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Representation Analysis of Magnetic Structures

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In the analysis of spin structures a 'natural' point of view looks for the set of symmetry operations which leave the magnetic structure invariant and has led to the development of magnetic or Shubnikov groups. A second point of view presented here simply asks for the transformation properties of a magnetic structure under the classical symmetry operations of the 230 conventional space groups and allows one to assign irreducible representations of the actual space group to all known magnetic structures. The superiority of representation theory over symmetry invariance under Shubnikov groups is already demonstrated by the fact proven here that the only invariant magnetic structures describable by magnetic groups belong to real one-dimensional representations of the 230 space groups. Representation theory on the other hand is richer because the number of representations is infinite, *i.e.* it can deal not only with magnetic structures belonging to one-dimensional real representations, but also with those belonging to one-dimensional complex and even to two-dimensional and three-dimensional representations associated with any **k** vector in or on the first Brillouin zone.

We generate from the transformation matrices of the spins a representation Γ of the space group which is reducible. We find the basis vectors of the irreducible representations contained in Γ.

The basis vectors are linear combinations of the spins and describe the structure. The method is first applied to the $\mathbf{k}=0$ case where magnetic and chemical cells are identical and then extended to the case where magnetic and chemical cells are different ($\mathbf{k}\neq 0$) with special emphasis on **k** vectors lying on the surface of the first Brillouin zone in non-symmorphic space groups. As a specific example we consider several methods of finding the two-dimensional irreducible representations and its basis vectors associated with $\mathbf{k}=\frac{1}{2}\,\mathbf{b}_2=[0\frac{1}{2}0]$ in space group *Pbnm* (D_{2h}^{16}).

We illustrate the physical context of representation theory by constructing an effective spin Hamiltonian H invariant under the crystallographic space group and under spin reversal. H is even in the spins and automatically invariant under the (isomorphous) magnetic group. We show by the example of CoO that the invariants in H, formed with the help of basis vectors, give information on the nature of spin coupling as for instance isotropic (Heisenberg–Néel) coupling, vectorial (Dzialoshinski–Moriya) and anisotropic symmetric couplings.

Magnetic structures, cited in the text to show the implications of the representation theory of space groups are $ErFeO_3$, $ErCrO_3$, $TbFeO_3$, $TbCrO_3$, $DyCrO_3$, $YFeO_3$, V_2CaO_4, β-$CoSO_4$, Er_2O_3, CoO and RMn_2O_5 (R = Bi, Y or rare earth).

Representation theory of *magnetic* groups must be considered when the Hamiltonian contains terms which are odd in the spins. The case may occur when the magnetic energy is coupled with other forms of energy as for instance in the field of magneto-electricity. Here again representation theory correctly predicts the couplings between magnetic and electric polarizations as shown on $LiCoPO_4$ and (previously) on $FeGaO_3$.

1. Introduction

We develop here a method characterized as 'macroscopic' which is able to predict all possible magnetic couplings in the frame of the known 230 crystallographic space groups.

When we state that 'a crystal has a space group' we evoke the concept of invariance of atomic positions under the symmetry operations of the space group. In the same way one was naturally led to associate with a magnetic structure new sets of symmetry elements, the so-called magnetic or Shubnikov groups, which *should* describe the invariance of magnetic structures. We say 'should' because today there are many instances where known magnetic structures are not invariant under any Shubnikov groups.

In opposition to the (widely accepted) view of *symmetry invariance* under the Shubnikov groups we develop in § 2 a new point of view which investigates the *transformation properties of magnetic structures* under the operations of the 'trivial' 230 space groups. Moreover this new point of view will prove to be more general. We show indeed that all the magnetic groups can be generated from the knowledge of the ensemble of one-dimensional real representations of the 230 space groups; in other words the 'magnetic' groups can only describe those magnetic structures which belong to one-dimensional representations, having characters $+1$ or -1, of the classical space groups.

The general theory is outlined in § 3. It uses representation theory, the main problem being to find *irreducible representations* and the *basis functions* which belong to them and which are *able to describe the magnetic structures*, their transformation properties and even the magnetic couplings.

Although this sounds very abstract, the application is easy and is illustrated in § 4 by the simple case where chemical and magnetic cells are identical. Such structures are associated with a wave vector $\mathbf{k}=0$. Specific examples will show the advantage of the method and some of the difficulties already faced by Shubnikov groups with these structures.

In § 5 we extend the application of the method to any $\mathbf{k}$ vector in the first Brillouin zone (*i.e.* to any magnetic, even non-commensurable cell) with special emphasis on $\mathbf{k}$ vectors lying at the surface of the Brillouin zone in non-symmorphic space groups. Two methods are used: an algebraic one due to Olbrychski which finds the irreducible representations, and a more geometrical one which, starting from the transformation matrices, provides the irreducible representations *and* the basis functions. As an illustration of two-dimensional irreducible representations we consider more fully the wave vector $\mathbf{k}=[0\frac{1}{2}0]$ in space group *Pbnm*. We also indicate examples of structures ($TbCrO_3$, $DyCrO_3$, V_2CaO_4, RMn_2O_5) belonging to $\mathbf{k}$ vectors on the Brillouin zone and solved by the methods of § 5.

We examine in § 4 the physical context of representation theory. A basic role is played by the 'effective macroscopic spin Hamiltonian' which gives rise to the magnetic structure. We study the implications of the postulate that the 'effective spin Hamiltonian' is an even function of the spins and find that the time reversal operator is not needed for the analysis of magnetic structures. Conclusions are reached, concerning the coupling and decoupling of magnetic atoms in the approximation of a Hamiltonian of order two. The influence of higher order terms is also examined. From the knowledge of the basis vectors and the known magnetic structure one can not only construct a spin Hamiltonian, but also may infer the existence of the various *microscopic couplings* known as Heisenberg–Néel coupling, Dzialoshinski–Moriya coupling, crystal-field and dipolar or tensor coupling of spins. As a specific example we have chosen the magnetic structure of CoO as proposed by van Laar (1965).

As long as the time reversal operator R is defined by $R^2=1$, magnetic groups are strictly isomorphous with the classical groups and thus have the same irreducible representations. From §§ 1 to 6 the reader might conclude that magnetic groups may be disregarded. This is however untrue. Magnetic group theory must be considered when in the energy expression magnetic and non-magnetic terms are coupled in such a way that the spins or magnetic moments occur in odd powers. As a particular case we investigate in § 7 magnetoelectricity which can be described as originating from a coupling, bilinear in a magnetic and an electric polarization. Here again group theory is useful and predicts in all known instances the spatial relation between electric and magnetic polarization.

2. Symmetry invariance and representation theory

At first sight it seems natural to consider as far as the symmetry of a spin configuration is concerned all those symmetry operations which leave the spin structure invariant. Historically one has introduced new (primed) symmetry operations C_k', the so-called 'antielements' which are the product of the conventional (unprimed) symmetry elements C_k with the time- (or current-) reversal operator R of order two.

$$C_k'=C_kR=RC_k\,;\;\; R^2=1\,. \tag{2-1}$$

These new symmetry elements considerably enlarge the number of possible groups. The 32 crystalline classes grow to 90 classes and the 230 space groups increase to 1651 'magnetic groups'. Good accounts may be found in the following references: Belov, Neronova & Smirnova (1957), Donnay, Corliss, Donnay, Elliott & Hastings (1958), Opechowski & Guccione (1965).

From the point of view of representation theory it is equivalent to say that 'a crystal structure has a space group G' or that it 'transforms according to the identity representation of space group G', *i.e.* each symmetry operation of G may be represented by $+1$ and thus leaves the crystal invariant. In the same way, when a magnetic structure may be described by a Shubnikov group G' it belongs to the identity representation of that group G'. Although such a statement might appear as obvious as a 'vérité de La Palice'* it is of a very essential nature because it contains all the shortcomings of the use of magnetic groups in the analysis of magnetic structures.

Indeed the Shubnikov groups already meet with difficulties in the case of helical structures where 'colour' groups of order infinity would be needed.

Other difficulties arise as we shall see in § 4 for canted spin structures when different spin components may belong to different representations and also when spin structures belong to two- or three-dimensional irreducible representations.

An entirely different point of view asks the following question: How does a given spin configuration transform under 'classical' symmetry operations C_k of the space group G in which the crystal is embedded? It is then always possible to characterize the transformation properties of a spin structure by indicating the irreducible representations of the space group G according to which the spin components transform. There remains naturally the problem of how complete such a description might be. It is easy to show that we get *at least* from representation theory the same information which the magnetic groups are supposed to give.

Abstractly this may be stated as follows: 'The number of magnetic groups is equal to the number of one-dimensional space-group representations which are *distinct in the abstract sense* and have real characters $+1$

* La Palice (1470–1525) is synonymous with evident statements. He was reported to have been 'still living a quarter of an hour before his death'.

or $-1'$. Two representations are said to be 'distinct in the abstract sense' if they cannot be transformed into each other by another setting (changes of axes and origins).

Magnetic classes

As a first example, consider the relation between the representations of the 32 crystalline classes or point groups and the so-called 90 magnetic classes.

Tables 1, 2 and 3 reproduce the well known character tables of the representations of the point groups 222 (D_2), $2/m$ (C_{2h}) and 23 (T) respectively, the first line in each table being the identity representation. The second line in Table 1 contains the representation labelled B_1 in which the numbers $1, -1, -1, 1$ represent the symmetry operations E, 2_x, 2_y and 2_z respectively. We want to establish a one-to-one correspondence with a magnetic class, *i.e.* a correspondence of B_1 with the identity representation of the magnetic point group. The recipe is simple: 2_x and 2_y have the characters -1 in B_1 so that in order to get the character $+1$ we have only to replace 2_x and 2_y by the antielements $2'_x$ and $2'_y$. Thus B_1 is associated with the magnetic class $2'2'2$.

Table 1. *Point group D_2*

Here A, B_1, B_2, B_3 are used for 222 because any one of the twofold axes can be considered the principal one.

222	E	2_x	2_y	2_z
A	1	1	1	1
B_1	1	-1	-1	1
B_2	1	-1	1	-1
B_3	1	1	-1	-1

Table 2. *Point group C_{2h}*

$2/m$	E	2_z	m_z	$\bar{1}$
A_g	1	1	1	1
B_g	1	-1	-1	1
A_u	1	1	-1	-1
B_u	1	-1	1	-1

Table 3. *Point group T*

23	E	2_z	3	3^2
A	1	1	1	1
E	1	1	ω	ω^2
	1	1	ω^2	ω
T	3	-1	0	0

where $\omega = \exp(2\pi i/3)$.

With each one-dimensional real representation of a space (point) group we can associate a magnetic space (point) group by keeping the same elements when the character is $+1$ and changing them to antielements when the character is -1.

The B_2 and B_3 representations of Table 1 are not distinct from B_1 in the abstract sense because the three can transform into each other by a simple interchange of axes, or expressed otherwise, B_2 and B_3 would give rise to the magnetic classes $2'22'$ and $22'2'$ which are just other settings of $2'2'2$.

In Table 2 of $2/m$ we encounter formally the same four representations as in 222, but here they are all 'distinct' in the abstract sense and will give rise to four distinct magnetic classes

$$A_g \to 2/m;\ B_g \to 2'/m';\ A_u \to 2/m';\ B_u \to 2'/m\ . \quad (2\text{-}2)$$

Finally in the cubic (tetrahedral) point group 23, there is only one one-dimensional real representation, the trivial identity representation $A_g \to 23$.

By counting in the same way the number of *distinct* one-dimensional representations in the 32 crystal classes one arrives exactly at the 90 magnetic classes: the original 32 classes plus the additional 58 classes [see table in Hammermesh (1962)].

Magnetic space groups

As a first example for space groups, consider *Pbam* (D_{2h}^9) where we choose as generators two screw axes $2_{1,x}$ in $x\frac{1}{4}0$ and $2_{1,y}$ in $\frac{1}{4}y0$ and a centre of symmetry $\bar{1}$ in 000. There are 8 one-dimensional representations, associated with the wave-vector $\mathbf{k}=0$, and listed in Table 4 with just the characters of the generating elements in columns 2, 3, 4. In columns 5, 6, 7 are listed the elements and antielements which correspond respectively to characters $+1$ and -1 on the same line. Finally the last column summarizes the magnetic groups with the use of the following rules:

$$2_{1,x}\,.\,\bar{1}=b;\ 2_{1,y}\,.\,\bar{1}=a;\ 2_{1,x}\,.\,2_{1,y}\,.\,\bar{1}=m=2'_{1,x}\,.\,2'_{1,y}\,.\,\bar{1}$$
$$2'_{1,x}\,.\,\bar{1}=2_{1,x}\,.\,\bar{1}'=b';\ 2'_{1,y}\,.\,\bar{1}=2_{1,y}\,.\,\bar{1}'=a';$$
$$2'_{1,x}\,.\,2_{1,y}\,.\,\bar{1}=2_{1,x}\,.\,2'_{1,y}\,.\,\bar{1}=2_{1,x}\,.\,2_{1,y}\,.\,\bar{1}'=m'\ . \quad (2\text{-}3)$$

Table 4. *Representations and magnetic groups in Pbam* ($\mathbf{k}=0$)

Representations	Characters of the generators			Elements and antielements			Magnetic groups
	2_{1x}	2_{1y}	$\bar{1}$				
Γ_1	1	1	1	2_x	2_y	$\bar{1}$	*Pbam*
Γ_2	1	-1	1	2_x	$2_y'$	$\bar{1}$	*Pba'm'*
Γ_3	-1	1	1	$2_x'$	2_y	$\bar{1}$	*Pb'am'*
Γ_4	-1	-1	1	$2_x'$	$2_y'$	$\bar{1}$	*Pb'a'm*
Γ_5	1	1	-1	2_x	2_y	$\bar{1}'$	*Pb'a'm'*
Γ_6	1	-1	-1	2_x	$2_y'$	$\bar{1}'$	*Pb'am*
Γ_7	-1	1	-1	$2_x'$	2_y	$\bar{1}'$	*Pba'm*
Γ_8	-1	-1	-1	$2_x'$	$2_y'$	$\bar{1}'$	*Pbam'*

The eight magnetic groups listed in Table 4 are not all distinct: *Pba'm'* and *Pb'am'* can be transformed into each other by an interchange of the x and y axes (as well as the corresponding representations Γ_2 and Γ_3). This is also true for *Pb'am* and *Pba'm* so that we have constructed six abstract magnetic groups (including *Pbam*). To exhaust the space group *Pbam* we must first determine which $\mathbf{k}$ vectors in the first Brillouin zone have the full point symmetry G_0 and finally among the corresponding group representations we must consider those which are real and one-dimensional. In orthorhombic groups the $\mathbf{k}$ vectors to be considered are $\frac{1}{2}\mathbf{b}_1$, $\frac{1}{2}\mathbf{b}_2$, $\frac{1}{2}\mathbf{b}_3$, $\frac{1}{2}(\mathbf{b}_2+\mathbf{b}_3)$, $\frac{1}{2}(\mathbf{b}_3+\mathbf{b}_1)$, $\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)$ and $\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2+\mathbf{b}_3)$ where the $\mathbf{b}_j$ ($j=1,2,3$) are the reciprocal vectors of the lattice vectors $\mathbf{a}_j$ in direct space. It can be shown (see § 5 and Appendix 1) that only for $\mathbf{k}=\frac{1}{2}\mathbf{b}_3$ are there 8 one-dimensional real representations, identical with the preceding ones. (The representations are still one-dimensional for $\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)$ and for $\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2+\mathbf{b}_3)$ but complex and two-dimensional for all the other vectors).

The meaning of the propagation vector $\mathbf{k}=\frac{1}{2}\mathbf{b}_3$ is that the phase factor $\exp 2\pi i\mathbf{k}\,.\,\mathbf{t}$ associated with the translation $\mathbf{t}$ becomes -1 for $\mathbf{t}=\mathbf{a}_3$, *i.e.* the magnetic cell is doubled in the z direction or $\mathbf{a}_3=\mathbf{c}'$ is an 'antitranslation' accompanied by spin reversal. Here too some of the 8 magnetic groups obtained can be transformed into each other by changes of origin or different settings, and one is finally left with 3 different magnetic groups $P_{2c}bam$, $P_{2c}b'am$ and $P_{2c}b'a'm$ where $2c$ denotes the new periodicity along the $\mathbf{c}$ direction.

Finally we have associated with *Pbam* a family of 9 magnetic groups (including *Pbam*).

As a second example more fully studied in §§ 4 and 5 we consider the very frequently encountered space group *Pnma* (D_{2h}^{16}) or in another setting, *Pbnm*. Here one finds by the same procedure 8 different magnetic groups associated with the vector $\mathbf{k}=0$ (*cf.* Table 5 and 6) and no others. Those associated with the aforementioned $\mathbf{k}$ vectors are all two-dimensional with the exception of $\mathbf{k}=\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)$ where the representation is one-dimensional but complex.

Table 5. *Character table for Pbnm* ($\mathbf{k}=0$) (*and point group mmm* D_{2h})

	e	2_x	2_y	2_z	$\bar{1}$	$2_x\bar{1}$	$2_y\bar{1}$	$2_z\bar{1}$
$\Gamma_1=\Gamma_{1g}$	1	1	1	1	1	1	1	1
$\Gamma_2=\Gamma_{2g}$	1	1	-1	-1	1	1	-1	-1
$\Gamma_3=\Gamma_{3g}$	1	-1	1	-1	1	-1	1	-1
$\Gamma_4=\Gamma_{4g}$	1	-1	-1	1	1	-1	-1	1
$\Gamma_5=\Gamma_{1u}$	1	1	1	1	-1	-1	-1	-1
$\Gamma_6=\Gamma_{2u}$	1	1	-1	-1	-1	-1	1	1
$\Gamma_7=\Gamma_{3u}$	1	-1	1	-1	-1	1	-1	1
$\Gamma_8=\Gamma_{4u}$	1	-1	-1	1	-1	1	1	-1

The reader may convince himself that we have found exactly the same magnetic groups associated with *Pbam* and *Pbnm* as other authors have found by very different procedures.

Finally we have shown that one may associate a magnetic group with each one-dimensional representation of characters ± 1 of a classical space group.

Conversely, starting from a magnetic space group, we get a one-dimensional representation of the isomorphous space group by putting characters of elements equal to $+1$ and those of antielements equal to -1.

We might summarize our discussion by saying that the 'invariant magnetic structures' described by magnetic groups correspond to real one-dimensional representations of the 230 space groups. It is from now on evident that representation theory is richer because it can deal not only with magnetic structures belonging to one-dimensional real representations of space groups (and invariant under magnetic groups) but also with those which belong to one-dimensional complex representations, and even to two-dimensional and three-dimensional representations.

3. General theory

Let C_g be a symmetry operation of a crystallographic space group G. Operate with C_g on a spin component $S_{i\alpha}=S_j$. Here α stands for x,y,z and i numbers the symmetry-equivalent points ($i=1,\ldots,n$) so that the index j varies from 1 to $3n$. The spin vectors are considered as axial vectors. We write then

$$C_g S_j = \sum_k D(C_g)_{kj}\,.\,S_k\,. \tag{3-1}$$

Here the matrix $D(C_g)$ is the transpose* of the transformation matrix of the spins (see examples in §§ 4 and 5). The matrices $D(C_g)$ form a representation Γ of the space group G. Γ of dimension $3n$ is generally reducible.

Our first step will be the construction of the transformation matrices and of their transposes. The second step will be the reduction of Γ which is synonymous with finding out the irreducible representations and its base vectors. If character tables of the irreducible representations $\Gamma^{(\nu)}$ of G are available it is easy to recognize from the well known orthogonality relations between characters (3-2) how many times $a^{(\nu)}$ the representation $\Gamma^{(\nu)}$ is contained in Γ. Here the $\chi^{\Gamma}(C_g)$ are the traces of the transformation matrices.

If the irreducible representations $\Gamma^{(\nu)}$ of G are explicitly known the techniques of projection operators

* For the reason for taking not the transformation matrices themselves but their transposes, see Heine (1960).

Table 6. *Transformation properties in space group Pbnm* (*cf. Table* 12)

Representation	Generators $2_{1,x}$	$2_{1,y}$	$\bar{1}$	Transition element in 4(a) or 4(b) x	y	z	Rare earth in 4(c) x	y	z	Magnetic group	
$\Gamma_1=\Gamma_{1g}$	+	+	+	A	G	C	.	.	C	*Pbnm* or	*Pnma*
$\Gamma_2=\Gamma_{2g}$	+	−	+	F	C	G	F	C	.	*Pbn'm'*	*Pn'm'a*
$\Gamma_3=\Gamma_{3g}$	−	+	+	C	F	A	C	F	.	*Pb'nm'*	*Pnm'a'*
$\Gamma_4=\Gamma_{4g}$	−	−	+	G	A	F	.	.	F	*Pb'n'm*	*Pn'ma'*
$\Gamma_5=\Gamma_{1u}$	+	+	−	.	.	.	G	A	.	*Pb'n'm'*	*Pn'm'a'*
$\Gamma_6=\Gamma_{2u}$	+	−	−	.	.	.	.	.	A	*Pb'nm*	*Pnma'*
$\Gamma_7=\Gamma_{3u}$	−	+	−	.	.	.	.	.	G	*Pbn'm*	*Pn'ma*
$\Gamma_8=\Gamma_{4u}$	−	−	−	.	.	.	A	G	.	*Pbnm'*	*Pnm'a*

(3-3) applied to a spin component or a suitable linear combination of spin components Ψ will 'project out' those linear combinations Ψ_{ij} which form the basis of irreducible representations.

$$a^{(\nu)}=g^{-1}\sum_{C_g}\chi^{\Gamma}(C_g)\chi^{(\nu)*}(C_g) \qquad (3\text{-}2)$$

$$\Psi_{ij}^{(\nu)}=\sum_{C_g}D_{ij}^{(\nu)}(C_g)\,.\,C_g\Psi\,. \qquad (3\text{-}3)$$

Here the summations are over all the g symmetry operations of the group. $D^{(\nu)}(C_g)$ is the matrix representative of C_g in the representation $\Gamma^{(\nu)}$ and $D_{ij}^{(\nu)}(C_g)$ is a matrix element. It is often sufficient to consider successively the spin components S_{1x}, S_{1y} and S_{1z} for Ψ in order to find a convenient set of Ψ_{ij} which are 'partners of vectors belonging to the representation $\Gamma^{(\nu)}$'.

If the representations $\Gamma^{(\nu)}$ are unknown, they may be constructed for instance by the algebraic method of Olbrychski (1963), and combined with the transformation properties they will yield the basis functions with the use of (3-3).

It is also possible to reduce directly the matrices $D(C_g)$ of Γ and to find simultaneously the basic vectors and the irreducible representations.

All these methods, briefly indicated here, will be examplified in the next two sections.

Once the basis of irreducible representations is known, it is easy to construct bilinear combinations of the base vectors which are invariants and represent the magnetic couplings allowed in the group G (§ 6).

4. Representations and base functions for $\mathbf{k}=0$

We consider first the case where magnetic and chemical cells are identical. The wave vector associated with the magnetic structure is $\mathbf{k}=0$ and has the full point group symmetry G_0 (G_0 contains all the rotational or dyadic parts of G but without the translational components). Our first example will be the centrosymmetric and orthorhombic space group *Pbnm* (D_{2h}^{16}). The underlying point group $G_0=D_{2h}$ has the 8 symmetry elements e, 2_x, 2_y, $2_z=2_x2_y$, $\bar{1}$, $\bar{1}\cdot 2_x$, $\bar{1}\cdot 2_y$ and $2_z\cdot\bar{1}$ which are all

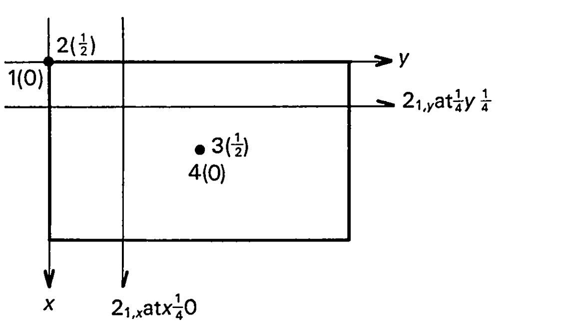

Fig. 1. Point transformation of the 4(*a*) positions in *Pbnm*, $\mathbf{k}=0$. $2_{1,x}$ turns 1 to 4, 2 to 3 *etc.*; $2_{1,y}$ turns 1 to 3, 2 to 4 *etc.* The number in parenthesis is the z coordinate.

binary and commute. The 8 one-dimensional representations of D_{2h} are listed in Table 5.

As generators of the group *Pbnm* one may take of course the Hermann–Mauguin symbols b,n,m themselves. Instead it is easier to consider as generators the two screw axes, $2_{1,x}$ at $x\frac{1}{4}0$ and $2_{1,y}$ at $\frac{1}{4}y\frac{1}{4}$ and the symmetry centre $\bar{1}$ at 000. Let us place spins $\mathbf{S}_j$ ($j=1,2,3,4$) into the fourfold sites 4(*a*) 000 (1); $00\frac{1}{2}$ (2); $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (3); $\frac{1}{2}\frac{1}{2}0$ (4). These 4 points are (equivalent) centres of symmetry.

The drawing of Fig. 1 allows us to write the following equations of transformation for the spin components of spin $\mathbf{S}_1$.

$$\begin{aligned}
&2_{1,x}S_{1x}=S_{4x};\ 2_{1,y}S_{1x}=-S_{3x};\ 2_{1,z}S_{1x}=-S_{2x}\\
&2_{1,x}S_{1y}=-S_{4y};\ 2_{1,y}S_{1y}=S_{3y};\ 2_{1,z}S_{1y}=-S_{2y}\\
&2_{1,x}S_{1z}=-S_{4z};\ 2_{1,y}S_{1z}=-S_{3z};\ 2_{1,z}S_{1z}=S_{2z}
\end{aligned} \qquad (4\text{-}1)$$

The operation $\bar{1}$ does not change any spin vector, which means that only the representations Γ_{jg} ($j=1,2,3,4$) of Table 6 are involved in the above mentioned 4-point problem (the indices g and u stand for 'gerade' = even and 'ungerade' = odd).

We are now prepared to apply the projection operator relation (3-3) to, say, $\Psi=S_{1x}$. All the representations being one-dimensional we drop the indices ij and obtain

$$\Psi_x^{(\nu)}=\chi^{(\nu)}(e)S_{1x}+\chi^{(\nu)}(2_x)2_xS_{1x}+\chi^{(\nu)}(2_y)2_yS_{1x}+\chi^{(\nu)}(2_z)2_zS_{1x}\,. \qquad (4\text{-}2)$$

$\Psi_x^{(\nu)}$ will be a base vector which transforms according to $\Gamma^{(\nu)}$.

We obtain in this way the vectors:

$$\begin{aligned}
&A_x=S_{1x}-S_{2x}-S_{3x}+S_{4x} \text{ belonging to } \Gamma_{1g}\\
&F_x=S_{1x}+S_{2x}+S_{3x}+S_{4x} \qquad \Gamma_{2g}\\
&C_x=S_{1x}+S_{2x}-S_{3x}-S_{4x} \qquad \Gamma_{3g}\\
&G_x=S_{1x}-S_{2x}+S_{3x}-S_{4x} \qquad \Gamma_{4g}\,.
\end{aligned} \qquad (4\text{-}3)$$

What is their physical meaning? A vector like F_x reaches a maximum value for $S_{1x}=S_{2x}=S_{3x}=S_{4x}$ and is zero for any antiferromagnetic sign combination. It characterizes a ferromagnetic $++++$ configuration. In the same way the $\mathbf{G}$ vector is maximized by the spin arrangement $\mathbf{S}_1=-\mathbf{S}_2=\mathbf{S}_3=-\mathbf{S}_4$ and is zero for every other antiferromagnetic or ferromagnetic sign combination. Thus it characterizes the $\mathbf{G}$ mode or a $+-+-$ spin configuration. In the same way the $\mathbf{A}$ and $\mathbf{C}$ vectors characterize respectively $+--+$ and $++--$ configurations.

The reader may complete the first part of Table 6 for the y and z components of the base vectors. Note that no 'ferromagnetic' component belongs to the identity representation.

It is easily checked that the same vector components are obtained with spins placed in the four equivalent symmetry centres in 4(*b*)

$$\tfrac{1}{2}00\ (1);\ \tfrac{1}{2}0\tfrac{1}{2}\ (2);\ 0\tfrac{1}{2}\tfrac{1}{2}\ (3);\ 0\tfrac{1}{2}0\ (4)\,.$$

The linear spin combinations $\mathbf{F},\mathbf{G},\mathbf{C},\mathbf{A}$ could have been guessed intuitively. The reader should verify that their components effectively belong to the indicated representations. For instance with the help of (4-1) and Fig. 1 one finds

$$2_{1,x}G_x = -G_x;\ 2_{1,y}G_x = -G_x;\ \bar{1}G_x = G_x\,, \tag{4-4}$$

so that, from the characters $-1, -1, +1$ of the respective generators $2_{1,x}$, $2_{1,y}$ and $\bar{1}$, G_x belongs to Γ_{4g} according to Table 5.

As a second example we consider the positions 4(c) in

$xy\frac{1}{4}$ (1); $\bar{x}\bar{y}\frac{\bar{1}}{4}$ (2); $\frac{1}{2}+x, \frac{1}{2}-y, \frac{\bar{1}}{4}$ (3); $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}$ (4).

The transformation properties for spin $\mathbf{S}_1$ are given by:

$$\begin{aligned} &2_{1,x}S_{1x} = S_{3x};\ 2_{1,y}S_{1y} = S_{4y};\ 2_{1,z}S_{1z} = S_{2z};\\ &\bar{1}\mathbf{S}_1 = \mathbf{S}_2;\ 2_{1,x}\,.\,\bar{1}S_{1x} = S_{4x};\ 2_{1,y}\,.\,\bar{1}S_{1y} = S_{3y};\\ &2_{1,z}\,.\,\bar{1}S_{1z} = S_{1z}\,, \end{aligned} \tag{4-5}$$

and obvious relations for the missing components. Here the $\bar{1}$ operation transforms $\mathbf{S}_1$ into $\mathbf{S}_2$ so that the Γ_{ju} representations will be relevant. Application of relation (3-3) to S_{1x} and S_{1y} in the representation $\Gamma_7 = \Gamma_{3u}$ yields

$$\begin{aligned} \Psi_x^{(\Gamma_7)} = {} & S_{1x} - S_{3x} + (-S_{4x})\\ & - (-S_{2x}) - S_{2x} + S_{4x} - (-S_{3x}) + (-S_{1x}) = 0 \end{aligned} \tag{4-6}$$

and similarly $\Psi_y^{(\Gamma_7)} = 0\,.$

This indicates that there is no x,y vector transforming according to Γ_7. However for the z component we get

$$\begin{aligned} \Psi_z^{(\Gamma_7)} = {} & S_{1z} - (-S_{3z}) + (-S_{4z}) - (-S_{2z}) - (S_{2z}) + (-S_{4z})\\ & + S_{1z} = 2(S_1 - S_2 + S_3 - S_4)_z = 2G_z\,, \end{aligned} \tag{4-7}$$

so that 'G_z belongs to Γ_7'. In the same way one constructs the whole of Table 6.

Transformation matrices

Finally let us show how to use the transformation matrices of the spin vectors. Table 7 summarizes the transformation properties of the points 4(c) numbered 1,2,3,4. The parenthesis following these numbers indicates the lattice translations (see also Fig. 2) which we disregard for the moment. We write the transformation properties not only for the spin S_1 but for all the spins. For instance

$$\begin{aligned} &2_{1,x}S_{1x} = S_{3x};\ 2_{1,x}S_{2x} = S_{4x};\\ &\qquad 2_{1,x}S_{3x} = S_{1x};\ 2_{1,x}S_{4x} = S_{2x} \end{aligned} \tag{4-8}$$

and similar equations for the y and z components. Relation (4-8) may be written in the matrix-form

$$\alpha\begin{bmatrix} S_{1x}\\ S_{2x}\\ S_{3x}\\ S_{4x}\end{bmatrix} = \begin{bmatrix} S_{3x}\\ S_{4x}\\ S_{1x}\\ S_{2x}\end{bmatrix} \quad \text{with} \quad \alpha = \begin{bmatrix} \cdot & \cdot & 1 & \cdot\\ \cdot & \cdot & \cdot & 1\\ 1 & \cdot & \cdot & \cdot\\ \cdot & 1 & \cdot & \cdot \end{bmatrix}, \tag{4-9}$$

where dots are written for zeros.

The complete transformation matrix $(2_{1,x})$ of order 12 may be written

$$(2_{1,x}) = \begin{array}{c} \begin{array}{ccc} x & y & z \end{array}\\ \begin{bmatrix} \alpha & \cdot & \cdot\\ \cdot & -\alpha & \cdot\\ \cdot & \cdot & -\alpha \end{bmatrix} \end{array}. \tag{4-10}$$

In the same way one obtains

$$(2_{1,y}) = \begin{array}{c} \begin{array}{ccc} x & y & z \end{array}\\ \begin{bmatrix} -\beta & \cdot & \cdot\\ \cdot & \beta & \cdot\\ \cdot & \cdot & -\beta \end{bmatrix} \end{array} \text{ with } \beta = \begin{bmatrix} \cdot & \cdot & \cdot & 1\\ \cdot & \cdot & 1 & \cdot\\ \cdot & 1 & \cdot & \cdot\\ 1 & \cdot & \cdot & \cdot \end{bmatrix} \tag{4-11}$$

and

$$(\bar{1}) = \begin{bmatrix} \gamma & \cdot & \cdot\\ \cdot & \gamma & \cdot\\ \cdot & \cdot & \gamma \end{bmatrix} \quad \text{with} \quad \gamma = \begin{bmatrix} \cdot & 1 & \cdot & \cdot\\ 1 & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & 1\\ \cdot & \cdot & 1 & \cdot \end{bmatrix}. \tag{4-12}$$

One constructs the eight transformation matrices by appropriate multiplications of the 'generating' matrices $(2_{1,x})$, $(2_{1,y})$ and $(\bar{1})$.

For instance

$$(m) = (2_{1,z}\,.\,\bar{1}) = (2_{1,x})(2_{1,y})(\bar{1}) = \begin{bmatrix} -\delta & \cdot & \cdot\\ \cdot & -\delta & \cdot\\ \cdot & \cdot & \delta \end{bmatrix}$$

with

$$\delta = \alpha\beta\gamma = \begin{bmatrix} 1 & \cdot & \cdot & \cdot\\ \cdot & 1 & \cdot & \cdot\\ \cdot & \cdot & 1 & \cdot\\ \cdot & \cdot & \cdot & 1 \end{bmatrix}. \tag{4-13}$$

The traces of these eight matrices are zero except for

$$\chi(e) = 12 \quad \text{and} \quad \chi(2_z\,.\,\bar{1}) = -4 \tag{4-14}$$

Table 7. *Point transformation in Pbnm. Sites* 4(c)

$xy\frac{1}{4}$ (1); $\bar{x}\bar{y}\frac{\bar{1}}{4}$ (2); $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{\bar{1}}{4}$ (3); $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{4}$ (4), $2_{1,x}$ at x, $\frac{1}{4}$, 0; $2_{1,y}$ at $\frac{1}{4}$, y, $\frac{1}{4}$; $\bar{1}$ at 0, 0, 0.

Operations e	$2_{1,x}$	$2_{1,y}$	$2_{1,x}2_{1,y}$	$\bar{1}$	$2_{1,x}\,.\,\bar{1}$	$2_{1,y}\,.\,\bar{1}$	$2_{1,x}2_{1,y}\,.\,\bar{1}$
1	3	4	2 (100)	2	4	3	1 (10$\bar{1}$)
2	4	3 (001)	1 (10$\bar{1}$)	1	3	4	2 (100)
3	1 (100)	2 (011)	4 (0$\bar{1}\bar{1}$)	4 ($\bar{1}\bar{1}$0)	2 (010)	1 (100)	3 (100)
4	2 (100)	1 (010)	3 (0$\bar{1}$0)	3 ($\bar{1}\bar{1}$0)	1 (010)	2 (101)	4 (10$\bar{1}$)

$2_{1,x}$ transforms point 1 to 3, 2 to 4, 3 to 1 plus a translation 1, 0, 0 and 4 to 2 plus a translation 1, 0, 0.

Reduction

The application of (3-2) indicates

$$a^{(\nu)}=\tfrac{1}{8}[12-4\,.\,\chi^{(\nu)}(2_{1,z}\,.\,\bar{1})] \qquad (4\text{-}15)$$

so that the representations $\Gamma_1,\Gamma_4,\Gamma_6,\Gamma_7$ are contained once ($\chi^{(\nu)}(2_{1,z}\,.\,\bar{1})=+1$) and the representations $\Gamma_2,\Gamma_3,\Gamma_5,\Gamma_8$ twice ($\chi^{(\nu)}(2_{1,z}\,.\,\bar{1})=-1$). This exactly corresponds to the findings of Table 6.

The eight transformation matrices 'represent the space group' and form a representation Γ of order 12 which may be reduced. A first reduction into 3 subspaces of order 4, corresponding to the x, y and z components is obvious. It is also easy to see that all the fourfold matrices of a subspace may be simultaneously reduced to diagonal form by the matrix Φ (4-16) the columns of which correspond precisely to the **F**, **G**, **C** and **A** vectors.

$$\begin{array}{cc} & \begin{array}{cccc}\mathbf{F} & \mathbf{G} & \mathbf{C} & \mathbf{A}\end{array} \\ \Phi=\tfrac{1}{2} & \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{bmatrix}=\Phi^{-1}\,. \end{array} \qquad (4\text{-}16)$$

For instance for the subspace x one finds

$$\Phi^{-1}\alpha\Phi=\begin{bmatrix} 1 & . & . & . \\ . & 1 & . & . \\ . & . & -1 & . \\ . & . & . & -1 \end{bmatrix};$$

$$\Phi^{-1}(-\beta)\Phi=\begin{bmatrix} -1 & . & . & . \\ . & 1 & . & . \\ . & . & 1 & . \\ . & . & . & -1 \end{bmatrix};$$

$$\Phi^{-1}\gamma\Phi=\begin{bmatrix} 1 & . & . & . \\ . & -1 & . & . \\ . & . & 1 & . \\ . & . & . & -1 \end{bmatrix}; \qquad (4\text{-}17)$$

so that in the respective operations 2_{1x}, 2_{1y} and $\bar{1}$ from (4-16) and (4-17)

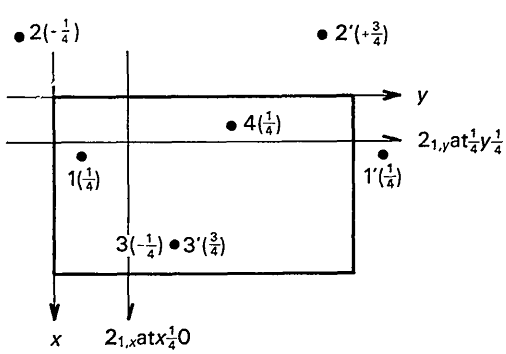

Fig. 2. Point transformation of the 4(c) positions in *Pbnm*, $\mathbf{k}=[0\tfrac{1}{2}0]$. $2_{1,y}$ in $\tfrac{1}{4}y\tfrac{1}{4}$ turns 1 to 4, 2 to 3', 3 to 2' and 4 to 1'. The number in parenthesis is the z coordinate.

F_x has the characters $1,\bar{1},1$ and belongs to Γ_2

G_x	$1,1,\bar{1}$	Γ_6
C_x	$\bar{1},1,1$	Γ_3
A_x	$\bar{1},\bar{1},\bar{1}$	Γ_8

(see Table 5).

Other examples of matrix representations are found in the next section.

At this point we may already note connexions with the Shubnikov groups and some of their difficulties.

Consider the example of $ErFeO_3$ (Koehler, Wollan & Wilkinson, 1960) or $ErCrO_3$ (Bertaut & Maréschal, 1967*a*). At low temperatures the spin components of Fe (or Cr) belong to a **G** mode with x *and* y components and those of Er to a **C** mode along Oz. Actually G_x (Fe,Cr) belongs to Γ_4 whereas G_y (Fe,Cr) and C_z (Er) belong to Γ_1 so that *different* magnetic groups be involved, say $Pb'n'm$ and $Pbnm$ (see last column of Table 6). The 'global magnetic symmetry' would be the intersection of these two magnetic groups, say the monoclinic group $P2_1/m$.

Another example is $TbFeO_3$ (Bertaut, Chappert, Maréschal, Rebouillat & Sivardière, 1967) where one finds at 1·5°K the Fe-spins in a G_x mode belonging to Γ_4 or $Pb'n'm$ and the Tb-spins in a non-collinear A_xG_y arrangement belonging to Γ_8 or $Pbnm'$. Here the two magnetic groups have the intersection $P2_1'2_1'2_1$.

In the two cases we see that it is possible to indicate a 'global Shubnikov group' which is of lower symmetry than the Shubnikov groups associated with the representations of the individual ions.

We may say that the interactions between different ions will have the symmetry of the global Shubnikov group. However there is no reason to believe that interactions between ions of the same nature would not have the higher symmetry associated with their representations. To be explicit, the Tb–Tb interactions in $TbFeO_3$ may have the symmetry $Pbnm'$, the Fe–Fe interactions would belong to the symmetry $Pb'n'm$ and only Fe–Tb interactions (if any) would have the lower symmetry $P2_1'2_1'2_1$.

We must conclude that the concept of global magnetic symmetry invariance has not the same strength as the concept of say positional invariance of a crystal under the operations of its space group.

From the point of view of representation theory there is, however, no conceptual difficulty in admitting that in the same crystallographic space group there might be spin components belonging to different representations. The physical reasons will become more apparent in § 6. We should like to point out the similarity with the problem of cryptosymmetry discussed by Niggli & Wondratschek (1960) and Wondratschek & Niggli (1961).

5. Representations and base functions for $\mathbf{k}\neq 0$

The division of this section roughly follows the needs of the projection operator method, which are the knowledge of irreducible space group representations and of the properties of transformation of spin vectors, both associated with the wave vector $\mathbf{k}$. The first part, recalling essential notions and including the Olbrychski (1963) method will be quite abstract. The second part dealing with the transformation properties is easy again and has been extended to show that the basis functions obtainable by the projection operator method may also be gained from the transformation properties themselves.

Any symmetry operator C_α of a space group G may be written in the form (5-1) where α is a (proper or improper) rotation and $\boldsymbol{\tau}_\alpha$ its translational part. The multiplication law is (5-2).

$$C_\alpha = \{\alpha|\boldsymbol{\tau}_\alpha\} . \qquad (5\text{-}1)$$

$$C_\alpha C_\beta = \{\alpha|\boldsymbol{\tau}_\alpha\}\{\beta|\boldsymbol{\tau}_\beta\} = \{\alpha\beta|\alpha\boldsymbol{\tau}_\beta + \boldsymbol{\tau}_\alpha\} . \qquad (5\text{-}2)$$

The wave vector $\mathbf{k}$ numbers the representations of the subgroup T of primitive translations $\mathbf{R}_n$

$$\mathfrak{D}^{(\mathbf{k}_\nu)}\{e|\mathbf{R}_n\} = \exp(2\pi i\mathbf{k} . \mathbf{R}_n) . \mathbf{1}^{(\nu)} . \qquad (5\text{-}3)$$

Here $\mathbf{1}^{(\nu)}$ is the unit matrix in the representation numbered ν.

The wave-vector groups G^k and their representations are defined as follows. The set of all rotational elements which leave the vector $\mathbf{k}$ invariant is a group noted G_0^k which is identical with one of the 32 point groups. Let $\mathfrak{D}^{(\nu)}(\beta)$ be a representation of the point group G_0^k numbered by the index ν. (For instance there are eight representations $\nu = 1, \ldots, 8$ when $G_0^k = mmm$ (see Table 5). Then the representations of the wave-vector group G^k are given by

$$\mathfrak{D}^{(\mathbf{k}_\nu)}(\{\beta|\boldsymbol{\tau}_\beta\}) = \exp(2\pi i\mathbf{k} . \boldsymbol{\tau}_\beta)\mathfrak{D}^{(\nu)}(\beta) , \qquad (5\text{-}4)$$

with some restrictions however. Formula (5-4) holds *at the interior* of the first Brillouin zone for all groups. *At the surface* it still holds for the symmorphic space groups, *i.e.* those in which $\boldsymbol{\tau}_\beta$ is a lattice translation.

In the 157 non-symmorphic space groups relation (5-4) does not hold in general. (For instance, for the D_{2h}^j groups one would expect, from relation (5-4) and Table 5, to find only one-dimensional representations. This is no longer true on the surface of the first Brillouin zone).

Remark: We do not deal more specifically with relation (5-4) except for the simplest case when G_0^k has no element except the identity e which may happen for an incommensurable wave vector $\mathbf{k}$. The oscillating spin [in chromium (Shirane & Takei, 1962)]

$$\mathbf{S}(\mathbf{R}_n) = S_0\mathbf{x}\cos(2\pi\mathbf{k} . \mathbf{R}_n + \varphi) \qquad (5\text{-}5)$$

and the helical spin [in dysprosium (Wilkinson, Koehler, Wollan & Cable, 1961)]

$$\mathbf{S}(\mathbf{R}_n) = S_0[\mathbf{x}\cos(2\pi\mathbf{k} . \mathbf{R}_n + \varphi) + \mathbf{y}\sin(2\pi\mathbf{k} . \mathbf{R}_n + \varphi)] \qquad (5\text{-}6)$$

appear to be vectors belonging to particularly simple representations of the vector $\mathbf{k}$.

The Olbrychski method

In this method one chooses first a convenient set of generators of the group. In a second step one forms the complete set of relations between the generators which induce relations between their matrix representatives. Finally one looks for the explicit form of these matrices which yield the desired irreducible representations.

We illustrate the method by applying it to the space groups D_{2h}^j and more particularly to two examples *Pbam* (D_{2h}^9) and *Pbnm* (D_{2h}^{16}) when the $\mathbf{k}$ vectors have the full point symmetry of G_0, say *mmm*.

One may take as generators the Hermann–Mauguin symbols themselves. However, other choices are as well suited. We select here the binary screw axes $2_{1,x}$ and $2_{1,y}$ and the symmetry centre $\bar{1}$ taken at the origin. We write

$$2_{1,x} = \{2_x|\boldsymbol{\tau}_x\};\ 2_{1,y} = \{2_y|\boldsymbol{\tau}_y\};\ \bar{1} = \{I|0\} , \qquad (5\text{-}7)$$

where $2_x, 2_y$ are binary axes and I is the inversion, which may be represented by matrices of order 3. The translations $\boldsymbol{\tau}_x, \boldsymbol{\tau}_y$ must be specified for each space group D_{2h}^j (see Appendix 1).

In the underlying point group $G_0^k = G_0$, the six defining relations between the generators $2_x, 2_y$ and I are

$$2_x^2 = 2_y^2 = I^2 = e;\ 2_x 2_y = 2_y 2_x;\ 2_x I = I 2_x . \qquad (5\text{-}8)$$

One finds correspondingly

$$\begin{array}{lll} 2_{1,x}^2 & = \{e|\mathbf{t}_1\} & \text{with } \mathbf{t}_1 = (2_x + e)\boldsymbol{\tau}_x \\ 2_{1,y}^2 & = \{e|\mathbf{t}_2\} & \text{with } \mathbf{t}_2 = (2_y + e)\boldsymbol{\tau}_y \\ (\bar{1})^2 & = \{e|0\} & \\ 2_{1,x} . \bar{1} & = \{e|\mathbf{t}_{13}\}\ \bar{1} . 2_{1,x} & \text{with } \mathbf{t}_{13} = 2\boldsymbol{\tau}_x \\ 2_{1,y} . \bar{1} & = \{e|\mathbf{t}_{23}\}\ \bar{1} . 2_{1,y} & \text{with } \mathbf{t}_{23} = 2\boldsymbol{\tau}_y \\ 2_{1,x} . 2_y & = \{e|\mathbf{t}_{12}\}\ 2_{1,y} . 2_{1,x} & \text{with } \mathbf{t}_{12} = (2_x - e)\boldsymbol{\tau}_y \\ & & \qquad - (2_y - e)\boldsymbol{\tau}_x . \end{array} \qquad (5\text{-}9)$$

The last equation of (5-9) is derived in Appendix 1 with the values of the translations $\mathbf{t}$ in groups *Pbam* and *Pbnm*.

Let us call A_1, A_2 and A_3 the matrix representations of $2_{1,x}$, $2_{1,y}$ and $\bar{1}$ respectively and remember that the representative of the translation $\mathbf{t}$ in the space group representation associated with the wave-vector $\mathbf{k}$ is $\mathbf{1} . \exp 2\pi i\mathbf{k} . \mathbf{t}$, where $\mathbf{1}$ is a unit matrix. The relations (5-9) become

$$\left.\begin{array}{l} A_j^2 = \varepsilon_j . \mathbf{1};\ A_i A_j = A_j A_i \varepsilon_{ij};\ i,j = 1,2,3 \\ \text{with} \\ \varepsilon_j = \exp(2\pi i\mathbf{k} . \mathbf{t}_j);\ \varepsilon_{ij} = \exp(2\pi i\mathbf{k} . \mathbf{t}_{ij}) . \end{array}\right\} \qquad (5\text{-}10)$$

One has in *Pbnm* (see Appendix 1)

$$\begin{array}{l} \varepsilon_1 = \exp[2\pi i k_1];\ \varepsilon_2 = \exp[2\pi i k_2];\ \varepsilon_3 = 1 \\ \varepsilon_{12} = \exp[2\pi i(k_1 - k_2 - k_3)];\ \varepsilon_{13} = \exp[2\pi i(k_1 + k_2)] \\ \varepsilon_{23} = \exp[2\pi i(k_1 + k_2 + k_3)] . \end{array} \qquad (5\text{-}11)$$

Here the k_j $(j=1,2,3)$ are the components of the wave-vector $\mathbf{k}$

$$\mathbf{k}=k_1\mathbf{b}_1+k_2\mathbf{b}_2+k_3\mathbf{b}_3\,. \tag{5-12}$$

It is worth while to tabulate the phase factors ε_j and ε_{jk} for those $\mathbf{k}$ vectors which are associated with the full point group symmetry (see Table 8). It is seen that only for $\mathbf{k}=0$ and $\mathbf{k}=\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)$ the matrices A_j $(j=1,2,3)$ commute (all ε_{ij} positive) so that their representations are one-dimensional real for $\mathbf{k}=0$ $(\varepsilon_i=+1)$ and complex for $\mathbf{k}=\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)$. Their derivation is of course trivial.

We shall derive here the irreducible representations belonging to the wave-vector $\mathbf{k}=\frac{1}{2}\mathbf{b}_2$ for which the equations (5-10) read

$$A_1^2=A_2^2=\mathbf{1}\,;\; A_3^2=-\mathbf{1}$$
$$A_iA_j=-A_jA_i \quad \text{for} \quad i,j=1,2,3\;(i\neq j)\,. \tag{5-13}$$

Because in (5-13) there are anti-commuting matrices, there cannot be any one-dimensional representation. There cannot be any three-dimensional representation, because $3^2=9$ exceeds the order 8 of the group. Finally we are left with two two-dimensional representations because $g=8=2^2+2^2$. Their explicit form, given by the simple identification procedure of Appendix 2, is tabulated in Table 9.

Transformation properties for $\mathbf{k}=\frac{1}{2}\mathbf{b}_2$ *in Pbnm* (D_{2h}^{16})

The transformation properties of the points 4(*c*) can be simply gained from geometrical inspection. We read from Fig. 2 that the screw axis $2_{1,y}$ sends point 1 to 4, point 2 to 3′ (=3 plus a translation $\mathbf{a}_3$), point 3 to point 2′ (=2 plus a translation $\mathbf{a}_2+\mathbf{a}_3$) and point 4 to point 1′ (=1 plus translation $\mathbf{a}_2$). Keeping in mind that spin reversal takes place after a translation $\mathbf{a}_2$ one has the following relations for the spin vectors

$$2_{1,y}S_{1y}=S_{4y}\,;\; 2_{1,y}S_{2y}=S_{3y}\,;$$
$$2_{1,y}S_{3y}=S'_{2y}=-S_{2y}\,;\; 2_{1,y}S_{4y}=S'_{1y}=-S_{1y}\,. \tag{5-14}$$

In the way described above one derives the transformation properties for points already summarized in Table 7 and for the spin vectors given in Table 10.

To use relation (3-3) it is convenient to consider for Ψ the following linear spin combinations*

$$\Psi^+=\tfrac{1}{2}(S_{1x}+S_{2x})\,;\; \Psi^-=\tfrac{1}{2}(S_{1x}-S_{2x})\,. \tag{5-15}$$

With the help of the matrices of the representation Γ_{k1} (Table 9) and the transformation properties of the x components (Table 10) one finds from Ψ^+:

$$\Psi_{11}^+=F_x\,;\; \Psi_{12}^+=-F_x$$
$$\Psi_{21}^+=-C_x\,;\; \Psi_{22}^+=C_x \tag{5-16}$$

and from Ψ^-:

$$\Psi_{11}^-=G_x\,;\; \Psi_{12}^-=G_x$$
$$\Psi_{21}^-=A_x\,;\; \Psi_{22}^-=A_x\,. \tag{5-17}$$

* One might take as well $\psi=S_{1x}$ for instance. The functions obtained in this way are, however, less symmetrical.

Table 8. *Phase factors* ε_j *and* ε_{ij} *in Pbnm*

$\mathbf{k}$	ε_1	ε_2	ε_3	ε_{12}	ε_{23}	ε_{31}	Order of irreducible representations	Nature and number	
0	1	1	1	1	1	1	1	Real	8
$\frac{1}{2}\mathbf{b}_1$	−1	1	1	−1	−1	−1	2	Real	2
$\frac{1}{2}\mathbf{b}_2$	1	−1	1	−1	−1	−1	2	Real	2
$\frac{1}{2}\mathbf{b}_3$	1	1	1	−1	−1	1	2	Real	2
$\frac{1}{2}(\mathbf{b}_2+\mathbf{b}_3)$	1	−1	1	1	1	−1	2	Complex	2
$\frac{1}{2}(\mathbf{b}_3+\mathbf{b}_1)$	−1	1	1	1	1	−1	2	Real	2
$\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)$	−1	−1	1	1	1	1	1	Complex	8
$\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2+\mathbf{b}_3)$	−1	−1	1	−1	−1	1	2	Complex	2

Table 9. *Irreducible representations of Pbnm. Wave-vector* $\mathbf{k}=[0\frac{1}{2}0]$

Γ_{1k}	e	A_1	A_2	A_1A_2	A_3	A_1A_3	A_2A_3	$A_1A_2A_3$
	$\begin{bmatrix}1 & \cdot\\ \cdot & 1\end{bmatrix}$	$\begin{bmatrix}1 & \cdot\\ \cdot & -1\end{bmatrix}$	$\begin{bmatrix}\cdot & 1\\ -1 & \cdot\end{bmatrix}$	$\begin{bmatrix}\cdot & 1\\ 1 & \cdot\end{bmatrix}$	$\begin{bmatrix}\cdot & -1\\ -1 & \cdot\end{bmatrix}$	$\begin{bmatrix}\cdot & -1\\ 1 & \cdot\end{bmatrix}$	$\begin{bmatrix}-1 & \cdot\\ \cdot & 1\end{bmatrix}$	$\begin{bmatrix}-1 & \cdot\\ \cdot & 1\end{bmatrix}$

A_1, A_2 and A_3 are the representatives of $2_{1,x}$, $2_{1,y}$ and $\bar{1}$. Γ_{2k} is obtained by reversing the sign of A_3.

Table 10. *Spin transformations in Pbnm. Sites* 4(*c*). $\mathbf{k}=[0\frac{1}{2}0]$. *x components*

e	$2_{1,x}$	$2_{1,y}$	$2_{1,z}$	$\bar{1}$	$2_{1,x}\,.\,\bar{1}$	$2_{1,y}\,.\,\bar{1}$	$2_{1,z}\,.\,\bar{1}$
S_{1x}	S_{3x}	$-S_{4x}$	$-S_{2x}$	$\mathbf{S}_2$	S_{4x}	$-S_{3x}$	$-S_{1x}$
S_{2x}	S_{4x}	$-S_{3x}$	$-S_{1x}$	$\mathbf{S}_1$	S_{3x}	$-S_{4x}$	$-S_{2x}$
S_{3x}	S_{1x}	S_{2x}	S_{4x}	$-\mathbf{S}_4$	$-S_{2x}$	$-S_{1x}$	$-S_{3x}$
S_{4x}	S_{2x}	S_{1x}	S_{3x}	$-\mathbf{S}_3$	$-S_{1x}$	$-S_{2x}$	$-S_{4x}$

According to § 3 the functions Ψ_{ij} with j fixed are 'partners belonging to the jth row'. The physical meaning of the fact that G_x and A_x for instance are 'partners' in the two-dimensional representation Γ_{k1} is that they provide an equivalent description of the same physical reality. This fact is illustrated in Fig. 3. By applying also projection operators to the functions $\frac{1}{2}(S_{1y} \pm S_{2y})$ and $\frac{1}{2}(S_{1z} \pm S_{2z})$ one arrives at the results of Table 11. It is found that all the x and y vectors belong to Γ_{k1}, the z vectors to Γ_{k2}.

Table 11. *Partners of irreducible representations*

	Γ_{k1}				Γ_{k2}	
φ_1	F_x	G_x	C_y	A_y	C_z	A_z
φ_2	$-C_x$	A_x	$-F_y$	G_y	F_z	$-G_z$

The transformation matrices for $\mathbf{k}=[0\frac{1}{2}0]$

The transformation matrices $(2_{1,x})$, $(2_{1,y})$ and $(\bar{1})$ may be written in the same forms as in (4-10), (4-11), (4-12) with:

$$\alpha=\begin{bmatrix} \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \end{bmatrix};\quad \beta=\begin{bmatrix} \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & 1 & \cdot \\ \cdot & -1 & \cdot & \cdot \\ -1 & \cdot & \cdot & \cdot \end{bmatrix};$$

$$\gamma=\begin{bmatrix} \cdot & 1 & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & -1 \\ \cdot & \cdot & -1 & \cdot \end{bmatrix}. \tag{5-18}$$

Note that the transpose of β is $-\beta$. From (3-1) it follows that the transposes of $(2_{1,x})$, $(2_{1,y})$ and $(\bar{1})$, say A_1^Γ, A_2^Γ and A_3^Γ, generate a 12-dimensional representation Γ which is reducible. Of course, as the reader may check, *these matrices follow exactly the multiplication rules reached by the Olbrychski method* in (5-10) and in (5-13) so that the irreducible representations Γ_{k1} and Γ_{k2} could have been found by the same identification procedure as in Appendix 2.

The only non-zero traces are

$$\chi^\Gamma(e)=12\,;\ \chi^\Gamma(A_1A_2A_3)=-4\,, \tag{5-19}$$

so that from (5-20) the representations Γ_{k1} and Γ_{k2}

$$a^{(k1)}=\tfrac{1}{8}(2\cdot 12-2\,.\,(-4)=4$$
$$a^{(k2)}=\tfrac{1}{8}(24-8)=2 \tag{5-20}$$

are contained respectively 4 and 2 times in Γ. This is exactly the number of couples of partners in Table 11 for the respective representations.

The direct reduction method

This method is based on the explicit form of the transformation relations. For instance by simply adding the equations (5-14) one gets

$$2_{1,y}(S_1+S_2+S_3+S_4)_y=$$
$$2_{1,y}F_y=(S_4+S_3-S_2-S_1)_y=-C_y$$

and similarly

$$2_{1,y}(S_1+S_2-S_3-S_4)=$$
$$2_{1,y}C_y=F_y=-(-F_y)\,. \tag{5-21}$$

Relations (5-21) suggest already that C_y and $-F_y$ are partners in a two-dimensional representation. One finds in the same way

$$2_{1,x}C_y=C_y\,;\qquad \bar{1}C_y=-(-F_y)$$
$$2_{1,x}(-F_y)=-(-F_y)\,;\ \bar{1}(-F_y)=-C_y\,. \tag{5-22}$$

Thus we have derived in a very simple way the three following transformation matrices in the two-dimensional space of the vectors C_y and $-F_y$:

$$(2_{1,x})=\begin{bmatrix} 1 & \cdot \\ \cdot & -1 \end{bmatrix};\ (2_{1,y})=\begin{bmatrix} \cdot & -1 \\ 1 & \cdot \end{bmatrix};$$
$$(\bar{1})=\begin{bmatrix} \cdot & -1 \\ -1 & \cdot \end{bmatrix}. \tag{5-23}$$

Their transposes are exactly the matrices A_1, A_2 and A_3 of the representation Γ_{k1} so that C_y and $-F_y$ are partners in that representation. One can find in the same way the representation Γ_{k2} as well as all the other basis functions.

Remark: If one had taken C_y and $+F_y$ as partners one would have got another set of matrices for A_1, A_2 and A_3 corresponding to one of the equivalent forms shown in Appendix 2.

Generalization of the matrix method

The matrix-method is easily generalized to any $\mathbf{k}$ vector. For instance when 2_y is an element of G_0^k (*i.e.* an operation which leaves $\mathbf{k}$ invariant, which is only true for $2k_1=0$ or 1, $2k_3=0$ or 1), the transformation matrix $(2_{1,y})$ has the form

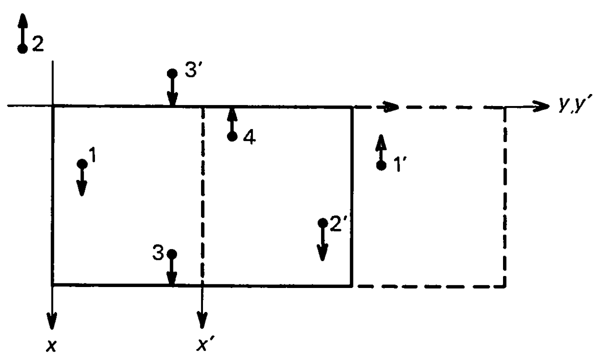

Fig. 3. Equivalence of the A_x and G_x configuration in *Pbnm*, $\mathbf{k}=[0\frac{1}{2}0]$. The spins 1, 2, 3, 4 form a $+-+-$ or G_x sequence. The spins 1′, 2′ and 3′ are displaced by $\mathbf{a}_2$, $\mathbf{a}_1+\mathbf{a}_2$ and $-\mathbf{a}_1$ with respect to 1, 2 and 3. Take a new origin at $0\frac{1}{2}0$ and call the coordinates of point 4: $x', y', \frac{1}{4}$. In the new (primed) coordinate system, our four-point sequence becomes 4, 3′, 2′, 1′ with spins $-++-$. This is an A_x sequence which describes the spin configuration as well.

$$(2_{1,y})=\begin{bmatrix} -\beta & . & . \\ . & \beta & . \\ . & . & -\beta \end{bmatrix}$$

with

$$\beta=\begin{bmatrix} . & . & . & 1 \\ . & . & \exp(2\pi i k_3) & . \\ . & \exp[2\pi i(k_2+k_3)] & . & . \\ \exp(2\pi i k_2) & . & . & . \end{bmatrix} \quad (5\text{-}24)$$

where the phase factors 'represent' the translations written in parenthesis after the transformed points of Table 9. The matrices which one gets after transposition play exactly the role of the Olbrychski matrices. One has for instance

$$(A_2^{\Gamma})^2=\exp(2\pi i k_2)\,.\,\mathbf{1} \quad (5\text{-}25)$$

in conformity with (5-10).

Examples

Examples of structures with $\mathbf{k}$ vectors *on* the Brillouin-zone are already found in the literature.

The spin configuration of Tb in $TbCrO_3$ (Bertaut, Maréschal & de Vries, 1967) is an example of a structure belonging to a two-dimensional irreducible representation of *Pbnm* associated with the wave-vector $\mathbf{k}=[0\frac{1}{2}0]$. Tb has an A_xG_y configuration (see Table 12).

The spin configuration of Dy in $DyCrO_3$ (Bertaut & Maréschal ,1967*b*) belongs to a complex one-dimensional irreducible representation of *Pbnm* associated with the wave-vector $\mathbf{k}=[\frac{1}{2}\frac{1}{2}0]$.

Let us now mention here an additional difficulty of Shubnikov groups. In the two preceding examples the rare-earth ordering requires enlargement of the unit cell in at least one direction whereas the Cr-spins retain the periodicity of the chemical cell. In $TbCrO_3$ for instance, the Tb-spin configuration would belong to a magnetic P_{2b} group whereas the Cr configuration remains in a simple *P* group.

Another example is the magnetic structure of V-spins in V_2CaO_4 (Bertaut & Nhung, 1967) belonging to a two-dimensional representation of *Pbnm* with $\mathbf{k}=[\frac{1}{2}0\frac{1}{2}]$. It is interesting to note that the same structure has been solved by Hastings, Corliss, Kunnmann & La Placa (1967) in monoclinic Shubnikov groups.

Finally the magnetic structure of the Mn atoms in RMn_2O_5 (R = rare earth or yttrium or bismuth) has been solved by the direct reduction method applied to the space group *Pbam* with $\mathbf{k}=[\frac{1}{2}0\frac{1}{2}]$ (Bertaut, Buisson, Quézel-Ambrunaz & Quézel, 1967).

6. Effective spin Hamiltonian and magnetic couplings

We consider purely magnetic interactions (*i.e.* interactions which are not coupled with other forms of energy – elastic, electric, and so on; see also § 7). Let us require that the effective spin Hamiltonian is invariant under the 'actual' crystallographic space group *and* under the reversal of *all* the spins. The physical foundation of this last requirement is that the magnetic energy of a single domain does not change (neglecting boundaries) by spin reversal and that nature always shows the coexistence of *A* domains and reversed *B* (= −*A*) domains.

The spin Hamiltonian must have the form:

$$H=\sum_{\substack{R,R',\alpha,\beta\\(\alpha,\beta=x,y,z)}} A_{\alpha\beta}(\mathbf{R},\mathbf{R}')S_\alpha(\mathbf{R})S_\beta(\mathbf{R}') + H_4+H_6+\ldots \quad (6\text{-}1)$$

Here $S_\alpha(\mathbf{R})$ is the α-component of a spin $\mathbf{S}$ localized in point $\mathbf{R}$. $A_{\alpha\beta}(\mathbf{R},\mathbf{R}')$ is a 3×3 matrix which represents a tensor of order two. By H_4 and H_6 we indicate the possible existence of terms of order 4 and 6 in the spins.

It is then a very trivial matter to see that if a Hamiltonian of the form (6-1) is invariant under an operation C_k of the crystallographic space group G, it is also invariant under the operation $C'_k=C_kR$ of the isomorphous magnetic space group G' and *vice versa* because $R^n=+1$ for n even. Thus H will be invariant under G and G'.

The construction of a Hamiltonian of form (6-1) may be quite cumbersome and it is advantageous to introduce, instead of the spins, the basis vectors of irreducible representations which are linear combinations of the spins. Indeed the linear system of the basis vectors may be resolved with respect to the spins*. In the approximation of a spin Hamiltonian of order two,

* For instance in the system (4–3) of the basis vectors **A**, **F**, **C** and **G** one has $4\mathbf{S}_1=\mathbf{F}+\mathbf{C}+\mathbf{G}+\mathbf{A}$ and so on.

Table 12. *Representations of axial vectors and polar vectors in Pnma'*

	Pnma [Sites 4(*c*)]						*Pnma'* [Sites 4(*c*)]						*Pnma* [Sites 4(*c*)]		
	Generators			Axial vectors			Generators			Axial vectors			Polar vectors		
Representation	$2_{1,x}$	$2_{1,z}$	$\bar{1}$	*x*	*y*	*z*	$2_{1,x}$	$2_{1,z}$	$\bar{1}$	*x*	*y*	*z*	*x*	*y*	*z*
$\Gamma_1=\Gamma_{1g}$	+	+	+	.	*C*	.	+	+	+	.	*A*	.	*A*	.	*G*
$\Gamma_2=\Gamma_{2g}$	+	−	+	*F*	.	*C*	+	−	+	*G*	.	*A*	.	*G*	.
$\Gamma_3=\Gamma_{3g}$	−	+	+	*C*	.	*F*	−	+	+	*A*	.	*G*	.	*A*	.
$\Gamma_4=\Gamma_{4g}$	−	−	+	.	*F*	.	−	−	+	.	*G*	.	*G*	.	*A*
$\Gamma_5=\Gamma_{1u}$	+	+	−	*A*	.	*G*	+	+	−	*C*	.	*F*	.	*C*	.
$\Gamma_6=\Gamma_{2u}$	+	−	−	.	*G*	.	+	−	−	.	*F*	.	*F*	.	*C*
$\Gamma_7=\Gamma_{3u}$	−	+	−	.	*A*	.	−	+	−	.	*C*	.	*C*	.	*F*
$\Gamma_8=\Gamma_{4u}$	−	−	−	*G*	.	*A*	−	−	−	*F*	.	*C*	.	*F*	.

one will get, after substitution, a *quadratic form* of the base vectors. The advantage of the new quadratic form is that one can only have products of basis vectors belonging to the same irreducible representation. This is due to the group theorem that only the direct product of an irreducible representation with itself† contains the identity representation and thus gives rise to invariants.

$$\Gamma_j \times \Gamma_j \text{ contains } \Gamma_0 \text{ (identity representation)}. \quad (6\text{-}2)$$

Physically one may explain in this way most of the so called 'canted' spin structures. For instance the occurrence of the non-zero product $a_{xz}F_xG_z$ in the spin Hamiltonian of group *Pbnm* ($\mathbf{k}=0$) means that a $++++$ sequence in the x direction is coupled with a $+-+-$ sequence of spins in the z direction. This is for instance the case in $YFeO_3$ where a 'weak' ferromagnetism F_x is seen magnetically (Bozorth, Williams & Walsh, 1956) whereas neutron diffraction mainly‡ observes a G_z configuration. Another example in the same space group *Pbnm* is the structure of β-$CoSO_4$ (Bertaut, Coing-Boyat & Delapalme, 1963) where A_x, G_y, C_z are seen to coexist (*cf.* Table 6 in Γ_1).

Remark: It is interesting to note in this context that one has to deal here with a 'phase problem'. Indeed in the last case, the observed magnetic lines are A or G or C lines (with no interferences) so that in fact one observes A_x^2, G_y^2, C_z^2. Thus the spin models are not unique and to the proposed solution A_x, G_y, C_z (Bertaut *et al.*, 1963) one must add three other possible solutions giving rise to exactly the same interference pattern, say $-A_x, +G_y, +C_z$; $+A_x, -G_y, +C_z$; $+A_x, +G_y, -C_z$ (Bertaut, 1966).

Several conclusions may be reached concerning the number of irreducible representations and the order of the Hamiltonian.

Case of one magnetic species of equivalent atoms

We have seen that a Hamiltonian of order two implies that the spin components must belong to the same irreducible representation. Conversely one may often conclude that if the spin components belong to the same irreducible representation, the approximation of a spin Hamiltonian of order two is sufficient. If the spin components $\mathbf{S}^{(\alpha)}$ and $\mathbf{S}^{(\beta)}$ belong to different irreducible representations $\Gamma^{(\alpha)}$ and $\Gamma^{(\beta)}$, the spin Hamiltonian must have terms of order four at least. Another consequence is that $\mathbf{S}^{(\alpha)}$ must be orthogonal to $\mathbf{S}^{(\beta)}$.

Indeed if

$$\mathbf{S}_\mathbf{R} = \mathbf{S}_\mathbf{R}^{(\alpha)} + \mathbf{S}_\mathbf{R}^{(\beta)} \quad (6\text{-}3)$$

one must have

$$S_R^2 = S_R^{(\alpha)2} + S_R^{(\beta)2} + 2\mathbf{S}_\mathbf{R}^{(\alpha)} \cdot \mathbf{S}_\mathbf{R}^{(\beta)} = \text{invariant}. \quad (6\text{-}4)$$

$\mathbf{S}_\mathbf{R}^{(\alpha)} \cdot \mathbf{S}_\mathbf{R}^{(\beta)}$ transforms according to the direct product $\Gamma^{(\alpha)} \times \Gamma^{(\beta)}$ (which does not contain the identity representation) and thus must disappear.

An example is the occurrence of 'conical spins' in which the linear and the helical components belong to different wave vectors and are orthogonal [for examples see Kaplan (1961), Elliott (1961) and Wilkinson *et al.* (1961)].

We remark finally that no spin can belong to more than three irreducible representations $\Gamma^{(\alpha)}, \Gamma^{(\beta)}, \Gamma^{(\gamma)}$ and that the three components $\mathbf{S}^{(\alpha)}, \mathbf{S}^{(\beta)}, \mathbf{S}^{(\gamma)}$ must be orthogonal (demonstration as above).

Case of two magnetic species (non-equivalent atoms)

If all the spin components belong to the same irreducible representation, we may suppose that coupling between the two species takes place within a Hamiltonian of order two: This is exemplified by $HoFeO_3$ (Koehler *et al.*, 1960) and $HoCrO_3$ (Bertaut, Maréschal, Pauthenet & Roult, 1964) where the moments of Ho and Fe, Cr belong to the representation Γ_2 of Table 6. Er_2O_3, where one finds 24 points of symmetry 2 and eight points of site symmetry $\bar{3}$ is another example for such a coupling (Bertaut & Chevalier, 1966; Moon, Koehler, Child & Raubenheimer, 1967).

May one have spin components belonging to different representations and still be satisfied with a Hamiltonian of order two? The answer is yes. An interesting example is $ErCrO_3$ (Bertaut & Maréschal, 1967*a*) where above 16·8°K the Cr moments are in a G_x configuration which belongs to Γ_4 (Table 6). Below 16·8°K the rare earth orders in a C_z configuration which belongs to Γ_1. At the same time the Cr moments rotate in the *Oxy* plane so that one is left with a G_x (Cr) component in Γ_4 and a new G_y (Cr) component in Γ_1, coupled with the rare earth.

If the spin components of each species belong to different representations, this may be interpreted as decoupling or coupling through a lower symmetry. An example is the spin structure of $TbFeO_3$ (Bertaut, Chappert, Maréschal, Rebouillat & Sivardière, 1967; *cf.* § 4).

Finally if the spin configurations of the two species belong to different $\mathbf{k}$ vectors as in $DyCrO_3$ (Bertaut & Maréschal, 1967*b*) one may assume complete decoupling (of order two) and (or) the presence of higher order terms (H_4, H_6).

Nature of the coupling

The tensor $A_{\alpha\beta}(\mathbf{R},\mathbf{R}')$ of (5-1) may be decomposed into a symmetrical and an antisymmetrical part (Bertaut, 1961, 1963). The latter one corresponds to the so-called Dzialoshinski–Moriya (Dzialoshinski, 1958; Moriya, 1960) vector $\mathbf{D}_{\mathbf{RR}'}$ and gives rise to an energy term of the form $\mathbf{D}_{\mathbf{RR}'} \cdot (\mathbf{S}_\mathbf{R} \times \mathbf{S}_{\mathbf{R}'})$. The symmetric part may again be split into two parts. The first one is a scalar and gives rise to the so called Heisenberg–Néel energy (Heisenberg, 1928; Néel, 1948), denoted by $-2\mathscr{J}_{RR'}\mathbf{S}_\mathbf{R} \cdot \mathbf{S}_{\mathbf{R}'}$, which represents a scalar or isotropic coupling. The second part is a traceless sym-

† If Γ_j is complex, one must take $\Gamma_j \times \Gamma_j^*$.

‡ The weak ferromagnetic component is here about one per cent of the antiferromagnetic one and can be evidenced with the help of polarized neutrons.

metric tensor of order two, often written in diadic form $\mathbf{\Phi}_{\mathbf{RR}'}$ and giving rise to the anisotropy energy $\mathbf{S}_{\mathbf{R}} \,.\, \mathbf{\Phi}_{\mathbf{RR}'} \,.\, \mathbf{S}_{\mathbf{R}'}$. R and R' may here coincide. The physical origins of $\mathbf{\Phi}_{\mathbf{RR}'}$ are dipolar, pseudodipolar and crystalline field interactions. $\mathscr{J}_{RR'}$ is called the exchange integral, $\mathbf{D}_{\mathbf{RR}'}$ is proportional to $\lambda\mathscr{J}_{RR'}$, and $\mathbf{\Phi}_{\mathbf{RR}'}$ to λ^2 where λ is the spin orbit coupling constant.

On the other hand group theory enables us to determine basis vectors, to construct invariants by product formation, and finally, expressing the basis vectors in terms of spins, to construct the spin Hamiltonian (5-1) which informs us about the nature of the couplings.

We illustrate this point by the example of CoO which in its magnetic ordering undergoes a tetragonal* deformation. Admitting that the 4_2 screw axis is conserved in the transition, there are two vectors V_1 and V_2 in the x,y plane which belong to the same irreducible representation associated with $\mathbf{k}=[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$.

$$V_1 = S_{1x} + S_{2y} - S_{3x} - S_{4y} \tag{6-5}$$

$$V_2 = S_{1y} - S_{2x} - S_{1y} + S_{4x}\,.$$

V_1^2, V_2^2 as well as $a(V_1^2 + V_2^2)$ are invariants. One has

$$a(V_1^2+V_2^2)=$$

$$a[\,\Sigma\, s^2 + 2\mathbf{z}\,.\,(\mathbf{s}_1\times\mathbf{s}_2+\mathbf{s}_2\times\mathbf{s}_3+\mathbf{s}_3\times\mathbf{s}_4+\mathbf{s}_4\times\mathbf{s}_1)$$

$$-2(\mathbf{s}_1\,.\,\mathbf{s}_3+\mathbf{s}_2\,.\,\mathbf{s}_4)]\,. \tag{6-6}$$

Here $\mathbf{z}$ is the unit vector in the z direction and small letters are used to denote the spin components in the Oxy plane [for the complete spin Hamiltonian see Bertaut (1967)]. (6-6) shows that strong Dzialoshinski–Moriya coupling may occur and that $a(V_1^2+V_2^2)$ is, minimized for a negative, $\mathbf{s}_1$ antiparallel to $\mathbf{s}_3, \mathbf{s}_2$ antiparallel to $\mathbf{s}_4$, but $\mathbf{s}_1$ orthogonal to $\mathbf{s}_2$, $\mathbf{s}_2$ orthogonal to $\mathbf{s}_3$ and so on. $2a\mathbf{z}$ plays the role of the Dzialoshinski–Moriya vector and is mainly responible for the tetragonal spin structure, recently proposed by van Laar (1965) and strongly supported by the large spin-orbit coupling observed in CoO.

Advantage of representation theory

Finally the advantage of representation theory over symmetry invariance (under the Shubnikov groups) is also reflected by the construction of the Hamiltonian itself. In the example of $DyCrO_3$ the Dy-spin configuration belongs to a one-dimensional complex representation of the space group *Pbnm* (D_{2h}^{16}) associated with the wave-vector $\mathbf{k}=[\frac{1}{2}\frac{1}{2}0]$. The Hamiltonian H(Dy) will be invariant under the *whole* set of the symmetry operators. On the other hand, the Dy-spin structure cannot be described in any Shubnikov group belonging to the *Pbnm* family so that we must lower the symmetry to a, say, monoclinic Shubnikov-group. As a consequence this will impose less stringent conditions on the coefficients in the Hamiltonian.

* MnO, FeO, NiO deform rhombohedrically at the Néel point.

7. Magnetoelectricity

The reader may get the impression that the author is hostile to the use of magnetic groups. In fact the author is only defending representation theory. The main objection of the reader might be that in the abstract sense magnetic and space groups are isomorphous* so that a structure belonging to a representation of a space group G (even when the representation is not one-dimensional real) also belongs to a representation of the isomorphous Shubnikov group G'. This is perfectly correct, but still means that we would abandon symmetry invariance in favour of representation theory.

Can we ignore magnetic groups entirely? The answer is no, not only in microscopic, say atomic systems† (Dimmock & Wheeler, 1962) but also macroscopically when a magnetic system is coupled with other forms of energy.

A specific example is magnetoelectricity.‡ Here the Hamiltonian expressed in the fields contains not only the even powers of magnetic and electric field components, but also bilinear invariant terms like $h_{m\alpha}h_{e\beta}$ where α and β specify directions. Actually the magnetic field variable $h_{m\alpha}$ is sensitive to time reversal whereas the electric field $h_{e\beta}$ (polar vector) is not. We require the invariance of such bilinear terms under a Shubnikov group and suppose of course that the magnetic group may be described by such a group. Instead of the field description we choose, as in the preceding sections, the moment description with a bilinear term of the form $F_{m\alpha}F_{e\beta}$ in the Hamiltonian. F_m and F_e denote magnetic and electric polarizations (=sums of moments). This is done in the following steps. First one constructs the table of *axial*§ basis vectors belonging to the irreducible representations of the space group G. From the knowledge of the magnetic structure one is able to indicate which elements have become anti-elements and to construct a new table of representations for axial vectors in the magnetic space group G'. Finally we construct the table of irreducible representations of *polar*§ basis vectors, which are representative of the electric moment structure.

As an example we have chosen $LiCoPO_4$ (Mercier, Gareyte & Bertaut, 1967) belonging to the space group *Pnma* with four Co atoms in positions $x\frac{1}{4}z$; $\bar{x}\frac{3}{4}\bar{z}$; $\frac{1}{2}-x,\frac{3}{4},\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z$ and numbered correspondingly. As generators we choose $2_{1,x}$ in $x\frac{1}{4}\frac{1}{4}$, $2_{1,z}$ in $\frac{1}{4}0z$ and $\bar{1}$ in 000. The first part of Table 12 corresponds

* macrospically speaking with $R^2=1$.

† where R is an operator of order 4 (Wigner, 1959).

‡ In a magnetoelectric compound an electric field provokes ordering of the magnetic domains and a magnetic field gives rise to an electric polarization [see Rado & Folen (1962) and literature cited there].

§ The language is improper. By axial or polar basis vector we mean a vector which is a linear combination of axial or polar vectors respectively.

to the representation of axial vectors in *Pnma* (with the notation of § 4). The spin structure (Santoro, Segal & Newnham, 1966) is described by A_y and belongs to the representation $\Gamma_7=\Gamma_{3u}$, from which we can infer that the generators of the magnetic group (see the prescription of § 2) are $2'_{1,x}$, $2_{1,z}$ and $\bar{1}'$ and consequently that the magnetic group is *Pnma'*. In order to get the representations of *Pnma'* we multiply the characters of the *Pnma* table (in columns 2,3,4) by $-,+,-$ respectively and reorder the representations accordingly. This is done in the central part of Table 12.

Finally in the third part we add the representations of polar vectors. Axial and polar vectors behave in the same way under $2_{1,x}$ and $2_{1,z}$. Only the $\bar{1}$ operation has different effects so that a Γ_g representation for axial vectors will become a Γ_u representation for polar vectors and *vice versa*. From comparing the axial vector representations in *Pnma'* and the polar vector representations in *Pnma* of the last 6 columns of Table 12 we read the existence of two invariants of the form $F_{my}F_{ex}(\Gamma_6)$ and $F_{mx}F_{ey}(\Gamma_8)$ which are effectively observed (Mercier *et al.*, 1967).* Note that none of the vectors $F_{m\alpha}$ or $F_{e\beta}$ belongs to the identity representation. Thus we have to do with an effect of 'induced' magnetoelectricity. (In the magnetoelectric $FeGaO_3$ (Rado, 1964) one finds an invariant $F_{mz}F_{ey}$ (Bertaut, Bassi, Buisson, Chappert, Delapalme, Pauthenet, Rebouillat & Aléonard, 1966) with F_{mz} and F_{ey} belonging to the identity representation.)

We are grateful to Professor David P. Shoemaker for many improvements of style and presentation and to Professor Louis Néel for unfailing encouragement.

Appendix 1

The last relation of (5-9) is obtained by comparing:

$$2_{1,x}\,.\,2_{1,y}=\{2_x\,.\,2_y|2_x\tau_y+\tau_x\}$$

and

$$2_{1,y}\,.\,2_{1,x}=\{2_x\,.\,2_y|2_y\tau_x+\tau_y\}\,, \qquad (A1\text{-}1)$$

expressions in which the second members only differ by the translation labelled $\mathbf{t}_{12}$.

The explicit forms of the matrices (2_x), (2_y) and $(\bar{1})$ being

$$(2_x)=\begin{bmatrix}1 & . & .\\ . & -1 & .\\ . & . & -1\end{bmatrix};\quad (2_y)=\begin{bmatrix}-1 & . & .\\ . & 1 & .\\ . & . & -1\end{bmatrix};$$

$$(\bar{1})=\begin{bmatrix}-1 & . & .\\ . & -1 & .\\ . & . & -1\end{bmatrix} \qquad (A1\text{-}2)$$

one has

$$(2_x+e)=\begin{bmatrix}2 & . & .\\ . & . & .\\ . & . & .\end{bmatrix};\quad (2_x-e)=\begin{bmatrix}. & . & .\\ . & -2 & .\\ . & . & -2\end{bmatrix}. \qquad (A1\text{-}3)$$

In *Pbnm* one has for the binary screw axis applied to the point xyz: $2_{1,x}(x,y,z)=\frac{1}{2}+x,\frac{1}{2}-y,\bar{z}$ from which

$$\tau_x=\tfrac{1}{2},\tfrac{1}{2},0 \text{ and similarly } \tau_y=\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\,. \qquad (A1\text{-}4)$$

One finds

$$\mathbf{t}_1=(2_x+e)\tau_x=1,0,0;\ \mathbf{t}_2=(2_y+e)\tau_y=0,1,0$$

$$\mathbf{t}_{12}=1,\bar{1},\bar{1};\ \mathbf{t}_{13}=1,1,0;\ \mathbf{t}_{23}=1,1,1\,. \qquad (A1\text{-}5)$$

To save space we have written row vectors instead of column vectors in (A1-4) and (A1-5).

In *Pbam* one finds

$$\tau_x=\tau_y=\tfrac{1}{2},\tfrac{1}{2},0$$

and

$$\mathbf{t}_1=1,0,0;\ \mathbf{t}_2=0,1,0;\ \mathbf{t}_{12}=1,\bar{1},0;$$

$$\mathbf{t}_{13}=\mathbf{t}_{23}=1,1,0\,. \qquad (A1\text{-}6)$$

Appendix 2
Determination of irreducible representations

To determine explicit forms, let us take A_1 diagonal and write A_2 and A_3 as follows,

$$A_1=\begin{bmatrix}\mu & .\\ . & \nu\end{bmatrix};\quad A_2=\begin{bmatrix}\alpha & \beta\\ \gamma & \delta\end{bmatrix};\quad A_3=\begin{bmatrix}a & b\\ c & d\end{bmatrix}. \qquad (A2\text{-}1)$$

Substitution in the six relations (5-13) yields identities which reduce the matrices to

$$A_1=\begin{bmatrix}\mu & .\\ . & -\mu\end{bmatrix};\ A_2=\begin{bmatrix}. & \beta\\ -\beta^{-1} & .\end{bmatrix};\ A_3=\begin{bmatrix}. & b\\ b & .\end{bmatrix} \qquad (A2\text{-}2)$$

with $\mu^2=b^2=1$. If we restrict ourselves to real values of β, one may take for β, μ and b any one of the eight sign combinations ± 1 which give rise to the eight representations of the following table

μ	+	+	−	−	+	+	−	−
β	+	−	+	−	+	−	+	−
b	+	+	+	+	−	−	−	−
	Γ'_1	Γ'_2	Γ'_3	Γ'_4	Γ'_5	Γ'_6	Γ'_7	Γ'_8.

The two labelled Γ_{k1} and Γ_{k2} correspond to the choices of signs $\mu=\beta=-b=1(\Gamma'_5)$ and $\mu=\beta=b=1(\Gamma'_1)$.

All the other sign combinations are either equivalent to Γ_{k1} or to Γ_{k2}.

$$\Gamma'_2 \doteq \Gamma'_3 \doteq \Gamma'_5 \doteq \Gamma'_8 \doteq \Gamma_{k1}$$
$$\Gamma'_1 \doteq \Gamma'_4 \doteq \Gamma'_6 \doteq \Gamma'_7 \doteq \Gamma_{k2}\,.$$

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* The group table given in this reference is a contracted version of Table 12: no distinction is made between Γ_g and Γ_u representations.

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