$
n-fold reflection-rotation	$\bar{n}$	$\bar{n}$	n
n-fold antireflection-rotation	$\bar{n}'$	$\bar{n}$	$\bar{n}$

(but not necessarily) the chemical space group of the crystal or one of its subgroups. If all $\underline{\tau}_i$ are set equal to zero in the corresponding group $G(\phi_i|\underline{\tau}_i)$, one obtains the so-called "underlying point group" $\{\phi_i\}$ which is one of the ordinary 32 point groups. It can be shown that the set $\{\theta_i\}$ also forms a point group, called the "aspect group" denoted by $G(\theta_i)$.[13]

All point group operations in the crystallographic point groups belong either to 6/mmm or to m3m.[11] Thus, enumeration of the operations of 6/mmm and m3m produces the complete catalog of $\{\phi_i\}$. To specify the rotation matrix (ϕ_i) of the operation ϕ_i, we write

$$(\underline{r}_i) = (\phi_i)(\underline{r}_o), \qquad (2.6)$$

or more explicitly,

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} \phi_{11} & \phi_{12} & \phi_{13} \\ \phi_{21} & \phi_{22} & \phi_{23} \\ \phi_{31} & \phi_{32} & \phi_{33} \end{pmatrix} \begin{pmatrix} x_o \\ y_o \\ z_o \end{pmatrix} . \qquad (2.7)$$

All possible rotation matrices (ϕ_i) are listed in condensed notation in Tables VI and VII (in which the operations are given in the Schoenflies notation). For example, the matrix for the operation C_{2z} (two-fold rotation around z-axis) is given as $\bar{x}\bar{y}z$ which in the form of (2.7) is to be understood as

$$\begin{pmatrix} \bar{x} \\ \bar{y} \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} . \qquad (2.8)$$

Two more complicated examples are provided by the following: the operation $S_6^5 = IC_3$ (three-fold rotation followed by inversion) for which Table VI gives $x-y, x, \bar{z}$ which stands for

$$\begin{pmatrix} x-y \\ x \\ \bar{z} \end{pmatrix} = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} , \qquad (2.9)$$

and the operation $S_{4z} = IC_{4z}$ (four-fold rotation around z-axis followed by inversion) for which Table VII gives $y\bar{x}\bar{z}$ which stands for

$$\begin{pmatrix} y \\ \bar{x} \\ \bar{z} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} . \qquad (2.10)$$

Table VI. Elements of D_{6h} (6/mmm) and the Corresponding Matrices (ϕ_i) in Condensed Notation

xyz	: E	$\bar{y},x-y,z$	: C_3	$y-x,\bar{x},z$	: C_3^2
$\bar{x}\bar{y}z$	: C_{2z}	$y,y-x,z$	: C_6^5	$x-y,x,z$	: C_6
$xy\bar{z}$	: σ_{2z}	$\bar{y},x-y,\bar{z}$	: S_3	$y-x,\bar{x},\bar{z}$	: S_3^{-1}
$\bar{x}\bar{y}\bar{z}$	: I	$y,y-x,\bar{z}$	: S_6^5	$x-y,x,\bar{z}$	: S_6
$yx\bar{z}$	: $C_2'(1)$	$\bar{x},y-x,\bar{z}$	: $C_2'(2)$	$x-y,\bar{y},\bar{z}$	: $C_2'(3)$
$\bar{y}\bar{x}\bar{z}$	: $C_2''(1)$	$x,x-y,\bar{z}$	: $C_2''(2)$	$y-x,y,\bar{z}$	: $C_2''(3)$
$\bar{y}\bar{x}z$	: $\sigma_2'(1)$	$x,x-y,z$	: $\sigma_2'(2)$	$y-x,y,z$	: $\sigma_2'(3)$
yxz	: $\sigma_2''(1)$	$\bar{x},y-x,z$	: $\sigma_2''(2)$	$x-y,\bar{y},z$	: $\sigma_2''(3)$

Table VII. Elements of O_h (m3m) and the Corresponding Matrices (ϕ_i) in Condensed Notation

xyz : E	zxy : $C_3(1)$	yzx : $C_3(1')$
$x\bar{y}\bar{z}$: C_{2x}	$\bar{z}\bar{x}y$: $C_3(2)$	$\bar{y}z\bar{x}$: $C_3(2')$
$\bar{x}y\bar{z}$: C_{2y}	$z\bar{x}\bar{y}$: $C_3(3)$	$\bar{y}\bar{z}x$: $C_3(3')$
$\bar{x}\bar{y}z$: C_{2z}	$\bar{z}x\bar{y}$: $C_3(4)$	$y\bar{z}\bar{x}$: $C_3(4')$
$\bar{x}\bar{y}\bar{z}$: I	$\bar{z}\bar{x}\bar{y}$: $S_6(1)$	$\bar{y}\bar{z}\bar{x}$: $S_6(1')$
$\bar{x}yz$: σ_{2x}	$\bar{z}xy$: $S_6(3)$	$\bar{y}zx$: $S_6(4')$
$x\bar{y}z$: σ_{2y}	$z\bar{x}y$: $S_6(4)$	$y\bar{z}x$: $S_6(2')$
$xy\bar{z}$: σ_{2z}	$zx\bar{y}$: $S_6(2)$	$yz\bar{x}$: $S_6(3')$
$\bar{x}\bar{z}\bar{y}$: C_{xd_1}	$\bar{z}\bar{y}\bar{x}$: C_{yd_1}	$\bar{y}\bar{x}\bar{z}$: C_{zd_1}
$\bar{x}zy$: C_{xd_2}	$z\bar{y}x$: C_{yd_2}	$yx\bar{z}$: C_{zd_2}
$x\bar{z}y$: C_{4x}	$\bar{z}yx$: C_{4y}	$\bar{y}xz$: C_{4z}
$xz\bar{y}$: $C_{4x'}$	$zy\bar{x}$: $C_{4y'}$	$y\bar{x}z$: $C_{4z'}$
xzy : σ_{xd_1}	zyx : σ_{yd_1}	yxz : σ_{zd_1}
$x\bar{z}\bar{y}$: σ_{xd_2}	$\bar{z}y\bar{x}$: σ_{yd_2}	$\bar{y}\bar{x}z$: σ_{zd_2}
$\bar{x}z\bar{y}$: S_{4x}	$z\bar{y}\bar{x}$: S_{4y}	$y\bar{x}\bar{z}$: S_{4z}
$\bar{x}\bar{z}y$: $S_{4x'}$	$\bar{z}\bar{y}x$: $S_{4y'}$	$\bar{y}x\bar{z}$: $S_{4z'}$

CHAPTER III

SYMMETRY OF THE INTERNAL MAGNETIC FIELD

In the magnetically ordered crystal, the internal magnetic field vector $\underline{B}(\underline{r})$ exhibits a repetition pattern governed by the magnetic space group of the crystal, and it is therefore a periodic function of the position vector $\underline{r}$. Since $\underline{B}(\underline{r})$ is an axial vector, the most general $\underline{B}(\underline{r})$ allowed by the symmetry at position $\underline{r}$ in the crystal should be determinable from the groups $G(\phi_i|\underline{\tau}_i)$ and $G(\theta_i)$ that are associated with the magnetic space group $S(s_i|\underline{\tau}_i)$ of the crystal.

The position vector $\underline{r}$ is said to be invariant under an operation $(\phi_i|\underline{\tau}_i)$ if $\phi_i \cdot \underline{r} + \underline{\tau}_i = \underline{r} + \underline{t}$, where $\underline{t}$ is any lattice translation, i.e., $\underline{t} = n_1\underline{a} + n_2\underline{b} + n_3\underline{c}$, where $\underline{a}$, $\underline{b}$, and $\underline{c}$ are unit vectors of the magnetic unit cell, and n_1, n_2, and n_3 are any set of integers. The set $\{\phi_i|\underline{\tau}_i\}$ of G which keeps $\underline{r}$ invariant forms a group[11], $G_i(\phi_i|\underline{\tau}_i)$. From this and (2.5) it follows that $\underline{B}$ at $\underline{r}$ has to satisfy

$$\underline{B}(\phi_i \cdot \underline{r} + \underline{\tau}_i) = \theta_i \cdot \underline{B}(\underline{r}) \qquad (3.1)$$

for all elements of $G_i(\phi_i|\underline{\tau}_i)$.

An immediate consequence of (3.1) is that if G_i contains T, then $\underline{B} \equiv 0$, since for T, $\underline{\tau}(T) = 0$, and Tables V and VII give $\phi(T) = (xyz)$

and $\theta(T) = (\bar{x}\bar{y}\bar{z})$. With these (3.1) gives $\underline{B}(\underline{r}) = -\underline{B}(\underline{r})$, hence $\underline{B} \equiv 0$.

As another example, if G_i is the group of order two containing E and 2_z, then $\phi(E) = (xyz)$, $\phi(2_z) = (\bar{x}\bar{y}z)$, $\theta(E) = (xyz)$, $\theta(2_z) = (\bar{x}\bar{y}z)$ and $\underline{\tau}(E) = \underline{\tau}(2_z) = 0$. With these, (3.1) gives $B_x = B_y = 0$, and only B_z may be non-zero at $\underline{r}$. Finally, if G_i is the group of order one (containing only E), then all three components of $\underline{B}(\underline{r})$ may be non-zero, hence $\underline{B}$ is arbitrary at $\underline{r}$. In this manner the behavior of $\underline{B}$ can be determined at all points of the magnetic cell.

The set S_k of points $(\underline{r}_k, \underline{r}_1, \ldots)$ is said to be a set of equivalent positions with respect to a given magnetic space group $S(s_i|\underline{\tau}_i)$ of the crystal if each point of S_k is related to all the other points of S_k by a set of operations $\{\phi_i|\underline{\tau}_i\}$ of $G(\phi_i|\underline{\tau}_i)$, i.e., for every pair $\underline{r}_k$, $\underline{r}_1$ of S_k there exists at least one operation $(\phi_i|\underline{\tau}_i)$ of G such that for that operation $(\phi_i|\underline{\tau}_i)$, $\underline{r}_k$, and $\underline{r}_1$ satisfy

$$\phi_i \cdot \underline{r}_k + \underline{\tau}_i = \underline{r}_1. \tag{3.2}$$

Thus for every point $\underline{r}_k$ in the crystal, one can find the group of operations $G_i(\phi_i|\underline{\tau}_i)$ under which $\underline{r}_k$ is invariant, and hence the set of operations $[G(\phi_i|\underline{\tau}_i) - G_i(\phi_i|\underline{\tau}_i)]$ under which $\underline{r}_k$ generates the set S_k of equivalent positions. In this way the symmetry of the internal magnetic field can be specifically determined for all points of S_k from (3.1), and the interrelation between the components of $\underline{B}$ at all points of S_k is taken into account through (2.5).

We now proceed to illustrate the above method with the seven magnetic space groups that derive from the ordinary space group $P4_222$ which belongs to the tetragonal system.[3] The chemical unit cell is primitive with vectors $a\underline{i}$, $a\underline{j}$, and $c\underline{k}$, where $\underline{i}$, $\underline{j}$, and $\underline{k}$ are the Cartesian unit vectors along the x, y, and z directions, respectively. The seven magnetic space groups are listed by Shubnikov and Belov[4] as tetragonal groups No. 119, 121 - 126, and are denoted by $P4_222$, $P4_2'22'$, $P4_2'2'2$, $P4_22'2'$, P_c4_222, P_C4_222, and P_I4_222. All of them are antiferromagnetic except $P4_22'2'$ which is ferromagnetic. Tetragonal group No. 120 is the grey space group which we omit. In Table VIII we list the elements of $P4_222$ (with origin[3] at 4_221). We introduce a running index number for these elements in order to have a more concise alternate designation.

In the magnetic space groups $P4_2'22'$, $P4_2'2'2$, and $P4_22'2'$ some of the elements of $P4_222$ become colored, and in Table IX these are designated by priming the corresponding running index number.

The magnetic space groups P_c4_222, P_C4_222, and P_I4_222 are obtained from $P4_222$ by adding, respectively, the antitranslation $(E|\underline{\tau})'$ with $\underline{\tau} = \frac{1}{2}c\underline{k}$ along the c-edge, the antitranslation $(E|\underline{\tau}_1)'$ with $\underline{\tau}_1 = \frac{1}{2}a(\underline{i}+\underline{j})$ along the diagonal of the c-face, and the antitranslation $(E|\underline{\tau}_2)'$ with $\underline{\tau}_2 = \frac{1}{2}a(\underline{i}+\underline{j}) + \frac{1}{2}c\underline{k}$ along the space-diagonal. These three magnetic space groups thus contain not only the elements of $P4_222$, but also these elements joined with the corresponding antitranslations. The <u>additional</u> elements of these three groups are given in Table X.

Table VIII. The Elements of the Space Group $P4_222$

Running index	Element $(\phi_i|\underline{\tau}_i)$	Description of the element $(\phi_i|\underline{\tau}_i)$
1	$(E|0)$	Identity operator
2	$(2_z|0)$	Counterclockwise rotation about z-axis through 180°
3	$(4_z|\underline{\tau})$	Counterclockwise rotation about z-axis through 90° followed by translation $\underline{\tau} = \frac{1}{2}c\underline{k}$
4	$(4_z^{-1}|\underline{\tau})$	clockwise rotation about z-axis through 90° followed by translation $\underline{\tau} = \frac{1}{2}c\underline{k}$
5	$(2_x|0)$	Counterclockwise rotation about x-axis through 180°
6	$(2_y|0)$	Counterclockwise rotation about y-axis through 180°
7	$(2_a|\underline{\tau})$	Counterclockwise rotation about $(\underline{i}+\underline{j})$ axis through 180° followed by translation $\underline{\tau}$
8	$(2_b|\underline{\tau})$	Counterclockwise rotation about $(\underline{i}-\underline{j})$ axis through 180° followed by translation $\underline{\tau}$

Table IX. The Elements of $P4_2'22'$, $P4_2'2'2$, and $P4_22'2'$

Running index of $P4_222$	Group $P4_2'22'$	Group $P4_2'2'2$	Group $P4_22'2'$
1	1	1	1
2	2	2	2
3	3'	3'	3
4	4'	4'	4
5	5	5'	5'
6	6	6'	6'
7	7'	7	7'
8	8'	8	8'

Table X. The Additional Elements of P_c4_222, P_C4_222, and P_I4_222

Group P_c4_222		Group P_C4_222		Group P_I4_222	
Running index	Element	Running index	Element	Running index	Element
1_c	$(E\|\underline{\tau})'$	1_C	$(E\|\underline{\tau}_1)'$	1_I	$(E\|\underline{\tau}_2)'$
2_c	$(2_z\|\underline{\tau})'$	2_C	$(2_z\|\underline{\tau}_1)'$	2_I	$(2_z\|\underline{\tau}_2)'$
3_c	$(4_z\|0)'$	3_C	$(4_z\|\underline{\tau}+\underline{\tau}_1)'$	3_I	$(4_z\|\underline{\tau}+\underline{\tau}_2)'$
4_c	$(4_z^{-1}\|0)'$	4_C	$(4_z^{-1}\|\underline{\tau}+\underline{\tau}_1)'$	4_I	$(4_z^{-1}\|\underline{\tau}+\underline{\tau}_2)'$
5_c	$(2_x\|\underline{\tau})'$	5_C	$(2_x\|\underline{\tau}_1)'$	5_I	$(2_x\|\underline{\tau}_2)'$
6_c	$(2_y\|\underline{\tau})'$	6_C	$(2_y\|\underline{\tau}_1)'$	6_I	$(2_y\|\underline{\tau}_2)'$
7_c	$(2_a\|0)'$	7_C	$(2_a\|\underline{\tau}+\underline{\tau}_1)'$	7_I	$(2_a\|\underline{\tau}+\underline{\tau}_2)'$
8_c	$(2_b\|0)'$	8_C	$(2_b\|\underline{\tau}+\underline{\tau}_1)'$	8_I	$(2_b\|\underline{\tau}+\underline{\tau}_2)'$

Given the magnetic space group, one can find the corresponding group $G(\phi_i|\underline{\tau}_i)$ from Table V, and then one can write down all possible sets of equivalent positions S_k for that group $G(\phi_i|\underline{\tau}_i)$. In Table XI, the coordinates of all equivalent positions are given for each set S_k for the seven groups under discussion. The symbols x,y, and z are here used for the general coordinates expressed as fractions of the unit cell edge lengths along the corresponding x, y, and z-axes. Special points like (½, ½, ¼) are read as the vector $\underline{r} = \frac{1}{2}a\underline{i} + \frac{1}{2}a\underline{j} + \frac{1}{4}c\underline{k}$ for our tetragonal system examples. One sees from Table V that the groups $G(\phi_i|\underline{\tau}_i)$ and $G_i(\phi_i|\underline{\tau}_i)$ that derive from the four groups $P4_222$, $P4_2'22'$, $P4_2'2'2$, and $P4_22'2'$ are identical. Thus the sets of equivalent positions for these four groups are those of $P4_222$ as given in the International Tables.[3] Here we have listed these positions in Table XI and we have designated them as S_1 through S_{16}.

Additional equivalent positions in Table XI are those generated by the translations $\underline{\tau}$, $\underline{\tau}_1$, and $\underline{\tau}_2$, respectively, in the three magnetic space groups P_c4_222, P_C4_222, and P_I4_222. For example, $S_{10}'(P_C)$ is the set generated from S_{10} by operating on every position of S_{10} with $(E|\underline{\tau}_1)$, $S_{10}'(P_I)$ is the set generated from S_{10} by operating on every position of S_{10} with $(E|\underline{\tau}_2)$. The sets $S_9'(P_c)$ and $S_9'(P_C)$ turn out to be identical sets and are simply designated by S_9'.

All points in the magnetic unit cell can be covered in terms of sets of equivalent positions, starting with the points of highest

Table XI. Coordinates of Equivalent Positions

Set	Equivalent positions (Origin at $4_{2}21$)
S_1	$(0,0,0)$, $(0,0,\frac{1}{2})$
S_2	$(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
S_3	$(0,\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$
S_4	$(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,0)$
S_5	$(0,0,\frac{1}{4})$, $(0,0,3/4)$
S_6	$(\frac{1}{2},\frac{1}{2},\frac{1}{4})$, $(\frac{1}{2},\frac{1}{2},3/4)$
S_7	$(0,0,z)$, $(0,0,\bar{z})$, $(0,0,\frac{1}{2}+z)$, $(0,0,\frac{1}{2}-z)$
S_8	$(\frac{1}{2},\frac{1}{2},z)$, $(\frac{1}{2},\frac{1}{2},\bar{z})$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2}+z)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2}-z)$
S_9	$(0,\frac{1}{2},z)$, $(0,\frac{1}{2},\bar{z})$, $(\frac{1}{2},0,\frac{1}{2}+z)$, $(\frac{1}{2},0,\frac{1}{2}-z)$
S_{10}	$(x,0,0)$, $(\bar{x},0,0)$, $(0,x,\frac{1}{2})$, $(0,\bar{x},\frac{1}{2})$
S_{11}	$(x,\frac{1}{2},\frac{1}{2})$, $(\bar{x},\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},x,0)$, $(\frac{1}{2},\bar{x},0)$
S_{12}	$(x,0,\frac{1}{2})$, $(\bar{x},0,\frac{1}{2})$, $(0,x,0)$, $(0,\bar{x},0)$
S_{13}	$(x,\frac{1}{2},0)$, $(\bar{x},\frac{1}{2},0)$, $(\frac{1}{2},x,\frac{1}{2})$, $(\frac{1}{2},\bar{x},\frac{1}{2})$
S_{14}	$(x,x,\frac{1}{4})$, $(\bar{x},\bar{x},\frac{1}{4})$, $(\bar{x},x,3/4)$, $(x,\bar{x},3/4)$
S_{15}	$(x,x,3/4)$, $(\bar{x},\bar{x},3/4)$, $(\bar{x},x,\frac{1}{4})$, $(x,\bar{x},\frac{1}{4})$
S_{16}	(x,y,z), $(\bar{x},\bar{y},z)$, $(\bar{y},x,\frac{1}{2}+z)$, $(y,\bar{x},\frac{1}{2}+z)$, $(x,\bar{y},\bar{z})$, $(\bar{x},y,\bar{z})$, $(y,x,\frac{1}{2}-z)$, $(\bar{y},\bar{x},\frac{1}{2}-z)$
S_9'	$(\frac{1}{2},0,z)$, $(\frac{1}{2},0,\bar{z})$, $(0,\frac{1}{2},\frac{1}{2}+z)$, $(0,\frac{1}{2},\frac{1}{2}-z)$

(continued on next page)

Table XI (cont'd.)

Set	Equivalent positions (Origin at $4_2 21$)
$S_{10}'(P_C)$	$(\frac{1}{2}+x,\frac{1}{2},0)$, $(\frac{1}{2}-x,\frac{1}{2},0)$, $(\frac{1}{2},\frac{1}{2}+x,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2}-x,\frac{1}{2})$
$S_{10}'(P_I)$	$(\frac{1}{2}+x,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2}-x,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2}+x,0)$, $(\frac{1}{2},\frac{1}{2}-x,0)$
$S_{11}'(P_C)$	$(\frac{1}{2}+x,0,\frac{1}{2})$, $(\frac{1}{2}-x,0,\frac{1}{2})$, $(0,\frac{1}{2}+x,0)$, $(0,\frac{1}{2}-x,0)$
$S_{11}'(P_I)$	$(\frac{1}{2}+x,0,0)$, $(\frac{1}{2}-x,0,0)$, $(0,\frac{1}{2}+x,\frac{1}{2})$, $(0,\frac{1}{2}-x,\frac{1}{2})$
$S_{12}'(P_C)$	$= S_{10}'(P_I)$
$S_{12}'(P_I)$	$= S_{10}'(P_C)$
$S_{13}'(P_C)$	$= S_{11}'(P_I)$
$S_{13}'(P_I)$	$= S_{11}'(P_C)$
$S_{14}'(P_C)$	$(\frac{1}{2}+x,\frac{1}{2}+x,\frac{1}{4})$, $(\frac{1}{2}-x,\frac{1}{2}-x,\frac{1}{4})$, $(\frac{1}{2}-x,\frac{1}{2}+x,3/4)$, $(\frac{1}{2}+x,\frac{1}{2}-x,3/4)$
$S_{14}'(P_I)$	$(\frac{1}{2}+x,\frac{1}{2}+x,3/4)$, $(\frac{1}{2}-x,\frac{1}{2}-x,3/4)$, $(\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{4})$, $(\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{4})$
$S_{15}'(P_C)$	$= S_{14}'(P_I)$
$S_{15}'(P_I)$	$= S_{14}'(P_C)$
$S_{16}'(P_c)$	$(x,y,\frac{1}{2}+z)$, $(\bar{x},\bar{y},\frac{1}{2}+z)$, $(\bar{y},x,z)$, $(y,\bar{x},z)$, $(x,\bar{y},\frac{1}{2}-z)$, $(\bar{x},y,\frac{1}{2}-z)$
	$(y,x,\bar{z})$, $(\bar{y},\bar{x},\bar{z})$
$S_{16}'(P_C)$	$(\frac{1}{2}+x,\frac{1}{2}+y,z)$, $(\frac{1}{2}-x,\frac{1}{2}-y,z)$, $(\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}+z)$, $(\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}+z)$,
	$(\frac{1}{2}+x,\frac{1}{2}-y,\bar{z})$, $(\frac{1}{2}-x,\frac{1}{2}+y,\bar{z})$, $(\frac{1}{2}+y,\frac{1}{2}+x,\frac{1}{2}-z)$, $(\frac{1}{2}-y,\frac{1}{2}-x,\frac{1}{2}-z)$
$S_{16}'(P_I)$	$(\frac{1}{2}+x,\frac{1}{2}+y,\frac{1}{2}+z)$, $(\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z)$, $(\frac{1}{2}-y,\frac{1}{2}+x,z)$, $(\frac{1}{2}+y,\frac{1}{2}-x,z)$,
	$(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z)$, $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$, $(\frac{1}{2}+y,\frac{1}{2}+x,\bar{z})$, $(\frac{1}{2}-y,\frac{1}{2}-x,\bar{z})$

symmetry and proceeding through points of intermediate symmetry to the general point (x,y,z). The number of equivalent positions in the set which contains the general point (x,y,z) is equal to the order of the Shubnikov group, and the number of equivalent positions in all other sets must be less than the order of the group and is, in fact, an integral divisor of the order of the group.

For every set of equivalent positions one can find from (3.1) the Shubnikov subgroups with elements $(s_i|\underline{\tau}_i)$ of the given magnetic space group which reduce, with T set equal to E, to the groups $G_i(\phi_i|\underline{\tau}_i)$ under which the equivalent positions remain invariant. These Shubnikov subgroup operations are given in Tables XII, XIII, and XIV. The first column gives the sets of equivalent positions, the subsequent column(s) list the elements $(s_i|\underline{\tau}_i)$ of the subgroups under which the equivalent positions of each set remain invariant, and the last column gives the number of points in the set. All the points in a given set may not be associated with the same subgroup in all cases. This occurs in Table XII for the sets S_{10} through S_{15}. For example, for the sets S_{10} through S_{13} of $P4_2'2'2$ the first two points are associated with the group with elements 1, 5', and the second two points are associated with the group with elements 1, 6'. In Table XII, this is indicated as: 1, 5'; 1, 6'. Similar remarks apply to Tables XIII and XIV.

After determining the groups $G_i(\phi_i|\underline{\tau}_i)$ one can find $G_i(\theta_i)$ from Table V for each set of equivalent positions. With this, as discussed at the beginning of this chapter, one can finally determine the

Table XII. Equivalent-Position Subgroups of $P4_222$, $P4_2'22'$, $P4_2'2'2$, and $P4_22'2'$

Sets of equivalent positions	$P4_222$	$P4_2'22'$	$P4_2'2'2$	$P4_22'2'$	No. of points in set
S_1, S_2, S_3, S_4	1, 2, 5, 6	1, 2, 5, 6	1, 2, 5', 6'	1, 2, 5', 6'	2
S_5, S_6	1, 2, 7, 8	1, 2, 7', 8'	1, 2, 7, 8	1, 2, 7', 8'	2
S_7, S_8, S_9	1, 2	1, 2	1, 2	1, 2	4
$S_{10}, S_{11}, S_{12}, S_{13}$	1, 5; 1, 6	1, 5; 1, 6	1, 5'; 1, 6'	1, 5'; 1, 6'	4
S_{14}, S_{15}	1, 7; 1, 8	1, 7'; 1, 8'	1, 7; 1, 8	1, 7'; 1, 8'	4
S_{16}	1	1	1	1	8

Table XIII. Equivalent-Position Subgroups of P_c4_222

Sets of equivalent positions	P_c4_222	No. of points in set
S_1, S_2, S_3, S_4	1, 2, 3_c, 4_c, 5, 6, 7_c, 8_c	2
S_5, S_6	1, 2, 3_c, 4_c, 5_c, 6_c, 7, 8	2
S_7, S_8	1, 2, 3_c, 4_c	4
S_9+S_9'	1, 2	8
$S_{10}+S_{12}$, $S_{11}+S_{13}$	1, 5; 1, 6	8
$S_{14}+S_{15}$	1, 7; 1, 8	8
$S_{16}+S_{16}'$	1	16

Table XIV. Equivalent-Position Subgroups of P_C4_222 and P_I4_222

Sets of equivalent positions	P_C4_222	P_I4_222	No. of points in set
S_1+S_2, S_3+S_4	1, 2, 5, 6	1, 2, 5, 6	4
S_5+S_6	1, 2, 7, 8	1, 2, 7, 8	4
S_7+S_8	1, 2	1, 2	8
S_9+S_9'	1, 2	---	8
S_9	---	1, 2, 3_I, 4_I	4
$S_{10}+S_{10}'$, $S_{11}+S_{11}'$, $S_{12}+S_{12}'$, $S_{13}+S_{13}'$	1, 5; 1, 6	1, 5; 1, 6	8
$S_{14}+S_{14}'$, $S_{15}+S_{15}'$	1, 7; 1, 8	1, 7; 1, 8	8
$S_{16}+S_{16}'$	1	1	16

allowed components of $\underline{B}$ at each point of these sets and the relation between these components of $\underline{B}$ at all points in the set. The results of these determinations for all sets of equivalent positions and for all seven groups are given in Tables XV, XVI, and XVII. The x, y, and z-components of the internal magnetic field $\underline{B}(\underline{r})$ are denoted by u, v, and w, respectively, and $\bar{u}$ stands for -u, etc. The entries list the components of the field which symmetry allows to be non-vanishing, and these components at the various points of a given set are listed in the same order as the points in Table XI. A zero entry designates that symmetry does not allow non-vanishing $\underline{B}$ at any point of the set. Use of Tables XV, XVI, and XVII is best described with the aid of two examples:

(1) The entries of Table XV for the set of equivalent positions S_7 should be understood to designate the following:

For $P4_222$,

$$B_z(0,0,z) = -B_z(0,0,\bar{z}) = B_z(0,0,\tfrac{1}{2}+z) = -B_z(0,0,\tfrac{1}{2}-z); \qquad (3.3)$$

for $P4_2'22'$,

$$B_z(0,0,z) = -B_z(0,0,\bar{z}) = -B_z(0,0,\tfrac{1}{2}+z) = B_z(0,0,\tfrac{1}{2}-z); \qquad (3.4)$$

for $P4_2'2'2$,

$$B_z(0,0,z) = B_z(0,0,\bar{z}) = -B_z(0,0,\tfrac{1}{2}+z) = -B_z(0,0,\tfrac{1}{2}-z); \qquad (3.5)$$

and for $P4_22'2'$,

$$B_z(0,0,z) = B_z(0,0,\bar{z}) = B_z(0,0,\tfrac{1}{2}+z) = B_z(0,0,\tfrac{1}{2}-z). \qquad (3.6)$$

The x and y-components were determined to be vanishing and are not listed.

Table XV. The Components of $\underline{B}(\underline{r})$ for $P4_222$, $P4_2'22'$, $P4_2'2'2$, and $P4_22'2'$

Sets of equivalent positions	$P4_222$	$P4_2'22'$	$P4_2'2'2$	$P4_22'2'$
S_1, S_2, S_3, S_4	0	0	$w,\bar{w}$	w,w
S_5, S_6	0	$w,\bar{w}$	0	w,w
S_7, S_8, S_9	$w,\bar{w},w,\bar{w}$	$w,\bar{w},\bar{w},w$	$w,w,\bar{w},\bar{w}$	w,w,w,w
$S_{10}, S_{11}, S_{12}, S_{13}$	$u,\bar{u},v,\bar{v}$	$u,\bar{u},\bar{v},v$	$v,\bar{v},u,\bar{u}$ $w,w,\bar{w},\bar{w}$	$v,\bar{v},\bar{u},u$ w,w,w,w
S_{14}, S_{15}	0	$w,w,\bar{w},\bar{w}$	0	w,w,w,w
S_{16}	$u,\bar{u},v,\bar{v},u,\bar{u},v,\bar{v}$ $v,\bar{v},\bar{u},u,\bar{v},v,u,\bar{u}$ $w,w,w,w,\bar{w},\bar{w},\bar{w},\bar{w}$	$u,\bar{u},\bar{v},v,u,\bar{u},\bar{v},v$ $v,\bar{v},u,\bar{u},\bar{v},v,\bar{u},u$ $w,w,\bar{w},\bar{w},\bar{w},\bar{w},w,w$	$u,\bar{u},\bar{v},v,\bar{u},u,v,\bar{v}$ $v,\bar{v},u,\bar{u},v,\bar{v},u,\bar{u}$ $w,w,\bar{w},\bar{w},w,w,\bar{w},\bar{w}$	$u,\bar{u},v,\bar{v},\bar{u},u,\bar{v},v$ $v,\bar{v},\bar{u},u,v,\bar{v},\bar{u},u$ w,w,w,w,w,w,w,w

Table XVI. The Components of $\underline{B}(\underline{r})$ for P_c4_222

Sets of equivalent positions	P_c4_222
S_1 through S_8	0
S_9+S_9'	$w,\bar{w},w,\bar{w},\bar{w},w,\bar{w},w$
$S_{10}+S_{12}$, $S_{11}+S_{13}$	$u,\bar{u},v,\bar{v},\bar{u},u,\bar{v},v$
$S_{14}+S_{15}$	0
$S_{16}+S_{16}'$	S_{16}: same as for $P4_222$; S_{16}': as for $P4_222$ with opposite sign

Table XVII. The Components of $\underline{B}(\underline{r})$ for P_C4_222 and P_I4_222

Sets of equivalent positions	P_C4_222	P_I4_222
S_1+S_2, S_3+S_4, S_5+S_6	0	0
S_7+S_8	$w,\bar{w},w,\bar{w},\bar{w},w,\bar{w},w$	$w,\bar{w},w,\bar{w},\bar{w},w,\bar{w},w$
S_9+S_9'	$w,\bar{w},w,\bar{w},\bar{w},w,\bar{w},w$	S_9: 0 S_9': not defined
$S_{10}+S_{10}'$, $S_{11}+S_{11}'$ $S_{12}+S_{12}'$, $S_{13}+S_{13}'$	$u,\bar{u},v,\bar{v},\bar{u},u,\bar{v},v$	$u,\bar{u},v,\bar{v},\bar{u},u,\bar{v},v$
$S_{14}+S_{14}'$, $S_{15}+S_{15}'$	0	0
$S_{16}+S_{16}'$	S_{16}: same as for $P4_222$ S_{16}': as for $P4_222$ with opposite sign	S_{16}: same as for $P4_222$ S_{16}': as for $P4_222$ with opposite sign

(2) As another example, consider S_{10} of $P4_2'2'2$ from Table XIV. This entry explicitly stands for:

$$B_y(x,0,0) = -B_y(\bar{x},0,0) = B_x(0,x,\tfrac{1}{2}) = -B_x(0,\bar{x},\tfrac{1}{2}), \tag{3.7}$$

and

$$B_z(x,0,0) = B_z(\bar{x},0,0) = -B_z(0,x,\tfrac{1}{2}) = -B_z(0,\bar{x},\tfrac{1}{2}). \tag{3.8}$$

It is also indicated from Table XV that the components of the field at the points of S_{11} (or S_{12}, or S_{13}) of $P4_2'2'2$ obey a set of relations similar to (3.7) and (3.8), i.e., for S_{11} one has

$$B_y(x,\tfrac{1}{2},\tfrac{1}{2}) = -B_y(\bar{x},\tfrac{1}{2},\tfrac{1}{2}) = B_x(\tfrac{1}{2},x,0) = -B_x(\tfrac{1}{2},\bar{x},0), \tag{3.9}$$

and

$$B_z(x,\tfrac{1}{2},\tfrac{1}{2}) = B_z(\bar{x},\tfrac{1}{2},\tfrac{1}{2}) = -B_z(\tfrac{1}{2},x,0) = -B_z(\tfrac{1}{2},\bar{x},0). \tag{3.10}$$

It is important to note, however, that the above magnitudes of the components of $\underline{B}$ in the set S_{11} cannot, from symmetry alone, be related to the magnitudes of the components of $\underline{B}$ in the set S_{10}. This applies, of course, generally in that the allowed components of $\underline{B}$ within any given set of equivalent positions cannot, from symmetry alone, be related to the allowed components of $\underline{B}$ in any other set of equivalent positions.

We have now completed the description of the solution of the first problem posed in Chapter I, viz., what is the symmetry of the most general time-averaged internal magnetic field $\underline{B}(\underline{r})$ allowed by a given magnetic space group, and we have given examples for purposes of illustration.

CHAPTER IV

NEUTRON SCATTERING FROM THE INTERNAL MAGNETIC FIELD

In order to study the scattering of a monochromatic beam of neutrons from the internal field $\underline{B}(\underline{r})$, a knowledge of the behavior of the Fourier components of this field is required. We therefore write

$$\underline{B}(\underline{r}) = \sum_{\underline{k}} \underline{F}(\underline{k}) \exp(i\underline{k} \cdot \underline{r}), \tag{4.1}$$

where $\underline{F}(\underline{k})$ is the axial vector amplitude of the k-th Fourier component of $\underline{B}(\underline{r})$, and $\underline{k}$ is a vector in the reciprocal lattice which can be written as $\underline{k} = 2\pi(l\underline{a}^* + m\underline{b}^* + n\underline{c}^*)$, where $\underline{a}^*$, $\underline{b}^*$, and $\underline{c}^*$ are the lattice vectors of the reciprocal magnetic unit cell and are related to $\underline{a}$, $\underline{b}$, and $\underline{c}$ which were defined in Chapter III as

$$\underline{a} \cdot \underline{a}^* = \underline{b} \cdot \underline{b}^* = \underline{c} \cdot \underline{c}^* = 1, \tag{4.2}$$

and l, m, and n are any set of integers.

If an incoming monochromatic neutron wave interacts with the internal magnetic field $\underline{B}(\underline{r})$ and is scattered elastically into an outgoing wave, then the matrix element of the interaction is given by $\langle \psi_i | \mathcal{H}_{int} | \psi_f \rangle$, where $\mathcal{H}_{int} = -\mu \cdot \underline{B}(\underline{r})$, and μ is the neutron magnetic moment vector. If the incoming neutron has momentum $\hbar \underline{k}_i$, and the outgoing neutron wave has momentum $\hbar\underline{k}_f$, then $\hbar\underline{k}_f = \hbar(\underline{k}_i-\underline{k})$, and $\hbar^2\underline{k}_i{}^2/2M = \hbar^2\underline{k}_f{}^2/2M$, where M is the mass of the neutron. If the spin state of the neutron is specified by spin index σ, and the state of the scattering system by an index n, then a state of the total system can be written as $|\underline{k}\sigma n\rangle$. Hence the matrix element $\langle\Psi_i|\mathcal{H}_{int}|\Psi_f\rangle$ takes the general form

$$\langle\Psi_i|\mathcal{H}_{int}|\Psi_f\rangle = \langle\underline{k}_i\sigma_i n_i|-\underline{\mu}(\underline{r})\cdot\underline{B}(\underline{r})|\underline{k}_f\sigma_f n_f\rangle.$$

Representing incoming and outgoing neutrons by plane waves,

$$\begin{aligned}\langle\Psi_i|\mathcal{H}_{int}|\Psi_f\rangle &= \langle\sigma_i n_i|\int[-\underline{\mu}(\underline{r})\cdot\sum_{\underline{k}'}\underline{F}(\underline{k}')]\exp[-i(\underline{k}-\underline{k}')\cdot\underline{r}]d\underline{r}|\sigma_f n_f\rangle\\ &= \langle\sigma_i n_i|-\underline{\mu}\cdot\sum_{\underline{k}'}\underline{F}(\underline{k}')\int\exp[-i(\underline{k}-\underline{k}')\cdot\underline{r}\;d\underline{r}]|\sigma_f n_f\rangle,\end{aligned}$$

where the integration is taken over the volume V of the magnetic unit cell. Carrying out the integration we obtain

$$\langle\Psi_i|\mathcal{H}_{int}|\Psi_f\rangle = -V\langle\sigma_i n_i|\underline{\mu}\cdot\underline{F}(\underline{k})|\sigma_f n_f\rangle. \tag{4.3}$$

The intensity of the neutron beam scattered into a final state with a particular polarization with an associated change in wave vector $\underline{k} = \underline{k}_i-\underline{k}_f$ is proportional to $|\langle\Psi_i|\mathcal{H}_{int}|\Psi_f\rangle|^2$, hence by (4.3) it is proportional to $|\langle\sigma_i n_i|\underline{\mu}\cdot\underline{F}(\underline{k})|\sigma_f n_f\rangle|^2$. If, for given $\underline{k}$, all three components of $\underline{F}(\underline{k})$ vanish, then $\langle\Psi_i|\mathcal{H}_{int}|\Psi_f\rangle = 0$, and there will be no scattered beam. If two components of $\underline{F}(\underline{k})$ vanish, the scattered beam may be linearly polarized, and if one component of $\underline{F}(\underline{k})$ vanishes, the scattered beam may be partially polarized.

We now wish to relate $\underline{F}(\underline{k})$ to the macroscopic magnetization $\underline{M}(\underline{r})$ of the crystal. We start with the well-known relation of classical electromagnetic theory[15]

$$\underline{B} = \underline{H} + 4\pi \underline{M}, \tag{4.4}$$

where $\underline{B}$ is the magnetic induction field, $\underline{H}$ is the magnetic field, and $\underline{M}$ is the magnetization (magnetic moment per unit volume). For the Fourier expansion of the magnetization we can write

$$\underline{M}(\underline{r}) = \sum_{\underline{k}} \underline{m}(\underline{k}) \exp(i\underline{k}\cdot\underline{r}), \tag{4.5}$$

and by Fourier inversion,

$$\underline{m}(\underline{k}) = (1/V)\int \underline{M}(\underline{r}) \exp(-i\underline{k}\cdot\underline{r})\, d\tau, \tag{4.6}$$

with the integration taken over the volume of the magnetic unit cell. Since all internal currents are described in terms of the magnetization $\underline{M}(\underline{r})$,

$$\nabla \times \underline{H} = 0 \tag{4.7}$$

which allows $\underline{H}$ to be written as the gradient of a scalar function ϕ,

$$\underline{H} = -\nabla\phi. \tag{4.8}$$

From (4.4),

$$\nabla\cdot\underline{B} = +4\pi\nabla\cdot\underline{M} + \nabla\cdot\underline{H}, \tag{4.9}$$

and since the divergence of the magnetic induction always vanishes, we obtain

$$4\pi\nabla\cdot\underline{M} = -\nabla\cdot\underline{H}, \tag{4.10}$$

and hence from (4.6) and (4.8),

$$\nabla^2\phi = 4\pi\nabla\cdot\underline{M} = 4\pi i \sum_{\underline{k}} \underline{k}\cdot\underline{m}(\underline{k}) \exp(i\underline{k}\cdot\underline{r}). \tag{4.11}$$

From this it follows by integrating over the volume of the magnetic unit cell that

$$\phi = -4\pi i \sum_{\underline{k}} [\underline{k}\cdot\underline{m}(\underline{k})/\underline{k}\cdot\underline{k}]\exp(i\underline{k}\cdot\underline{r}), \tag{4.12}$$

and thus

$$\underline{H} = -\nabla\phi = -4\pi \sum_{\underline{k}} [\underline{kk}\cdot\underline{m}(\underline{k})/\underline{k}^2]\exp(i\underline{k}\cdot\underline{r}), \tag{4.13}$$

and hence

$$\underline{B} = 4\pi \sum_{\underline{k}} [I - (\underline{kk}/\underline{k}^2)]\cdot\underline{m}(\underline{k}) \exp(i\underline{k}\cdot\underline{r}), \tag{4.14}$$

where I is the unit dyadic. By comparison of (4.14) with (4.1) we find that

$$\underline{F}(\underline{k}) = 4\pi[I - (\underline{kk}/\underline{k}^2)]\cdot\underline{m}(\underline{k}) \tag{4.15}$$

which is the desired relation between the Fourier components of the magnetic induction field and the Fourier components of the magnetization.

We now proceed to the study of the Shubnikov symmetry of $\underline{F}(\underline{k})$. The Fourier inversion of (4.1) is

$$\underline{F}(\underline{k}) = (1/V)\int\underline{B}(\underline{r}) \exp(-i\underline{k}\cdot\underline{r})\ d\tau, \tag{4.16}$$

from which we have that

$$\theta_i\cdot\underline{F}(\underline{k}) = (1/V)\int\theta_i\cdot\underline{B}(\underline{r})\exp(-i\underline{k}\cdot\underline{r})\ d\tau, \tag{4.17}$$

and with the aid of (2.5) we can write

$$\theta_i\cdot\underline{F}(\underline{k}) = (1/V)\int\underline{B}(\phi_i\cdot\underline{r}+\underline{\tau}_i) \exp(-i\underline{k}\cdot\underline{r})\ d\tau. \tag{4.18}$$

Now we set

$$\phi_i\cdot\underline{r} + \underline{\tau}_i = \underline{r}', \tag{4.19}$$

and hence

$$\underline{r} = \phi_i^{-1}\cdot(\underline{r}' - \underline{\tau}_i). \tag{4.20}$$

Thus with the use of (4.20), (4.18) can be written

$$\theta_i\cdot\underline{F}(\underline{k}) = (1/V)\int\underline{B}(\underline{r}')\exp(-i\underline{k}\cdot\phi_i^{-1}\cdot\underline{r}')\exp(i\underline{k}\cdot\phi_i^{-1}\cdot\underline{\tau}_i)\,d\tau \tag{4.21}$$

Replacing $\underline{k}$ by $\underline{k}\cdot\phi_i^{-1}$ and $\underline{r}$ by $\underline{r}'$ in (4.16), we obtain

$$\underline{F}(\underline{k}\cdot\phi_i^{-1}) = (1/V)\int\underline{B}(\underline{r}')\exp(-i\underline{k}\cdot\phi_i^{-1}\cdot\underline{r}')\,d\tau, \tag{4.22}$$

and using this in (4.21) we get[16]

$$\theta_i\cdot\underline{F}(\underline{k}) = \exp(i\underline{k}\cdot\phi_i^{-1}\cdot\underline{\tau}_i)\,\underline{F}(\underline{k}\cdot\phi_i^{-1}). \tag{4.23}$$

We now consider the set of operations $\{\phi_j|\underline{\tau}_j\}$ of the magnetic space group $S(s_j|\underline{\tau}_j)$ of the crystal that transform the reciprocal vector $\underline{k}_i$ such that

$$\underline{k}_i\cdot\phi_j^{-1} = \underline{k}_i. \tag{4.24}$$

This set of operations $\{\phi_j|\underline{\tau}_j\}$ for which (4.24) is valid, i.e., the operations under which $\underline{k}_i$ is invariant, and the corresponding set of operations $\{\theta_j\}$ of the magnetic space group $S(s_j|\underline{\tau}_j)$ form groups[10] which we denote, respectively, by $\mathcal{G}_i(\phi|\underline{\tau})$ and $\mathcal{G}_i(\theta)$. For each group $\mathcal{G}_i(\phi|\underline{\tau})$ for which (4.24) holds, (4.23) takes the form

$$[\underline{F}(\underline{k}_i) - \exp(-i\underline{k}_i\cdot\underline{\tau}_j)\,\theta_j]\cdot\underline{F}(\underline{k}_i) = 0, \tag{4.25}$$

or

$$[I - \exp(-i\underline{k}_i\cdot\underline{\tau}_j)\,\theta_j]\cdot\underline{F}(\underline{k}_i) = 0, \tag{4.26}$$

where θ_j and $(\phi_j|\underline{\tau}_j)$ belong to $\mathcal{G}_i(\theta)$ and $\mathcal{G}_i(\phi|\underline{\tau})$, respectively. The equation (4.26) must be satisfied for <u>each</u> element of $\mathcal{G}_i(\phi|\underline{\tau})$ and for every corresponding element of $\mathcal{G}_i(\theta)$. The most restricted common solution of (4.26), i.e., the "intersection" of the common solutions of the scattering amplitude equation (4.26), will represent the most general solution compatible with the symmetry of the crystal for the three components of $\underline{F}(\underline{k})$.

Since (4.26) is a matrix equation, the number of linearly independent solutions depends[10] on the rank r of the coefficient matrix $A = I - \exp(-i\underline{k}_i\cdot\underline{\tau}_j)\,\theta_j$. The order of the matrix A is three, thus the number of linearly independent solutions will be (3-r). If A is non-singular, its rank is three, and then $\underline{F}(\underline{k}_i)$ must vanish identically. For this $\underline{k}_i$, there will be no scattered beam. If only one component of $\underline{F}(\underline{k}_i)$ is non-vanishing for given $\underline{k}_i$, e.g., $F_z(\underline{k}_i) = \lambda$, and $F_x(\underline{k}_i) = F_y(\underline{k}_i) = 0$, then the corresponding linear polarization of the scattered neutrons is to be expected. If only one component of $\underline{F}(\underline{k}_i)$ vanishes, then the corresponding direction of polarization is expected to be absent from the scattered beam.

It is found that only a few types of symmetry operations of Shubnikov groups will satisfy (4.24). These are n-fold rotation or antirotation which keep invariant the vector $\underline{k}$ along the axis of rotation or antirotation, and any twofold reflection-rotation or antireflection-rotation which keep invariant the vector $\underline{k}$ in the plane of reflection or antireflection-rotation. In case $S(s_i|\underline{\tau}_i)$ contains an antitranslation $(E|\underline{\tau})'$, $\underline{k}$ must satisfy

$$\exp(i\underline{k}\cdot\underline{\tau}) = -1 \qquad (4.27)$$

in addition to satisfying the invariance condition (4.24). For in this case one must have

$$\underline{B}(\underline{r}) = -\underline{B}(\underline{r}+\underline{\tau}), \tag{4.28}$$

and thus from (4.1)

$$\sum_{\underline{k}'} \underline{F}(\underline{k}') \exp(i\underline{k}'\cdot \underline{r}) = -\sum_{\underline{k}'} \underline{F}(\underline{k}') \exp[i\underline{k}'\cdot(\underline{r}+\underline{\tau})]. \tag{4.29}$$

Multiplying both sides by $\exp(-i\underline{k}\cdot\underline{r})$ and integrating over the volume of the magnetic unit cell, one obtains (4.27).

The condition (4.27) has an important consequence, as may be seen from the following. Suppose $\underline{\tau} = \frac{1}{2}(\underline{a}+\underline{b}+\underline{c})$ and $\underline{k} = 2\pi(l\underline{a}^*+m\underline{b}^*+n\underline{c}^*)$. Then, from (4.27) one obtains

$$\exp[2\pi i(l\underline{a}^*+m\underline{b}^*+n\underline{c}^*)\cdot\tfrac{1}{2}(\underline{a}+\underline{b}+\underline{c})] = -1 \tag{4.30}$$

which requires $(l+m+n)$ to be an odd integer. Thus, for example, if $\underline{\tau} = \frac{1}{2}\underline{c}$, then n must be odd and hence one cannot choose $\underline{k}$ along the a-axis or b-axis since that would require n to be zero. Thus, in case of magnetic space groups containing an antitranslation, (4.27) represents restrictive conditions on the choice of $\underline{k}$ which are additional to those demanded by (4.24).

We now present all possible solutions of the scattering amplitude equation for the Shubnikov group operations which satisfy (4.24) in general, i.e., without taking into account possible antitranslations. We take all symmetry operations as passing through the origin, and we choose the z-axis (c-axis) as the n-fold rotation and antirotation axis and also as the twofold reflection-rotation and antireflection-rotation axis. The complete catalog of such operations is given in Table XVIII, and the solutions $\underline{F}(\underline{k})$ of (4.26) for the specific operations in Table XVIII are given in Tables XIX, XX, XXI, XXII, and XXIII. The details of calculation of such results will be illustrated in the next chapter.

As an example of how to use Tables XIX through XXIII, consider the first row of Table XIX which states that (a) the operations 2_z and $(2_z|\underline{\tau})$ for even n, and the operation $(2_z|\underline{\tau})'$ for odd n, with $\underline{\tau} = \frac{1}{2}\underline{c}$, keep invariant the vector $\underline{k} = 2\pi n\underline{c}^*$; and that (b) the most general solution $\underline{F}(\underline{k})$ of (4.26) is given by $F_{\parallel}(\underline{k}) = \gamma$, and $F_{\perp}(\underline{k}) = (0,0)$, i.e., the component of $\underline{F}(\underline{k})$ parallel to the z-axis (c-axis) is equal to a constant γ, and the components of $\underline{F}(\underline{k})$ perpendicular to the z-axis are zero. Other entries can be understood along the same lines.

Table XVIII. All Possible Shubnikov Group Operations which Satisfy Equation (4.24) and the Corresponding Invariant Reciprocal Vector

Shubnikov group operation (with $\underline{\tau}_i=0$)	Possible translational part $\underline{\tau}_i$ with the elements passing through the origin	Invariant reciprocal vector $\underline{k} = 2\pi(l\underline{a}^*+m\underline{b}^*+n\underline{c}^*)$
2_z, $2_z'$	0, $\frac{1}{2}\underline{c}$	$\underline{k} = 2\pi n\underline{c}^*$
$\bar{2}_z$, $\bar{2}_z'$	0, $\frac{1}{2}\underline{a}$, $\frac{1}{2}\underline{b}$, $\frac{1}{2}\underline{c}$ $\frac{1}{2}(\underline{a}+\underline{b})$, $\frac{1}{2}(\underline{b}+\underline{c})$, $\frac{1}{2}(\underline{c}+\underline{a})$, $\frac{1}{2}(\underline{a}+\underline{b}+\underline{c})$ $\frac{1}{4}(\underline{a}\pm\underline{b})$, $\frac{1}{4}(\underline{b}\pm\underline{c})$, $\frac{1}{4}(\underline{c}\pm\underline{a})$, $\frac{1}{4}(\underline{a}\pm\underline{b}\pm\underline{c})$	$\underline{k} = 2\pi(l\underline{a}^*+m\underline{b}^*)$
3_z	0, $\underline{c}/3$, $2\underline{c}/3$	$\underline{k} = 2\pi n\underline{c}^*$
4_z, $4_z'$	0, $\frac{1}{4}\underline{c}$, $\frac{1}{2}\underline{c}$, $3\underline{c}/4$	$\underline{k} = 2\pi n\underline{c}^*$
6_z, $6_z'$	0, $\underline{c}/6$, $\underline{c}/3$, $\frac{1}{2}\underline{c}$, $2\underline{c}/3$, $5\underline{c}/6$	$\underline{k} = 2\pi n\underline{c}^*$

Table XIX. Solutions $\underline{F}(\underline{k})$ of Equation (4.26) for the Operations $(2_z|\underline{\tau})$ and $(2_z|\underline{\tau})'$

Operation 2_z	Operation $2_z'$	$\underline{F}(2\pi n\underline{c}^*)$
$\underline{\tau} = 0$, for all n $\underline{\tau} = \frac{1}{2}\underline{c}$, for even n	$\underline{\tau} = \frac{1}{2}\underline{c}$, for odd n	$\underline{F}_{\parallel}(\underline{k}) = \gamma$; $\underline{F}_{\perp}(\underline{k}) = (0,0)$
$\underline{\tau} = \frac{1}{2}\underline{c}$, for odd n	$\underline{\tau} = 0$, for all n $\underline{\tau} = \frac{1}{2}\underline{c}$, for even n	$\underline{F}_{\parallel}(\underline{k}) = 0$; $\underline{F}_{\perp}(\underline{k}) = (\alpha,\beta)$

Table XX. Solutions $\underline{F}(\underline{k})$ of Equation (4.26) for the Operations $(\bar{2}_z|\underline{\tau})$ and $(\bar{2}_z|\underline{\tau})'$

Operation $\bar{2}_z$	Operation $\bar{2}_z'$	$\underline{F}[2\pi(l\underline{a}^*+m\underline{b}^*)]$
$\underline{\tau} = \frac{1}{2}\underline{a}, \frac{1}{2}(\underline{a}+\underline{c})$, l even $= \frac{1}{2}\underline{b}, \frac{1}{2}(\underline{b}+\underline{c})$, m even $= 0$, all values of l, m $= \frac{1}{2}(\underline{a}+\underline{b}), \frac{1}{2}(\underline{a}+\underline{b}+\underline{c})$, (l+m) even	$\underline{\tau} = \frac{1}{2}\underline{a}, \frac{1}{2}(\underline{a}+\underline{c})$, l odd $= \frac{1}{2}\underline{b}, \frac{1}{2}(\underline{b}+\underline{c})$, m odd $= \frac{1}{2}(\underline{a}+\underline{b}), \frac{1}{2}(\underline{a}+\underline{b}+\underline{c})$, (l+m) odd $= \frac{1}{4}(\underline{c}\pm\underline{a})$, l even $= \frac{1}{4}(\underline{b}\pm\underline{c})$, m even $= \frac{1}{4}(\underline{a}\pm\underline{b}), \frac{1}{4}(\underline{a}\pm\underline{b}\pm\underline{c})$, (l±m) even	$F_{\parallel}(\underline{k}) = (0,0)$, $F_{\perp}(\underline{k}) = \gamma$
$\underline{\tau} = \frac{1}{2}\underline{a}, \frac{1}{2}(\underline{a}+\underline{c})$, l odd $= \frac{1}{2}\underline{b}, \frac{1}{2}(\underline{b}+\underline{c})$, m odd $= \frac{1}{2}(\underline{a}+\underline{b}), \frac{1}{2}(\underline{a}+\underline{b}+\underline{c})$, (l+m) odd $= \frac{1}{4}(\underline{c}\pm\underline{a})$, l even $= \frac{1}{4}(\underline{b}\pm\underline{c})$, m even $= \frac{1}{4}(\underline{a}\pm\underline{b}), \frac{1}{4}(\underline{a}\pm\underline{b}\pm\underline{c})$, (l±m) even	$\underline{\tau} = \frac{1}{2}\underline{a}, \frac{1}{2}(\underline{a}+\underline{c})$, l even $= \frac{1}{2}\underline{b}, \frac{1}{2}(\underline{b}+\underline{c})$, m even $= \frac{1}{2}(\underline{a}+\underline{b}), \frac{1}{2}(\underline{a}+\underline{b}+\underline{c})$, (l+m) even $= 0$, all values of l, m	$F_{\parallel}(\underline{k}) = (\alpha,\beta)$, $F_{\perp}(\underline{k}) = 0$
$\underline{\tau} = \frac{1}{4}(\underline{c}\pm\underline{a})$, l odd $= \frac{1}{4}(\underline{b}\pm\underline{c})$, m odd $= \frac{1}{4}(\underline{a}\pm\underline{b}), \frac{1}{4}(\underline{a}\pm\underline{b}\pm\underline{c})$, (l±m) odd	$\underline{\tau} = \frac{1}{4}(\underline{c}\pm\underline{a})$, l odd $= \frac{1}{4}(\underline{b}\pm\underline{c})$, m odd $= \frac{1}{4}(\underline{a}\pm\underline{b}), \frac{1}{4}(\underline{a}\pm\underline{b}\pm\underline{c})$, (l±m) odd	$\underline{F}(\underline{k}) = 0$

Table XXI. Solutions $\underline{F}(\underline{k})$ of Equation (4.26) for the Operations $(3_z|\underline{\tau})$

Operation 3_z	$\underline{F}(2\pi n\underline{c}^*)$
$\underline{\tau}$ = 0, all values of n = $\underline{c}/3$, $2\underline{c}/3$, n = 3N, (N any integer)	$F_{\parallel}(\underline{k}) = \gamma$, $F_{\perp}(\underline{k}) = (0,0)$
$\underline{\tau}$ = $\underline{c}/3$, n = 3N+1 = $2\underline{c}/3$, n = 3N+2	$F_{\parallel}(\underline{k}) = 0$ $F_{\perp}(\underline{k}) = \beta[\frac{1}{2}(1+\sqrt{3}i),1]$
$\underline{\tau}$ = $\underline{c}/3$, n = 3N+2 = $2\underline{c}/3$, n = 3N+1	$F_{\parallel}(\underline{k}) = 0$ $F_{\perp}(\underline{k}) = \beta[\frac{1}{2}(1-\sqrt{3}i),1]$

Table XXII. Solutions $\underline{F}(\underline{k})$ of Equation (4.26) for the Operations $(4_z|\underline{\tau})$ and $(4_z|\underline{\tau})'$

Operation 4_z	Operation $4_z'$	$\underline{F}(2\pi n\underline{c}^*)$
$\underline{\tau} = 0$, all n $= \frac{1}{2}\underline{c}$, even n $= \frac{1}{4}\underline{c}, 3\underline{c}/4$, n = 4N, (N any integer)	$\underline{\tau} = \frac{1}{2}\underline{c}$, odd n $= \frac{1}{4}\underline{c}, 3\underline{c}/4$, n = 4N+2	$F_{\parallel}(\underline{k}) = \gamma$ $F_{\perp}(\underline{k}) = (0,0)$
$\underline{\tau} = \frac{1}{2}\underline{c}$, odd n $= \frac{1}{4}\underline{c}, 3\underline{c}/4$, n = 4N+2	$\underline{\tau} = 0$, all n $= \frac{1}{2}\underline{c}$, even n $= \frac{1}{4}\underline{c}, 3\underline{c}/4$, n = 4N	$\underline{F}(\underline{k}) = 0$
$\underline{\tau} = \frac{1}{4}\underline{c}$, n = 4N+1 $= 3\underline{c}/4$, n = 4N+3	$\underline{\tau} = \frac{1}{4}\underline{c}$, n = 4N+3 $= 3\underline{c}/4$, n = 4N+1	$F_{\parallel}(\underline{k}) = 0$ $F_{\perp}(\underline{k}) = \beta(i,1)$
$\underline{\tau} = \frac{1}{4}\underline{c}$, n = 4N+3 $= 3\underline{c}/4$, n = 4N+1	$\underline{\tau} = \frac{1}{4}\underline{c}$, n = 4N+1 $= 3\underline{c}/4$, n = 4N+3	$F_{\parallel}(\underline{k}) = 0$ $F_{\perp}(\underline{k}) = \alpha(1,i)$

Table XXIII. Solutions $\underline{F}(\underline{k})$ of Equation (4.26) for the Operations $(6_z|\underline{\tau})$ and $(6_z|\underline{\tau})'$

Operation 6_z	Operation $6_z'$	$\underline{F}(2\pi n\underline{c}^*)$
$\underline{\tau} = 0$, all n $= \frac{1}{2}\underline{c}$, even n $= \underline{c}/3,\ 2\underline{c}/3,\ n = 3N,$ (N any integer) $= \underline{c}/6,\ 5\underline{c}/6,\ n = 6N$	$\underline{\tau} = \frac{1}{2}\underline{c}$, odd n $= \underline{c}/6,\ 5\underline{c}/6,\ n = 3N+3$	$F_{\parallel}(\underline{k}) = \gamma$ $F_{\perp}(\underline{k}) = (0,0)$
$\underline{\tau} = \frac{1}{2}\underline{c}$, odd n $= \underline{c}/3,\ 2\underline{c}/3,\ n = 3N+1,$ $3N+2$ $= \underline{c}/6,\ 5\underline{c}/6,\ n = 6N+2,$ $6N+3,\ 6N+4$	$\underline{\tau} = 0$, all n $= \frac{1}{2}\underline{c}$, even n $= \underline{c}/3,\ 2\underline{c}/3,\ n = 3N$ $= \underline{c}/6,\ 5\underline{c}/6,\ n = 6N,$ $6N+1,\ 6N+5$	$\underline{F}(\underline{k}) = 0$
$\underline{\tau} = \underline{c}/6,\ n = 6N+5$ $= 5\underline{c}/6,\ n = 6N+1$	$\underline{\tau} = \underline{c}/3,\ n = 3N+1$ $= 2\underline{c}/3,\ n = 3N+2$ $= \underline{c}/6,\ n = 6N+2$ $= 5\underline{c}/6,\ n = 6N+4$	$F_{\parallel}(\underline{k}) = 0$ $F_{\perp}(\underline{k})$ $= \alpha[1, \frac{1}{2}(1+\sqrt{3}i)]$
$\underline{\tau} = \underline{c}/6,\ n = 6N+1$ $= 5\underline{c}/6,\ n = 6N+5$	$\underline{\tau} = \underline{c}/3,\ n = 3N+2$ $= 2\underline{c}/3,\ n = 3N+1$ $= \underline{c}/6,\ n = 6N+4$ $= 5\underline{c}/6,\ n = 6N+2$	$F_{\parallel}(\underline{k}) = 0$ $F_{\perp}(\underline{k})$ $= \alpha[1, \frac{1}{2}(1-\sqrt{3}i)]$

CHAPTER V

ILLUSTRATION OF THE CALCULATION OF THE FOURIER COMPONENTS OF THE INTERNAL FIELD

In this chapter we present all possible solutions of the neutron scattering amplitude equation (4.26) for the seven tetragonal magnetic space groups $P4_222$ through P_I4_222 introduced in Chapter III, and we give some examples of how these solutions were calculated.

Since the elements of the magnetic space groups under discussion consist only of rotations and antirotations followed by translations, one expects that the reciprocal vector which will be invariant in these magnetic space groups should lie along the axes of rotation and antirotation. In case of P_c4_222, P_C4_222, and P_I4_222, the reciprocal vector $\underline{k} = 2\pi(l\underline{a}^* + m\underline{b}^* + n\underline{c}^*)$ should further satisfy (4.27). The latter means that $\underline{k}$ must lie along the z-axis with n odd for P_c4_222, along the x and y-axes with l and m odd in case of P_C4_222, and along the x, y, and z-axes with l, m, and n odd in case of P_I4_222, taking the a, b, and c-axes, respectively, as the x, y, and z-axes. In Table XXIV are listed the reciprocal vectors $\underline{k}_i$ and the elements of the corresponding groups $\mathcal{G}_i(\phi|\underline{\tau})$ for which the $\underline{k}_i$ satisfy (4.26) and, if applicable, (4.27). The elements of the corresponding groups $\mathcal{G}_i(\theta)$ can be determined from Table V.

Table XXIV. Reciprocal Vectors $\underline{k}_i$ and the Elements of the Corresponding Groups $\mathcal{G}_i(\phi|\underline{\tau})$

Reciprocal vector $\underline{k}_i$	in component form	$P4_222$, $P4_2'22'$, $P4_2'2'2$, $P4_22'2'$	P_c4_222	P_C4_222	P_I4_222
$\underline{k}_1$	$2\pi(1,0,0)$	1, 5	---	1, 5, $1_C'$, $5_C'$, l odd	1, 5, $1_I'$, $5_I'$, l odd
$\underline{k}_2$	$2\pi(0,m,0)$	1, 6	---	1, 6, $1_C'$, $6_C'$, m odd	1, 6, $1_I'$, $6_I'$, m odd
$\underline{k}_3$	$2\pi(0,0,n)$	1, 2, 3, 4	1, 2, 3, 4, $1_c'$, $2_c'$, $3_c'$, $4_c'$, n odd	---	1, 2, 3, 4, $1_I'$, $2_I'$, $3_I'$, $4_I'$, n odd
$\underline{k}_4$	$2\pi(1,1,0)$	1, 7	---	---	---
$\underline{k}_5$	$2\pi(1,-1,0)$	1, 8	---	---	---

Thus we have available all quantities needed to solve the amplitude equation (4.26) for the seven magnetic space groups. Suppose, as an example, that we start with the reciprocal vector $\underline{k}_1 = 2\pi 1\underline{a}^*$ and the elements of the group $\mathcal{G}_1(\phi|\underline{\tau})$ which are given to be element 1 which is E, the identity, and element 5 which is 2_x, the two-fold rotation around the x-axis. These are the only two operations under which $\underline{k}_1$ is invariant for the group $P4_2'22'$. From Table VII one has that

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

and

$$2_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

and using ϕ = E, 2_x; θ = E, 2_x; $\underline{\tau}$ = 0, 0; and $\underline{k} = 2\pi 1\underline{a}^*$ in (4.26), one obtains

$$(E - E)\underline{F}(\underline{k}) \equiv 0 \tag{5.1}$$

and

$$(E - 2_x)\underline{F}(\underline{k}) \equiv 0\,. \tag{5.2}$$

The equation (5.1) allows all components of $\underline{F}(\underline{k})$ to be arbitrary.

However, (5.2) gives

$$\left[\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}-\begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}\right]\begin{pmatrix}F_x(2\pi l\underline{a}^*)\\F_y(2\pi l\underline{a}^*)\\F_z(2\pi l\underline{a}^*)\end{pmatrix}=\begin{pmatrix}0\\0\\0\end{pmatrix},$$

or

$$\begin{pmatrix}0&0&0\\0&2&0\\0&0&2\end{pmatrix}\begin{pmatrix}F_x\\F_y\\F_z\end{pmatrix}=\begin{pmatrix}0\\0\\0\end{pmatrix}. \tag{5.3}$$

The rank of the coefficient matrix

$$\begin{pmatrix}0&0&0\\0&2&0\\0&0&2\end{pmatrix}$$

is two, and thus there exists only one non-trivial solution of (5.3). It is found by multiplying out the matrix equation (5.3) which gives

$$0F_x = 0; \quad 2F_y = 0; \quad \text{and } 2F_z = 0. \tag{5.4}$$

This means that $F_x = \alpha$ or the parallel component of $\underline{F}(\underline{k})$, i.e., $F_{\parallel}(\underline{k})$, is arbitrary; and $F_y = F_z = 0$, or the perpendicular component of $\underline{F}(\underline{k})$, i.e., $F_{\perp}(\underline{k})$, is zero. Such a result will be designated by

$$\underline{F}(\underline{k}) = (\alpha,0,0). \tag{5.5}$$

As a more complicated example, consider $\underline{k}_3 = 2\pi n\underline{c}^*$ and the invariant group $\mathcal{G}_3(\phi|\underline{\tau})$ with elements 1 which is E, 2 which is 2_z, 3 which is $(4_z|\underline{\tau})$, and 4 which is $(4_z^{-1}|\underline{\tau})$, for the same magnetic space group $P4_2'22'$. The corresponding group $\mathcal{G}_3(\theta)$ consists of $\theta_1 = E$,

$\theta_2 = 2_z$, $\theta_3 = \bar{4}_z$, and $\theta_4 = \bar{4}_z^{-1}$ (where $\bar{4}_z = -4_z$ and $\bar{4}_z^{-1} = -4_z^{-1}$).
We substitute these values in (4.26) and thereby obtain the following equations:

$$(E - E)\cdot \underline{F}(\underline{k}) = 0, \tag{5.6}$$

$$(E - 2_z)\cdot \underline{F}(\underline{k}) = 0, \tag{5.7}$$

$$[E - \exp(-2\pi i n \underline{c}^* \cdot \tfrac{1}{2}\underline{c})\ \bar{4}_z]\cdot \underline{F}(\underline{k}) = 0, \tag{5.8}$$

and

$$[E - \exp(-2\pi i n \underline{c}^* \cdot \tfrac{1}{2}\underline{c})\ \bar{4}_z^{-1}]\cdot \underline{F}(\underline{k}) = 0. \tag{5.9}$$

More explicitly these equations read:

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \tag{5.6a}$$

$$\left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\right]\begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \tag{5.7a}$$

$$\left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \exp(-\pi i n)\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\right]\begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \tag{5.8a}$$

and

$$\left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \exp(-\pi i n)\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\right]\begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.9a}$$

The solutions thus depend on the value of n, and we first choose n to be even and obtain

$$0F_x = 0F_y = 0F_z = 0, \tag{5.6b}$$

$$2F_x = 2F_y = 0F_z = 0, \tag{5.7b}$$

$$(F_x - F_y) = (F_x + F_y) = 2F_z = 0, \tag{5.8b}$$

and

$$(F_x + F_y) = (-F_x + F_y) = 2F_z = 0. \tag{5.9b}$$

The only common solution for these four sets of equations is

$$\underline{F}(\underline{k}) = 0. \tag{5.10}$$

Thus, if n is even and $\underline{k} = 2\pi n \underline{c}^*$, then $\underline{F}(\underline{k}) = 0$.

Now we take n to be odd, and then we obtain:

$$0F_x = 0F_y = 0F_z = 0, \tag{5.6c}$$

$$2F_x = 2F_y = 0F_z = 0, \tag{5.7c}$$

$$(F_x + F_y) = (-F_x + F_y) = 0F_z = 0, \tag{5.8c}$$

and

$$(F_x - F_y) = (F_x + F_y) = 0F_z = 0. \tag{5.9c}$$

The common solution is thus $F_z = \gamma$ with γ arbitrary, and $F_x = F_y = 0$, i.e., $F_{\parallel}(\underline{k})$ is arbitrary and $F_{\perp}(\underline{k})$ is zero. Such a solution will be designated by

$$\underline{F}(\underline{k}) = (0,0,\gamma), \text{ n odd.} \tag{5.11}$$

In a similar manner, all the solutions of the scattering amplitude equation can be obtained for the seven Shubnikov groups and for the five types of reciprocal vectors, and the results are given in Table XXV. The first row of Table XXV gives the reciprocal vectors $\underline{k}_i$ and the subsequent rows give the solutions to (4.26) for our seven tetragonal groups.

Table XXV. Solutions for the Fourier Components $\underline{F}(\underline{k})$ of the Internal Magnetic Field

Group	$\underline{k} = 2\pi(n,0,0)$	$\underline{k} = 2\pi(0,n,0)$	$\underline{k} = 2\pi(0,0,n)$	$\underline{k} = 2\pi(n,n,0)$	$\underline{k} = 2\pi(-n,n,0)$
$P4_222$	$(\alpha,0,0)$	$(0,\beta,0)$	$(0,0,0)$ n odd, $(0,0,\gamma)$ n even	$(\alpha,\alpha,0)$	$(\alpha,-\alpha,0)$
$P4_2'22'$	$(\alpha,0,0)$	$(0,\beta,0)$	$(0,0,\gamma)$ n odd, $(0,0,0)$ n even	$\alpha(1,-1,0)$ $+\gamma(0,0,1)$	$\alpha(1,1,0)$ $+\gamma(0,0,1)$
$P4_2'2'2$	$\beta(0,1,0)$ $+\gamma(0,0,1)$	$\alpha(1,0,0)$ $+\gamma(0,0,1)$	$(0,0,\gamma)$ n odd, $(0,0,0)$ n even	$(\alpha,\alpha,0)$	$(\alpha,-\alpha,0)$
$P4_22'2'$	$\beta(0,1,0)$ $+\gamma(0,0,1)$	$\alpha(1,0,0)$ $+\gamma(0,0,1)$	$(0,0,0)$ n odd, $(0,0,\gamma)$ n even	$\alpha(1,-1,0)$ $+\gamma(0,0,1)$	$\alpha(1,1,0)$ $+\gamma(0,0,1)$
P_c4_222	---	---	$(0,0,0)$ n odd	---	---
P_C4_222	$(\alpha,0,0)$ n odd	$(0,\beta,0)$ n odd	---	---	---
P_I4_222	$(\alpha,0,0)$ n odd	$(0,\beta,0)$ n odd	$(0,0,0)$ n odd	---	---

CHAPTER VI

SUMMARY

Inclusion of time inversion as a possible symmetry operation for the study of crystallographic structure leads to interesting and significant generalizations of the ordinary crystallographic point and space groups. As a symmetry operation, time inversion may occur by itself or in combination with the spatial rotations, reflections, and translations. The resulting generalized point and space groups, the Heesch groups and the Shubnikov groups, respectively, are useful for the study of magnetically ordered crystallographic states.

We considered the time-averaged internal magnetic field of the ordered state to be a classical axial vector field. When the Shubnikov group of the magnetic state is given, it is possible to develop for all points of the unit cell the symmetry behavior of the internal field, as well as that of its Fourier components in reciprocal lattice space. The former is of most direct interest in nuclear magnetic resonance experiments, and the latter in elastic neutron scattering experiments.

In this dissertation the general theory for this problem is developed and discussed, and the procedure is illustrated through application to seven different Shubnikov groups all of which belong to the same chemical space group of the tetragonal system. The general theory is developed in sufficient detail to permit similar calculations to be made with ease for any of the 1651 possible Shubnikov groups.

If for a given chemical space group all possible Shubnikov groups are studied in this way, it will then be possible from the results of such a study to predict whether a unique assignment of the Shubnikov symmetry can be made from the available nmr or neutron diffraction data, or if not, what additional data one would have to attempt to produce to make the assignment unique.

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