MAGNETIC STRUCTURE ANALYSIS AND GROUP THEORY

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Résumé. — L'analyse de structures magnétiques par la théorie des groupes (analyse de représentations) est basée sur la transformation de vecteurs spins, situés dans une position cristallographique donnée, sous les opérations de symétrie d'un groupe d'espace **G** ou sous-groupe $\mathbf{G_k}$ du cristal dans lequel se trouve la structure magnétique. Le vecteur d'onde **k** caractérisant le groupe de translation est déduit de l'expérience de diffraction neutronique. Les équations de transformation linéaires induisent une représentation Γ de **G** ou de $\mathbf{G_k}$. On réduit Γ en représentations irréductibles (r. i.). Les vecteurs de base, sous-tendant les r. i. décrivent des structures magnétiques possibles de sorte que l'on n'a à comparer qu'un faible nombre de modèles avec l'expérience. La symétrie de l'hamiltonien (de la représentation irréductible) est généralement plus élevée que la symétrie de Shubnikov de la structure magnétique. Quant au schéma de classification d'Opechowski, notre schéma (C2) utilise d'une manière cohérente et exclusive les *groupes d'espace*, même pour des spins sinusoïdaux et hélicoïdaux alors que dans le schéma C1′ on doit ajouter des groupes *non cristallographiques* pour une description de ces cas.

Abstract. — The analysis of magnetic structures by group theory (representation analysis) is based on the transformation of spins on a given lattice site under the symmetry operations of a crystallographic space group **G** or a subgroup $\mathbf{G_k}$ of the crystal in which the magnetic structure is imbedded. The wave vector **k** labelling the translation group is taken from the neutron diffraction experiment. The linear transformation equations induce a representation Γ of **G** or $\mathbf{G_k}$. Γ is reduced to irreducible representations. Basis vectors, constructed from them, describe possible magnetic structures so that only a small number of models have to be compared with experiment. The symmetry of the hamiltonian (of the irreducible representation) is generally higher than the Shubnikov symmetry of the magnetic structure. As far as Opechowski's classification scheme is concerned our scheme (C2) uses *space* groups consistently, even for sinusoidal and helical spins whereas in the scheme C1′ one must add *non crystallographic* groups for a full description of the latter case.

Introduction. — Representation analysis of a magnetic structure is not only *a*) labelling or classifying a structure, but consists mainly of *b*) the search for the structure before it is known and of *c*) the discussion of the interactions which might explain the final structure model. Professor Opechowski has not evaluated the merits of representation analysis for *b*) and *c*). Thus I shall answer his criticism at the end of my lecture.

After stressing the difference between invariance and transformation properties, we show the analogy between the theory of magnetic modes and the group theoretical treatment of lattice vibration modes. In both cases linear transformations of vectors induce a matrix representation Γ of a space group **G**. We study in part I the structure of the matrix Γ taking advantage of the fact that the wave vector **k** of the translation group **T** of **G** is known from the diffraction experiment and also that spin-components transforming like Bloch-waves can be defined. In part II we reduce Γ to irreducible representations and illustrate the procedure using Mn_3GaN ($P\,m\,3\,m$), the perovskite family ($P\,b\,n\,m$) for $\mathbf{k} = 0$ and MnP ($\mathbf{k} \neq 0$) for the helical case. In part III it is shown that basis vectors of irreducible representations describe magnetic modes in a unique way for all structures including helical and sinusoidal ones.

The construction of invariants, which appear in an effective spin hamiltonian is briefly considered in part IV where we discuss also some interesting features of the length of spin components at individual sites. In part V we describe the procedure for finding the Shubnikov group when the irreducible representation to which the structure belongs is known. Finally (part VI) time reversal symmetry is shown to play a role in those cases in which **k** and $-\mathbf{k}$ are inequivalent vectors in the star of **k**.

I. **Invariance and transformation properties.** — There are two ways of stating the symmetry properties of a physical object under the symmetry operations of a group **G**.

a) The set of symmetry operations under which the physical object is invariant, generally a subgroup **H** of **G** ;

b) The specifications of the transformation properties under *all* the symmetry operations of **G**.

Let us give some specific examples. The crystallographer assigns a space group to a crystal. This means that the crystal is invariant, i. e. transforms into itself under all the operations of the space group. In the same way the quantum mechanical physicist constructs an hamiltonian, invariant under the symmetry operations of « the group of the hamiltonian ». However when considering the Schrödinger wave ψ, he does not look for the subgroup which leaves ψ invariant, but studies its transformation properties under the whole group of the hamiltonian.

The same is true in lattice dynamics where for a crystal of given space group symmetry **G** the neutron diffractonist, the spectroscopist (in ultraviolet, infrared, Raman effect work, etc.) studies the transformation properties of atomic displacements (i. e. lattice vibrations).

Transformation properties form an important part of representation theory. We shall remain within the framework of conventional space group theory ([1]). Finding the irreducible representations of a space group $\mathbf{G_k}$, associated with a **k**-vector in the first Brillouin-zone, has become a standard procedure [1-3].

Proceeding by analogy, we first consider the case of molecular vibrations. Given arbitrary displacements $\mathbf{u(R)}$ of the atoms at positions **R** in the molecule, one subjects the $\mathbf{u(R)}$ to the symmetry operations $\mathbf{P}_i$ of the point group of the molecule. The linear equations of transformation may be written in matrix form and it can be shown that the matrices $\mathbf{M}_i$ multiply like the symmetry operators $\mathbf{P}_i$ and thus form a matrix representation, say Γ of the point group. The irreducible representations of the 32 point groups are found in

([1]) Except in the last paragraph of the discussion of time reversal.

many text books [4]. One can determine which irreducible representations $\Gamma^{(\nu)}$ are contained in Γ and finally construct with the components of the $\mathbf{u}(\mathbf{R})$ certain linear combinations called « symmetry coordinates » [5] which transform according to the $\Gamma^{(\nu)}$'s.

The same procedure applies to lattice vibrations if one replaces the $\mathbf{u}(\mathbf{R})$ by normal coordinates, the point group by a space group, and irreducible representation $\Gamma^{(\nu)}$ of the point group by $\Gamma^{(k_\nu)}$ of the space group.

The atomic displacements are *polar* vectors ([2]). Our method of analyzing magnetic structures is exactly the same, except that we are concerned with spin vectors, i. e. « magnetic displacements » which are *axial* vectors. The analogy of the procedures is schematized in table I.

TABLE I

Vibrational and Magnetic Modes

	MOLECULAR AND LATTICE VIBRATIONS	MAGNETIC STRUCTURES
	POLAR VECTORS	AXIAL VECTORS
I	Linear Transformation induce a representation Γ	
II	Reduction of Γ to irreducible representations in	
	Point groups (molecular V.)	Space groups
	Space groups (lattice V.)	
III	BASIS VECTORS	
	Symmetry Coordinates	Magnetic Modes

The transformation equations of spin vectors in a given space group $\mathbf{G}$ induce a representation Γ which is decomposed into irreducible representations. Whereas the symmetry coordinates depict vibrational modes, the basis vectors of the irreducible representations in the magnetic case are « magnetic modes », i. e. describe possible spin arrangements.

I.1 THE BASIC EQUATIONS. — We shall analyze more closely the three steps required in the analysis by referring to three basic equations. The transformation induced representation Γ is described by (I) ; the decomposition into irreducible components is given by (II), and the construction of base vectors is described by (III).

$$CS_j = \sum_i D^{\Gamma}(C)_{ij}\, S_i \qquad \text{(I)}$$

$$\left.\begin{aligned} \Gamma &= \sum_\nu a_\nu\, \Gamma^{(\nu)} \\ \text{with} \quad a_\nu &= g^{-1} \sum_C \chi^{\Gamma}(C).\chi^{(\nu)}(C)^* \end{aligned}\right\} \qquad \text{(II)}$$

$$\psi_{ij}^{(\nu)} = \sum_C D_{ij}^{(\nu)*}(C).C\psi\ . \qquad \text{(III)}$$

([2]) The author has used the same method to study ferroelectric modes [6], electric displacements or moments being polar vectors.

I.2 THE REPRESENTATION Γ. — The most general symmetry operation of a crystallographic space group $\mathbf{G}$ is $(\mathrm{E} \mid \mathbf{R}_n)\ (\alpha \mid \tau_\alpha)$, the product of a lattice translation $(\mathrm{E} \mid \mathbf{R}_n)$ and the operation $(\alpha \mid \tau_\alpha)$. Here E is the identity operator, $\mathbf{R}_n$ a lattice translation belonging to the translation group $\mathbf{T}$, α a proper or an improper rotation belonging to a point group $\mathbf{g}$ and τ_α a fractional translation.

The space group may be expanded as follows

$$\mathbf{G} = \mathbf{T} + \mathbf{T}(\alpha_2 \mid \tau_2) + \cdots + \mathbf{T}(\alpha_g \mid \tau_g) \qquad \text{(I-1)}$$

and it is well known that the factor group $\mathbf{G}/\mathbf{T}$ is isomorphous with the point group $\mathbf{g}$ of order g.

I.2.1 *The translation group.* — The irreducible representations of $\mathbf{T}$ are labelled by a wave-vector $\mathbf{k}$ and the character ([3]) $\chi(\mathbf{R})$ of a lattice-translation $\mathbf{R}$ is $\exp(2\pi\, \mathrm{i}\mathbf{k}.\mathbf{R}$. Fortunately $\mathbf{k}$ is known, so to speak, experimentally. As in X-ray crystallography where general extinction rules ([4]) and the positions of the reflexions (irrespective of their intensities) determine the crystallographic translation groups (i. e. Bravais lattices), similar extinction rules determine the magnetic translation lattices. If the neutron diffractionist says that he can index all the magnetic lines in the chemical unit cell, it means that $\mathbf{k} = 0$. The character of any lattice translation is + 1 and the spin arrangement conserves the periodicity of the chemical cell.

The classical magnetic structure of MnO with sublattices as foreseen by Néel [7] and confirmed by the first magnetic structure determination of Shull and Smart [8] illustrates clearly the theory presented here. Indeed the appearance of only (odd, odd, odd) lines in a unit cell doubled in three directions $2\,a_1$, $2\,a_2$, $2\,a_3$ implies the existence of a wave vector $\mathbf{k} = [\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}]$, so that

$$\exp(2\pi\, \mathrm{i}\mathbf{k}.\mathbf{R}) = \exp \pi\, \mathrm{i}(x + y + z) = \sigma(\mathbf{R})\,. \qquad \text{(I-2)}$$

Here x, y, z are the coordinates of the positions $\mathbf{R}$ of Mn expressed in units of the *chemical* cell. One easily checks that $\sigma(\mathbf{R})$ gives the correct signs of the Mn-spins. (For instance $\sigma(\mathbf{R}) = +1$ for $\mathbf{R}$ in 000, in 200, 020, 002 but $\sigma(\mathbf{R}) = -1$ for 100, 010, 001, $\frac{1}{2}\ \frac{1}{2}\ 0$, etc. Note also that in planes defined by $\mathbf{k}.\mathbf{R}$ = constant, the spins keep the same phase.)

We can reach an even more important conclusion from the MnO example. Consider a spin $\mathbf{S}(\mathbf{R})$ in $\mathbf{R}$ and let $\mathrm{P}_{\Delta\mathbf{R}}$ be the operator which brings the spin to $\mathbf{R} + \Delta\mathbf{R}$, $\Delta\mathbf{R}$ being a lattice translation. One then has

$$\mathrm{P}_{\Delta\mathbf{R}}\, \mathbf{S}(\mathbf{R}) = \mathbf{S}(\mathbf{R} + \Delta\mathbf{R}) = \\ = \exp(2\pi\, \mathrm{i}\mathbf{k}.\Delta\mathbf{R}).\mathbf{S}(\mathbf{R})\,. \qquad \text{(I-3)}$$

This equation expresses a Bloch-wave like behavior

([3]) This is only true for one dimensional representations of the wave-vector group $\mathbf{G}_\mathbf{k}$. More precise definitions are given later. It is clear of course that corresponding to the law of addition, $\mathbf{R}_1 + \mathbf{R}_2 = \mathbf{R}_3$, we have the multiplication law $\exp 2\pi\, \mathrm{i}\mathbf{k}.\mathbf{R}_1.\exp(2\pi\, \mathrm{i}\mathbf{k}.\mathbf{R}_2) = \exp(2\pi\, \mathrm{i}\mathbf{k}.\mathbf{R}_3)$.

([4]) An extinction rule is said to be « general » when it is valid for *all* reflexions (*hkl*). For instance, the rule (*hkl*) only exists for $h + k + l = 2n$, determines an I (centered) lattice ; the rule (*hkl*) only exists for $h + k + l = 2n + 1$, an I_P (anti-centered) lattice, and so on.

TABLE II

Magnetic Translation Lattices and Invariant Wave-vectors

System	Lattice O & G[27]	Lattice B[36]	Vector k	System	Lattice O & G[27]	Lattice B[36]	Vector k
Triclinic	P	P	0 0 0	Orthorhombic	F	F	0 0 0
	P_{2s}	P_s	0 0 ½		F_C	C_A	0 0 1
Monoclinic	P	P	0 0 0	Tetragonal	P	P	0 0 0
	P_{2a}	P_a	½ 0 0		P_{2c}	P_c	0 0 ½
	P_{2b}	P_b	0 ½ 0		P_P	P_C	½ ½ 0
	P_C	C_a	½ ½ 0		P_I	I_c	½ ½ ½
	C	C	0 0 0		I	I	0 0 0
	C_{2c}	C_c	0 0 ½		I_P	P_I	0 0 1
	C_P	P_C	1 0 0	Rhombohedral	R	R	0 0 0
Orthorhombic	P	P	0 0 0		R_R	R_I	½ ½ ½
	P_{2a}	P_a	½ 0 0	Hexagonal	P	P	0 0 0
	P_C	C_a	½ ½ 0		P_{2c}	P_c	0 0 ½
	P_F	F_s	½ ½ ½	Cubic	P	P	0 0 0
	C	C	0 0 0		P_F	F_s	½ ½ ½
	C_{2c}	C_c	0 0 ½		J	I	0 0 0
	C_P	P_C	1 0 0		I_P	P_I	0 0 1
	C_I	I_c	1 0 ½		F	F	0 0 0
	I	I	0 0 0				
	I_P	P_I	0 0 1				

of spins. Thus the fact that the neutron diffractionist can characterize a magnetic translation lattice by a wave vector **k** is already an experimental proof of a Bloch-wave like nature of spin-components. The magnetic translation lattices and wave vectors are compared in table II with the Opechowski-Guccione [27] and Belov [36] notations.

In the foregoing discussion of magnetic translation lattices with rational multiple cells, $\exp(2\pi\, i\mathbf{k}.\mathbf{R})$ takes only the values + 1 (translation) or − 1 (anti-translation).

There is an obvious generalisation for helical and sinusoidal spin configurations. We shall write [5] more generally

$$\mathbf{S}(\mathbf{R}) = \mathbf{S}_k(\mathbf{R}) + \mathbf{S}_{-k}(\mathbf{R}) \qquad \text{(I-4)}$$

with

$$\mathbf{S}_k(\mathbf{R}) = (\mathbf{x}a \exp i\alpha + \mathbf{y}b \exp i\beta + \mathbf{z}c \exp i\gamma) \exp(2\pi\, i\mathbf{k}.\mathbf{R})$$
$$\mathbf{S}_k^*(\mathbf{R}) = \mathbf{S}_{-k}(\mathbf{R}) . \qquad \text{(I-5)}$$

Here **x**, **y**, **z** are unit vectors along the crystallographic axes, a, b, c are positive quantities, α, β, γ phase angles to be determined by the experiment. The $\mathbf{S}_k(\mathbf{R})$-components behave like Bloch-waves, i. e.

$$P_{\Delta R}\, \mathbf{S}_k(\mathbf{R}) = \exp(2\pi\, i\mathbf{k}.\Delta\mathbf{R})\, \mathbf{S}_k(\mathbf{R}) = \mathbf{S}_k(\mathbf{R} + \Delta\mathbf{R}) . \qquad \text{(I-6)}$$

One has the conjugate complex relation for $\mathbf{S}_{-k}(\mathbf{R})$.

In the helical or sinusoidal case the neutron diffractionist determines the **k**-vector from satellite reflexions. It can also be shown from (I-5) that the turn angle $\varphi(\Delta\mathbf{R})$ between two helical spins $\mathbf{S}(\mathbf{R})$ and $\mathbf{S}(\mathbf{R} + \Delta\mathbf{R})$, $\Delta\mathbf{R}$ being a lattice translation is $\varphi(\Delta\mathbf{R}) = 2\pi\mathbf{k}.\Delta\mathbf{R}$. We postpone the proof to the discussion of invariants.

Once **k** is known, one may construct the irreducible representations of **G** and its subgroups associated with **k**.

We recall here some definitions in order to avoid the existing confusion in the nomenclature. Among the $(\alpha \mid \tau_\alpha)$ operators (their number is g) consider those $(\beta \mid \tau_\beta)$ wity the following property

$$\beta\mathbf{k} = \mathbf{k} + \mathbf{K}_\beta . \qquad \text{(I-7)}$$

The rotational operators β which conserve the wave vector **k** modulo a vector $\mathbf{K}_\beta$ of the reciprocal lattice [6] form a group, called the point group of the wave vector **k** and denoted here by $\mathbf{g}_\mathbf{k}$. If g_k is the order of the group, one has

$$g_k = \sum_\nu \delta_\nu^2 \qquad \text{(I-8)}$$

where δ_ν is the dimension of an irreducible representation of $\mathbf{g}_\mathbf{k}$.

The subgroup of **G**, composed of the $(\beta \mid \tau_\beta)$ operators defined above and the translation group **T** is a space group, called the wave-vector group and denoted by $\mathbf{G}_\mathbf{k}$. In an irreducible representation $\Delta^{(k_\nu)}$ of dimension d_ν of $\mathbf{G}_\mathbf{k}$, a lattice translation $\mathbf{R}_n$ is represented by

$$D^{(k_\nu)}(\mathbf{R}_n) = \mathbf{1}.\exp(2\pi\, i\mathbf{k}.\mathbf{R}_n) \qquad \text{(I-9)}$$

(5) We have defined earlier [9, 10]

$$\mathbf{S}_k(\mathbf{R}) = \frac{\mathbf{S}}{2}(\mathbf{u} - i\mathbf{v}) \exp(2\pi\, i\mathbf{k}.\mathbf{R}) \exp i\varphi ,$$

u and **v** being orthonormal vectors ; one has obviously $S_k^2 = 0$. The need for the definition above (1-5) has recently arisen in the discussion of the helical structure of $(UFeO_4)_{0.75}(UCrO_4)_{0.25}$, see this conference [11]. The two definitions can be shown to be equivalent, but **u** and **v** are not necessarily parallel to crystallographic axes.

(6) One must distinguish between reciprocal *lattice* and reciprocal *space*. One has $\mathbf{K} = K_1\mathbf{b}_1 + K_2\mathbf{b}_2 + K_3\mathbf{b}_3$ with K_j integer ($j = 1, 2, 3$) for a reciprocal lattice-vector where $\mathbf{b}_j$, the reciprocal cell edge, is defined by $\mathbf{a}_i.\mathbf{b}_j = \delta_{ij}$, the $\mathbf{a}_i$ being the cell vectors of the direct lattice.

where **1** is a unit matrix of dimension d_ν. The rule

$$g_k = \sum_\nu d_\nu^2 \qquad \text{(I-10)}$$

still applies, but of course the d_ν and δ_ν need not be the same.

Finally there is the « full group **G** » in which all operators $(\alpha \mid \tau_\alpha)$ (and not only the $(\beta \mid \tau_\beta)$ defined by (I-7)) have matrix representatives in irreducible representations [12] associated with **k**. The full group representation of a lattice translation $\mathbf{R}_n$ is

$$\mathrm{D}^{(\mathbf{k}_\nu)}(\mathbf{R}_n) = \begin{bmatrix} 1_q \exp 2\pi i \mathbf{k}_1 . \mathbf{R}_n & & \\ & \ddots & \\ & & 1_q \exp 2\pi i \mathbf{k}_p . \mathbf{R}_n \end{bmatrix} \qquad \text{(I-11)}$$

where the $\mathbf{k}_j$ $(j = 1, ..., p)$ form the star of the vector **k**, i. e. the set of p independant vectors (not related by (I-7)) generated from one of them by the application of *all* the operators α of the $(\alpha \mid \tau_\alpha)$.

Here we shall be satisfied with the discussion of $\mathbf{G}_\mathbf{k}$ only ([7]).

I.2.2 *Structure of the matrix representation* Γ. — Let be C an operator of the space group **G**, acting on the spin component $S_{k,i,\alpha}$ at $\mathbf{R}_i$. Here **k** is the vector labelling the translation group, i is an index which numbers the sites in the crystal, α stands for the components x, y, z. We can renumber the spin components in some convenient order and use *one* collective index j so that $S_{k,i,\alpha} = S_j$. The operator C will transform S_j to some other spin component say S_l. If these transformations are written in the form of equation (I), they define a matrix $\mathrm{D}^\Gamma(C)$. The matrices $\mathrm{D}^\Gamma(C)$ represent the group ([8]) i. e. they form a representation Γ of the group **G**. These matrices would have very high dimensions if C acted on all the spins of the crystal ; here would also be a very great number of operators C (theoretically an infinity) to deal with.

Fortunately the knowledge of the translation group and its representation (I-9) reduces both the dimension of $\mathrm{D}^\Gamma(C)$ as well as the number of operators C to be included. Indeed we have only to consider the g operatores $(\alpha_j \mid \tau_{\alpha j})$ $(j = 1, ..., g)$. Their action on a point xyz with no point symmetry (except the identity element) gives rise to g points, called « general positions » and tabulated in the International Tables (I. T.) [14]. In most cases, paramagnetic ions are located in « special positions », i. e. positions having a site symmetry, which is also indicated in I. T. If n is the number of atoms in « special positions » and m the order of the site symmetry group one has $mn = g$. The positions in I. T. are defined modulo a lattice translation.

We can proceed as follows. We number the spins $\mathbf{S}(\mathbf{R}_i)$ on a lattice site of order n from $i = 1$ to n in some definite order. They will be called « reference spins ».

We apply to a spin component $S_k(\mathbf{R}_i)_\alpha$ $(\alpha = x, y, z)$ an operation $C = (\beta \mid \tau_\beta)$ which does two things.

First it transforms the index α to some index $\alpha' = xyz$ with or without a change of sign according to the transformation law of axial vectors.

Secondly it sends point $\mathbf{R}_i$ to some point $\mathbf{R}_{j'}$.

In symmorphic groups ($\tau_\alpha \equiv 0$ for each α) one can always choose the reference points in such a way that $\mathbf{R}_{j'}$ is again on a reference point ($(\alpha \mid 0)$ or $(\beta \mid 0)$ are « closed » operations) so that there is no problem, whatever **k** may be.

In non symmorphic groups (at least *one* $\tau_\alpha \neq 0$), where « open » [15] symmetry operations occur, $\mathbf{R}_{j'}$ may not belong to the reference points, but will always be related to some reference point, say $\mathbf{R}_j$, by a lattice translation $\Delta\mathbf{R}$

$$\mathbf{R}_{j'} = \mathbf{R}_j + \Delta\mathbf{R} \qquad \text{(I-12)}$$

so that we can still express the transformed spin component in terms of the component of a reference spin in $\mathbf{R}_j$, as

$$S_k(\mathbf{R}_{j'})_{\alpha'} = \exp(2\pi i \mathbf{k}.\Delta\mathbf{R}) . S_k(\mathbf{R}_j)_{\alpha'} . \qquad \text{(I-13)}$$

This introduces a phase factor $\exp(2\pi i \mathbf{k}.\Delta\mathbf{R})$ into the corresponding coefficient of the matrix. Thus we can always construct matrices $\mathrm{D}^\Gamma(C)$ of dimension $3n$, representing an operation C of the space group $\mathbf{G}_\mathbf{k}$. This is a tractable problem for n up to six, but becomes quite cumbersome for say $n = 24$.

Another simplification arises from the remark already made. The axial vector transformation operating on the lower index α and on the sign of the spin component is governed by an axial vector representation ([9]) which will be noted $\tilde{\mathrm{V}}$ and has matrices of dimension 3 at most. The operation which sends $\mathbf{R}_i$ to $\mathbf{R}_{j'}$ is governed by a permutation representation denoted by $\Gamma_{\text{perm.}}$ which has matrices of order n only. The two operations are independant, which means that the resulting representation Γ is the direct product of those representations

$$\Gamma = \tilde{\mathrm{V}} \times \Gamma_{\text{perm.}} . \qquad \text{(I-14)}$$

In the same way, one has for the corresponding matrices the direct product relation

$$\mathrm{D}^\Gamma(\alpha \mid \tau_\alpha) = \mathrm{D}^{\tilde{\mathrm{V}}}(\alpha) \times \mathrm{D}^{\Gamma_{\text{perm.}}}(\alpha \mid \tau_\alpha) . \qquad \text{(I-15)}$$

II. Reduction of the Representation Γ. — As we have already said, once the wave-vector **k** is known, the irreducible representations $\Delta(\mathrm{k}_\nu)$ of the wave-vector space group $\mathbf{G}_\mathbf{k}$ may be constructed. If $\chi^\Gamma(C)$ is the character in the representation Γ, $\chi^{(\Delta(\mathrm{k}_\nu))}(C)$ the character in the irreducible representation $\Delta(\mathrm{k}_\nu)$ of the operator C, the relation (II) indicates how many times a_ν the representation $\Delta(\mathrm{k}_\nu)$ is contained in Γ. The summation is in principle over the g_k elements $(\beta \mid \tau_\beta)$, but may be restricted further in the following way. One has from the direct product relation (I-14)

$$\chi^\Gamma(\alpha \mid \tau_\alpha) = \chi^{\tilde{\mathrm{V}}}(\alpha) . \chi^{\Gamma_{\text{perm.}}}(\alpha \mid \tau_\alpha) . \qquad \text{(II-1)}$$

([7]) In $UCoO_4$ the full group representation has been taken into account [13].

([8]) If C_1, C_2 and C_3 are operators of **G** so that $C_1 C_2 = C_3$, then also $\mathrm{D}(C_1)\ \mathrm{D}(C_2) = \mathrm{D}(C_3)$.

([9]) We use the notation of Sivardière and Waintal [16] namely V for a polar and $\tilde{\mathrm{V}}$ for an axial vector representation, given for instance in the cubic group $m\,3\,m$ by the 3×3 matrices of $\Gamma_{4g}(\mathrm{T}_1)$.

In the permutation representation $\Gamma_{\text{perm.}}$, the only non zero traces are due to points which stay invariant (modulo a lattice translation) under the symmetry operation which therefore must belong to the site symmetry group of order m. Thus the summation in II can be restricted to those of the m elements of the site symmetry group which belong to $\mathbf{G}_k$.

For instance in the rare earth perovskites belonging to the space group $P\,b\,n\,m$, the rare earth site symmetry group is composed of two elements, the identity E and a mirror m. The identity will always contribute, the mirror m only if $m\mathbf{k} = \mathbf{k} + \mathbf{K}$.

In the axial vector representation $\tilde{\mathrm{V}}$ which clearly is the 3-dimensional representation Γ_{4g}, also denoted by T_1 of the point group $m\,3\,m$, $\chi^{\tilde{\mathrm{V}}}(3) = 0$, so that a ternary axis in a cubic group or subgroup of a cubic group will not contribute to $\chi^{\Gamma}(C)$. Other reductions are apparent from the direct product relation (I-14).

We shall discuss the three following cases :

1° $\mathbf{k} = 0$ (chemical = magnetic cell!),

2° $\mathbf{k}$ is an invariant vector on the surface of the Brillouin zone,

3° $\mathbf{k}$ is at the interior of the Brillouin zone.

1° $\mathbf{k} = 0$. In this case on has

$$\mathbf{g}_k = \mathbf{g} \tag{II-2}$$

and the only relevant irreducible representations are those of the point group $\mathbf{g}$ even if $\mathbf{G}$ is a non symmorphic group.

The matrices of the permutation representation have coefficients which are either 0 or + 1. The relevant matrices of the representation $\tilde{\mathrm{V}}$ are those of $\Gamma_{4g}(\mathrm{T}_1)$ in $m\,3\,m$, restricted to the point group $\mathbf{g}$, if it is a subgroup ([10]) of $m\,3\,m$. If $\mathbf{g}$ is an orthorhombic group, $\tilde{\mathrm{V}}$ decomposes into three representations of $\mathbf{g}$, corresponding to three subspaces x, y, z which thus can be considered separately. If $\mathbf{g}$ is a uniaxial point group, splitting into two subspaces z and (xy) occurs.

We illustrate these considerations by two examples. The first one chosen is m 3 m, the second one is m m m.

Example 1. Mn_3GaN crystallises in the cubic space group P m 3 m and all magnetic lines can be indexed in the chemical unit cell. The Mn atoms are in the positions 3 c and will be numbered 1, 2, 3 as follows : $0\,\frac{1}{2}\,\frac{1}{2}$ (1) ; $\frac{1}{2}\,0\,\frac{1}{2}$ (2) ; $\frac{1}{2}\,\frac{1}{2}\,0$ (3).

A fourfold axis, 4, along Oz changes 1 to 2, 2 to 1 and 3 to 3 (modulo a lattice translation) ; thus the matrix (4_z) in $\Gamma_{\text{perm.}}$ is

$$(4_z) = \begin{bmatrix} . & 1 & . \\ 1 & . & . \\ . & . & 1 \end{bmatrix}. \tag{II-3}$$

One has obviously

$$(4_z)^2 = (4_z^2) = \begin{bmatrix} 1 & . & . \\ . & 1 & . \\ . & . & 1 \end{bmatrix} = (2_z). \tag{II-4}$$

([10]) Any point group is a subgroup of $m\,3\,m$ or of $6/m\,m\,m$. In this latter event one is again in the uniaxial case.

The twofold axis along $x\,x\,0$, denoted by 2′ has the same matrix as (4_z) so that the non zero traces are

$$\chi^{\Gamma_{\text{perm.}}}(\mathrm{E}) = \chi^{\Gamma_{\text{perm.}}}(2) = 3\,;$$

$$\chi^{\Gamma_{\text{perm.}}}(4) = \chi^{\Gamma_{\text{perm.}}}(2') = 1\,. \tag{II-5}$$

One then finds easily from the group character table [4] that

$$\Gamma_{\text{perm.}} = \mathrm{A}_1 + \mathrm{E} \tag{II-6}$$

and from (I-14)

$$\Gamma = \mathrm{T}_1 \times (\mathrm{A}_1 + \mathrm{E}) = 2\,\mathrm{T}_1 + \mathrm{T}_2 \quad (\text{or } 2\,\Gamma_4 + \Gamma_5)\,. \tag{II-7}$$

Thus no magnetic structure may belong to Γ_1, Γ_2, Γ_3 of the cubic group. The investigation has shown that the structure, in fact, belongs to Γ_5 [17].

Example 2. Consider the four Cr or Fe positions in the family of rare earth perovskites [3] belonging to P b n m. The point group $\mathbf{g} = \mathrm{m\,m\,m}$ is of order eight and has eight representations Γ_{gj} and Γ_{uj} ($j = 1, 2, 3, 4$) (Γ_{g_1} is the identity representation). The point symmetry is $\bar{1}$. The only non zero characters in $\Gamma_{\text{perm.}}$ are $\chi^{\Gamma_{\text{perm.}}}(\mathrm{E}) = \chi^{\Gamma_{\text{perm.}}}(\bar{1}) = 4$. Thus $\Gamma_{\text{perm.}}$ contains each even representation once

$$\Gamma_{\text{perm.}} = \Gamma_{g_1} + \Gamma_{g_2} + \Gamma_{g_3} + \Gamma_{g_4}\,. \tag{II-8}$$

The representation $\tilde{\mathrm{V}}$ splits as follows

$$\tilde{\mathrm{V}} = \Gamma_{g_2} + \Gamma_{g_3} + \Gamma_{g_4} \tag{II-9}$$

and the direct product Γ (I-14) reduces to

$$\Gamma = 3(\Gamma_{g_1} + \Gamma_{g_2} + \Gamma_{g_3} + \Gamma_{g_4})\,. \tag{II-10}$$

Here we have used the relation $\Gamma_{gj}^2 = \Gamma_{g_1}$;

$$\Gamma_{g_2} \times \Gamma_{g_3} = \Gamma_{g_4}, \text{ etc.}$$

Relation (II-10) shows that each representation is contained three times or in other words there will be three basis vectors per representation as can be easily checked (see table 6 in ref. [3]).

The splitting of $\tilde{\mathrm{V}}$ corresponds to the three subspaces x, y and z and one can prove easily that each even representation exists once in each subspace.

Of course the same results may be obtained by the direct construction of the matrices D^{Γ} [3] [17].

2° $\mathbf{k} \neq 0$ is invariant.

Point group representations are still sufficient for symmorphic groups, but special care is needed for non symmorphic groups where for the case of $\mathbf{k}$-vectors on the surface of the Brillouin zone the Olbrychski-procedure [1-3] provides us with the needed irreducible representations. The coefficients in the matrices of $\Gamma_{\text{perm.}}$ are 0, + 1 and also − 1 (due to the action of phase coefficients $\exp(2\,\pi\,i\mathbf{k}.\Delta\mathbf{R})$. The representation of $\tilde{\mathrm{V}}$ is still handled as in the case $\mathbf{k} = 0$. There are numerous examples in the litterature [3] that fall under this classification.

The dimension of the irreducible representations increases generally.

3° $\mathbf{k} \neq 0$ at the interior of the first Brillouin zone.

We only consider the representations of the space group $\mathbf{G}_k$, simply given by (see any textbook on group theory)

$$\mathrm{D}^{(\nu)}(\beta \mid \tau_\beta) = \exp(2\,\pi\,i\mathbf{k}.\tau_\beta).\mathrm{D}^{(\nu)}(\beta) \tag{II-11}$$

where $D^{(\nu)}(\beta)$ is the matrix representative of β in the irreducible representation $\Gamma^{(\nu)}$ of the point group $\mathbf{g_k}$.

The non zero coefficients in the matrices of $\Gamma_{\text{perm.}}$ are generally complex numbers of the form $\exp(2\pi\, \mathbf{i k}.\Delta\mathbf{R})$.

Here we come back to the example of MnP, already considered briefly in [9], because we shall complete it later when discussing the role of time reversal.

MnP belongs to the space group $P\,b\,n\,m$. There are four atoms Mn with coordinates

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

$$\tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{4}\,(4)\,. \quad \text{(II-12)}$$

In the low temperature form the propagation vector is $\mathbf{k} = [h\ 0\ 0]$ [18, 19] for the « double helix » structure. For the time being let us be satisfied with the subgroup $P\,2_1$ of $P\,b\,n\,m$ containing the identity E and the twofold helical axis 2_{1x} in $x\,\frac{1}{4}\,0$, described by

$$2_{1x} = (2_x \mid \tau_x) \text{ with } \tau_x = \tfrac{1}{2}\,\tfrac{1}{2}\,0 \quad \text{(II-13)}$$

The point group of $\mathbf{k}$ is $\mathbf{g_k}(\mathrm{E}, 2_x)$ and has the usual irreducible representations $\Gamma_1(+1, +1)$ and $\Gamma_2(+1, -1)$ of a binary group. From (II-11), the space group $P\,2_1$ has the following irreducible representations

$P2_1$	E	2_{1x}
Γ_1	1	a
Γ_2	1	$-a$; $\quad a = \exp \pi i h$

(II-14)

The axis 2_{1x} brings point 1 to 3, point 2 to 4, point 3 to point 1 *plus* a translation 1 0 0 and point 4 to point 2 plus a translation 1 0 0. Thus the couple of points 1, 3 is disconnected from the couple 2, 4, so that they can be discussed separately.

III. **Basis Vectors.** — Whereas for the reduction of Γ, the knowledge of the characters of Γ and of $\Gamma^{(\nu)}$ was sufficient, we need for the construction of basis vectors according to relation (III) the matrices of the irreducible representations $D^{\nu}(C)$ themselves ([11]). In formula (III), ψ is a function from which one wants to project out the part transforming according to $\Gamma^{(\nu)}$, and described by $\psi_{ij}^{(\nu)}$. Here j is a *fixed* index whereas i varies from 1 to d_ν, the dimension of $\Gamma^{(\nu)}$. The summation in (III) is over all relevant symmetry operations. For the function ψ we shall take successively the spin components of $\mathbf{S}_{k,1}$ say $S_{k,1x}$, $S_{k1,y}$, $S_{k1,z}$. The result, on the left side, will be some linear combination of spins. This procedure is sufficient if the symmetry operations in the summation connect point 1 to all the other points.

It happens however that, for peculiar wave-vectors $\mathbf{k}$ in $\mathbf{G_k}$, the crystallographic site of order n in $\mathbf{G}$ of the International Tables splits into disconnected sets, in which case one repeats the procedure above for one point in each separate set. This is the case for $\mathbf{k} = [h, \bar{h}, 0]$ in spinels for the octahedral or B-sites [20].

([11]) Of course, characters and matrices coincide in a one dimensional representation.

Theorem. *The specification of the non zero basis vectors describes the structure.* Indeed such an information, combined with the fact that every other basis vector is zero gives rise to a set of linear equations which can be solved with respect to the individual spins. To prove the theorem, we only show that the number of spin components to be determined, say $3\,n$ is equal to the total number of components of basis vectors. This is exactly what one finds by taking in the first equation (II), the traces of the unit matrices in the first and second member

$$3\,n = \sum_{\nu} a_\nu\, d_\nu\,. \quad \text{(III-1)}$$

The basis vectors for the sites 4*a*) or 4*b*) in space group P b n m are shown in table VI reference [3], which is valid for the rare earth perovskite family and for β-$CoSO_4$ in the case of $\mathbf{k} = 0$.

If we refer to a $G_x\,F_z$ configuration we mean that

$$G_x = (S_1 - S_2 + S_3 - S_4)_x \neq 0\,;$$
$$F_z = (S_1 + S_2 + S_3 + S_4)_z \neq 0 \quad \text{(III-2)}$$

These equations combined with those obtained by setting all other basis vectors equal to zero, yield

$$S_{1x} = -S_{2x} = +S_{3x} = -S_{4x}\,;$$
$$S_{1z} = S_{2z} = S_{3z} = S_{4z} \quad \text{(III-3)}$$

The same is true for table IV describing the basis vectors for the MnP-structure in $P\,2_1$. If we say that the magnetic structure belongs to Γ_2, the basis vectors of Γ_1, are zero, leading to the conclusion (see table IV)

$$S_{k,1\alpha} = \exp(-\pi i h)\, S_{k,3\alpha}\,;\ (\alpha = y, z)\,. \quad \text{(III-4)}$$

Finally, let us mention that the magnetic structure factor, $\mathbf{F_M}$ linear function of the spins (III-5) can always be expressed in terms of the basis vectors of irreducible representations. This fact enormously simplifies model calculations [21].

$$\mathbf{F_M} = \sum_j \mathbf{S}_j \exp 2\pi\, \mathbf{i h}.\mathbf{R}_j\,. \quad \text{(III-5)}$$

IV. **Invariants.** — It is well known that the product $\Gamma^{(\mu)} \times \Gamma^{(\nu)}$ of two irreducible representations contains the identity representation only for $\Gamma^{(\mu)} = \Gamma^{(\nu)}$ for real and $\Gamma^{(\mu)} = \Gamma^{(\nu)*}$ for complex irreducible representations. Thus when we want to construct an effective spin hamiltonian of order two in the spins and invariant under a group $\mathbf{G_k}$ ([12]), we form products of two basis vectors belonging to the same real or to two conjugate complex representations of $\mathbf{G_k}$. For instance $G_x\,F_z$ in (III-2) (see table 6 in [3]) is an invariant product.

We note here that, in accordance with Curie's symmetry principle ([13]), we consider the *highest* possible symmetry of the hamiltonian and *not* its restriction to the Shubnikov group (which will be defined later).

An hamiltonian of order two in the spins is the exact analogue of the so-called « harmonic approxi-

([12]) Sometimes, for $\mathbf{k} \neq 0$, the full group is required. See [13].

([13]) « The characteristic symmetry of a phenomenon is the maximum symmetry compatible with the existence of the phenomenon » [22].

mation » in the theory of lattice vibrations. Only anharmonicity, i. e. the existence of higher order terms and in our case of higher order products of spin components can couple different irreducible representations ([14]). The hamiltonians constructed by the indicated pair multiplication can give information as already discussed in the existing literature on the nature (isotropic, symmetric, antisymmetric, « one-ion » anisotropic) of the magnetic couplings in CoO [24], $DyCrO_3$ [25] and in alloys [26].

Another interesting invariant is the « local length » of a spin component $\mathbf{S}_k^{(\nu)}(\mathbf{R})$ belonging to a definite representation $\Delta(k_\nu)$.

One has indeed for $\mathbf{S}_k^{(\nu)}(\mathbf{R})$ complex

$$\left.\begin{aligned}(\mathbf{S}^{(\nu)}(\mathbf{R}))^2 &= 2\,\mathbf{S}_k(\mathbf{R}).\mathbf{S}_k^*(\mathbf{R}) \text{ with}\\ (\mathbf{S}_k^{(\nu)})^2 &= (\mathbf{S}_k^{(\nu)*})^2 = 0\end{aligned}\right\} \quad \text{(IV-1)}$$

because only products transforming like $\Gamma^{(\nu)} \times \Gamma^{(\nu)*}$ can be invariant.

As an example one proves in the same way from (I.4), (I.5) and (III.4) that in the case of MnP

$$\mathbf{S}_1.\mathbf{S}_3 = \mathbf{S}_{1k}.\mathbf{S}_{3k}^* + \mathbf{S}_{1k}^*.\mathbf{S}_{3k} = S^2 \cos \pi h \quad \text{(IV-2)}$$

i. e. the angle between $\mathbf{S}_1$ and $\mathbf{S}_3$ is $\varphi_{13} = \pi h$.

Another interesting consequence is that spin-components of the same spin $\mathbf{S}(\mathbf{R})$ belonging to *different representations must be orthogonal* [3].

V. **Shubnikov groups.** — A magnetic space group $\mathbf{G}_m$ or Shubnikov group leaves a magnetic structure invariant. Thus it is a subgroup [27] of the direct product of a space group $\mathbf{G}$ and the time inversion group $(\mathrm{E}, \bar{\mathrm{E}})$ defined in such a way that it does not contain the time reversal operator alone but only in combination with other symmetry elements, giving rise to the so-called antisymmetry elements.

The one-to-one correspondance between Shubnikov groups and one dimensional real representations has been pointed out by several authors [27]-[29], [3]. The antisymmetry elements having the character — 1, we can immediately indicate the Shubnikov group corresponding to a one-dimensional real representation.

In the case of a one dimensional complex representation the Shubnikov group is the restriction to the real elements. We loose the symmetry elements having imaginary characters and still relevant in the hamiltonian.

In the case of an irreducible representation $\Gamma^{(\nu)}$ of higher dimension one might think of a « symmetry descent » à la Bethe [30] leading at least to *one* one-dimensional real representation, i. e. to a possible Shubnikov group. Such a procedure is however lengthy and often not unique. Indeed the three-dimensional representation $\Gamma_{5g} = \mathrm{T}_{2g}$ of group $m\ 3\ m$ can split into a one- plus a two-dimensional representation in a ternary group 32 $(= \mathrm{A}_1 + \mathrm{E})$ as well as in a tetragonal group 422 $(= \mathrm{B}_1 + \mathrm{E})$.

The following procedure is much simpler. In a first step one selects those symmetry elements which leave the magnetic structure invariant. They form a subgroup say $\mathbf{K}$. In a second step one decomposes the restriction to $\mathbf{K}$ of the original matrices of $\Gamma^{(\nu)}$ according to the irreducible representations of $\mathbf{K}$. If the restriction contains a one-dimensional real representation, this one corresponds to the Shubnikov group.

As an example, the non zero basis-vector $\mathrm{V}(\Gamma_{5g})$ (V-1) of Mn_3GaN implies the relations (V-2)

$$\mathrm{V}(\Gamma_{5g}) = \begin{bmatrix}\mathrm{S}_{2x} - \mathrm{S}_{3x}\\ \mathrm{S}_{3y} - \mathrm{S}_{1y}\\ \mathrm{S}_{1z} - \mathrm{S}_{2z}\end{bmatrix} \quad \text{(V-1)}$$

$$\mathrm{S}_{2x} = -\mathrm{S}_{3x} = \mathrm{S}_{3y} = -\mathrm{S}_{1y} = \mathrm{S}_{1z} = -\mathrm{S}_{2z} \quad \text{(V-2)}$$

The operations (3) (2') and $(\bar{1})$ in Γ_{5g} permute the components of $\mathrm{V}(\Gamma_{5g})$, but do not change the relations (V-2). The subgroup $\mathbf{K}$ is $R\ \bar{3}\ m$ and the restriction to $\mathbf{K}$ gives rise to the decomposition

$$\mathrm{T}_2 = \mathrm{A}_1 + \mathrm{E} \quad \text{(V-3)}$$

Thus the Shubnikov group is $R\ \bar{3}\ m$.

Another example, also discussed by Opechowski and Dreyfus [31] is $TbCrO_3$ [32]. Here $\mathbf{k} = [0\ \frac{1}{2}\ 0]$ and the diagonal matrices of the two-dimensional representation, say e, 2_{1x}, $2_{1y}\ \bar{1}$, $2_{1z}\ \bar{1}$ give rise to the equations

$$\begin{aligned}&2_{1x}.\mathrm{G}_x = \mathrm{G}_x\,;\ 2_{1y}.\bar{1}.\mathrm{G}_x = 2_{1z}.\bar{1}.\mathrm{G}_x = -\mathrm{G}_x\\ &2_{1x}.\mathrm{A}_x = -\mathrm{A}_x = 2_{1z}.\bar{1}.\mathrm{A}_x\,;\\ &2_{1y}.\bar{1}.\mathrm{A}_x = \mathrm{A}_x\,.\end{aligned} \quad \text{(V-4)}$$

The Shubnikov group conserving G_x is $\mathrm{P}_{2b}\ 2_1\ \mathrm{n}'\ \mathrm{m}'$ and that conserving A_x is $\mathrm{P}_{2b}\ 2_1'\ \mathrm{n}\ \mathrm{m}$. They are equivalent.

In our language, A_x and G_x describe equivalent magnetic structures, in other words they give rise to S-type magnetic twins ([15]). The simple connection between the theory outlined here and the theory of magnetic twins will be considered by Sivardière [33] in a separate publication.

To summarize, knowing the irreducible representation leads easily to the description by means of Shubnikov groups and at the same time gives information about magnetic twins.

VI. **Time Reversal Symmetry.** — In our earlier paper [3] time invariance did not play a role in magnetic structures because we had put special emphasis on the cases $\mathbf{k} = 0$ and $\mathbf{k}$ invariant. Thus $\mathbf{k}$ and $-\mathbf{k}$ are equivalent, crystallographic and magnetic space groups have the same number of elements and the same representations.

This no longer holds in those $\mathbf{G}_\mathbf{k}$ groups (subgroup of $\mathbf{G}$) in which $\mathbf{k}$ and $-\mathbf{k}$ are inequivalent as when $\mathbf{G}$ contains an element $(\rho \mid \tau)$ such that

$$\rho\mathbf{k} = -\mathbf{k} + \mathbf{K}_\rho \quad \text{(VI-1)}$$

Then the combined operator $a_0 = \theta.(\rho \mid \tau)$ where θ is the time reversal operator ([16]) ($\theta\mathbf{k} = -\mathbf{k}$) will also be in $\mathbf{G}_\mathbf{k}$.

([14]) The criticism expressed by Herpin [23] that the « theory of Bertaut » cannot take into account anisotropy and higher order terms (biquadratic for instance) is incorrect. See also [3].

([15]) These show up in the diffraction pattern. The domain walls are here magnetic « stacking faults ».

([16]) The notation here is that of Wigner [34] and of Dimmock and Wheeler [35].

This means that to the operations, already outlined, that act on a spin-component (axial vector transformation and point permutation) we must add the following : *a*) change of sign and *b*) complex conjugation. Thus an antiunitary operation will connect S_k and S_{-k} components and introduce new phase relations between them.

To illustrate this point, we complete, in the example of MnP, the group P 2_1 with $\mathbf{k} = [h\,0\,0]$, having the elements e and 2_{1x} in $\mathbf{G_k}$, by a centre of symmetry $\mathrm{I} = (\bar{1} \mid 0)$. I is not in $\mathbf{G_k}$ so that nothing would change without time reversal symmetry. Actually I plays the role of the element $(\rho \mid \tau)$ above (VI-1) so that, taking time reversal symmetry into account, $a_0 = \theta.\mathrm{I}$ as well as $\theta\mathrm{I}\,2_{1x}$ are in $\mathbf{G_k}$. The four representations of $\mathbf{G_k}$ are given in table III where the lower index + or − indicates the character of $\theta\mathrm{I}$.

TABLE III

Representations of the group P 2_1/b with time reversal for $\mathbf{k} = [h\ 0\ 0]$

	e	2_{1x}	$\theta.\mathrm{I}$	$2_{1x}\,\theta\mathrm{I}$
Γ_{1+}	1	a	1	a^*
Γ_{2+}	1	$-a$	1	$-a^*$
Γ_{1-}	1	a	-1	$-a^*$
Γ_{2-}	1	$-a$	-1	$+a^*$

$a = \exp \pi i h$.

One has the following transformation equations

$$\theta(\bar{1} \mid 0)\,\mathbf{S}_{k,1} = -\mathbf{S}^*_{k,2} = -\mathbf{S}_{-k,2}$$

$$\theta(2_x \mid \tau_x)\,(\bar{1} \mid 0)\,\mathrm{S}_{k,1\alpha} = \mathrm{S}^*_{k,2\alpha} \quad (\alpha = \mathrm{y},\ \mathrm{z}) \qquad \text{(VI-2)}$$

and analogous equations, so that the couples of points (1, 3) and (2, 4), previously disconnected ([17]) are connected again. It is easy to see that the non zero y, z components of the basis vector $\psi(\Gamma_{2-})$ in table IV

TABLE IV

Basis Vectors in MnP, *group P 2_1/b for* $\mathbf{k} = [h\ 0\ 0]$

	x-component	$\alpha = y$ and z components
$\psi(\Gamma_{1+})$	$V^+_{k,1x} - (V^+_{k,2x})^*$	$V^-_{k,1\alpha} - (V^-_{k,2\alpha})^*$
$\psi(\Gamma_{2+})$	$V^-_{k,1x} - (V^-_{k,2x})^*$	$V^+_{k,1\alpha} - (V^+_{k,2\alpha})^*$
$\psi(\Gamma_{1-})$	$V^+_{k,1x} - (V^+_{k,2x})^*$	$V^-_{k,1\alpha} + (V^-_{k,2\alpha})^*$
$\psi(\Gamma_{2-})$	$V^-_{k,1x} + (V^-_{k,2x})^*$	$V^+_{k,1\alpha} + (V^+_{k,2\alpha})^*$

$$V^+_{k,1\beta} = S_{k,1\beta} + a^* S_{k,3\beta}\ ;\quad V^-_{k,1\beta} = S_{k,1\beta} - a^* S_{k,3\beta}$$

$$V^+_{k,2\beta} = S_{k,2\beta} + a^* S_{k,4\beta}\ ;\quad V^-_{k,2\beta} = S_{k,2\beta} - a^* S_{k,4\beta}$$

$$\beta = x, y, z$$

Time reversal symmetry has added the quantities (...)*. In P 2_1 one has only $\psi(\Gamma_{1+})$ and $\psi(\Gamma_{2+})$ without the quantities (...)*.

describe the structure. The relations (VI-3) imply indeed (VI-4)

$$S_{k,1\alpha} = S^*_{k,2\alpha} = a^*\,\mathbf{S}_{k,3\alpha} = aS^*_{k,4\alpha} \qquad \text{(VI-3)}$$

$$\mathbf{S}_1 = \mathbf{S}_2\ ;\ \mathbf{S}_3 = \mathbf{S}_4\ ;\ \varphi_{13} = \pi h\ . \qquad \text{(VI-4)}$$

([17]) Of course if there is no centre I in G, the couples (1, 3) and (2, 4) would remain disconnected.

One might formulate the following objection : « The Bloch-wave like behavior is only formal. The relation $\theta\mathbf{k} = -\mathbf{k}$ might not be valid in a static structure ». We remark however that there is no inconsistency with still considering **k** as a crystal momentum. Indeed the minimizing condition for the hamiltonian equation of motion in the **k**, q representation

$$\frac{1}{\mathrm{h}}\nabla_{\mathrm{k}}\mathcal{H}(\mathbf{k}) = \frac{\mathrm{dr}}{\mathrm{dt}} = \mathbf{v} = 0 \qquad \text{(VI-5)}$$

(VI-5) shows that no motion is associated with the wave vector **k**, the velocity **v** being zero. For the same reason, one has also

$$\frac{\mathrm{dk}}{\mathrm{dt}} = \frac{\mathrm{e}}{\mathrm{c}}\mathbf{v} \times \mathbf{H} = 0 \quad (\mathbf{H} = \text{magnetic field})\,. \qquad \text{(VI-6)}$$

One may go one step further by replacing our « point spin » description by a « spin density » description, replacing $\mathbf{S}_k(\mathbf{R}_i)$ by $\mathbf{S}_k(\mathbf{R})\ \delta(\mathbf{R} - \mathbf{R}_i)$ or even $\mathbf{S}_k(\mathbf{R})\ \rho(\mathbf{R} - \mathbf{R}_i)$, δ and ρ denoting respectively a Dirac or ordinary density function [37].

Answer to the criticism of Professor Opechowski. — In the C 2 label (corresponding to representation analysis) I would prefer the specification of the basis vectors to that of spins arrangements. When a physicist says that the iron spins rotate from the $G_x F_z$ to the $G_z F_x$ configuration in some perovskite this is for him more descriptive and appealing than saying that the Shubnikov-group has changed from $P\,b'\,n'\,m$ to $P\,b\,n'\,m'$ or that the representation has changed from Γ_{4g} to Γ_{2g}. A good nomenclature for basis vectors is still needed.

I have claimed the superiority of classification C 2 over that by Shubnikov groups, and *not* over the classification C 1′, as defined by Professor Opechowski.

I certainly have said [3], thinking of helical and sinusoidal spins that « there are many instances where known magnetic structures are not invariant under any Shubnikov group ». If I had added « except in $P\,1$, $p\,1$ and 1 » this would have avoided some misunderstanding. But such low symmetries are not very useful for the physicist : The reason why I have not talked about magnetic groups of non crystallographic nature is that in representation analysis all ordered magnetic structures, including helical and sinusoidal ones, are handled consistently in the frame of the 230 space groups. Professor Opechowski, in his description of an helical spin introduces « extra symmetries in the spin-vector space », i. e. infinite rotation (non crystallographic) groups, whereas I still describe the helix by indicating basis-vectors $(S_{k,1\alpha} + \exp(-\pi i h).\ S_{k,3\alpha}$ and so on in the case of MnP ; see Table IV).

It is in this sense that I have claimed representation analysis to offer a wider frame than invariance under a Shubnikov group.

If one is willing to accept all isometric groups including non crystallographic ones, then, of course, C 1′ and C 2 describe magnetic structures uniquely.

On the other hand it is always easy to deduce from representation analysis the underlying Shubnikov-group. I do not think that the converse is that easy (see the case of $TbCrO_3$). According to Professor Opechowski, « C 2 may in some cases meet with mathe-

matical difficulties when one is not willing to impose cyclic boundary conditions ». As far as I understand, cyclic boundary conditions are the mathematical trick to handle infinite groups (translation and space groups) on the same footing as finite groups and have led to the success of space group theory. I am not willing to abandon these achievements if there is no better theory available.

As far as usefulness is concerned I still think that C 2 gives more immediate information than C 1'. There is no difficulty in using both descriptions jointly and, as a common practice, I indicate the Shubnikov group (except P 1) in my writings.

Conclusion. — Representation analysis is, first of all, a tool for finding magnetic structures. The description of a magnetic structure by basis vectors of irreducible representations is certainly useful. Finally the construction of an effective spin hamiltonian using *all* the symmetry elements of the irreducible representation becomes possible. Of course, physicists did not wait for the theory presented here to build their hamiltonian in the helimagnetic case. But when minimizing the isotropic part of the hamiltonian, say $J_1 \cos \pi l + J_2 \cos 2\pi l$ in the case of say the dysprosium or $AuMn_2$-helix, they may have got some feeling from this lecture that their hamiltonian is invariant under the wave vector group $\mathbf{G_k}$ ($= P 6_3 m c$) with $\mathbf{k} = [0\,0\,l]$ and that the helical spin configuration may belong to a two-dimensional representation of $\mathbf{G_k}$ [10].

Thus we reach this final conclusion. When the spin arrangement belongs to an irreducible representation of order higher than one or to a complex representation, the effective spin hamiltonian has a symmetry higher than the symmetry (Shubnikov-symmetry) which leaves the magnetic structure invariant.

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