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Classifications of Magnetic Structures

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(*Received* 17 *August* 1970)

Two different classification schemes have been used for concise characterization of magnetic structures: one (called here $C1'$) making use of magnetic groups, and another, more recent (called here $C2$), in which representations of space groups play an essential part. While the mathematical principles of $C1'$ have already been formulated in all their generality, this is not so in the case of $C2$ (although many magnetic structures have been discussed from the point of view of $C2$). In this paper the principles of $C2$ are formulated in a mathematically general way, a link between $C1'$ and $C2$ is established, and a few illustrative examples of magnetic structures are discussed. It turns out that $C1'$ and $C2$ are equivalent in a precise mathematical sense, provided cyclic boundary conditions are imposed on the crystal; each magnetic structure has then its appropriate label in both classifications. If, however, one is not willing to impose such conditions, $C2$ may in some cases (as for example helical structures) meet with mathematical difficulties while $C1'$ never does. Claims made by Bertaut (*Acta Cryst.* (1968). A**24**, 217) that $C2$ is 'more general' than $C1'$ are thus unjustified.

1. Introduction

The phrase *magnetic structure* has many connotations in solid state physics. When discussing the problem of classification of magnetic structures we will take this phrase to mean nothing else than an axial vector function that changes sign under time inversion and is defined on a set of points ('atoms') which form an ideal crystal, or any other atom arrangement. To stress that only this particular meaning is to be attached to the term magnetic structure, we shall most of the time use instead of it the term *spin arrangement*, and shall call, as is customary, the vectors *spin vectors*.

An assignment of a label to each spin arrangement is called here a *classification* of all spin arrangements if

(*a*) the label characterizes the spin arrangement completely; that is, the label allows one, from the information contained in it, to construct the whole spin arrangement;
(*b*) one obtains a list of all spin arrangements by letting the symbols occurring in the label vary over a specified class of symbols.

The problem of classification of all spin arrangements is thus a special case of the general mathematical problem of classification of all (scalar or vector or tensor *etc.*) functions defined on a discrete set of points.

If one applies an element of the space group F of a crystal to a scalar or vector function defined on it, then the function will either remain unchanged or be transformed into another function defined on the came crystal. This trivial remark makes it clear that there are two obvious ways of classifying all such functions: (1) by assigning to each function the subgroup H of F consisting of all those elements of F which leave the function unchanged (we shall call this *classification* $C1$); (2) by assigning to each function all those distinct functions which arise from it by applying the elements of F; this is equivalent to assigning a permutation representation of F according to which those distinct functions transform, or, as it will turn out, an appropriate component of such representation (we shall call this *classification* $C2$).

If a function changes sign under time inversion, as spin arrangements do, classification $C1$ can be use-

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fully replaced, as is well known, by a classification (to be called here *classification* $C1'$) in which the role of F is taken over by the direct product group $F \times A$, where A is the time-inversion group, and the role of H by a subgroup of $F \times A$ which is some magnetic group m. (One could consider of course still another classification, *classification* $C2'$, which is in the same relation to $C2$ as $C1'$ is to $C1$, but it turns out that $C2'$ is a trivial modification of $C2$, not worth further consideration).

The idea of classification $C1'$ of spin arrangements seems to have first been proposed by Landau & Lifshitz (1951). Donnay, Corliss, Donnay, Elliott & Hastings (1958) and Le Corre (1958) were the first to assign (in the sense of $C1'$) magnetic groups to magnetic structures as determined experimentally, after Belov, Neronova & Smirnova (1955) established a list of all magnetic space groups (called by them 'Shubnikov groups').

In all their generality the group theoretical principles of classification $C1'$ of all spin arrangements on crystals have been formulated by Opechowski & Guccione (1965), who have shown that every spin arrangement, however low its symmetry group may be, has its appropriate place in $C1'$ (in particular, this is true of helical spin arrangements).

The principles of classification $C2$ have never been formulated in an equally general manner. We present such a formulation in this paper. We also consider and answer the question, to which extent the two classifications, $C1'$ and $C2$, can be regarded as equivalent in a precise mathematical sense.

An extensive paper on this subject has recently been published by Bertaut (1968), who strongly advocates classification $C2$ (he calls it 'representation analysis of magnetic structures'; it should be added that he often means by this phrase more than just a classification of magnetic structures). Although representations of space groups have already been used earlier in this connexion (Bertaut, 1963; Alexander, 1962) it is only in that paper that, for the first time, the general idea of $C2$ is sketched and explained by means of a few examples. However, Bertaut's presentation of $C2$ is by far not general enough to make a valid comparison between $C2$ and $C1'$ possible. Despite that, Bertaut did attempt such a comparison, and arrived at a conclusion which he reaffirmed in a more recent paper (Bertaut, 1969) in these words: '... surprisingly enough, this new point of view' – this is $C2$ – 'offers a wider frame for the description and analysis of magnetic structures than invariance under Shubnikov groups. It can be shown indeed that Shubnikov groups can only describe magnetic structures which belong to one-dimensional real representations of the 230 space groups. In our theory there is no limitation either on the nature, real or complex, nor on the dimension of the irreducible representation'.

Since Bertaut has not pointed out any specific errors in the general formulation of $C1'$, one is very much puzzled by this conclusion. The solution of the puzzle is that what Bertaut finds 'surprising' is simply not true; see examples 2 and 3 in § 6. A possible reason for Bertaut's conclusion is discussed in § 6, example 1.

The plan of this paper is as follows. In § 2, after preliminaries concerning notation and terminology, we formulate four elementary group theoretical lemmas which we shall repeatedly use. In § 3, we briefly discuss, as an introduction to the subject, classification $C1$ of scalar functions defined on any atom arrangement. In § 4, we concentrate our attention on scalar and vector functions which change sign under time inversion, hence in particular on spin arrangements, and we present the principles of $C1'$ in a form convenient for comparison with $C2$. In § 5 we formulate the principles of $C2$ in a general way for any scalar or vector function defined on any atom arrangement. In § 6 we formulate and discuss the relation between $C1'$ and $C2$; we also illustrate it with examples. Finally, we summarize our general conclusions.

2. Preliminaries

We begin with a few preliminary remarks concerning some notations, terminology and conventions used in this paper.

A definite choice of a Cartesian coordinate system in the three-dimensional Euclidean space will always be understood without, in general, being specified explicitly. A discrete set of points $\{\mathbf{r}_1, \mathbf{r}_2, \ldots\}$, where $\mathbf{r}_k (k = 1,2, \ldots)$ stands for the 3 coordinates of a point, will be referred to as an *atom arrangement* of identical atoms, provided the number of points in any finite domain is finite. If the set is finite we shall call it a *molecule* (consisting of identical atoms located at $\mathbf{r}_1$, $\mathbf{r}_2$, ...).

As is well known, an element K of any finite or infinite group K of isometries is always of the form $(R|\mathbf{v})$, where R is a (proper or improper) rotation and $\mathbf{v}$ is a translation. *Applying* K to $\mathbf{r}$ means replacing $\mathbf{r}$ by another point ('atom') which will be denoted by $K\mathbf{r}$ or $(R|\mathbf{v})\,\mathbf{r}$ or $R\mathbf{r}+\mathbf{v}$ where R is a 3×3 matrix, $\mathbf{r}$ and $\mathbf{v}$ are 3-row column matrices.

If an atom arrangement $\{\mathbf{r}_1, \mathbf{r}_2, \ldots\}$ can be *generated* by applying to one of its atoms, $\mathbf{r}_1$ say, all elements of K in turn, it will be denoted by $\mathsf{K}\mathbf{r}_1$ and called a *simple* atom arrangement. We shall speak, in particular, of *simple molecules* and *simple crystals*, the latter being atom arrangements $\mathsf{F}\mathbf{r}$, where F is any space group. A simple crystal is thus a crystal whose atoms occupy one set of 'equivalent positions' in the sense of *International Tables of X-ray Crystallography* (1952). An arbitrary (composite) atom arrangement can always be considered as consisting of a finite number of interlocking simple atom arrangements.

An atom arrangement A is called *invariant* under an isometry K if $\{K\mathbf{r}_1, K\mathbf{r}_2, \ldots\} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots\}$, that is, if the effect of K on A is a permutation of its atoms. The group G of all those isometries under which A is in-

variant is called its *symmetry group*. If Kr is a simple atom arrangement, and G its symmetry group, then $\mathsf{Kr}=\mathsf{Gr}$ and $\mathsf{G}\supseteq\mathsf{K}$. When denoting a simple atom arrangement by Gr we shall always tacitly assume that G has been chosen to be its symmetry group.

The set of all those elements G of the symmetry group G of an atom arrangement $\{\mathbf{r}_1, \mathbf{r}_2, \ldots\}$ for which $G\mathbf{r}_k=\mathbf{r}_k$ forms a subgroup of G to be called the *site group of (the atom at)* $\mathbf{r}_k$ and denoted by $\mathsf{G}(\mathbf{r}_k)$. Site groups of the atoms of a simple atom arrangement A are conjugate subgroups of the symmetry group of A.

We will make use of the following lemmas:

L1: Quite generally, if

$$\mathsf{K}=\mathsf{K}(\mathbf{r}_1)+K_2\mathsf{K}(\mathbf{r}_1)+K_3\mathsf{K}(\mathbf{r}_1)+\ldots$$

is the decomposition of K into left-cosets of $\mathsf{K}(\mathbf{r}_1)$ then for any two distinct left-cosets $K_\alpha\mathsf{K}(\mathbf{r}_1)$ and $K_\beta\mathsf{K}(\mathbf{r}_1)$, $\alpha\neq\beta$, the sets of atoms $K_\alpha\mathsf{K}(\mathbf{r}_1)\,\mathbf{r}_1$ and $K_\beta\mathsf{K}(\mathbf{r}_1)\,\mathbf{r}_1$ of the atom arrangement Kr_1 have no atoms in common. Hence the number of atoms of the atom arrangement is equal to the index of $\mathsf{K}(\mathbf{r}_1)$ in K, which may of course be finite or infinite.

L2: On the other hand, if L is an arbitrary subgroup of K and if

$$\mathsf{K}=\mathsf{L}+\mathsf{L}K_2+\mathsf{L}K_3+\ldots$$

is the decomposition of K into right-cosets of L, then any two sets of atoms $\mathsf{L}K_\alpha\mathbf{r}$ and $\mathsf{L}K_\beta\mathbf{r}$ are either identical or have no atoms in common. Furthermore, if L is of index l' in K, we may write by omitting redundant cosets

$$\mathsf{Kr}=\mathsf{Lr}+\mathsf{L}K_2\mathbf{r}+\ldots+\mathsf{L}K_{l''}\mathbf{r}\,,\quad l''\leq l'\,.$$

That means that the atom arrangement Kr can also be regarded as composed of l'' interlocking simple atom arrangements generated by L from the atoms located at $\mathbf{r}$, $K_2\mathbf{r}$, ..., $K_{l''}\mathbf{r}$.

L3: Each subgroup L of an arbitrary finite or infinite discrete group K generates a representation of that group, a transitive permutation representation P_L [see for example Speiser (1956)]. To obtain P_L one simply makes correspond to an element K of K the permutation $P_\mathsf{L}(K)$,

$$\begin{pmatrix}\mathsf{L} & \mathsf{L}K_2 & \mathsf{L}K_3 & \ldots\\ \mathsf{L}K & \mathsf{L}K_2K & \mathsf{L}K_3K\ldots & \end{pmatrix}$$

of the right-cosets of L in K. One then shows that $P_\mathsf{L}(K_\alpha)P_\mathsf{L}(K_\beta)=P_\mathsf{L}(K_\gamma)$ if $K_\alpha K_\beta=K_\gamma$. From such a representation of K by permutations one obtains a representation of K by matrices as follows: if $\mathsf{L}K_\alpha K=\mathsf{L}K_\beta$ ($\alpha=1,2,\ldots$) then one makes correspond to the element K of K the matrix whose αth row consists of zeros except for the entry in the βth column which is unity. The dimension of the matrix representation so obtained is equal to the index of L in K. Henceforward 'permutation representation' will always mean such a matrix representation; it will be denoted as before by P_L and its matrices by $P_\mathsf{L}(K)$. A permutation representation is never irreducible (except in the trivial case $\mathsf{L}=\mathsf{K}$).

L4: Let Δ be a (reducible or irreducible) d-dimensional representation of a group K, and $\mathbf{b}_1, \mathbf{b}_2, \ldots \mathbf{b}_d$ be a basis in the carrier space of Δ such that

$$K\mathbf{b}_\alpha=\sum_{\beta=1}^{d}\mathbf{b}_\beta\Delta(K)_{\beta\alpha}\,.$$

Then $\mathbf{a}=a_1\mathbf{b}_1+a_2\mathbf{b}_2+\ldots+a_d\mathbf{b}_d$ is a vector invariant under a subgroup L of K if an only if

$$a_\alpha=\sum_{\beta=1}^{d}\Delta(L)_{\alpha\beta}a_\beta$$

for all elements L of L.

Finally, we would like to emphasize that we do not attach the same meaning to the two expressions 'd functions form a basis in the carrier space of the representation Δ' and 'd functions transform according to the representation Δ'. The former implies that the d functions are linearly independent, whereas the latter does not.

3. Classification *C*1

Let us consider a simple atom arrangement $\mathsf{Gr}_1=\{\mathbf{r}_1, \mathbf{r}_2, \ldots\}$. Let us denote the orders of G and $\mathsf{G}(\mathbf{r}_1)$ by g and s, and the index of $\mathsf{G}(\mathbf{r}_1)$ in G by n; g and n may be infinite but s is always finite: $g/s=n$.

Scalar functions

We now consider an arbitrary (real or complex) function $f(\mathbf{r})$ defined on Gr_1, and the effect of *applying* the elements of G to it. This means as usual replacing the function $f(\mathbf{r})$ by the function $f(G^{-1}\mathbf{r})$, to be denoted by $Gf(\mathbf{r})$, that is

$$Gf(\mathbf{r})=f(G^{-1}\mathbf{r})\,. \tag{3·1}$$

If $Hf(\mathbf{r})=f(\mathbf{r})$, where H is in G, the function $f(\mathbf{r})$ is said to be *invariant under* H, and H is said to be a *symmetry element of* $f(\mathbf{r})$. The set of all symmetry elements of $f(\mathbf{r})$ constitutes a subgroup H of G, called the *symmetry group of* $f(\mathbf{r})$. Any subgroup of H is called an *invariance group of* $f(\mathbf{r})$.

If H is the symmetry group of $f(\mathbf{r})$ then the conjugate subgroup $G\mathsf{H}G^{-1}$ is the symmetry group of $Gf(\mathbf{r})$, for

$$(G\mathsf{H}G^{-1})Gf(\mathbf{r})=G\mathsf{H}f(\mathbf{r})=Gf(\mathbf{r})\,.$$

Given an atom arrangement Gr_1, one can construct all those functions defined on it which have a given symmetry group $H\subseteq G$ as follows:

Decompose G into right-cosets of H:

$$\mathsf{G}=\mathsf{H}+\mathsf{H}G_2+\ldots\mathsf{H}G_{h'} \tag{3·2}$$

(if G is infinite h' need not be finite);
correspondingly decompose Gr_1 (see *L2*) into $h''\leq h'$ disjoint sets of atoms:

$$\mathsf{Gr}_1=\mathsf{H}\mathbf{r}_1+\mathsf{H}G_2\mathbf{r}_1+\ldots+\mathsf{H}G_{h''}\mathbf{r}_1\,. \tag{3·3}$$

Choose h'' arbitrary numbers $a_1, a_2 \ldots a_{h''}$, and define the function $f(\mathbf{r})$ by putting, for all elements of H

$$f(\mathbf{r})=a_\alpha\,, \quad \text{if} \quad r=H\mathbf{r}_\alpha \qquad \text{where} \quad \mathbf{r}_\alpha=G_\alpha\mathbf{r}_1\ (\alpha=1,2,\ \ldots\ h'')\ .$$

The function $f(\mathbf{r})$ then clearly has H as an invariance group whatever the choice of $a_1, a_2 \ldots a_{h''}$.

By choosing each possible set of h'' numbers a_1, $a_2 \ldots a_{h''}$ in turn, we thus obtain, in the way just described, all those possible functions on Gr_1 whose symmetry group is either H or contains H as a proper subgroup. The latter may occur if $a_\alpha=a_\beta$ for some $\alpha\neq\beta$ (for example, in the extreme case where all h'' numbers a_α are equal the symmetry group of $f(\mathbf{r})$ will be G itself). But this only means that when constructing in this way the functions $f(\mathbf{r})$ for each subgroup H of G in turn, we obtain some functions more than once. When classifying all the functions defined on Gr_1, according to their symmetry groups this redundancy can easily be removed.

A full classification label of $f(\mathbf{r})$ is then

$$[\mathsf{G},\ \mathsf{H};\ \mathbf{r}_1, \mathbf{r}_2, \ \ldots\ \mathbf{r}_{h''};\ a_1, a_2\ \ldots\ a_{h''}]\,, \qquad (3{\cdot}4)$$

and $f(\mathbf{r})$ can completely be determined from it.

By letting, in the classification label (3·4), H vary over the set of all subgroups of G, and $\{a_1, a_2 \ldots a_{h''}\}$ over the set of all h''-plets of numbers with no regard to their order (this means that, for example, $\{2,3,5\}=\{3,2,5\}$), we obtain a list of all functions on Gr_1.

This classification of all scalar functions defined on simple atom arrangements will be referred to as *classification* $C1$ or, simply $C1$.

The generalization of $C1$ to the case of composite atom arrangements (that is, whose atoms occupy more than one set of equivalent positions) is straightforward and we shall not discuss it here.

Vector functions

After having discussed the principles of a classification of all scalar functions on atom arrangements by means of symmetry groups, we should next consider the problem of an analogous classification of all (real or complex) vector functions on atom arrangements. (Here 'vector' when used in the phrase 'vector function' will always mean a vector in a three-dimensional Euclidean vector space. On the other hand, we shall also speak of vectors in carrier spaces of representations of groups; in particular, the term 'invariant vector' is used in this latter sense).

Applying an element $G=(R|\mathbf{v})$ of a group G of isometries to a vector function $\mathbf{B}(\mathbf{r})$ defined on Gr_1 means replacing $\mathbf{B}(\mathbf{r})$ by the function $[G]\,\mathbf{B}(\mathbf{r})$ defined as usual by

$$[G]\mathbf{B}(\mathbf{r})=\delta_R\, R\mathbf{B}(G^{-1}\mathbf{r}) \qquad (3{\cdot}5)$$

where $\delta_R=\det R=+1$ if $\mathbf{B}(\mathbf{r})$ are axial vectors, and $\delta_R=1$ if $\mathbf{B}(\mathbf{r})$ are polar vectors; more explicitly, in terms of components $B^{(i)}(\mathbf{r})$ of $\mathbf{B}(\mathbf{r})$.

$$[G]B^{(i)}(\mathbf{r})=\sum_{j=1}^{3}\delta_R R_{ij}B^{(j)}(G^{-1}\mathbf{r}). \qquad (3{\cdot}5A)$$

Such a vector function is called *invariant* under G if $[G]\mathbf{B}(\mathbf{r})=\mathbf{B}(\mathbf{r})$. The definitions of symmetry elements, invariance groups and symmetry groups are then introduced in the same way as in the case of scalar functions.

The next step would be the construction of all possible vector functions with a given symmetry group $\mathsf{H}\subseteq\mathsf{G}$ on a given simple atom arrangement Gr_1, and finally their classification $C1$. However, we are primarily interested in the case of spin arrangements. To discuss these we shall make use (in § 4) of magnetic groups and arrive at a classification (to be called $C1'$) appropriate for this case. The general case of arbitrary vector functions could then easily be obtained by an obvious modification of the argument given there for spin arrangements; therefore we do not treat it explicitly.

4. Classification $C1'$

One can generalize the concept of the symmetry group of a function defined on an atom arrangement by taking into account the permutations of its distinct values. One defines for this purpose the *colour groups* (the distinct values of a function are often called *colours* in this context) in such a way that a symmetry group generalized in this sense is always some colour group. A mathematically most satisfactory but very concise discussion of this question was given by Van der Waerden & Burckhardt (1961), where references to earlier work can be found.

For our purpose it is more appropriate, however, to make use of another generalization of the concept 'symmetry group of a function'. We are here not particularly interested in a classification by symmetry groups of arbitrary scalar or vector functions defined on atom arrangements. We are only interested in such a classification of spin arrangements, that is, axial-vector functions which have the additional property of changing sign under time inversion, while atom arrangements on which they are defined are invariant under this operation. Elements of symmetry groups generalized for this purpose will thus be pairs (G,A), where G is an element of a discrete group of isometries G, and A is an element of a group A which consists of the identity E and time inversion E'; the generalized symmetry groups themselves will be certain subgroups of the direct product $\mathsf{G}\times\mathsf{A}$.

Every scalar function $f(\mathbf{r})$ is either a time-inversion even function, $E'f(\mathbf{r})=f(\mathbf{r})$, or a time-inversion odd function, $E'f(\mathbf{r})=-f(\mathbf{r})$, or a linear combination of an even and an odd function. We shall simply say *E'-even* and *E'-odd*, and we shall use the same definitions and terminology in the case of vector functions. Thus spin arrangements are E'-odd vector functions defined on atom arrangements; the atom arrangements themselves are E'-even functions on the Euclidean space.

While spin arrangements, that is, arrangements of magnetic dipoles, are E'-odd axial vector functions, similar arrangements of electric dipoles are E'-even polar vector functions.

We begin with a few well-known definitions, which we repeat here to explain our notation and possibly avoid misunderstandings.

Applying an element (G,A) to a scalar function $f(\mathbf{r})$ defined on an atom arrangement $\mathbf{Gr}_1$ means replacing it by the function $(G,A)f(\mathbf{r})$, where

$$(G,A)f(\mathbf{r}) = \varepsilon_A G f(\mathbf{r}) = \varepsilon_A f(G^{-1}\mathbf{r}) \quad \text{if} \quad f(\mathbf{r}) \text{ is } E'\text{-odd} \qquad (4{\cdot}1)$$

$$(G,A)f(\mathbf{r}) = G f(\mathbf{r}) = f(G^{-1}\mathbf{r}) \quad \text{if} \quad f(\mathbf{r}) \text{ is } E'\text{-even}, \qquad (4{\cdot}2)$$

and $\varepsilon_A = +1$ or -1 according as $A = E$ or $A = E'$; ε_A is called the *signature* of the element (G,A).

Similarly, if $G = (R|\mathbf{v})$, *applying* (G,A) to a spin arrangement (or any other E'-odd axial vector function) $\mathbf{S}(\mathbf{r})$ defined on $\mathbf{Gr}_1$ means replacing it by the spin arrangement $[G,A]\mathbf{S}(\mathbf{r})$, where

$$[G,A]\mathbf{S}(\mathbf{r}) = \varepsilon_A [G]\mathbf{S}(\mathbf{r}) \qquad (4{\cdot}3)$$

and [this is definition (3·5*A*)]

$$[G]S^{(i)}(\mathbf{r}) = \sum_{j=1}^{3} \delta_R R_{ij} S^{(j)}(G^{-1}\mathbf{r}), \quad i = 1,2,3. \qquad (4{\cdot}4)$$

In the case of an E'-even axial vector function $\mathbf{P}(\mathbf{r})$ it means replacing it by

$$[G,A]\mathbf{P}(\mathbf{r}) = [G]\mathbf{P}(\mathbf{r}). \qquad (4{\cdot}5)$$

In the case of polar vector functions (E'-odd or E'-even) definitions (4·3) and (4·4) remain unchanged except for replacing δ_R by unity.

These definitions are of course compatible with our assumption that, for any atom position $\mathbf{r}$ of an atom arrangement, one has $[G,A]\mathbf{r} = G\mathbf{r}$.

The definitions (4·1) to (4·4) make it possible to attach in the present case of E'-odd functions a meaning to such phrases as 'invariance' or 'symmetry element of a spin arrangement' *etc.*, analogous to their meaning as defined in § 3.

Since we consider only single valued functions, no scalar or vector E'-odd function can remain unchanged when the element (E,E') of $\mathsf{G} \times \mathsf{A}$ is applied to it. Therefore invariance groups of such functions, and in particular of spin arrangements, cannot contain this element. In other words, each such invariance group is necessarily a magnetic group. For *magnetic groups* can be defined as precisely those subgroups of $\mathsf{G} \times \mathsf{A}$ (G is here any discrete group of isometries) which do not contain the element (E,E').* According to this definition, all groups of isometries, and hence, in particular, all space groups and their subgroups are magnetic groups; they are called *trivial* magnetic groups.

To avoid a possible misunderstanding we should perhaps mention that usually one restricts the term 'magnetic group' to the case, most important in practice, when G is a space group F or any subgroup of a space group (in particular, any crystallographic point group).

All essential properties of magnetic groups have been derived, starting out from the above definition, by Opechowski & Guccione (1965). We assume here these properties as known, and we shall use the terminology, conventions and notation introduced in that reference unless otherwise stated. (One exception is that both, (G,A) and $[G,A]$, are simply denoted there by GA). However, we will repeat one such convention explicitly: we shall call an element (G,A) a *primed element* if $A = E'$, and an *unprimed element* if $A = E$; correspondingly we shall often use a simplified notation: G' for (G,E') and G for (G,E).

The prescriptions for constructing all scalar functions $f(\mathbf{r})$ and all spin arrangements $\mathbf{S}(\mathbf{r})$ defined on a given atom arrangement $\mathbf{Gr}_1$ and having a non-trivial magnetic group $\mathsf{m} \subset \mathsf{G} \times \mathsf{A}$ as an invariance group are analogous to the prescriptions formulated for scalar functions in § 3; analogous but somewhat more complicated.

A non-trivial magnetic group m is always of the form

$$\mathsf{m} = \mathsf{H} + \mathsf{H}L_2', \qquad (4{\cdot}6)$$

where

$$\mathsf{L} = \mathsf{H} + \mathsf{H}L_2 \qquad (4{\cdot}7)$$

is some discrete group of isometries and L_2 is an element of L not in H. Whenever necessary, we shall denote m more explicitly by $\mathsf{m}_{\mathsf{L}}(\mathsf{H})$. In particular, if L is a three-dimensional space group, the symbol m would be replaced by M and the group M called a *magnetic space group* or *Shubnikov group*. However, we want to emphasize that the prescriptions we are about to formulate are perfectly general, and presuppose nothing about the non-trivial magnetic group m.

We decompose G into right-cosets of L,

$$\mathsf{G} = \mathsf{L} + \mathsf{L}G_2 + \ldots + \mathsf{L}G_{l'}, \qquad (4{\cdot}8)$$

and correspondingly (see *L*2)

$$\mathbf{Gr}_1 = \mathsf{L}\mathbf{r}_1 + \mathsf{L}G_2\mathbf{r}_1 + \ldots + \mathsf{L}G_{l''}\mathbf{r}_1, \; l'' \leq l'. \qquad (4{\cdot}9)$$

We next define the magnetic site group $\mathsf{m}(\mathbf{r}_\alpha)$ of $\mathbf{r}_\alpha = G_\alpha \mathbf{r}_1$ as the magnetic group consisting of all those elements $m(\mathbf{r}_\alpha)$ of m for which $m(\mathbf{r}_\alpha)\mathbf{r}_\alpha = \mathbf{r}_\alpha$:

$$\mathsf{m}(\mathbf{r}_\alpha) = \begin{cases} \mathsf{H}(\mathbf{r}_\alpha) + \mathsf{H}(\mathbf{r}_\alpha)L_3' \text{ if there exists } L_3' \text{ in } \mathsf{m} \\ \quad \text{such that } L_3\mathbf{r}_\alpha = \mathbf{r}_\alpha \\ \mathsf{H}(\mathbf{r}_\alpha) \quad \text{otherwise}; \quad \alpha = 1,2,\ldots l''. \end{cases} \qquad (4{\cdot}10)$$

Whenever necessary we shall denote the elements of m more explicitly by (L,A), where $L = (P|\mathbf{u})$, and the elements of $\mathsf{m}(\mathbf{r}_\alpha)$ by $((C_\alpha|\mathbf{w}_\alpha), A_\alpha)$.

We deal with the case of scalar E'-odd functions and with that of spin arrangements separately.

* If A is interpreted as the symmetric group on two variables, and E' as a permutation of two 'colours' rather than time inversion, then this definition becomes the definition of a *two-colour group*, also called a *black-and-white group*.

Scalar E′-odd functions

As we have seen in § 3, it is always possible to construct, for a given subgroup H of G, a scalar function defined on an arbitrary atom arrangement Gr_1 and invariant under H. This is no longer true when H is replaced by a non-trivial magnetic subgroup m of $\mathsf{G}\times\mathsf{A}$.

A necessary and sufficient condition for the existence of an E'-odd scalar function $f(\mathbf{r})\not\equiv 0$ defined on Gr_1 and invariant under m is that $\mathsf{m}(\mathbf{r}_1)$ be a trivial magnetic group.

The condition is necessary because from $mf(\mathbf{r})=f(\mathbf{r})$ it follows that $f(m\mathbf{r})=\varepsilon_m f(\mathbf{r})$, where ε_m is the signature of m, and hence, by putting $\mathbf{r}=\mathbf{r}_1$, one obtains $f(\mathbf{r}_1)=\varepsilon_{m(\mathbf{r}_1)}f(\mathbf{r}_1)$; hence $\varepsilon_{m(\mathbf{r}_1)}=1$.

If $\mathsf{m}(\mathbf{r}_1)$ is a trivial magnetic group, then the function $f(\mathbf{r})$ defined by putting

$$f(\mathbf{r})=\varepsilon_m a_\alpha \text{ for } \mathbf{r}=m\mathbf{r}_\alpha=L\mathbf{r}_\alpha\,, \qquad (4\cdot11)$$

where $a_1, a_2, \ldots a_{l''}$ are arbitrary numbers, is single-valued (because $\mathsf{m}(\mathbf{r}_1)$ is a trivial magnetic group) and invariant under m; hence the condition is also sufficient.

Equation (4·11) thus constitutes a prescription for constructing all those E'-odd scalar functions which have m as an invariance group. If $\mathsf{m}(\mathbf{r}_\alpha)$ are not all trivial, such functions on Gr_1 do not exist.

Proceeding further as in § 3 we arrive at a classification label of an E'-odd function $f(\mathbf{r})$ whose symmetry group is $\mathsf{m}_L(\mathsf{H})$:

$$[\mathsf{G};\ \mathsf{m}_L(\mathsf{H});\ \mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_{l''};\ a_1, a_2, \ldots a_{l''}]\,. \qquad (4\cdot12)$$

We shall refer to the classification of E'-odd functions which makes use of such labels as *classification* $C1'$ or simply $C1'$.

If we had disregarded the existence of magnetic groups, we would have missed half of the symmetry elements of an E'-odd function, and its $C1$-label would be almost twice as complicated because the number of positions $\mathbf{r}$, at which one would have to specify the values of the function, would be $2l''=h''$:

$$[\mathsf{G};\ \mathsf{H};\ \mathbf{r}_1, \mathbf{r}_1', \mathbf{r}_2, \mathbf{r}_2' \ldots, \mathbf{r}_{l''}, \mathbf{r}_{l''}';\ a_1, -a_1, a_2, -a_2, \ldots a_{l''}, -a_{l''}]\,. \qquad (4\cdot13)$$

In this way the link between $C1$ and $C1'$ for scalar functions is established.

We see that a necessary (but not sufficient) condition for an E'-odd function $f(\mathbf{r})$ to have a non-trivial magnetic symmetry group is that a number and its negative must occur the same number of times as values of $f(\mathbf{r})$.

Spin arrangements

The treatment of this case given by Opechowski & Guccione (1965) is in some respects unnecessarily complicated; moreover, for brevity, some of the essential proofs had to be omitted there. That is why we present it here again, in a simpler way; but, of course, we shall not repeat the discussion of the specific questions connected with the important case of magnetic space groups (that is, $\mathsf{G}=\mathsf{F}$).

We formulate a convenient necessary and sufficient condition for the existence of a spin arrangement $\mathbf{S}(\mathbf{r})$ defined on Gr_1 and invariant under m: such a spin arrangement exists if, and only if, for each $\mathbf{r}_\alpha=G_\alpha\mathbf{r}_1$ the equations

$$[\mathsf{m}(\mathbf{r}_\alpha)]\mathbf{S}(\mathbf{r}_\alpha)=\mathbf{S}(\mathbf{r}_\alpha)\ \ (\alpha=1,2,\ldots l'') \qquad (4\cdot14)$$

or, more explicitly,

$$\sum_{j=1}^{3}(\varepsilon_{m(\mathbf{r}_\alpha)}\delta_{C_\alpha}C_{\alpha ij}-\delta_{ij})S^{(j)}(\mathbf{r}_\alpha)=0\ (i=1,2,3)\,, \qquad (4\cdot14A)$$

have at least one set of (non-vanishing) solutions $S^{(j)}(\mathbf{r}_\alpha)$ satisfying (4·14A) for all elements of $\mathsf{m}(\mathbf{r}_\alpha)$.

Any E'-odd axial vector $\boldsymbol{\sigma}_\alpha$ whose components satisfy these equations is called a spin vector *admissible at* $\mathbf{r}_\alpha$. In other words, a spin vector admissible at $\mathbf{r}_\alpha$ is the simultaneous eigenvector of all the matrices of $\mathsf{m}(\mathbf{r}_\alpha)$ belonging to the eigenvalue $+1$.

We show that the condition is necessary. In fact, from

$$[m]\mathbf{S}(\mathbf{r})=\mathbf{S}(\mathbf{r})\,,\quad m=(L,A)\,,\quad L=(P|\mathbf{u})\,,$$

and [see (4·3) and (4·4)]

$$[m]S^{(i)}(\mathbf{r})=\varepsilon_m\sum_{j=1}^{3}\delta_P P_{ij}S^{(j)}(L^{-1}\mathbf{r})\,,\quad i=1,2,3\,, \qquad (4\cdot15)$$

it immediately follows that, if $\mathbf{r}=LG_\alpha\mathbf{r}_1=L\mathbf{r}_\alpha$ then

$$\varepsilon_{m(\mathbf{r}_\alpha)}\delta_{C_\alpha}C_\alpha\mathbf{S}(\mathbf{r}_\alpha)=\mathbf{S}(\mathbf{r}_\alpha)\,,$$

which is another way of writing (4·14A).

To show that the condition is sufficient, we make use of it to construct a spin arrangement $\mathbf{S}(\mathbf{r})$ invariant under m. Let $\boldsymbol{\sigma}_\alpha$ be an admisible spin vector at $\mathbf{r}_\alpha$, $\alpha=1, 2, \ldots l''$; we assume here that the magnitudes of these l'' admissible spin vectors are all equal (see, however, the final paragraph of this section). Then the spin arrangement in which the spin vector $\mathbf{S}(\mathbf{r})$ at

$$\mathbf{r}=m\mathbf{r}_\alpha=L\mathbf{r}_\alpha$$

is given by

$$S^{(i)}(\mathbf{r})=\varepsilon_m\sum_{j=1}^{3}\delta_P P_{ij}\sigma_\alpha^{(j)}\,,\quad i=1,2,3, \qquad (4\cdot16)$$

is single-valued and invariant under m. (More specifically, each of the l'' 'sub'-spin arrangements (4·16) on the l'' interlocking atom arrangements $LG_\alpha\mathbf{r}_1$, see equation (4·9), which constitute the atom arrangement Gr_1, is invariant under m). Perhaps it is useful to emphasize that in a spin arrangement constructed according to the prescription (4·16) the spin vectors at $\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_{l''}$ are just the selected admissible vectors: $\mathbf{S}(\mathbf{r}_\alpha)\equiv\boldsymbol{\sigma}_\alpha$, $\alpha=1,2,\ldots l''$.

We first show that the spin arrangement (4·16) is single-valued; that is, we show that for any two elements m and $\bar{m}$ of m the equality $m\mathbf{r}_\alpha=\bar{m}\mathbf{r}_\alpha$ implies that the right-hand side of equation (4·16) has the same value. The same equality also implies that $m^{-1}\bar{m}$ belongs to $\mathsf{m}(\mathbf{r}_\alpha)$. Hence $\bar{m}=m\,m(\mathbf{r}_\alpha)$. The right-hand side of (4·16) for $m\,m(\mathbf{r}_\alpha)$ is:

$$\varepsilon_{mm(\mathfrak{r}\alpha)} \sum_j \delta_{PC_\alpha}(PC_\alpha)_{ij}\sigma_\alpha^{(j)} = \varepsilon_m \sum_k \delta_P P_{ik}(\varepsilon_{m(\mathfrak{r}\alpha)} \sum_j \delta_{C_\alpha} C_{\alpha kj}\sigma_\alpha^{(j)}) .$$

Using (4·14*A*) this becomes equal to the right-hand side of (4·16) for m.

We next show that the spin arrangement (4·16) is invariant under any $\bar{m}$ belonging to m. From (4·16) it follows that

$$S^{(i)}(\bar{L}^{-1}\mathbf{r}) = S^{(i)}(\bar{L}^{-1}L\mathbf{r}_\alpha) = \varepsilon_{\bar{m}}\varepsilon_m \sum_k \delta_{\bar{P}}\delta_P \sum_l (\bar{P}^{-1})_{jl}P_{lk}\sigma_\alpha^{(k)} .$$

By substituting this expression in (4·15) where we first replace m by $\bar{m}$ one obtains immediately

$$[\bar{m}]S^{(i)}(\mathbf{r}) = S^{(i)}(\mathbf{r}) , \quad i=1,2,3 . \qquad Q.E.D.$$

Prescription (4·16) for constructing spin arrangements on Gr_1 presupposes the existence of admissible spin vectors $\boldsymbol{\sigma}_\alpha$, $\alpha=1,2,\ldots l''$. Admissible spin vectors always exist if the atoms of a simple atom arrangement occupy general positions (that is, if $\mathbf{r}_1$ is a general position) because then every spin vector is admissible at any position. If the atoms occupy special positions admissible spin vectors may not exist, and hence, no spin arrangements will exist in such a case. The number $n_\alpha(0\leq n_\alpha\leq 3)$ of linearly independent admissible vectors $\boldsymbol{\sigma}_\alpha$ is given by

$$n_\alpha = \frac{1}{s_\alpha}\sum_{m(\mathfrak{r}\alpha)} \varepsilon_{m(\mathfrak{r}\alpha)}\delta_{C\alpha}\ \mathrm{trace}\ C_\alpha , \qquad (4\cdot17)$$

where s_α is the order of $\mathsf{m}(\mathbf{r}_\alpha)$.

Since the condition (4·14*A*) is also necessary, all possible spin arrangements will be obtained from (4·16), by taking in turn each simple atom arrangement Gr_1, and, given Gr_1, each magnetic group $\mathsf{m_L(H)}$ for which L is a subgroup of G, and each set $\{\boldsymbol{\sigma}_1\equiv\mathbf{S}(\mathbf{r}_1), \boldsymbol{\sigma}_2\equiv\mathbf{S}(\mathbf{r}_2), \ldots \boldsymbol{\sigma}_{l''}\equiv\mathbf{S}(\mathbf{r}_{l''})\}$ of admissible vectors. In general one will obtain in this way each spin arrangement more than once, but this redundancy is easily removed.

The classification label

$$[\mathsf{G};\ \mathsf{m_L(H)};\ \mathbf{S}(\mathbf{r}_1),\ \mathbf{S}(\mathbf{r}_2),\ \ldots\ \mathbf{S}(\mathbf{r}_{l''})] \qquad (4\cdot18)$$

of a spin arrangement $\mathbf{S}(\mathbf{r})$ determines it uniquely if $\mathsf{m_L(H)}$ is its symmetry group (rather than one of its invariance groups). We shall refer to the classification of spin arrangements which makes use of such labels as *classification* $C1'$ or simply $C1'$.

In some cases it may not be necessary to specify all the l'' spin vectors occurring in the $C1'$ label of a spin arrangement. It may be sufficient to specify a smaller number of them together with some algebraic relations. This point has already been discussed by Opechowski & Guccione (1965), § IV, 2, *h* and § IV, 3. As explained there in detail, it is sufficient, for example, in the case of a simple helical spin arrangement to specify one single spin vector together with a group which generates the countable infinity of all other spin vectors from that one; thus, in the $C1'$ label, one would indicate one spin vector at $\mathbf{r}_1$ (say) and the group which generates the others – see also example 4 in § 6 below. Such groups, that is, groups whose elements operate in the spin vector space only, are closely related to 'spin space groups' introduced by Brinkman & Elliott (1966) and to groups considered by Kitz (1965). We shall not discuss this question here.

So far we have considered only simple atom arrangements. The generalization of $C1'$ to the case of composite atom arrangements (that is, atom arrangements whose atoms, no longer necessarily identical, occupy more than one set of equivalent positions, or whose otherwise identical atoms have spins of different magnitudes) is straightforward: spin arrangements on each of the several component atom arrangements are assigned their own $C1'$ label. Since magnetic groups occurring in the several $C1'$ labels may be different, several magnetic groups will, in general, be assigned to such a composite atom arrangement. There is nothing surprising or objectionable in such a situation. Characterizing the spin arrangement defined on a composite atom arrangement by means of the intersection of the several magnetic groups would not be useful; just as it would not be useful to say that a plane geometrical figure consisting of a triangle and a square which have a common centre has no symmetry at all.

5. Classification $C2$

In § 3 we have described the principles of a classification, $C1$, of all functions $f(\mathbf{r})$ defined on atom arrangements by means of the symmetry groups of such functions. However, in the case of E'-odd functions, $C1$ has the disadvantage of not taking into account the additional symmetry elements (the 'primed symmetry elements') which E'-odd functions may possess. Classification $C1'$ (described in § 4) of all E'-odd functions and all spin arrangements (which are E'-odd axial vector functions) by means of magnetic groups is free from this disadvantage.

In this section, we shall consider scalar functions and spin arrangements again disregarding the fact that the latter are E'-odd, and the former may be E'-odd, and show that:

(*A*) to each spin arrangement (or scalar function) with symmetry group H, according to $C1$, a representation Γ of G can be assigned in a well-defined way;

(*B*) if a given finite-dimensional representation Γ of G satisfies certain conditions then a set of spin arrangements (or scalar functions) transforming according to Γ can be constructed, which makes it possible to establish still another classification, to be called $C2$, of spin arrangements.

(*A*) We first discuss scalar functions.

Let us arrange the values of the g functions defined on Gr_1 (g is the order of G),

$$f(\mathbf{r}),\ G_2f(\mathbf{r}),\ \ldots,\ G_gf(\mathbf{r}) \qquad (5\cdot1)$$

into a rectangular array whose rows are labelled by the elements of G, and columns by the positions of the atoms of $\mathbf{Gr}_1$:

$$\begin{aligned} &f(\mathbf{r}_1), f(\mathbf{r}_2) \ \ldots \ f(\mathbf{r}_n)\,, \\ &G_2 f(\mathbf{r}_1),\ G_2 f(\mathbf{r}_2) \ \ldots \ G_2 f(\mathbf{r}_n)\,, \\ &Ggf(\mathbf{r}_1),\ Ggf(\mathbf{r}_2) \ \ldots \ G_g f(\mathbf{r}_n)\,. \end{aligned} \tag{5·2}$$

The array may be infinite because g and n may be infinite; this is the case when G is a space group and $\mathbf{Gr}_1$ a crystal. We list some of the properties of the array:

The numbers in each row are permutations of the numbers constituting the first row, that is, a value a_j of $f(\mathbf{r})$ occurs the same number, n_j, of times in each row (if $f(\mathbf{r}_k)\neq f(\mathbf{r}_l)$ for any two k and l, $k\neq l$, then $n_j=1$ for all j).

Each value of $f(\mathbf{r})$ occurs sn_j times in each column, where $s=g/n$ is the order of the site group $\mathsf{G}(\mathbf{r}_1)$. This is so because the site groups of $\mathbf{r}_1, \mathbf{r}_2 \ \ldots \ \mathbf{r}_n$ are all conjugate subgroups of G, and for this reason a position $\mathbf{r}_k$ is mapped into each position $\mathbf{r}_l$ by exactly s different elements of G.

If H (order h; index h' in G) is the symmetry group of $f(\mathbf{r})$ then the above array consists of h' different sets of h identical rows each. In other words, only h' of the g functions represented by the array are distinct. More specifically, two functions $G_a f$ and $G_b f$ are equal if and only if G_a and G_b belong to the same left-coset of H in G. We take these h' distinct functions to be

$$f_\mu(\mathbf{r})=G_\mu^{-1}f(\mathbf{r})\,,\ f_1(\mathbf{r})=f(\mathbf{r})\,,\ \mu=1,2,\ \ldots\ h'\,, \tag{5·3}$$

where G_μ are the coset representatives in the decomposition

$$\begin{aligned} \mathsf{G} &= \mathsf{H}+G_2^{-1}\mathsf{H}+\ldots+G_{h'}^{-1}\mathsf{H} \\ &= \mathsf{H}+\mathsf{H}G_2\ +\ldots+\mathsf{H}G_{h'}\,. \end{aligned} \tag{5·4}$$

The functions f_μ satisfy, for all elements of G, the relations

$$Gf_\mu(\mathbf{r})=\sum_{\mu=1}^{h'} f_\nu(\mathbf{r})P_{\mathsf{H}}(G)_{\nu\mu}\,, \tag{5·5}$$

where $P_{\mathsf{H}}(G)$ are the matrices of the permutation representation P_{H} of G, generated by the right-cosets of H in G (see $L3$ in § 2).

If the index h' of H in G is infinite, the matrices $P_{\mathsf{H}}(G)$ are countably infinite, but they are well-defined and so is the representation P_{H} itself. However, in what follows we assume h' to be finite because certain parts of our argument would, in general, not be correct if h' were infinite. We briefly discuss this difficulty later on in this section.

The h' functions f_μ constitute a basis in the carrier space of P_{H} if they are linearly independent. If only $d<h'$ among them are linearly independent, one can always find (see, for example, Van der Waerden (1932), page 74, Hilfssatz 1) d orthogonal linear combinations of them, $\varphi_\alpha(\mathbf{r})$, $\alpha=1,2\ \ldots\ d$, such that for all elements of G

$$G\varphi_\alpha(\mathbf{r})=\sum_{\beta=1}^{d}\varphi_\beta(\mathbf{r})\Gamma_{\mathsf{H}}(G)_{\beta\alpha}\,, \tag{5·6}$$

where Γ_{H} is a unitary representation of G and

$$P_{\mathsf{H}}=\Gamma_{\mathsf{H}}\oplus\ \Delta_{\mathsf{H}}\,, \tag{5·7}$$

where Δ_{H} is another unitary representation of G. One can of course always choose the linear combinations such that $\varphi_1(\mathbf{r})=f_1(\mathbf{r})=f(\mathbf{r})$, without loss of generality. The representation Γ_{H} may be reducible or irreducible.

We have thus shown that, to each function $f(\mathbf{r})$ defined on $\mathbf{Gr}_1$ and having the symmetry group H with a finite index h' in G, one can assign a finite-dimensional unitary representation Γ_{H} of G, which is uniquely determined apart from an equivalence transformation; and that one can choose a basis $\varphi_1, \varphi_2, \ldots$ in the carrier space of Γ_{H} such that $f(\mathbf{r})=\varphi_1(\mathbf{r})$. A representation Γ_{H} which has the latter property will be called a *representation of* G *associated with* $f(\mathbf{r})$.

The procedure for associating a representation Γ_{H} of G with a given vector function $\mathbf{B}(\mathbf{r})$ defined on $\mathbf{Gr}_1$ and having H as the symmetry group is, apart from obvious trivial modifications, exactly the same as in the case of scalar functions, so that it is sufficient to indicate those modifications. We shall explicitly consider the case of spin arrangements, but we shall treat them just as any other axial vector functions, that is, we shall ignore the fact that they are E'-odd axial vector functions.

If we arrange the spin vectors $\mathbf{S}(\mathbf{r}_m)$, $m=1,2\ \ldots\ n$, of the g spin arrangements

$$\mathbf{S}(\mathbf{r}),\ [G_2]\,\mathbf{S}(\mathbf{r}),\ \ldots\ [G_g]\mathbf{S}(\mathbf{r}) \tag{5·1s}$$

into an array similar to (5·2), then it is no longer true that the spin vectors,

$$[G_k]\mathbf{S}(\mathbf{r}_1),\ [G_k]\mathbf{S}(\mathbf{r}_2),\ \ldots\ [G_k]\mathbf{S}(\mathbf{r}_n),\ k=1,2,\ldots g$$

of a row of the array are permutations of the spin vectors of the first row ($k=1$, $G_1=E$); they are permutations of the spin vectors

$$\delta_{R_k}R_k\mathbf{S}(\mathbf{r}_1),\ \delta_{R_k}R_k\mathbf{S}(\mathbf{r}_2),\ \ldots\ \delta_{R_k}R_k\mathbf{S}(\mathbf{r}_n)$$

[compare definition (4·4)].

Once the symmetry group H of $\mathbf{S}(\mathbf{r})$ has been determined, the argument leading in the case of scalar functions to equations (5·3), (5·5) and (5·6) can be repeated without any change, except the change in notation. One thus obtains:

$$\mathbf{S}_\mu(\mathbf{r})=[G_\mu^{-1}]\mathbf{S}(\mathbf{r}),\ \mathbf{S}_1(\mathbf{r})=\mathbf{S}(\mathbf{r}),\ \mu=1,2,\ \ldots,\ h'; \tag{5·3s}$$

$$[G]\mathbf{S}_\mu(\mathbf{r})=\sum_{\mu=1}^{h'}\mathbf{S}_\nu(\mathbf{r})P_{\mathsf{H}}(G)_{\nu\mu}; \tag{5·5s}$$

and

$$[G]\mathbf{\Lambda}_\alpha(\mathbf{r})=\sum_{\beta=1}^{d}\mathbf{\Lambda}_\beta(\mathbf{r})\Gamma_{\mathsf{H}}(G)_{\beta\alpha},\ \alpha=1,2\ \ldots\ d\leq h'\,, \tag{5·6s}$$

the definition of P_{H} and equation (5·7) remaining unchanged; the spin arrangements $\mathbf{\Lambda}_\alpha(\mathbf{r})$ form a basis in

the carrier space of Γ_H and are orthogonal linear combinations of the spin arrangements $\mathbf{S}_\mu(\mathbf{r})$; moreover, $\mathbf{S}_1(\mathbf{r})=\mathbf{S}(\mathbf{r})=\mathbf{\Lambda}_1(\mathbf{r})$.

The finite dimensional representation Γ_H of G, uniquely determined in this way apart from an equivalence transformation, will be called a *representation of* G *associated with the spin arrangement* $\mathbf{S}(\mathbf{r})$ defined in $\mathbf{Gr}_1$ (*N.B.* Only those equivalence transformations are allowed under which the condition $\mathbf{\Lambda}_1(\mathbf{r})=\mathbf{S}(\mathbf{r})$ is preserved).

As has already been mentioned, it is essential for the validity of the above argument that the index h' of H in G be finite. If h' is infinite, then P_H is an infinite-dimensional permutation representation of G, and its decomposition into a direct sum (5·7) cannot be established in the way indicated for finite h'. We have not further examined this problem; its treatment would require an approach based on the theory of infinite-dimensional representations of groups, as developed by Mackey and others [see, for example, Coleman (1968)].

If the symmetry group H of a spin arrangement defined on a crystal is a three-dimensional space group (which means, that its magnetic symmetry group is a trivial or non-trivial three-dimensional magnetic space group), then h' is necessarily finite. In other words, every spin arrangement that is invariant under some three-dimensional discrete group of translations (which, in general, will be a proper subgroup of the translation group of the crystal) has a representation Γ_H associated with it.

If, however, the symmetry group H of a spin arrangement defined on a crystal is, for example, a two-dimensional space group, as is often the case with the helical spin arrangements, then Γ_H cannot be defined in the above described manner (if at all!); one can assign to such a spin arrangement only the infinite-dimensional permutation representation P_H.

To avoid such difficulties one can, of course, introduce cyclic boundary conditions on the crystal (thus making the group G finite); or, on the spin arrangements only (thus enforcing invariance of spin arrangements under some three-dimensional discrete groups of translations).

(*B*) Let an arbitrary (reducible or irreducible) representation Γ (dimension d) of G, and an atom arrangement $\mathbf{Gr}_1$ be given. We may assume without any loss of generality that Γ is unitary. For if a set of spin arrangements (or scalar functions) defined on $\mathbf{Gr}_1$ and transforming according to Γ is to exist at all, the representation Γ must be equivalent to one of the representation Γ_H defined in (5·7) and those could always be taken to be unitary.

To avoid awkward repetitions we shall discuss here, contrary to what we have done in (*A*), spin arrangements first, and obtain the conclusions concerning scalar functions as a byproduct.

Since we shall no longer consider explicitly the spin arrangements $\mathbf{S}_\mu(\mathbf{r})$, introduced in (*A*), which transform according to the permutation representation P_H, but only those transforming according to some given representation Γ (which may be equal to P_H, but this is here irrelevant), we may denote the latter by $\mathbf{S}_\alpha(\mathbf{r})$, $\alpha=1,2\ \ldots\ d$, rather than by $\mathbf{\Lambda}_\alpha(\mathbf{r})$, without introducing confusion. If the spin arrangements $\mathbf{S}_\alpha(\mathbf{r})$ (defined on $\mathbf{Gr}_1$, and transforming according to Γ) exist at all, then (5·6*s*) can be written as

$$[G]S_\alpha^{(i)}(\mathbf{r})=\sum_{\beta=1}^{d} S_\beta^{(i)}(\mathbf{r})\Gamma(G)_{\beta\alpha}\,,\quad i=1,2,3\,, \tag{5·8}$$

where the left-hand side of this equation is defined by (4·4), assuming that $G=(R|\mathbf{v})$. By multiplying both sides of (5·8) by $\delta_R(R^{-1})_{ki}$ and summing over i, the left-hand side of (5·8) becomes

$$\sum_i\sum_j (R^{-1})_{ki}R_{ij}S_\alpha^{(j)}(G^{-1}\mathbf{r})=S_\alpha^{(k)}(G^{-1}\mathbf{r})=GS_\alpha^{(k)}(\mathbf{r}) \tag{5·9}$$

[where the last equality follows from definition (3·1)], while the right-hand side of (5·8) becomes

$$\sum_i\sum_\beta \delta_R(R^{-1})_{ki}S_\beta^{(i)}(\mathbf{r})\Gamma(G)_{\beta\alpha} = \sum_i\sum_\beta S_\beta^{(i)}(\mathbf{r})\delta_R R_{ik}\Gamma(G)_{\beta\alpha}\,. \tag{5·10}$$

Equating (5·9) and (5·10) one obtains

$$GS_\alpha^{(k)}(\mathbf{r})=\sum_i\sum_\beta S_\beta^{(i)}(\mathbf{r})D(G)_{i\beta;k\alpha}\,, \tag{5·11}$$

where $D(G)_{i\beta;k\alpha}$ are the elements of the direct product matrix

$$D(G)=\delta_R R\otimes\Gamma(G)\,. \tag{5·12}$$

We have thus shown that if the d vector functions $\mathbf{S}_\alpha(\mathbf{r})$, $\alpha=1,2,\ \ldots\ d$, form a basis of the d-dimensional representation Γ of G, then the $3d$ functions $S_\alpha^{(i)}(\mathbf{r})$, $i=1,2,3$, transform according to the $3d$-dimensional unitary representation D of G, whose matrices are given by (5·12).

In the case of scalar functions $\varphi_\alpha(\mathbf{r})$, equations (5·8) do not differ from equations (5·11) because matrix R in this case becomes a number, namely unity, and, hence, $D=\Gamma$; thus

$$G\varphi_\alpha(\mathbf{r})=\sum_{\beta=1}^{d}\varphi_\beta(\mathbf{r})\Gamma(G)_{\beta\alpha}\,. \tag{5·13}$$

We now formulate a theorem that one may use for constructing all possible sets of spin arrangements (if any!) which transform according to a given representation Γ of G:

A set of spin arrangements $\mathbf{S}_\alpha(\mathbf{r})$, $\alpha=1,2,\ \ldots\ d$, defined on $\mathbf{Gr}_1$ and transforming according to (5·8),

$$[G]S_\alpha(\mathbf{r})=\sum_{\beta=1}^{d}S_\beta(\mathbf{r})\Gamma(G)_{\beta\alpha}\,, \tag{5·8*A*}$$

for all elements G of G, exists if and only if the restriction of the representation D [defined by (5·12)] to the site group $\mathbf{G}(\mathbf{r}_1)$ contains the identity representation at least once.

The condition is necessary. We replace in (5·11), which, as has just been shown, follows from (5·8), G

by G^{-1} and make use of the unitarity of D; we obtain:

$$S_\alpha^{(k)}(G\mathbf{r}) = \sum_i \sum_\beta S_\beta^{(i)}(\mathbf{r}) D(G)^*_{k\alpha;i\beta} .$$

We put in this equation $\mathbf{r}=\mathbf{r}_1$ and specialize it further by choosing for G any element $G(\mathbf{r}_1)=(C|\mathbf{w})$ of $\mathsf{G}(\mathbf{r}_1)$; then

$$S_\alpha^{(k)}(\mathbf{r}_1)^* = \sum_i \sum_\beta D[G(\mathbf{r}_1)]_{k\alpha;i\beta} S_\beta^{(i)}(\mathbf{r}_1)^* , \quad (5\cdot14)$$

where

$$D[G(\mathbf{r}_1)]_{k\alpha;i\beta} = \delta_C C_{ki} \Gamma[G(\mathbf{r}_1)]_{\alpha\beta} .$$

Equation (5·14) means, according to (*L*4), that the linear combination

$$J(\mathbf{r}) = \sum_k \sum_\alpha S_\alpha^{(k)}(\mathbf{r}_1)^* S_\alpha^{(k)}(\mathbf{r}) \quad (5\cdot15)$$

of the vectors $S_\alpha^{(k)}(\mathbf{r})$ of the carrier space of D is invariant under $\mathsf{G}(\mathbf{r}_1)$; or, in other words, that the restriction of D to $G(\mathbf{r}_1)$ contains the identity representation at least once.

The condition is sufficient. Since the restriction of D to $\mathsf{G}(\mathbf{r}_1)$ contains the identity representation, there exists, according to (*L*4), a set of $3d$ numbers $\sigma_\alpha^{(k)}$ which satisfy the relations (5·14),

$$\sigma_\alpha^{(k)*} = \sum_i \sum_\beta D[G(\mathbf{r}_1)]_{k\alpha;i\beta} \sigma_\beta^{(i)*} \quad (5\cdot16)$$

for all elements of $\mathsf{G}(\mathbf{r}_1)$. We make use of these numbers and construct d spin arrangements $\mathbf{S}_\alpha(\mathbf{r})$, $\alpha = 1,2, \ldots d$, on $\mathsf{G}\mathbf{r}_1$ by assigning to the atom at $\mathbf{r}=\mathsf{G}\mathbf{r}_1$ in the spin arrangement $S_\alpha(\mathbf{r})$ the spin vector

$$S_\alpha^{(k)}(\mathbf{r}) = \sum_i \sum_\beta D(G)^*_{k\alpha;i\beta} \sigma_\beta^{(i)} , \quad k=1,2,3. \quad (5\cdot17)$$

We next show (*a*) that the d spin arrangements constructed in this way are single-valued vector functions on $\mathsf{G}\mathbf{r}_1$, and (*b*) that they indeed transform according to (5·8*A*). (We omit the proof that they cannot all vanish identically; it consists in showing that this would imply $\sigma_\alpha^{(k)}=0$ for each k and α.)

The proof of (*a*) and (*b*) is a generalization of the proof that the spin arrangement defined by (4·16) is single-valued and invariant under m.

To prove (*a*) we show that, for any two elements G and $\bar{G}$ of G for which $G\mathbf{r}_1 = \bar{G}\mathbf{r}_1$, the right-hand side of equation (5·17) has the same value:

$$\sum_i \sum_\beta D(\bar{G})^*_{k\alpha;i\beta} \sigma_\beta^{(i)} = \sum_i \sum_\beta D(G)^*_{k\alpha;i\beta} \sigma_\beta^{(i)} . \quad (5\cdot18)$$

Since $G^{-1}\bar{G}$ belongs to $\mathsf{G}(\mathbf{r}_1)$, we may put $\bar{G}=GG(\mathbf{r}_1)$. By substituting this in the left-hand side of (5·18) and using (5·16) we obtain:

$$\sum_i \sum_\beta D[GG(\mathbf{r}_1)]^*_{k\alpha;i\beta} \sigma_\beta^{(i)} = \sum_i \sum_\beta \sum_j \sum_\gamma D(G)^*_{k\alpha;j\gamma} \times D[G(\mathbf{r}_1)]^*_{j\gamma;i\beta} \sigma_\beta^{(i)} = \sum_\gamma \sum D(G)^*_{k\alpha;j\gamma} \sigma_\gamma^{(j)} ;$$

and this is, in fact, the right-hand side of (5·18).

To prove (*b*) we apply an element $\bar{G}=(\bar{R}|\bar{\mathbf{v}})$ of G to the spin arrangement (5·17) and we obtain (5·8*A*), taking into account (4·4), (5·17) and (5·12), as follows:

$$\begin{aligned}
[\bar{G}]S_\alpha^{(k)}(\mathbf{r}) &= \sum_j \delta_{\bar{R}} \bar{R}_{kj} \sum_i \sum_\beta D(\bar{G}^{-1})^*_{j\alpha;i\beta} \sigma_\beta^{(i)} \\
&= \sum_j \sum_l \sum_\gamma \delta_{\bar{R}} \bar{R}_{kj} D(\bar{G}^{-1})^*_{j\alpha;l\gamma} S_\gamma^{(l)}(\mathbf{r}) \\
&= \sum_j \sum_l \sum_\gamma \delta_{\bar{R}} \bar{R}_{kj} \delta_{\bar{R}} (\bar{R}^{-1})_{jl} \Gamma(\bar{G}^{-1})^*_{\alpha\gamma} S_\gamma^{(l)}(\mathbf{r}) \\
&= \sum_\gamma S_\gamma^{(k)}(\mathbf{r}) \Gamma(\bar{G})_{\gamma\alpha} , \quad k=1,2,3 .
\end{aligned}$$

This completes the proof of the sufficiency of the condition stated in the theorem.

The same theorem and the same proof hold for the case of scalar functions, provided (5·8*A*), D, R and $\boldsymbol{\sigma}_\alpha$ are replaced by (5·13), Γ, unity and a_α respectively. This is also true of all statements in the remainder of this section.

If Γ is irreducible the d spin arrangements (5·17) are linearly independent. If, however, Γ is reducible they need not be. We continue the discussion of this point at the end of this section.

We next proceed to assign to each $\mathbf{S}(\mathbf{r})$ a classification label which specifies the representation Γ of G associated with $\mathbf{S}(\mathbf{r})$. The full classification label is:

$$[\mathsf{G},\mathbf{r}_1;\ \Gamma(K_1),\ \Gamma(\mathrm{K}_2)\ \ldots\ \Gamma(K_q);\ \boldsymbol{\sigma}_1,\ \boldsymbol{\sigma}_2,\ \ldots\ \boldsymbol{\sigma}_d] . \quad (5\cdot19)$$

Here $\Gamma(K_1), \ldots, \Gamma(K_q)$ are the matrices which correspond to the generating elements $K_1, \ldots, K_q$ of G (in the case of space groups, $q \leq 6$). The d vectors $\boldsymbol{\sigma}_\alpha$ (components $\sigma_\alpha^{(1)}$, $\sigma_\alpha^{(2)}$, $\sigma_\alpha^{(3)}$) satisfy (5·16), and, as is clear from (5·17), are equal to the vectors $\mathbf{S}_\alpha(\mathbf{r}_1)$ located at $\mathbf{r}_1$ in the d spin arrangements $\mathbf{S}_\alpha(\mathbf{r})$.

We shall refer to this classification as *classification* $C2$ or simply $C2$. A $C2$ classification label determines $\mathbf{S}(\mathbf{r})$ uniquely.

For scalar functions the $C2$ classification label would be:

$$[\mathsf{G},\mathbf{r}_1;\ \Gamma(K_1),\ \Gamma(K_2),\ \ldots\ \Gamma(K_q);\ a_1,\ a_2,\ \ldots\ a_d] . \quad (5\cdot20)$$

By definition of Γ_H a $C2$ classification label is attached to the spin arrangement $\mathbf{S}_1(\mathbf{r})$ rather than to any of the other d–1 spin arrangements given by (5·17). This implies a good deal of redundant information in such a label. However, this cannot be avoided if one wishes to use representations as a classification criterion.

If for a given $\mathsf{G}\mathbf{r}_1$ the restriction of a representation Γ of G to $\mathsf{G}(\mathbf{r}_1)$ does not contain the identity representation, the corresponding $C2$ classification label does not exist (that is, there are no d non-vanishing spin arrangements transforming according to Γ).

By letting Γ vary over all those finite-dimensional irreducible and reducible representations of G whose restrictions to $\mathsf{G}(\mathbf{r}_1)$ contain the identical representation, and letting the set $\{\boldsymbol{\sigma}_1, \ldots, \boldsymbol{\sigma}_d\}$ vary over all solutions of (5·16) for a given Γ, we obtain a list of all spin arrangements on $\mathsf{G}\mathbf{r}_1$ describable by finite-dimensional representations in the sense of $C2$. We should

emphasize that by 'all ... representations' we really mean all, and not just one from each set of equivalent representations.

The list we obtain in this way will contain many spin arrangements more than once. We shall discuss here only one of the reasons for this redundancy. If, for a given label, the spin arrangements (5·17) are not linearly independent, then there exists, in analogy to an argument given earlier in this section [see (5·6) and (5·7)] another set of $\bar{d}<d$ spin arrangements $\bar{\mathbf{S}}(\mathbf{r})$ transforming according to a representation $\bar{\Gamma}$ contained in Γ and with $\bar{\mathbf{S}}_1(\mathbf{r})=\mathbf{S}_1(\mathbf{r})$. Therefore we may drop that particular label from the list.

Furthermore, we may drop from the list all those labels in which $\bar{\Gamma}$ is replaced by a representation equivalent to it and having as its 'first' basis vector $\mathbf{S}_1(\mathbf{r})$.

We illustrate this point with an example. For simplicity we consider the case of scalar functions defined on a 'square' molecule. Its two-dimensional symmetry group G is $4mm$ (order 8). We choose $\mathbf{r}_1\neq 0$ on the m_x reflexion line; then $\mathsf{G}(\mathbf{r}_1)$ is the group m_x (order 2). We want to construct four scalar functions which transform according to the unitary representation Γ of $4mm$ given by the matrices

$$\Gamma(4_z)=\begin{pmatrix} \cdot\cdot\cdot 1\\ 1\cdot\cdot\cdot\\ \cdot 1\cdot\cdot\\ \cdot\cdot 1\cdot \end{pmatrix},\quad \Gamma(m_x)=\begin{pmatrix} \cdot\cdot\cdot 1\\ \cdot\cdot 1\cdot\\ \cdot 1\cdot\cdot\\ 1\cdot\cdot\cdot \end{pmatrix}.$$

We easily find that Γ restricted to $\mathsf{G}(\mathbf{r}_1)$ contains the identical representation twice, and that

$$a_1=1,\ a_2=0,\ a_3=0,\ a_4=1$$

are the components of one of the invariant vectors. Prescription (5·17) becomes in the case of scalar functions

$$\varphi_\alpha(\mathbf{r})=\sum_\beta \Gamma(G)^*_{\alpha\beta}a_\beta\,. \tag{5·21}$$

Using it, we obtain 4 functions whose values at the atoms of the molecule are:

$$\begin{array}{cccc} 0\ 1 & 1\ 1 & 1\ 0 & 0\ 0\\ \varphi_1: & \varphi_2: & \varphi_3: & \varphi_4:\\ 0\ 1 & 0\ 0 & 1\ 0 & 1\ 1\,. \end{array}$$

These 4 functions are not linearly independent:

$$\varphi_1-\varphi_2+\varphi_3-\varphi_4=0\,.$$

The functions φ_1, φ_2 and φ_3 do constitute a basis of the reducible representation $\bar{\bar{\Gamma}}$ given by:

$$\bar{\bar{\Gamma}}(4_z)=\begin{pmatrix} \cdot\cdot & 1\\ 1\cdot & -1\\ \cdot 1 & 1 \end{pmatrix},\quad \bar{\bar{\Gamma}}(m_x)=\begin{pmatrix} 1\cdot\cdot\\ -1\cdot 1\\ \cdot\cdot 1\cdot \end{pmatrix}.$$

The representation $\bar{\Gamma}$ which occurs in the $C2$ label of φ_1 is a unitary representation equivalent to $\bar{\Gamma}$ and having φ_1 as its 'first' basis vector, while the $C2$ label in which $\bar{\bar{\Gamma}}$ occurs in a completely reduced form is no longer a label of φ_1 but of $\varphi_1+\varphi_3$, as is easily verified.

Finally, we would like to mention that in order to assign a representation to a given spin arrangement one could use instead of the method described in part A of this section, the well-known method of projection operators, which however turns out to be much more laborious in practice.

6. Relation between classifications $C1'$ and $C2$

In this section we discuss the relation between the classification $C1'$ (and $C1$) and $C2$. We first formulate and prove a theorem, which we shall refer to as the *$C2$–$C1'$ linking theorem.*

Let a set of spin arrangements $\mathbf{S}_\alpha(\mathbf{r})$ defined on an atom arrangement $\mathsf{G}\mathbf{r}_1$ constitute the basis of a representation Γ of G:

$$[G]\mathbf{S}_\alpha=\sum_{\beta=1}^{d}\mathbf{S}_\beta\Gamma(G)_{\beta\alpha}\quad(\alpha=1,2,\ \ldots\ d)\,. \tag{6·1}$$

The non-trivial magnetic group

$$\mathsf{m}_\mathsf{L}(\mathsf{H})=\mathsf{H}+\mathsf{H}L_2',\quad \mathsf{L}\subseteq\mathsf{G}\,, \tag{6·2}$$

is the symmetry group of the spin arrangement $\mathbf{S}_\gamma$ if and only if the matrices of the restriction of Γ to L, and no other matrices of Γ, have the property that for all elements of H

$$\Gamma(H)_{\beta\gamma}=\delta_{\beta\gamma} \tag{6·3}$$

and

$$\Gamma(HL_2)_{\beta\gamma}=-\delta_{\beta\gamma} \tag{6·3'}$$

where γ is fixed and $\beta=1,2\ \ldots\ d$.

The condition is necessary. If $\mathsf{m}_\mathsf{L}(\mathsf{H})$ is the symmetry group of $\mathbf{S}_\gamma$, then for all H

$$[H]\mathbf{S}_\gamma=\mathbf{S}_\gamma\,, \tag{6·4}$$

$$[HL_2']\mathbf{S}_\gamma=\mathbf{S}_\gamma\quad\text{or}\quad[HL_2]\mathbf{S}_\gamma=-\mathbf{S}_\gamma\,. \tag{6·4'}$$

Substituting this in (6·1) for G belonging to L, one obtains

$$\sum_\beta \mathbf{S}_\beta(\Gamma(H)_{\beta\gamma}-\delta_{\beta\gamma})=0\,,$$

and

$$\sum_\beta \mathbf{S}_\beta(\Gamma(HL_2)_{\beta\gamma}+\delta_{\beta\gamma})=0$$

wherefrom (6·3) and (6·3') follow immediately.

The condition is sufficient. If (6·3) and (6·3') hold then (6·1) implies (6·4) and (6·4'), which means that all elements of the two cosets in (6·2) are symmetry elements of $\mathbf{S}_\gamma$. *Q.E.D.*

It should be clear from this proof that the theorem remains valid, and becomes *$C2$–$C1$ linking theorem*, if one replaces $\mathsf{m}_\mathsf{L}(\mathsf{H})$ by H and at the same time omits equation (6·3').

It should also be clear that the theorem remains valid for E'-odd scalar functions if one replaces in its formulation and proof the spin arrangements by such functions; and for any scalar function, if $\mathsf{m}_\mathsf{L}(\mathsf{H})$ is replaced by H and equation (6·3') dropped.

The $C2$–$C1$ linking theorem shows how to find, from a $C2$ label, the symmetry group (appearing in the $C1$ label) of a (E'-even or E'-odd) scalar or vector function specified by such label. The $C2$–$C1'$ linking theorem shows how to find, from a $C2$ label of an E'-odd function or a spin arrangement, the magnetic symmetry group (appearing in the $C1'$ label) of that function or spin arrangement. In both cases according to the convention introduced in § 5 one has only to specialize the linking theorem for the case $\gamma=1$.

The converse question, how to determine from a given $C1$ label the representation Γ which appears in the $C2$ label, has already been answered in part A of § 5, where we have indicated how to find the representation Γ_{H} associated with a scalar function or spin arrangement whose symmetry group is H. If in the case of spin arrangement (or E'-odd function) the $C1'$ label rather than $C1$ label is given, the question of finding the representation Γ in the $C2$ label is answered by observing that if $\mathsf{m_L(H)}$ appears in the $C1'$ label then H will appear in the corresponding $C1$ label.

From the above discussion it should be clear in what precise mathematical sense $C1'$ and $C2$ are equivalent.

We next illustrate these general statements concerning the link between classifications $C1'$ and $C2$ of spin arrangements with a few examples.

Example 1

A mathematically almost trivial but important example of the general link between $C1'$ and $C2$ just described is provided by the case where the $C2$ label of a spin arrangement is $[\mathsf{G};\ \Gamma_{\mathrm{alt}}(\mathsf{D^G});\ \mathbf{S}(\mathbf{r}_1)]$, where $\Gamma_{\mathrm{alt}}(\mathsf{D^G})$ is the alternating representation of G in which $+1$ corresponds to the elements of the subgroup $\mathsf{D^G}$ of index 2 in G. Then, according to the $C2$–$C1'$ linking theorem, the $C1'$ label of the same spin arrangement is $[\mathsf{G};\ \mathsf{m_G(D^G)};\ \mathbf{S}(\mathbf{r}_1)]$. Conversely, this $C1'$ label implies that the permutation representation P_{DG} of G is of dimension 2, and (since $\mathbf{S}_1(\mathbf{r})=-\mathbf{S}_2(\mathbf{r})\not\equiv 0$ in this case) that the representation Γ_{DG} associated with the spin arrangement is $\Gamma_{\mathrm{alt}}(\mathsf{D^G})$ as indicated in the $C2$ label.

This case is important because many actual magnetic structures can be assigned such simple $C1'$ or $C2$ labels.

In this connexion we want to emphasize that (as is clear from the $C1'$ and $C2$ classification labels) neither a magnetic space group by itself in the case of $C1'$, nor a representation of the space group of the crystal by itself in the case of $C2$, are sufficient to characterize a spin arrangement completely. Therefore the well-known one-to-one correspondence pointed out by Niggli (1959), between the alternating representations of a space group and its subgroups of index 2 (and, hence, the magnetic space groups of its 'family'), and repeatedly used by Bertaut (1968), is sufficient to establish the link between $C1'$ and $C2$ only in the special case considered in this example, but not in general. In fact Bertaut concludes that this is the only case for which the classification $C1'$ by means of magnetic space groups is at all possible, and he arrives in this way at the point of view expressed in the passage quoted in § 1.

The next two examples are those of the magnetic structures discussed by Bertaut and his collaborators from the point of view of cllassfication $C2$. We shall see that these structures are characterized by magnetic space groups in the sense of $C1'$, although they belong to two-dimensional representations in the sense of $C2$.

In the sequel, the symbol $\langle G_a, G_b, \ldots\rangle$ will denote the group generated by the elements $G_a, G_b, \ldots$.

Example 2

We consider the spin arrangement of the Tb spins in $TbCrO_3$ (Bertaut, Mareschal & de Vries, 1967). In this case

$$\mathsf{G}=Pbnm\equiv\langle(2_x),\ (2_y),\ \bar{1}\rangle\ ,$$

where here, and in what follows:

$$(2_x)=(2_x|\tfrac{1}{2}\tfrac{1}{2}0)\ ,\quad (2_y)=(2_y|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\ ,$$
$$(2_z)=(2_z|00\tfrac{1}{2})\ ,\quad \bar{1}=(\bar{1}|000)\ ,\quad b=(m_x|\tfrac{1}{2}\tfrac{1}{2}0)\ ,$$
$$n=(m_y|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\ ,\quad m=(m_z|00\tfrac{1}{2})\ .$$

The Tb atoms are all located at the positions obtained from $\mathbf{r}_1=(x,y,\frac{1}{4})$ by applying to it all elements of *Pbnm*. Further, $\mathsf{G}(\mathbf{r}_1)=\langle m\rangle$ is of order 2. Hence

$$\mathsf{G}=\sum_{\mathbf{t}}(1|\mathbf{t})\{\langle m\rangle+(2_x)\langle m\rangle+(2_y)\langle m\rangle+\bar{1}\langle m\rangle\}\ .$$

Write $\mathbf{t}=(n_1n_2n_3)$ and choose

$$\mathbf{r}_2=\ \bar{1}\mathbf{r}_1+(111)=(1-x,1-y,\tfrac{3}{4})$$
$$\mathbf{r}_3=(2_x)\mathbf{r}_1+(001)=(\tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{3}{4})$$
$$\mathbf{r}_4=(2_y)\mathbf{r}_1\ \ \ \ \ \ \ \ \ \ \ \ =(\tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{4})$$

The Tb spin arrangement is then given by:

$$\mathbf{S}(\mathbf{r}_1+\mathbf{t})=(-1)^{n_2}(A,B,0),$$
$$\mathbf{S}(\mathbf{r}_2+\mathbf{t})=(-1)^{n_2}(A,B,0)\ ,\quad \mathbf{S}(\mathbf{r}_3+\mathbf{t})=(-1)^{n_2}(\bar{A},B,0),$$
$$\mathbf{S}(\mathbf{r}_4+\mathbf{t})=(-1)^{n_2}(A,\bar{B},0)\ .$$

Here $(A.\ B,\ 0)$ are the components of $\mathbf{S}(\mathbf{r}_1)$; $\bar{A}=-A$, $\bar{B}=-B$. To assign the $C1'$ label to this spin arrangement, we first determine its magnetic group $\mathsf{M_L(H)}$. We find

$$\mathsf{M_L(H)}\equiv\langle\mathsf{H},L_2'\rangle=P_{2b}\,2_1'nm'$$
$$\equiv\langle\langle(2_x)(1|010),n,(1|020)\rangle,(1|010)'\rangle\ ;$$

this means that $\mathsf{L}=P2_1nm$, and

$$\mathsf{G}=\mathsf{L}+\mathsf{L}(\bar{1}|111)$$
$$\mathsf{G}\mathbf{r}_1=\mathsf{L}\mathbf{r}_1+\mathsf{L}\mathbf{r}_2\ ,\quad l''=l'=2\ .$$

The spin vectors $\mathbf{S}(\mathbf{r}_1)=\mathbf{S}(\mathbf{r}_2)=(A,B,0)$ are admissible at $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively. The $C1'$ label of the Tb spin arrangement is thus, according to (4·18), as follows:

$$[Pbnm;\ P_{2b}2_1'nm';\ \mathbf{S}(\mathbf{r}_1)=\mathbf{S}(\mathbf{r}_2)=(A,B,0)]\ .$$

Given this label, the Tb magnetic structure can be completely reconstructed by means of (4·16).

Next we assign the $C2$ label to the same magnetic structure. We use equation (5·4) with G and H as just defined, and

$$G_2=(\bar{1}|000)\,,\quad G_3=(1|010)\,,\quad G_4=(\bar{1}|010)\,.$$

Hence, according to (5·3s),

$$\mathbf{S}_1(\mathbf{r})=\mathbf{S}(\mathbf{r})\,,\qquad \mathbf{S}_2(\mathbf{r})=[(\bar{1}|000)]\mathbf{S}(\mathbf{r})\,,$$
$$\mathbf{S}_3(\mathbf{r})=[(1|0-10)]\mathbf{S}(\mathbf{r})\,,\quad \mathbf{S}_4(\mathbf{r})=[(\bar{1}|010)]\mathbf{S}(\mathbf{r})\,,$$

or, explicitly,

$$\mathbf{S}_\alpha(\mathbf{r}_j+\mathbf{t})=(-1)^{n_2}\mathbf{S}_\alpha(\mathbf{r}_j)\quad \alpha,j=1,2,3,4$$

where

$$\mathbf{S}_1(\mathbf{r}_1)=\mathbf{S}_1(\mathbf{r}_2)=(A,B,0)\,,\quad \mathbf{S}_1(\mathbf{r}_3)=-\mathbf{S}_1(\mathbf{r}_4)=(\bar{A},B,0)\,,$$
$$\mathbf{S}_2(\mathbf{r}_1)=\mathbf{S}_2(\mathbf{r}_2)=(\bar{A},\bar{B},0)\,,\quad \mathbf{S}_2(\mathbf{r}_3)=-\mathbf{S}_2(\mathbf{r}_4)=(\bar{A},B,0)\,,$$
$$\mathbf{S}_3(\mathbf{r})=-\mathbf{S}_1(\mathbf{r})\,,$$
$$\mathbf{S}_4(\mathbf{r})=-\mathbf{S}_2(\mathbf{r})\,.$$

These 4 spin arrangements transform according to the permutation representation P_{H} of G. Since only 2 of them are linearly independent, the representation Γ_{H} of G associated with $\mathbf{S}(\mathbf{r})$ will be two-dimensional. We choose as its (orthogonal) basis $\mathbf{S}_1(\mathbf{r})=\mathbf{S}(\mathbf{r})$ and $\mathbf{S}_2(\mathbf{r})$. By applying to these two spin arrangements the three generating elements of *Pbnm* specified earlier, we obtain after some calculation the matrices of Γ_{H} which correspond to these three elements. They are the same, apart from an equivalence transformation, as those found by Bertaut, Mareschal & de Vries (1967). The representation Γ_{H} is irreducible. According to (5·19) the $C2$ label is thus:

$$\left[Pbnm;\ (2_x)\to\begin{pmatrix}-1 & .\\ . & 1\end{pmatrix},\ (2_y)\to\begin{pmatrix}. & 1\\ -1 & .\end{pmatrix},\ \bar{1}\to\begin{pmatrix}. & 1\\ 1 & .\end{pmatrix};\right.$$
$$\left.\mathbf{S}_1(\mathbf{r}_1)=-\mathbf{S}_2(\mathbf{r}_1)=(A,B,0)\right]$$

Given this label, the Tb structure can completely be reconstructed, using (5·17); if one only wants to determine its magnetic symmetry group from the $C2$ label, the $C2$–$C1'$ linking theorem is sufficient.

Example 3

We next consider the spin arrangement of the Dy spins in $DyCrO_3$ (Bertaut & Mareschal, 1968). The space group G of the crystal is in this case the same as that of $TbCrO_3$, and the positions $\mathbf{Gr}_1$ occupied by the Dy atoms are again those obtained by taking $\mathbf{r}_1=(x,y,\frac{1}{4})$, only the numerical values of x and y being different. Therefore we may and shall use the notations of example 2. The Dy spin arrangement is then given by

$$\mathbf{S}(\mathbf{r}_1+\mathbf{t})=(-1)^{n_1+n_2}(A,\bar{B},0)\,,$$
$$\mathbf{S}(\mathbf{r}_2+\mathbf{t})=(-1)^{n_1+n_2}(\bar{A},B,0)\,,$$
$$\mathbf{S}(\mathbf{r}_3+\mathbf{t})=(-1)^{n_1+n_2}(\bar{B},\bar{A},0)\,,$$
$$\mathbf{S}(\mathbf{r}_4+\mathbf{t})=(-1)^{n_1+n_2}(B,A,0)\,.$$

By following the same procedure as in example 2 we find for this spin arrangement the $C1'$ label:

$$[Pbnm;\ P_{2a}2_1/m;\ \mathbf{S}(\mathbf{r}_1)=(A,\bar{B},0)\,,\ \mathbf{S}(\mathbf{r}_3)=(\bar{B},\bar{A},0)]\,,$$

where

$$P_{2a}2_1/m=\langle\langle(2_z),(\bar{1}|100),(1|110),(1|200),\rangle,(1|100)'\rangle,$$

and the $C2$ label:

$$\left[Pbnm;\ (2_x)\to\begin{pmatrix}. & -1\\ 1 & .\end{pmatrix},\ (2_y)\to\begin{pmatrix}. & -1\\ 1 & .\end{pmatrix},\bar{1}\to\right.$$
$$\left.\begin{pmatrix}-1 & .\\ . & -1\end{pmatrix};\ \mathbf{S}_1(\mathbf{r}_1)=(A,\bar{B},0),\mathbf{S}_2(\mathbf{r}_1)=(B,\bar{A},0)\right].$$

The representation Γ_{H} occurring in this $C2$ label is reducible into two complex one-dimensional representations, which are those found by Bertaut & Mareschal (1968). The reduction is obtained by means of an equivalence transformation given by the matrix $\begin{pmatrix}1 & -i\\ -i & 1\end{pmatrix}$.

Example 4

Here we consider a case of a helical spin arrangement, the 'double helix' in the metamagnetic phase of MnP (Felcher, 1966; Bertaut, 1969). The space group G of the crystal, and the positions $\mathbf{Gr}_1$ occupied by the Mn atoms are (apart from their numerical values) the same as in examples 2 and 3. Therefore we use the same notation as in those two examples. The $C1'$ label of the double helix spin arrangement is then:

$$[Pbnm;\ p1;\ \mathbf{S}(\mathbf{r}_1+\mathbf{t}_{n_1})=R_\psi^{2n_1}\mathbf{S}(\mathbf{r}_1)\,,$$
$$\mathbf{S}(\mathbf{r}_3+\mathbf{t}_{n_1})=R_\psi^{2n_1+1}(\mathbf{r}_1);\ \mathbf{S}(\mathbf{r}_4+\mathbf{t}_{n_1})=R_\psi^{2n_1}\mathbf{S}(\mathbf{r}_4)\,,$$
$$\mathbf{S}(\mathbf{r}_2+\mathbf{t}_{n_1})=R_\psi^{2n_1+1}\mathbf{S}(\mathbf{r}_4);\ \mathbf{S}(\mathbf{r}_4)=R_\psi\mathbf{S}(\mathbf{r}_1)]$$

where

$$p1=\langle(1|010),(1|001)\rangle\,,\quad \mathbf{t}_{n_1}=(n_100)$$

and R_ψ is a rotation through ψ about the x axis. [For a discussion of the numerical value of ψ, see Felcher (1966)]. Instead of an infinity of spin vectors, the $C1'$ label specifies just two spin vectors, $\mathbf{S}(\mathbf{r}_1)$ and $\mathbf{S}(\mathbf{r}_4)$, a relation between them, and indicates how an infinite rotation group (generated by R_ψ and R_ψ^{-1}) determines all the other spin vectors; for more details on this way of describing helical spin arrangements, see Opechowski & Guccione (1965), § IV, 2,*h*.

As far as the $C2$ label is concerned, there are two possibilities: either to assign the infinite-dimensional permutation representation of *Pbnm* generated by $p1$, or to introduce cyclic boundary conditions and in this way reduce the problem to the standard form discussed in § 5.

After having dealt with examples of spin arrangements, we want to make a few more general remarks.

Using the $C2$–$C1'$ linking theorem, one easily finds that the symmetry groups of the two spin arrangements, $\mathbf{S}_1(\mathbf{r})$ and $\mathbf{S}_2(\mathbf{r})$ in example 2 above are conjugate subgroups of $\mathsf{G}=Pbnm$; or, in other words, that the magnetic symmetry groups of $\mathbf{S}_1(\mathbf{r})$ and $\mathbf{S}_2(\mathbf{r})$ are conjugate subgroups of $\mathsf{G}\times\mathsf{A}=Pbnm\ 1'$. For this reason the two spin arrangements may be regarded as not essentially different. Each of them can be used to describe the same physical situation if appropriate conventions are introduced; or, if one prefers, one may say with Bertaut (1968, page 226) 'that they provide an equivalent description of the same physical reality.'

In general, however, it is not true that the spin arrangements which constitute the basis of an irreducible representation Γ of G have symmetry groups which are conjugate subgroups of G. These symmetry groups need not even be isomorphic, as is illustrated by example 5 below. True is only the statement that it is always possible to find a basis with that property (but then such basis may not be orthogonal). This can be seen as follows. The symmetry groups of the h' spin arrangements $\mathbf{S}_\mu(\mathbf{r})$ defined by (5·3s) are $G_\mu^{-1}\mathsf{H}G_\mu$, where H is the symmetry group of $\mathbf{S}_1(\mathbf{r})$. Therefore they are conjugate subgroups of G. If the dimension of Γ_H is d, then exactly d of the h' spin arrangements $\mathbf{S}_\mu(\mathbf{r})$ will be linearly independent. If we choose these d spin arrangements as a basis of the carrier space of Γ_H, then this particular basis will have the required property.

Example 5

For simplicity we consider an 'octahedral' molecule (6 atoms). Its symmetry group G is $m3m=\langle 4_z,3,\bar{1}\rangle$. We choose $\mathbf{r}_1\neq 0$ on the 4_z-axis; then $\mathsf{G}(\mathbf{r}_1)=\bar{4}_z2m$, and

$$\mathsf{G}=\sum_{k=1}^{6} G_k\mathsf{G}(\mathbf{r}_1)\,,$$

where

$$G_1=1\,,\quad G_6=\bar{1}\,,\quad G_{m+2}=4_z^m3\ (m=0,1,2,3)\,.$$

We suppose the following irreducible unitary representation of $m3m$ is given:

$$\Gamma(4_z)=\begin{pmatrix}1&.&.\\.&.&1\\.&1&.\end{pmatrix},\quad \Gamma(3)=\tfrac{1}{2}\begin{pmatrix}.&\sqrt{2}&-\sqrt{2}\\\sqrt{2}&1&1\\\sqrt{2}&-1&-1\end{pmatrix},$$

$$\Gamma(\bar{1})=\begin{pmatrix}-1&.&.\\.&-1&.\\.&.&-1\end{pmatrix}.$$

The restriction of Γ to $\bar{4}_z2m$ is no longer irreducible; it contains the identity representation, and the corresponding invariant vector has the components $a_1=1/\sqrt{2}$, $a_2=a_3=0$. Substituting these components, and the elements of the matrices of Γ in (5·21) one obtains the three functions φ_1, φ_2, φ_3 which form an orthogonal basis in the carrier space of Γ. Their values are arranged into the following self-explanatory Table, in which $\mathbf{r}_k=G_k\mathbf{r}_1$ ($k=1,2,\ldots 6$):

	$\mathbf{r}_1$	$\mathbf{r}_2$	$\mathbf{r}_3$	$\mathbf{r}_4$	$\mathbf{r}_5$	$\mathbf{r}_6$
$\sqrt{2}\varphi_1=$	1	0	0	0	0	−1
$2\varphi_2=$	0	1	1	−1	−1	0
$2\varphi_3=$	0	1	−1	−1	1	0

The symmetry group of φ_1 is $\bar{4}_z2m$ (order 8); the symmetry groups of φ_2 and φ_3 are conjugate subgroups of $m3m$, both belonging to the class $mm2$ (order 4).

What is then our conclusion? Is the classification $C2$ as general as $C1'$, that is, has every spin arrangement, however low its symmetry may be, its appropriate label in $C2$? If one is willing to impose the usual cyclic boundary conditions on the crystal, the answer to this question is 'yes', $C2$ and $C1'$ are rigorously equivalent. If one is not, then the answer is 'possibly, yes'. For, in the latter case, a mathematically rigorous answer would require a study of certain infinite-dimensional reducible representations of space groups, which we have not done. However, for the class of all those spin arrangements whose magnetic symmetry groups contain some three-dimensional discrete group of translations as a subgroup, it is not necessary to introduce cyclic boundary conditions to prove the rigorous equivalence of $C1'$ and $C2$; but this class does not comprise the helical spin arrangements.

Is one of the two classifications preferable? The answer to this question will evidently depend on what one wants to use a classification for. If, however, the purpose which the classification labels are to serve is not specified, then $C1'$ is preferable to $C2$ for the simple reason that it takes fewer steps (for example, in the sense of a computer program) to assign a $C1'$ label to a given spin arrangement than to assign to it a $C2$ label.

Although each magnetic structure has its label in both, $C1'$ and $C2$ (in the latter case, subject to the qualification just mentioned), it is obvious that for certain, possibly hypothetical, magnetic structures both classifications become of doubtful value. For example, this would be so if a spin arrangement on a simple crystal were a superposition of two (or more) substructures of which one has high symmetry, and in the other the spin vectors were oriented partially at random. For all such cases a classification which makes allowance for a probability distribution of spin vectors would be more appropriate.

We are indebted to Dr M. Boon for a discussion of infinite-dimensional representations of space groups. This work was supported in part by the National Research Council of Canada. One of the authors (TD) wishes to thank the Canada Council for a 'bourse de perfectionnement'.

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Quasi-Harmonic Analysis of the Thermodynamic Data for Gold and an Estimate of $\Theta^M(T)$

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(*Received* 21 *August* 1970)

The moments of the Au frequency spectrum have been calculated in the usual manner from available thermodynamic data. These results are expressed in terms of the effective Debye temperatures, $\Theta^D(n)$. Unlike many materials, the values of $\Theta^D(n)$ for Au increase monotonically with increasing n. Values of the characteristic temperature associated with the Debye–Waller factor are determined [$\Theta^M(0, V_0) = 171 \pm 2$ °K and $\Theta^M(300, V_{300}) = 163 \pm 1$ °K], and the temperature dependence of $\Theta^M(T, V_T)$ is estimated. Our results are compared with recent Mössbauer and X-ray data. The comparison with the Mössbauer measurements, which were performed at $4{\cdot}2 \leq T \leq 100$ °K., yields a value of $\sim 4{\cdot}4$ for the internal conversion coefficient, α, for the 77 keV, γ-ray line of Au^{197}; this agrees well with a recent independent determination of $\alpha = 4{\cdot}23 \pm 0{\cdot}09$. However, our results for $\Theta^M(T, V_T)$ disagree, to within quoted estimates of error, with the results of published X-ray measurements. It is suggested that additional X-ray experiments extending to low temperatures would help to resolve these discrepancies.

Introduction

It is well known that the moments of the frequency spectrum can be determined, within the quasi-harmonic approximation, from an analysis of thermodynamic data; also, the Debye–Waller factor or its effective Debye temperature, $\Theta^M(T, V_T)$ can be estimated with reasonable accuracy from these moments. Our results for $\Theta^M(T, V_T)$ may be compared to very recent Mössbauer measurements and to previously published X-ray determinations of the Debye–Waller factor. We mention that Au was of special interest because relevant experiments for Au indicate that at room temperature, Θ^M is greater than the Debye temperature determined from elastic constants, Θ^E; this is contrary to what is found in other studied materials, as noted by Synecek, Chessin & Simerska (1970).

Calculations

The moments of the frequency spectrum are defined as follows:

$$\overline{\omega^n} = \int_0^\infty \{\omega^n G(\omega)\, d\omega\} \Big/ \int_0^\infty G(\omega)\, d\omega, \qquad (1)$$

where $G(\omega)$ is the lattice frequency distribution function. These moments can be related to an effective Debye temperature, $\Theta^D(n)$:

$$\Theta^D(n) = \frac{\hbar}{k}\left\{\frac{1}{3}(n+3)\overline{\omega^n}\right\}^{1/n}, \quad \begin{matrix} n > -3\,, \\ n \neq 0 \end{matrix} \qquad (2)$$

where $\hbar$ and k have their usual meaning and the limits $n = -3$ and 0 exist. Low-temperature specific heat or elastic-constant data yield a value for $\Theta^D(-3)$ and Barron, Berg & Morrison (1957) have shown how the