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THE PHASE COMPARISON METHOD APPLICATION TO THE COMPLEX MAGNETIC STRUCTURE OF $REMn_2O_5$ (RE = Rare Earth)

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Résumé. — On construit d'abord une matrice d'interaction $\eta(\mathbf{q})$ à partir d'un hamiltonien de spins classiques. La méthode de comparaison de phases est une simple méthode d'identification, obtenant d'abord les vecteurs propres de $\eta(\mathbf{q})$ qui sont directement liés à la structure magnétique. Dans un deuxième temps on trouve les racines, reliées à l'énergie magnétique et les conditions de stabilité. L'application de la méthode aux composés $REMn^{3+}Mn^{4+}O_5$ (RE = terre rare) aboutit à un modèle dans lequel des chaînes linéaires de spins hélicoïdaux de Mn^{4+} sont couplées au moyen de paires de spins de Mn^{3+}. Le système hélimagnétique de Mn induit aux basses températures un ordre des spins RE qui est hélicoïdal pour une faible et sinusoïdal pour une forte anisotropie du site. Des corrélations de spins orthogonaux, rencontrées dans le présent traitement matriciel sont prouvées être compatibles avec la théorie des groupes.

Abstract. — One first derives from a classical spin hamiltonian an interaction matrix $\eta(\mathbf{q})$. The phase comparison method is a simple identification procedure obtaining at once the eigenvectors of $\eta(\mathbf{q})$ which are directly related to the magnetic structure. In a second step one finds the roots, related to the magnetic energy and the stability conditions. The application of this method to the compounds $REMn^{3+}Mn^{4+}O_5$ (RE = rare earth) results in a model where Mn^{4+}-chains of helical spins are coupled together by pairs of Mn^{3+}-spins, the system of helical Mn-spins inducing at low temperatures a spin ordering of RE, helical for negligible and sinusoidal for high one ion anisotropy. Orthogonal spin correlations occurring in the present matrix approach are shown to be compatible with group theory.

1. **Introduction.** — The microscopic or Fourier-method, developed by the author for the search of magnetic structures is a matrix method [1] which reduces to an eigenvalue problem in the case of equivalent atoms. When there are coupled systems of non equivalent magnetic atoms, the method is more difficult to handle and consists essentially in the search of a convenient combination of magnetic modes of the isolated (uncoupled) systems.

We present here a simple method called *phase comparison method* which does not need an explicit knowledge of eigenvectors or eigenvalues and only uses the fact that the linear equations under consideration and belonging to a same eigenvalue can be made either identical or conjugate.

We outline first the matrix method as far as needed here. We show further that eigenvalues and eigenvectors do not depend on atomic positions (part 1). We check then the *phase comparison method* on simple examples of equivalent atoms (part 2) and finally apply it to coupled systems (part 3).

Recently, a neutron diffraction study has been undertaken on the compounds $RE_2O_3.Mn_2O_3.2\ MnO_2$ or $REMn_2O_5$ where RE is Nd, Er, Ho, Tb or Y. The results [2, 10] are in essential agreement with the predictions of the theory presented here on coupled helical Mn-spins and helical or sinusoïdal RE-spins.

We study the stability conditions, first neglecting super-superexchange (part 4) and secondly taking it into account in order to explain Buisson's present data [2] (part 5). The coupling of the RE-to the Mn-spin system is considered in the approximation of isotropic exchange for negligible anisotropy (part 6) and for very high one ion anisotropy (part 7). In the discussion one relates the spin structure to the relevant exchange interactions.

Finally we connect the *microscopic* matrix method [1] to the *macroscopic* method of group theory (representation analysis) and show the perfect compatibility of these methods (part 8).

1.1 THE MATRIX METHOD. — We use a Heisenberg hamiltonian (1.1) where $\mathfrak{J}_{ij}$ is the usual exchange integral and $\mathbf{S}_i$ the spin at point $\mathbf{r}_i$. The minimisation of the hamiltonian (1.1) under the constraint S_i^2 = constant as well as the fact that $\mathrm{d}\mathbf{S}_i/\mathrm{d}t = 0$ in a static spin configuration are conducive to a system of linear eq. (1.2) with (positive) Lagrange parameters λ_i

$$\mathcal{H} = -2\sum_{i,j}\mathfrak{J}_{ij}\,\mathbf{S}_i.\mathbf{S}_j = -2\sum_i \lambda_i S_i^2 \qquad (1.1)$$

$$\lambda_i\,\mathbf{S}_i = \sum_j \mathfrak{J}_{ij}\,\mathbf{S}_j\,. \qquad (1.2)$$

After a Fourier transformation (1.2) can be written as a matrix equation

$$(\zeta(\mathbf{q}) - (\lambda))\,\mathbf{T}(\mathbf{q}) = 0\,. \qquad (1.3)$$

Here $\mathbf{T}(\mathbf{q})$ is a column vector having components $\mathbf{T}_j(\mathbf{q})$ which are the Fourier transforms of the $\mathbf{S}_j = \mathbf{S}(\mathbf{r}_j)$

$$\mathbf{T}_j(\mathbf{q}) = \sum_{r_j}\mathbf{S}(\mathbf{r}_j)\exp i\mathbf{q}.\mathbf{r}_j \qquad (1.4a)$$

$$\mathbf{S}(\mathbf{r}_j) = \sum_q \mathbf{T}_j(\mathbf{q})\exp -i\mathbf{q}.\mathbf{r}_j\,. \qquad (1.4b)$$

The summation in (1 4*a*) is over all points $\mathbf{r}_j$ belonging to the same Bravais lattice *j*. The interaction matrix $\zeta(\mathbf{q})$ is hermitian and has elements

$$\zeta_{ij}(\mathbf{q}) = \sum_{r_j}\mathfrak{J}_{ij}\exp i\mathbf{q}.(\mathbf{r}_{i0} - \mathbf{r}_j)\,. \qquad (1.5)$$

Here the indices *i* and *j* denote Bravais lattices *i* and *j*. $\mathbf{r}_{i0}$ is a reference point on the Bravais lattice *i*. The summation is first over all those points $\mathbf{r}_j$ of the Bravais lattice *j*, belonging to the same exchange integral J_{ij} and secondly over several exchange integrals if needed. The dimension of the matrix $\zeta(\mathbf{q})$, of the diagonal matrix (λ) and of the column vector $\mathbf{T}(\mathbf{q})$ is equal to the total number of Bravais lattices under consideration. The construction of matrix elements $\zeta_{ij}(\mathbf{q})$ is illustrated by the tables I and II.

As an example consider two systems I and II, each one containing four equivalent Bravais lattices. The matrices $\zeta(\mathbf{q})$ and (λ) will have the structure

$$\zeta(\mathbf{q}) = \begin{pmatrix} \zeta_{\mathrm{I}}(\mathbf{q}) & \zeta_{\mathrm{I-II}}(\mathbf{q}) \\ \zeta_{\mathrm{II-I}}(\mathbf{q}) & \zeta_{\mathrm{II}}(\mathbf{q}) \end{pmatrix} \qquad (1.6)$$

$$(\lambda) = \begin{pmatrix} (\lambda_{\mathrm{I}}) & 0 \\ 0 & (\lambda_{\mathrm{II}}) \end{pmatrix}. \qquad (1.7)$$

Here $\zeta_{\mathrm{I}}(\mathbf{q})$ and $\zeta_{\mathrm{II}}(\mathbf{q})$ are the interaction matrices of the separated systems I and II respectively, $\zeta_{\mathrm{I-II}}(\mathbf{q})$ is

TABLE I

Neighbours of $\mathrm{Mn_I}(1)$ *in xyO and Interaction Matrix*

Lattice *j*	Number of neighbours	Coordinates	Contribution to $\zeta_{1j}(\mathbf{q})$	Distance in Å	Angles (or Observations)
—	—	—	—	—	—
1	2	$x,\ y, \frac{1}{2} = \mathbf{r}_1 + 0, 0, \frac{1}{2}$ $x,\ y, \bar{1} = \mathbf{r}_1 + 0, 0, \bar{1}$	$2J_1(1.1)\cos q_3$	5.68	super-superexchange
2	1	$\bar{x},\ \bar{y}, 0 = \mathbf{r}_2$	$J_1(1.2)\exp i\mathbf{q}.(r_1 - r_2)$	2.855	91.5°
3	2	$\frac{1}{2} - x, \frac{1}{2} + y, 0 = \mathbf{r}_3$ $\frac{1}{2} - x, -\frac{1}{2} + y, 0 = \mathbf{r}_3 + 0, \bar{1}, 0$	$J_1(1.3)\exp i\mathbf{q}.(r_1 - r_3) \times$ $\times (1 + \exp iq_2)$	4.864	
4	2	$\frac{1}{2} + x, -\frac{1}{2} - y, 0 = \mathbf{r}_4 + 0, \bar{1}, 0$ $-\frac{1}{2} + x, -\frac{1}{2} - y, 0 = \mathbf{r}_4 + 1, 1, 0$	$J_1(1.4)\exp i\mathbf{q}.(r_1 - r_4) \times$ $\times \exp iq_2(1 + \exp iq_1)$	4.04	117°
5	1	$\frac{1}{2},\ 0, z = \mathbf{r}_5$	$J_{1,\mathrm{II}}(1.5)\exp i\mathbf{q}.(\mathbf{r}_1 - \mathbf{r}_5)$	3.55	131°
6	1	$\frac{1}{2},\ 0, \bar{z} = \mathbf{r}_6$	$J_{1,\mathrm{II}}(1.6)\exp i\mathbf{q}.(\mathbf{r}_1 - \mathbf{r}_6)$	3.55	131°
7	1	$0,\ -\frac{1}{2}, z = \mathbf{r}_7$	$J'_{1,\mathrm{II}}(1.7)\exp i\mathbf{q}.(\mathbf{r}_1 - \mathbf{r}_7)$	3.34	113°
8	1	$0,\ -\frac{1}{2}, \bar{z} = \mathbf{r}_8$	$J'_{1,\mathrm{II}}(1.8)\exp i\mathbf{q}.(\mathbf{r}_1 - \mathbf{r}_8)$	3.34	113°

The contribution to $\eta_{1j}(\mathbf{q})$ is obtained by suppressing the factor $\exp i\mathbf{q}.(\mathbf{r}_1 - \mathbf{r}_j)$ in $\zeta_{1j}(\mathbf{q})$.

TABLE II

Neighbours of $\mathrm{Mn_{II}}(5)$ *in* $\frac{1}{2}\ 0\ z$ *and Interaction Matrix*

Lattice *j*	Number of neighbours	Coordinates	Contribution to $\zeta_{5j}(\mathbf{q})$	Distance in Å	Angles
—	—	—	—	—	—
6	2	$\frac{1}{2},\ 0,\ -z = \mathbf{r}_6$ $\frac{1}{2},\ 0, 1 - z = \mathbf{r}_6 + 0, 0, 1$	$J_{\mathrm{II}}(5.6)\exp i\mathbf{q}.(\mathbf{r}_5 - \mathbf{r}_6)$ $J'_{\mathrm{II}}(5.6^+)\exp I\mathbf{q}.(\mathbf{r}_5 - \mathbf{r}_6)\exp -iq_3$	2.75 Å 2.93	95° 98°
7	4	$0,\ \frac{1}{2},\ z = \mathbf{r}_7$ $0, -\frac{1}{2},\ z = \mathbf{r}_7 + 0, \bar{1}, 0$ $1,\ \frac{1}{2},\ z = \mathbf{r}_7 + 1, 0, 0$ $1, -\frac{1}{2},\ z = \mathbf{r}_7 + 1, \bar{1}, 0$	$J_{\mathrm{II}}(5.7)\exp i\mathbf{q}.(\mathbf{r}_5 - \mathbf{r}_7)f(q_1, q_2)$	5.61	
8	4	$0, \pm\frac{1}{2},\ -z = \mathbf{r}_8 + \text{transl.}$ $1, \pm\frac{1}{2},\ -z = \mathbf{r}_8 + \text{transl.}$	$J_{\mathrm{II}}(5.8)\exp iq.(r_5 - r_8)f(q_1, q_2)$	6.25	
	4	$0, \pm\frac{1}{2}, 1 - z = \mathbf{r}_8 + \text{transl.}$ $1, \pm\frac{1}{2}, 1 - z = \mathbf{r}_8 + \text{transl.}$	$J'_{\mathrm{II}}(5.8)\exp iq.(r_5 - r_8)f(q_1, q_2)$	6.92	

$f(q_1, q_2) = (1 + \exp -iq_1)(1 + \exp iq_2)$; 6^+ is the point $\frac{1}{2}, 0, 1 - z$.
The contribution to $\eta_{5j}(\mathbf{q})$ is obtained by suppressing the factor $\exp i\mathbf{q}.(\mathbf{r}_5 - \mathbf{r}_j)$ in $\zeta_{5j}(\mathbf{q})$.

the matrix describing the interaction between the systems I and II. (λ_I) and (λ_{II}) are diagonal matrices of the form

$$(\lambda_I) = \lambda_I.\mathbf{1}\,; \qquad (\lambda_{II}) = \lambda_{II}.\mathbf{1} \tag{1.8}$$

where $\mathbf{1}$ is a diagonal matrix of dimension four; λ_I and λ_{II} are scalars.

The matrix $\zeta(\mathbf{q})$ still depends on atomic coordinates. It is however easy to see that one can write

$$\zeta_{ij}(\mathbf{q}) = \eta_{ij}(\mathbf{q}) \exp i\mathbf{q}.(\mathbf{r}_{i0} - \mathbf{r}_{j0}) \tag{1.9}$$

where η_{ij} only depends on Bravais lattice translations and no longer on atomic coordinates. It is advantageous to replace the $\mathbf{T}_j(\mathbf{q})$ (1.4) by new vectors $\mathbf{Q}_j(\mathbf{q})$ defined by

$$\mathbf{Q}_j(\mathbf{q}) = \mathbf{T}_j(\mathbf{q}) \exp - i\mathbf{q}.\mathbf{r}_{j0} \tag{1.10}$$

so that the matrix eq. (1.3) is replaced by

$$(\eta(\mathbf{q}) - (\lambda))\,\mathbf{Q} = 0\,. \tag{1.11}$$

Here $\eta(\mathbf{q})$ and consequently (λ) and $\mathbf{Q}$ will no longer depend on atomic coordinates. In the case of only one propagation vector $\mathbf{q}$, reference spins are simply given by

$$\mathbf{S}(\mathbf{r}_{j0}) = \mathbf{Q}_j(\mathbf{q}) + \mathbf{Q}_j^*(\mathbf{q}) \tag{1.12}$$

with

$$\mathbf{Q}_j^*(\mathbf{q}) = \mathbf{Q}_j(-\mathbf{q})\,. \tag{1.13}$$

We shall consider solutions of the form

$$\mathbf{Q}_j = \tfrac{1}{2}(\mathbf{u} + i\mathbf{v})\, S_j.Q_j \tag{1.14}$$

$\mathbf{u}$ and $\mathbf{v}$ are orthonormal unit vectors and Q_j is a phase factor of the form

$$Q_j = \exp - i\psi_j\,. \tag{1.15}$$

Thus the spin $\mathbf{S}(\mathbf{r}_{j0})$ (1.12) becomes

$$\mathbf{S}(\mathbf{r}_{j0}) = S_j(\mathbf{u}\cos\psi_j + \mathbf{v}\sin\psi_j) \tag{1.16}$$

and the angle between spins in $\mathbf{r}_{i0}$ and $\mathbf{r}_{j0}$ becomes $(\psi_i - \psi_j)$.

1.1.1 *Remark* 1. — A sinusoidal spin can be expressed by (1.16) with $\mathbf{v} = 0$.

1.1.2 *Remark* 2. — It is often convenient to introduce unitary spins $\boldsymbol{\sigma}_j$ defined by (1.17) and to incorporate the spin values in new exchange constants defined by (1.18)

$$\boldsymbol{\sigma}_j = \mathbf{S}_j/S_j \tag{1.17}$$

$$\hat{J}_{ij} = S_i\, \mathcal{J}_{ij}\, S_j\,. \tag{1.18}$$

When this is done, the components of the column vector $\mathbf{Q}$ in (1.11) are directly proportional to the phase factors Q_j (1.15), the constant factor being $\frac{1}{2}(\mathbf{u} + i\mathbf{v})$. From now on we shall use the convention of unitary spins for the manganese systems in $REMn_2O_5$. This is equivalent to replace S_j by 1 in (1.14).

2. **Equivalent atoms (the Mn-system).** — 2.1 PRELIMINARIES. — Figure 1 shows the projection of the structure along *c*.

The compounds crystallize in the space group *Pbam*. The atomic positions will be numbered as follows :

Mn^{3+} in 4g :

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

Mn^{4+} in 4f :

$\frac{1}{2}, 0, z$	(5);	$\frac{1}{2}, 0, \bar{z}$	(6);
$0, \frac{1}{2}, z$	(7);	$0, \frac{1}{2}, \bar{z}$	(8);

RE in 4h :

$x, y, \frac{1}{2}$	(9);	$\bar{x}, \bar{y}, \frac{1}{2}$	(10);
$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2}$	(11);	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2}$	(12).

There are four kinds of oxygenes O_I in 8i, O_{II} in 4g; O_{III} in 4h; O_{IV} in 4e. Their parameters are found in [3]. We only repeat those of the cations, as found from a refinement of $HoMn_2O_5$ [3] : for Mn^{3+} $x = 0.088$, $y = -.150$; for Mn^{4+} $z = .242$; for Ho $x = .140$, $y = .171$, $a = 7{,}33$ Å; $b = 8.49$ Å; $= 5.68$ Å.

(Cf. also lattice parameters of isomorphous substances [4] and a structure refinement of $DyMn_2O_5$ [5].)

For the sake of brevity, we note $Mn^{3+} = Mn_I$ and $Mn^{4+} = Mn_{II}$. We consider first the order of the manganese moments alone. The exchange integrals are of several types, J_I between moments of Mn_I, J_{II} between moments Mn_{II} and $J_{I,II}$ between moments Mn_I and Mn_{II}. Tables I and II show respectively the environments of the atoms $Mn_I(1)$ in $x, y, 0$ and of $Mn_{II}(5)$ in $\frac{1}{2}, 0, z$ and illustrate the construction of the matrix elements $\zeta_{ij}(\mathbf{q})$ and $\eta_{ij}(\mathbf{q})$. The $\eta(\mathbf{q})$ matrix has the following form, analogous to (1.6)

$$\eta(\mathbf{q}) = \begin{pmatrix} \eta_I & \eta_{I,II} \\ \eta_{II,I} & \eta_{II} \end{pmatrix}. \tag{2.1}$$

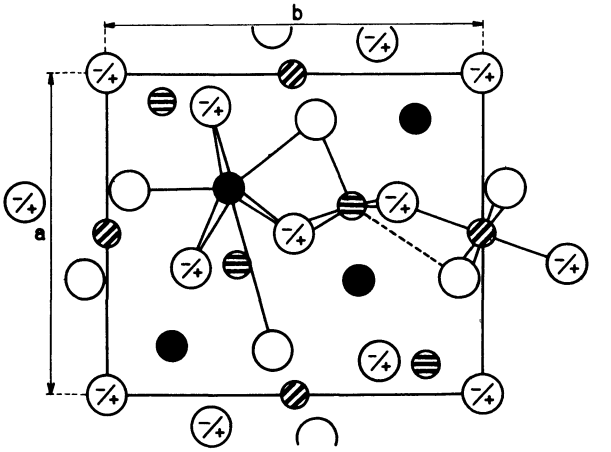

FIG. 1. — Projection of the crystal structure of $REMn_2O_5$ along *c*. White circles for O in $z = 0$ and $z = \frac{1}{2}$; circles $\pm$ for O in $z = \pm\frac{1}{4}$; black circles for RE in $z = \frac{1}{2}$; circles hatched horizontally for Mn_I^{3+} in $z = 0$ and obliquely for Mn_{II}^{4+} in $z \simeq \pm 0.24$. The environments are prismatic for RE, a (nearly) square pyramid for Mn_I and an octahedron for Mn_{II}.

Here η_{I} and η_{II} are the 4 × 4 matrices of the sublattices $\mathrm{Mn_I}$ and $\mathrm{Mn_{II}}$ alone. $\eta_{\mathrm{I,II}}$ is the interaction matrix between the sublattices $\mathrm{Mn_I}$ and $\mathrm{Mn_{II}}$. $\eta_{\mathrm{II,I}}$ is the conjugate transpose of $\eta_{\mathrm{I,II}}$.

The wave vector $\mathbf{q}$ has been found to be [2] $[\frac{1}{2}\ 0\tau]$ or explicitely

$$\mathbf{q} = (\tfrac{1}{2}\,\mathbf{a}^* + \tau\mathbf{c}^*).2\,\pi\,. \tag{2.2}$$

Here $\mathbf{a}^*$ and $\mathbf{c}^*$ are the reciprocal vectors of $\mathbf{a}$ and $\mathbf{c}$ respectively. All matrix elements are real except for η_{II}.

One has

$$\eta_{\mathrm{I}} = \begin{pmatrix} A_{\mathrm{I}} & B_{\mathrm{I}} & C_{\mathrm{I}} & O \\ B_{\mathrm{I}} & A_{\mathrm{I}} & O & -C_{\mathrm{I}} \\ C_{\mathrm{I}} & O & A_{\mathrm{I}} & B_{\mathrm{I}} \\ O & -C_{\mathrm{I}} & B_{\mathrm{I}} & A_{\mathrm{I}} \end{pmatrix};$$

$$\eta_{\mathrm{I,II}} = \begin{pmatrix} a & a & b & b \\ -a & -a & b & b \\ b & b & a & a \\ b & b & -a & -a \end{pmatrix};$$

$$\eta_{\mathrm{II}} = \begin{pmatrix} A_{\mathrm{II}} & B_{\mathrm{II}} & O & O \\ B_{\mathrm{II}}^* & A_{\mathrm{II}} & O & O \\ O & O & A_{\mathrm{II}} & B_{\mathrm{II}} \\ O & O & B_{\mathrm{II}}^* & A_{\mathrm{II}} \end{pmatrix}. \tag{2.3}$$

In the foregoing equations we have used the following abbreviations (cf. tables I and II)

$$\begin{gathered} 2\,J_{\mathrm{I}}(1.1)\cos q_3 = A_{\mathrm{I}};\quad J_{\mathrm{I}}(1.2) = B_{\mathrm{I}}; \\ 2\,J_{\mathrm{I}}(1.3) = C_{\mathrm{I}};\quad J_{\mathrm{I,II}}(1.5) = a; \\ J'_{\mathrm{I,II}}(1.7) = b;\quad 2\,J_{\mathrm{II}}(5.5)\cos q_3 = A_{\mathrm{II}}; \\ J_{\mathrm{II}}(5.6) + J'_{\mathrm{II}}(5.6^+)\exp - iq_3 = B_{\mathrm{II}};\quad 2\,\pi\tau = q_3\,. \end{gathered} \tag{2.4}$$

The (λ) matrix has the structure (1.7) (1.8) where λ_{I} and λ_{II} are the roots for the $\mathrm{Mn_I}$ and $\mathrm{Mn_{II}}$ moments, determined by the phase comparison method.

2.2 System $\mathrm{Mn_I}$. — Consider the $\mathrm{Mn_I}$ system alone which should obey the matrix equation

$$(\eta_{\mathrm{I}} - \lambda_{\mathrm{I_0}})\,Q_{\mathrm{I}} = 0\,. \tag{2.5}$$

Multiply the four eq. (2.5) by Q_1^{-1}, Q_2^{-1}, Q_3^{-1} and Q_4^{-1} respectively and rewrite the equations, labeled (1′) to (4′), so that terms with the same coefficients can be readily compared. For instance the eq. (1′) and (4′) are respectively

$$\begin{aligned} -\lambda_{\mathrm{I_0}} + A_{\mathrm{I}} + B_{\mathrm{I}}\,Q_2\,Q_1^{-1} + C_{\mathrm{I}}\,Q_3\,Q_1^{-1} &= 0 \\ -\lambda_{\mathrm{I_0}} + A_{\mathrm{I}} + B_{\mathrm{I}}\,Q_3\,Q_4^{-1} - C_{\mathrm{I}}\,Q_2\,Q_4^{-1} &= 0\,. \end{aligned} \tag{2.6}$$

Since the equations must be either identical or conjugate, inspection shows that one has symbolically

$$(1') = (2')^* = (3')^* = (4')\,. \tag{2.7}$$

From the comparison of eq. (1′) and (4′), we get

$$Q_2\,Q_1^{-1} = Q_3\,Q_4^{-1};\quad Q_3\,Q_1^{-1} = -\,Q_2\,Q_4^{-1}\,. \tag{2.8}$$

It can be checked that there are no other relations. The corresponding angular relations are

$$\begin{aligned} \psi_4 - \psi_3 &= \psi_1 - \psi_2 + 2\,\pi m\,; \\ \psi_1 - \psi_3 &= \psi_4 - \psi_2 + \pi + 2\,\pi n \end{aligned} \tag{2.9}$$

so that ψ_4 and ψ_3 can be expressed in terms of ψ_1 and ψ_4 respectively as follows (m, n integer)

$$\begin{aligned} \psi_3 &= \psi_2 - \frac{\pi}{2} - \pi(m+n)\,; \\ \psi_4 &= \psi_1 - \frac{\pi}{2} + \pi(m-n)\,. \end{aligned} \tag{2.10}$$

According to the parities of m and n, there will be two types of solutions, say *a*) and *b*).

2.2.1 *Solution a).* — m and n are of the same parity.

In this case

$$Q_3 = iQ_2\,;\qquad Q_4 = iQ_1\,. \tag{2.11}$$

This means geometrically that the spins $\mathbf{S}_2$ and $\mathbf{S}_3$ must be orthogonal and the same holds for spins $\mathbf{S}_1$ and $\mathbf{S}_4$.

Substituting the results (2.11) in the eq. (1′) and (2′) defined above, we have

$$\begin{aligned} \lambda_{\mathrm{I_0}} - A_{\mathrm{I}} &= \text{real quantity} = (B_{\mathrm{I}} + iC_{\mathrm{I}})\,Q_2\,Q_1^{-1} \\ &= (B_{\mathrm{I}} - iC_{\mathrm{I}})\,Q_1\,Q_2^{-1}\,. \end{aligned} \tag{2.12}$$

Define a phase φ by

$$B_{\mathrm{I}} + iC_{\mathrm{I}} = \sqrt{B_{\mathrm{I}}^2 + C_{\mathrm{I}}^2}\,\exp i\varphi\,. \tag{2.13}$$

We get from (2.12)

$$\exp i\varphi.Q_2^2 = \exp - i\varphi.Q_1^2 \tag{2.14}$$

so that finally a simple ([1]) solution is

$$Q_1 = \exp i\frac{\varphi}{2} = \pm\,Q_2^* = Q_{\mathrm{I}}\,. \tag{2.15}$$

2.2.2 *Solution b).* — m and n have different parities.

One finds the relations (2.16) and (2.17) analogous to (2.11) and (2.15)

$$Q'_3 = -\,iQ'_2\,;\qquad Q'_4 = -\,iQ'_1 \tag{2.16}$$

$$Q'_1 = \exp -\frac{i}{2}\varphi = \pm\,(Q'_2)^* = Q'_{\mathrm{I}}\,. \tag{2.17}$$

([1]) The most general solution is

$$Q_1 = \exp i\left(\frac{\Phi}{2} + \alpha\right);\quad Q_2 = \exp i\left(-\frac{\Phi}{2} + \alpha\right)$$

with α arbitrary.

Finally the eigenvector matrix (Q) of the uncoupled Mn_I system becomes

$$(Q) = \begin{pmatrix} Q & Q & Q' & Q' \\ -Q^* & Q^* & -Q'^* & Q'^* \\ -iQ^* & iQ^* & iQ'^* & -iQ'^* \\ iQ & iQ & -iQ' & -iQ' \end{pmatrix} . \quad (2.18)$$

Here columns 1 and 2 belong to solution *a*), columns 3 and 4 to solution *b*).

2.2.3 *Roots.* — From (2.12) we can evaluate directly the roots

$$\lambda_{I_0}^{+} = A_I + \sqrt{B_I^2 + C_I^2}\,; \qquad \lambda_{I_0}^{-} = A_I - \sqrt{B_I^2 + C_I^2}\,. \quad (2.19)$$

Columns 1 and 3 of (Q) (2.18) are conjugate and belong to one root λ^+, columns 2 and 4 belong to the other root.

One may equivalently write a parametric representation of the roots, splitting (2.12) into a real and an imaginary part. Thus

$$\lambda_{I_0}^{+} = A_I - B_I \cos 2\psi_I + C_I \sin 2\psi_I \quad (2.20a)$$

with

$$B_I \sin 2\psi_I + C_I \cos 2\psi_I = 0 \quad (2.20b)$$

so that

$$\operatorname{tg} 2\psi_I = -C_I/B_I\,. \quad (2.21)$$

2.3 SYSTEM Mn_{II}. — The same procedure as above, applied to the matrix η_{II} gives rise to the phase relations

$$Q_5 = \pm Q_6^*\,; \qquad Q_7 = \pm Q_8^*\,. \quad (2.22)$$

No phase relation is found between Q_5 and Q_7 because there is no matrix element connecting them. This inherent degeneracy will be lifted in the coupled system.

It is instructive to consider a root λ_{II_0} in the parametrized and the non parametrized form. With the abbreviations (cf. (2.4))

$$J_{II}(5.5) = J_c\,; \quad J_{II}(5.6) = J\,; \quad J'_{II}(5.6') = J'\,; \quad \psi_{II} = \psi_5\,; \quad q = 2\pi\tau \quad (2.23)$$

the root parametrized in ψ_{II} is

$$\lambda_{II_0} = 2J_c \cos q + J \cos 2\psi_{II} + J' \cos(q - 2\psi_{II}) \quad (2.24)$$

with the conditions

$$J \sin 2\psi_{II} + J' \sin(2\psi_{II} - q) = 0 \quad (2.25a)$$

$$2J_c \sin q + J' \sin(q - 2\psi_{II}) = 0\,. \quad (2.25b)$$

The form non parametrized in ψ_{II} is

$$\lambda_{II_0} = 2J_c \cos q + (J^2 + (J')^2 + 2JJ' \cos q)^{1/2}\,. \quad (2.26)$$

The discussion shows that if $J_c = 0$, there is no helical solution, i. e. $\sin q = 0$. Thus even in the asymmetric chain $(J \neq J')$ the second neighbour interaction is needed for a helical arrangement. In this event one finds :

$$\cos^2 \frac{q}{2} = \frac{JJ'}{16 J_c^2} - \frac{(J - J')^2}{4JJ'} \quad (2.27)$$

which reduces to the classical result

$$\cos \frac{q}{2} = -\frac{J}{4J_c} \quad \text{for} \quad J = J'\,,$$

i. e. for the case of the symmetrical chain.

For completeness we also give the value of $\cos 2\psi_{II}$ and λ_{II_0} for the asymmetric chain

$$\cos 2\psi_{II} = -\frac{1}{4}\frac{J'}{J_c} + \frac{J_c}{J}\left(\frac{J'}{J} - \frac{J}{J'}\right) \quad (2.28)$$

$$\lambda_{II_0} = -[(JJ')^2 + 2J_c^2(J^2 + (J')^2)]/(JJ'J_c)\,. \quad (2.29)$$

The positivity of λ_{II_0} implies the negativity of the product $JJ'J_c$.

3. **Coupled systems.** — We could have started from the beginning with comparing the phases of the coupled systems. It is however obvious that the phase relations between the Q_j of the coupled systems must functionally still satisfy those of the uncoupled systems although the values of the individual phases will change in the coupling. Thus the symbolic relations (2.7) must still be valid and all previous phase relations can be used. More precisely, we conserve the phase vector of the first column of (2.18) with

$$Q_1 = Q_I\,; \qquad Q_2 = -Q_I^*\,; \qquad Q_3 = -iQ_I^*\,; \qquad Q_4 = iQ_I \quad (3.1a)$$

or equivalently

$$\psi_1 = \psi_I\,; \qquad \psi_2 = \pi - \psi_I\,; \qquad \psi_3 = \frac{\pi}{2} - \psi_I\,; \qquad \psi_4 = \psi_I - \frac{\pi}{2}\,. \quad (3.1b)$$

In the first four equations of the matrix η (2.1), Q_5 and Q_6 on one hand, Q_7 and Q_8 on the other hand always occur with the same coefficients so that we put

$$Q_5 + Q_6 = F\,; \qquad Q_7 + Q_8 = G\,. \quad (3.2)$$

We examplify the procedure by writing explicitely the first two equations of the coupled system :

$$(A_I-\lambda_I)\,Q_1+B_I\,Q_2+C_I\,Q_3+aF+bG=0 \quad (3.3)$$

$$B_I^*\,Q_1+(A_I-\lambda_I)\,Q_2-C_I\,Q_4-aF+bG=0\,. \quad (3.4)$$

Multiplying them by Q_1^{-1} and Q_2^{-1} respectively and taking into account the conjugate character of the equations thus obtained (cf. (2.7)) one has from the comparison of the coefficients of a and b and from (3.1)

$$\begin{aligned} FQ_1^{-1} &= -\,(FQ_2^{-1})^* = -\,F^*\,Q_2 = F^*\,Q_1^{-1} \\ GQ_1^{-1} &= (GQ_2^{-1})^* = G^*\,Q_2 = -\,G^*\,Q_1^{-1}\,. \end{aligned} \quad (3.5)$$

Thus F must be real and G imaginary

$$F = F^*; \qquad G = -\,G^* \quad (3.6)$$

whence

$$Q_5 = Q_6^*; \qquad Q_7 = -\,Q_8^*\,. \quad (3.7)$$

From the comparison of the first and fourth equation of our matrix equation we deduce the condition

$$G = -\,iF\,. \quad (3.8)$$

Finally comparing the coefficients of a and b in the fifth and seventh equation formed with η (2.1) one gets

$$Q_5 = iQ_7; \qquad Q_6 = iQ_8\,. \quad (3.9)$$

These relations satisfy the condition (3.8) and mean that $\mathbf{S}_7$ and $\mathbf{S}_8$ are respectively orthogonal to $\mathbf{S}_5$ and $\mathbf{S}_6$. The orthogonality relations (2.11) and (3.9) have provided the key for the solution of the magnetic structures studied by Buisson [2].

The eigenvector of the Mn_{II} system can be expressed in terms of Q_5 alone

$$\begin{aligned} Q_5 &= Q_{II}; \qquad Q_6 = Q_{II}^*; \\ Q_7 &= -\,iQ_{II}; \quad Q_8 = -\,iQ_{II}^* \end{aligned} \quad (3.10a)$$

or equivalently

$$\begin{aligned} \psi_5 &= \psi_{II}; \qquad \psi_6 = -\,\psi_{II}; \\ \psi_7 &= \psi_{II}+\frac{\pi}{2}; \quad \psi_8 = -\,\psi_{II}+\frac{\pi}{2}\,. \end{aligned} \quad (3.10b)$$

The phase relations (3.1) and (3.10) with

$$Q_I = \exp -\,i\psi_I; \quad Q_{II} = \exp -\,i\psi_{II} \quad (3.11)$$

define the following system of reference spins (3.12) where we take $\mathbf{u}$ along the x-axis and $\mathbf{v}$ along the y-axis :

$$\begin{aligned} \boldsymbol{\sigma}_1 &= \mathbf{u}\cos\psi_I + \mathbf{v}\sin\psi_I \\ \boldsymbol{\sigma}_2 &= -\,\mathbf{u}\cos\psi_I + \mathbf{v}\sin\psi_I \\ \boldsymbol{\sigma}_3 &= \mathbf{u}\sin\psi_I + \mathbf{v}\cos\psi_I \\ \boldsymbol{\sigma}_4 &= \mathbf{u}\sin\psi_I - \mathbf{v}\cos\psi_I \\ \boldsymbol{\sigma}_5 &= \mathbf{u}\cos\psi_{II} + \mathbf{v}\sin\psi_{II}\,; \\ \boldsymbol{\sigma}_6 &= \mathbf{u}\cos\psi_{II} - \mathbf{v}\sin\psi_{II}\,; \\ \boldsymbol{\sigma}_7 &= -\,\mathbf{u}\sin\psi_{II} + \mathbf{v}\cos\psi_{II} \\ \boldsymbol{\sigma}_8 &= \mathbf{u}\sin\psi_{II} + \mathbf{v}\cos\psi_{II}\,. \end{aligned} \quad (3.12)$$

This information combined with the assumption of mainly negative interactions between spins of Mn_I and Mn_{II} gives already a fair picture of allowed structures, taking ψ_I and ψ_{II} in the vicinity of 0° and 180° respectively.

At this point we emphasize once more that our eigenvectors (3.1) and (3.10) or equivalently our structure model (3.12) have been obtained by the phase comparison method without solving for the values of λ_I and λ_{II}. The present example also shows that orthogonal spin situations (cf. the couples of spins (1 ; 4), (2 ; 3), (5 ; 7), (6 ; 8)) can arise in the presence of only isotropic interactions without the need of anisotropic exchange. We return to our system of eight eq. (1.11) which is now reduced to only two complex equations, say the first and the fifth for instance

$$\left.\begin{aligned} &(A_I-\lambda_I)\,Q_I-(B_I+iC_I)\,Q_I^*+ \\ &\quad+(a-ib)\,(Q_{II}+Q_{II}^*)=0 \\ &(A_{II}-\lambda_{II})\,Q_{II}+B_{II}\,Q_{II}^*+ \\ &\quad+(a+ib)\,Q_I+(a-ib)\,Q_I^*=0 \end{aligned}\right\}. \quad (3.13)$$

Multiply the first and second equation of (3.13) by Q_I^* and Q_{II}^* respectively and split into real and imaginary parts. One gets the four eq. (3.14*a*, *b*, *c*, *d*) where we have used the notations (2.4) and (2.23)

$$\begin{aligned} \lambda_I &= A_I - B_I\cos 2\psi_I + C_I\sin 2\psi_I + \\ &\quad+2(a\cos\psi_I + b\sin\psi_I)\cos\psi_{II} \quad (3.14a) \\ \lambda_{II} &= A_{II} + J\cos 2\psi_{II} + J'\cos(q-2\psi_{II}) + \\ &\quad+2(a\cos\psi_I + b\sin\psi_I)\cos\psi_{II} \quad (3.14b) \\ &-(B_I\sin 2\psi_I + C_I\cos 2\psi_I) + \\ &\quad+2(a\sin\psi_I - b\cos\psi_I)\cos\psi_{II}=0 \quad (3.14c) \\ &J\sin 2\psi_{II} + J'\sin(2\psi_{II}-q) + \\ &\quad+2(a\cos\psi_I + b\sin\psi_I)\sin\psi_{II}=0\,. \quad (3.14d) \end{aligned}$$

It is easily checked that for a and b tending to zero, λ_I and λ_{II} tend to the roots λ_{I_0} (2.20*a*) and λ_{II_0} (2.24) of the uncoupled systems. At the same time conditions (3.14*c*) and (3.14*d*) tend to the conditions (2.20*b*) and (2.25*a*) of the uncoupled systems, as it should be.

The magnetic energy of the couple of ions $Mn_I + Mn_{II}$ is given by

$$W_M = -\,2(\lambda_I+\lambda_{II})\,. \quad (3.15)$$

It is seen that (3.14*c*) and (3.14*d*) express the conditions of an extremum of W_M with respect to the variates ψ_I and ψ_{II} respectively. With the abbreviations

$$A_I + A_{II} = 4\,\bar{J}_c \cos q = j_c \cos q \qquad (3.16)$$

where $\bar{J}_c$ is the average exchange integral of Mn_I and Mn_{II} with their neighbours at the distance c, one finds a further equilibrium condition (3.14*e*) by equating to zero the derivative of W_M with respect to the wave vector component $q = 2\,\pi\tau$ (cf. (2.25*b*)) :

$$j_c \sin q + J' \sin (q - 2\,\psi_{II}) = 0\,. \qquad (3.14e)$$

3.1 REMARK. — In the foregoing lines the phase relations (3.10) were derived with the help of the four first equations of the matrix system (1.11) belonging to λ_I. If we had taken the second set of equations belonging to λ_{II}, multiplied by Q_5^* to Q_8^* and labeled (5′) to (8′) respectively, we would have got the same result.

The reader may check the symbolic relations, completing (2.7)

$$(5') = (6')^* = (7') = (8')^*\,. \qquad (3.17)$$

4. **Negligible super-superexchange.** — For a first orientation we neglect super-superexchange at the distance $c \sim 5.7$ Å ($j_c \sim 0$). Thus from (3.14*e*)

$$\sin (q - 2\,\psi_{II}) = 0\,. \qquad (4.1)$$

From (3.14*d*) we derive two solutions, a solution $\sin \psi_{II} = 0$, implying also $\sin q = 0$, which case will be studied at the end of this chapter, and the solution

$$\cos \psi_{II} = -\,(a \cos \psi_I + b \sin \psi_I)/J \qquad (4.2)$$

which substituted into (3.14*c*) determines ψ_I by

$$\operatorname{tg} 2\,\psi_I = (2\,ab - C_I J)/(B_I J + a^2 - b^2)\,. \qquad (4.3)$$

$\cos \psi_{II}$ can now be expressed as follows

$$\cos \psi_{II} = -\,(a\sqrt{1 + r} + b\sqrt{1 - r})/(J\sqrt{2}) \qquad (4.4)$$

where

$$r = 1/\sqrt{1 + \operatorname{tg}^2 2\,\psi_I}\,. \qquad (4.5)$$

Thus the angles ψ_I and ψ_{II} are expressible in terms of the exchange integrals alone.

With the help of these relations, it is also possible to indicate explicite expressions for the eigenvalues λ_I and λ_{II} (3.14*ab*). We find after some tedious but straightforward algebra (neglecting A_I and A_{II})

$$\lambda_I = \left(\left(B_I + \frac{a^2 - b^2}{J}\right)^2 + \left(\frac{2\,ab}{J} - C_I\right)^2\right)^{1/2} - \frac{a^2 + b^2}{J} \qquad (4.6)$$

$$\lambda_{II} = -\,J + J' \cos (q - 2\,\psi_{II}) = -\,J + |\,J'\,| \qquad (4.7)$$

where the last equation is justified in (4.9).

4.1 LOCAL STABILITY CONDITIONS. — The quadratic form constructed on the second derivatives of W_M with respect to the variates ψ_I, ψ_{II} and q_3 should be definite positive, or expressed otherwise, the determinant Δ (4.8) and all its principal minors should be positive for a minimum of W_M :

$$\Delta = \begin{vmatrix} \dfrac{\delta^2 W}{\delta \psi_I^2} & \dfrac{\delta^2 W}{\delta \psi_I\, \delta \psi_{II}} & \dfrac{\delta^2 W}{\delta \psi_I\, \delta q} \\ \dfrac{\delta^2 W}{\delta \psi_{II}\, \delta \psi_I} & \dfrac{\delta^2 W}{\delta \psi_{II}^2} & \dfrac{\delta^2 W}{\delta \psi_{II}\, \delta q} \\ \dfrac{\delta^2 W}{\delta q\, \delta \psi_I} & \dfrac{\delta^2 W}{\delta q\, \delta \psi_{II}} & \dfrac{\delta^2 W}{\delta q^2} \end{vmatrix}\,. \qquad (4.8)$$

We discuss here the most significant ones in the approximation of negligible super-superexchange ($j_c = 0$). From

$$\frac{\delta^2 W}{\delta q^2} > 0$$

we deduce the condition

$$J'.\cos (q_3 - 2\,\psi_{II}) > 0\,. \qquad (4.9)$$

Thus there are two choices from (4.1), either

$$J' > 0 \quad \text{and} \quad 2\,\psi_{II} = q_3 + 2\,\pi n \qquad (4.9a)$$

or

$$J' < 0 \quad \text{and} \quad 2\,\psi_{II} = q_3 + 2\,\pi n + \pi\,. \qquad (4.9b)$$

From

$$\frac{\delta^2 W}{\delta \psi_{II}^2} > 0 \text{ and } \frac{\delta^2 W}{\delta \psi_{II}^2} \cdot \frac{\delta^2 W}{\delta q^2} - \left(\frac{\delta^2 W}{\delta \psi_{II}\, \delta q}\right)^2 > 0 \qquad (4.10)$$

one derives the conditions

$$\left.\begin{aligned} -\,J \sin^2 \psi + J' \cos (q_3 - 2\,\psi_{II}) > 0 \\ \text{and} \\ -\,JJ' \cos (q_3 - 2\,\psi_{II}) > 0 \end{aligned}\right\}\,. \qquad (4.11)$$

The last relation (4.11) compared to (4.9) implies the important result

$$J < 0 \qquad (4.12)$$

Thus (4.9) and (4.12) tend to make λ_{II} positive.

We may conjecture that B_I, a and b are negative so that $J < 0$ also increases λ_I (4.6). We may also conjecture that with the shortest distances are associated the most negative exchange integrals with $|\,b\,| < |\,a\,| \leqslant B_I$ or J so that $|\,ab\,|$ would be small with respect to $|\,B_I J\,|$ and from (4.3) the angle ψ_I would be small too (C_I is probably negligible).

Table III summarizes the result of the discussion of relations (4.1) and (4.9*a*, *b*) and contains the values of $\cos \psi_{II}$ and $\sin \psi_{II}$, the signs of the exchange integrals J' (between Mn_{II} — moments at z and

TABLE III

Values of the phases ψ_{II} and φ_5 and signs of exchange J' and a

Value of $2\psi_{II}$	J'	n	a	$\cos\psi_{II}$	$\sin\psi_{II}$	$\cos\varphi_5$	$\sin\varphi_5$
$2\psi_{II} = q + 2\pi n$	+	0	+	$\cos\frac{1}{2}q$	$\sin\frac{1}{2}q$	$\cos\frac{1}{4}q$	$\sin\frac{1}{4}q$
	+	1	−	$-\cos\frac{1}{2}q$	$-\sin\frac{1}{2}q$	$-\cos\frac{1}{4}q$	$-\sin\frac{1}{4}q$
$2\psi_{II} = q + 2\pi n + \pi$	−	0	−	$-\sin\frac{1}{2}q$	$\cos\frac{1}{2}q$	$-\sin\frac{1}{4}q$	$\cos\frac{1}{4}q$
	−	1	+	$+\sin\frac{1}{2}q$	$-\cos\frac{1}{2}q$	$\sin\frac{1}{4}q$	$-\cos\frac{1}{4}q$

$1 - z$) and a (between $Mn_I(1)$ and $Mn_{II}(5)$) and the values of $\cos\varphi_5$ and $\sin\varphi_5$, defined below (4.13).

4.2 COMPARISON WITH EXPERIMENT. — Actually the phases accessible to the observation by neutron diffraction are not the phases ψ_j, but phases φ_j defined by (4.13) and related to ψ_j by (4.14)

$$\mathbf{S}_j = S_j(\mathbf{u}\cos(\mathbf{q}.\mathbf{r}_j + \varphi_j) + \mathbf{v}\sin(\mathbf{q}.\mathbf{r}_j + \varphi_j)) \quad (4.13)$$

$$\psi_j = \varphi_j + 2\pi\tau z_j . \quad (4.14)$$

Choosing for the cosine and sine functions of (4.13) the complex representation, the magnetic structure factor (4.15) splits into two parts, corresponding to satellite reflections at $\mathbf{h}^+ = \mathbf{H} + \boldsymbol{\tau}$ and $\mathbf{h}^- = \mathbf{H} - \boldsymbol{\tau}$ ($|\boldsymbol{\tau}| = \tau$) :

$$\mathbf{F}(\mathbf{h}) = \sum f_j \mathbf{S}_j \exp(2\pi i\mathbf{h}.\mathbf{r}_j) = \mathbf{F}(\mathbf{h}^+) + \mathbf{F}(\mathbf{h}^-)$$

with

$$\mathbf{F}(\mathbf{h}^\pm) = \tfrac{1}{2}(\mathbf{u} \pm i\mathbf{v})(1 - (-1)^H)\sum_j f_j S_j \times \times \exp(2\pi i\mathbf{H}.\mathbf{r}_j)\exp \mp i\varphi_j . \quad (4.15)$$

Here $\mathbf{H}$ is a vector (HKL) of the reciprocal lattice in a unit cell doubled along a. H is always odd. f_j is the magnetic form factor. From (4.14) one has

$$\left.\begin{aligned} &\varphi_j = \psi_j \quad \text{for} \quad j = 1, 2, 3, 4 ; \\ &\varphi_5 = \psi_{II} - 2\pi\tau z_5 \simeq \psi_{II} - \frac{1}{4}q_3 \\ &\varphi_6 = -\varphi_5 ; \ \varphi_7 = \frac{\pi}{2} + \varphi_5 ; \ \varphi_8 = \frac{\pi}{2} - \varphi_5 \end{aligned}\right\} . \quad (4.16)$$

It is then an easy matter to calculate the structure factors which are explicitly (with $x' = x/2 \sim 0.044$; $y = -0.150$; $z = 0.242$) :

$$\mathbf{F}(\mathbf{h}^\pm)_{Mn_I} = 2i(\mathbf{u} \pm i\mathbf{v})\{\sin(2\pi(Hx' + Ky) \mp \varphi_1) \pm \pm \sin(2\pi(Hx' - Ky) \mp \varphi_1)(-1)^{K+(H+1/2)}\} f_I S_I \quad (4.17)$$

$$\mathbf{F}(\mathbf{h}^\pm)_{Mn_{II}} = \mp 2i(\mathbf{u} \pm i\mathbf{v})\cos(2\pi Lz \mp \varphi_5) \times \times (-1)^K (1 \pm (-1)^{K+(H+1/2)}) f_{II} S_{II} .$$

Although most of the satellites are obscured by nuclear reflections, the intensity of $\{300\}^\pm$ is definitely much higher than that of $\{100\}^\pm$. The comparison of their intensities $I(\mathbf{h})$ evaluated according to

$$I(\mathbf{h}) = |F(\mathbf{h})|^2 - |\mathbf{F}.\mathbf{h}/|\mathbf{h}||^2 \quad (4.18)$$

already shows qualitatively that $\cos\varphi_5$ must be negative. Table III shows that only two solutions are possible, corresponding to (4.9*a*) and (4.9*b*) respectively, say

$$\cos\varphi_5 = -\cos\tfrac{1}{4}q \text{ with } \psi_{II} = \tfrac{1}{2}q_3 + \pi \quad (4.19a)$$

and

$$\cos\varphi_5 = -\sin\tfrac{1}{4}q \text{ with } \psi_{II} = \tfrac{1}{2}q_3 + \tfrac{1}{2}\pi . \quad (4.19b)$$

Experimentally $\cos(q - 2\psi_{II})$ is positive for RE = Tb, Ho, Er and negative for RE = Nd. Thus for RE = Tb, Ho, Er the solution (4.19*a*) corresponding to $J' > 0$ and $a < 0$ is favoured. It is represented in the figure 2. The solution (4.19*b*) would correspond to the same figure, interchanging moments 5 with 6, and also 7 with 8.

Thus $J < 0$ would be associated with the smaller distance Mn_{II}-Mn_{II} (2.75 Å) and the smaller angle Mn_{II}-O-Mn_{II} (95°) and $J' > 0$ with the larger distance (2.93 Å) and the larger angle (98°).

It is believed that negative direct exchange here competes with positive superexchange and that the

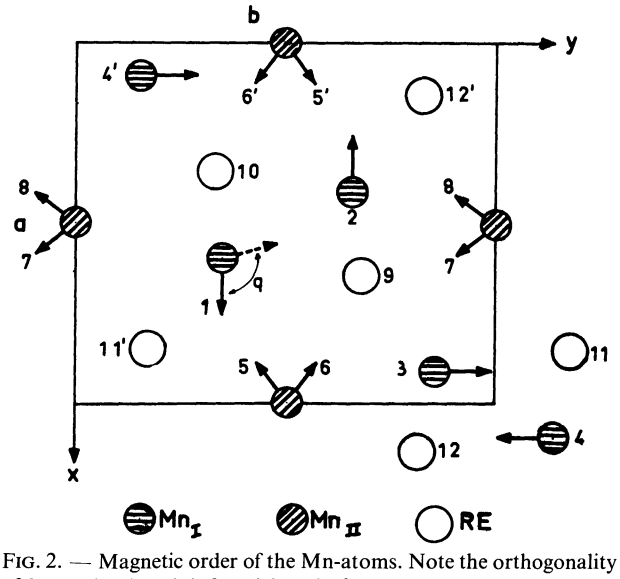

FIG. 2. — Magnetic order of the Mn-atoms. Note the orthogonality of Mn_I-spins 1 and 4, 2 and 3 and of Mn_{II}-spins 5 and 7, 6 and 8. A translation a changes the sign of spins, a translation c rotates every spin by q_3 indicated by the dashed arrow at spin 1.

absolute value of direct exchange decreases more rapidly with distance than super-exchange [6, 7, 8], as observed in the right angle exchange Cr^{3+}-X-Cr^{3+} (X = O, S, Se, Te). Note that Cr^{3+} is isoelectronic with Mn^{4+}. Thus $|J'| < |J|$.

Table IV shows the values of $q_3 = 2\pi\tau$, τ, ψ_{IB} and ψ_{IIB} according to Buisson's powder datae [2], and of $\psi_{II\,cal}$ calculated according to (4.9*a*) with $n = 1$, neglecting j_c. In all cases ψ_I is small; ψ_{IIB} is in acceptable agreement with $\psi_{II\,cal}$ only for RE = Tb, Ho, Er and is systematically smaller than $\psi_{II\,cal}$. Actually the turn angle between spin 5 at height z and spin 6 at height $\bar{z}$ is $2\psi_{II}$; the turn angle between spin 5 and spin 6^+ at height $1 - z$ is $q - 2\psi_{II}$. Thus the neglect of super-superexchange j_c is equivalent to saying that the moments of 5 and 6^+ are parallel. In fact the tabulation of $q - 2\psi_{IIB}$ shows that they are not!

TABLE IV

Angles and Propagation Vectors of Mn-*spins in* $REMn_2O_5$

RE	Nd	Tb	Ho	Er	Y
τ	.365	.306	.271	.247	.320
q^0	131.4°	110.2°	97.6°	88.9°	115.2°
ψ_{IB}	12°	18°	3°	10°	0°
ψ_{IIB}	187.9°	219.5°	219.4°	222.2°	193.8°
$\psi_{II\,cal}$	245.7°	235.1°	228.4°	224.5°	237.6°
$q - 2\psi_{IIB}$	115.6°	31.2°	18.8°	4.5°	87.6
ζ	− 1.2	− .56	− .32	− .08	− 1.10

τ is the propagation vector along Oz, expressed in fractions of the reciprocal length $c^* = \frac{1}{c}$; q^0 is the turn angle after a translation c. ψ_{IB} and ψ_{IIB} are the angles of the reference spins 1 and 5 with Ox according to Buisson. ζ is the ratio (4.20) j_c/J'.

It is seen that (4.9*a*) implies $\sin 2\psi_{II} > 0$ and $\cos 2\psi_{II} < 0$ while (4.9*b*) implies $\sin 2\psi_{II} < 0$ and $\cos 2\psi_{II} > 0$. None of these solutions is compatible with Buisson's datae [2] for which simultaneously $\sin 2\psi_{II} > 0$ and $\cos 2\psi_{II} > 0$ hold. The last line of table IV shows the ratio, calculated from (3.14*e*)

$$\zeta = j_c/J' = -\sin(q_3 - 2\psi_{IIB})/\sin q_3 \qquad (4.20)$$

which is not negligible. Thus we have to reexamine the stability conditions for non negligible super-superexchange j_c. Geometrically there is only one magnetic path corresponding to J' against four magnetic paths for j_c. As already stated, the exchange between two Mn^{4+}-cations turns from negative at small distances (J) to positive at large distances. Thus near to the crossover the ratio ζ (4-20) may become significant. Of course these are only plausibility arguments.

On the other hand the neutron diffraction powder data are not precise enough to make definite statements. Only a structure refinement of the Mn^{4+}-positions at low temperatures and magnetic measurements combined with neutron data on single crystals could shed more light on these questions.

4.3 REMARK ON THE RANGE OF q_3. — We finally study the equilibrium solution $\sin\psi_{II} = 0$ implying $\sin q_3 = 0$ with $\psi_{II} = \pi$; $q_3 = \pi$, i. e. for a propagation vector $\mathbf{k} = [\frac{1}{2}\,0\,\frac{1}{2}]$ in the case of negligible super-exchange. The condition

$$\frac{\delta^2 W}{\delta q^2} > 0$$

shows that here

$$J' < 0\,. \qquad (4.21)$$

It is also seen that the condition

$$J > 0 \qquad (4.22)$$

favours the equilibrium condition and the positivity of λ_{II} which becomes (neglecting b)

$$\lambda_{II} = J - J' - 2a\,. \qquad (4.23)$$

The results is at first sight surprising because the signs of J and J' are just opposite to those of the non commensurate case discussed above. In fact, one has precisely $\mathbf{k} = [\frac{1}{2}\,0\,\frac{1}{2}]$ in $BiMn_2O_5$ [9] where the structure refinement has shown that the z-parameter of Mn_{II} is $z = 0.27$ (while in $REMn_2O_5$ $z < 0.25$). Consequently again the larger distance (3.10 Å) is associated with a positive exchange (here J) and the smaller one (2.65 Å) with negative exchange (here J') as it should be.

5. **Non negligible super-superexchange.** — 5.1 STABILITY CONDITIONS. — The condition $\delta^2 W/\delta q^2 > 0$ leads to

$$J' \sin 2\psi_{II}/\sin q > 0 \qquad (5.1)$$

(by eliminating j_c). q being contained in the first Brillouin zone, $\sin q$ is supposed positive so that we have the important condition (5.2) which also holds for the isolated system

$$J' \sin 2\psi_{II} > 0\,. \qquad (5.2)$$

Thus

$$J' > 0;\quad \sin 2\psi_{II} > 0;\quad j_c < 0 \qquad (5.3a)$$

or

$$J' < 0;\quad \sin 2\psi_{II} < 0;\quad j_c > 0\,. \qquad (5.3b)$$

Buisson's data [2] for ψ_{II} favour the conditions (5.3*a*).

The equilibrium conditions (4.10) read now

$$-J\sin^2\psi + J'(\sin\psi.\sin(q-\psi) + \tfrac{1}{2}\cot g\,\psi.\sin q) > 0 \qquad (5.4)$$

and

$$-J\sin^2\psi + J'\sin(q-2\psi)\times\sin^2(q-\psi)/\sin 2\psi > 0\,. \qquad (5.5)$$

In both relations the coefficient of J' is positive ($\sin\psi$ and $\sin(q-\psi)$ are negative everywhere; $\cot g\,\psi$,

$\sin 2\psi$ and $\sin(q - 2\psi)$ are positive everywhere [2]) so that there is always compatibility with $J' > 0$ and $J < 0$. One also checks that for vanishing j_c (i. e. $\sin(q_3 - 2\psi_{II}) \to 0$) the relation (5.5) is conducive to $J < 0$.

Another way of checking the plausibility of the signs we have assigned to the various exchange integrals is : to write down the linear relations (3.14*a*, *b*, *c*, *d*, *e*) with the observed angles ψ_I, ψ_{II} and wave vector component q_3, to eliminate a, b and j_c and to compute $\lambda_I + \lambda_{II}$ which must be positive.

In the case of Nd we get successively from Buisson's data [2]

$$\begin{aligned} j_c &= -1{,}2\,J'; \\ a &= -0.05\,B_I - 0.1\,C_I + J - 3.3\,J' \\ b &= 0.2\,B_I + 0.45\,C_I + 0.2\,J - 0.7\,J' \\ \lambda_I + \lambda_{II} &= -1.26\,B_I - 0.35\,C_I - 3.08\,J + 13.73\,J'. \end{aligned} \tag{5.6}$$

In the case of Tb

$$\begin{aligned} j_c &= -0.55\,J'; \\ a &= -0.12\,B_I + 0.16\,C_I + 0.73\,J - 0.39\,J' \\ b &= 0.37\,B_I + 0.50\,C_I + 0.24\,J - 0.13\,J' \\ \lambda_I + \lambda_{II} &= -0.80\,B_I + 0.6\,C_I - 2.17\,J + 2.32\,J'. \end{aligned} \tag{5.7}$$

It is seen that the coefficient of strong negative exchange integrals is negative (B_I and J), the coefficient of positive exchange J' is positive. C_I is probably negligible with respect to B_I. If B_I ($= J_I$ (1.2)) is of the same order of magnitude as J, it is also seen that a is more negative than b. If J' was negative for Nd, $|J'|$ should be very small compared to $|J|$.

5.2 Relations between turn angles and exchange. — Figure 3 shows the relation between the angle $\psi = \psi_{II}$ and the wave vector component q_3 for various values of ζ (4.20) taken from the relation (3.14*e*) which can be written

$$\operatorname{tg} q_3 = \sin 2\psi/(\cos 2\psi + \zeta) \tag{5.8}$$

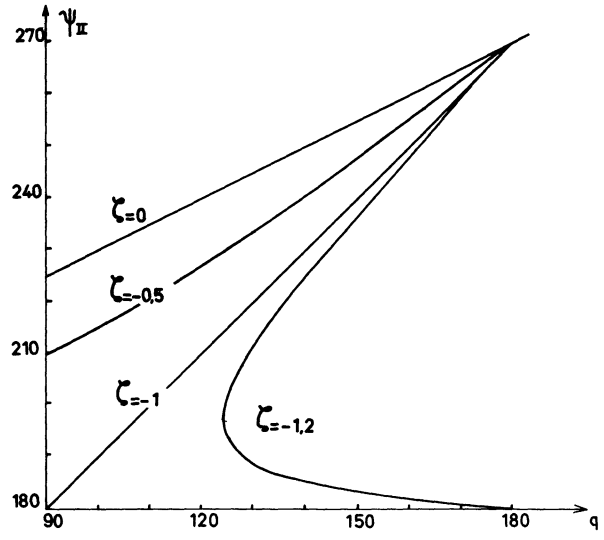

FIG. 3. — Relation between the propagation vector q and the angle ψ_{II} for various values of the super-superexchange parameter ζ.

or after inversion

$$\sin 2\psi = u \sin q_3 \tag{5.9}$$

with

$$u = \zeta \cos q_3 + \varepsilon(1 - \zeta^2 \sin^2 q_3)^{1/2}.$$

The last equation is double-valued with $\varepsilon = +1$ for Tb, Ho, Er, Y and $\varepsilon = -1$ for Nd. $\zeta = 0$ corresponds to $\psi = \frac{1}{2} q_z + \pi$; $\zeta = -1$ corresponds to $\psi = q_z + \pi/2$ (but also to $\psi = 0$ and q_3 arbitrary).

By appropriate eliminations between the relations (3.14*c*, *d*, *e*) one obtains relations in only one variate ψ (5.10), q_3 (5.11), $\cos(\psi - q_3)$ (5.12) versus the ratios of exchange integrals ζ, η and ρ. They are given here for completeness

$$\eta^2 \cos^2\psi = (\rho + \cos\psi)^2((1 - \zeta)^2 + 4\,\zeta \cos^2\psi) \tag{5.10}$$

$$(u + \eta)^2 \sin^2 q_3 = 2\,\rho^2(1 + \zeta - u \cos q_3) \tag{5.11}$$

$$y^2(1 - \zeta)^2 = \left(\rho + \frac{\eta y}{1 + \zeta}\right)^2 ((1 + \zeta)^2 - 4\,\zeta y^2). \tag{5.12}$$

Here we have introduced the following abbreviations

$$\left.\begin{aligned} &\eta = j_c/J; \quad \rho = a'/J \\ &y = \cos(\psi - q_3) \\ &a' = a\cos\psi_I + b\sin\psi_I \simeq a \end{aligned}\right\}. \tag{5.13}$$

5.3 Discussion. — The ratio of exchange integrals η is small; ρ is near to unity and positive. For negligible superexchange (ζ and η negligible) we find the result

$$-\cos\psi = +\rho = \cos\frac{q}{2} \tag{5.14}$$

which is approximately satisfied for the Er-compound with $\rho \simeq 0.7$.

For important super-superexchange with ζ in the vicinity of -1, ψ is in the vicinity of π. Setting

$$\psi = \pi + \kappa \tag{5.15}$$

where κ is a small positive quantity, one finds from (3.14*d*, *e*)

$$\kappa = \frac{\eta}{2(\rho - 1)\sqrt{-\zeta}}. \tag{5.16}$$

In the cases of Nd and Y, κ is a small positive angle (7.9° and 13.8°). Thus one may conclude that here $\rho = a'/J > 1$ for $\eta > 0$ and $\rho < 1$ for $\eta < 0$. This is also evident from the eq. (3.14*d*) which may be written

$$\rho = -\cos\psi - \eta \sin q/(2\sin\psi). \tag{5.17}$$

With the observed values of ψ and q, one has the following relations

$$\begin{aligned} \rho &= 1 \quad + 2.53\,\eta \text{ for Nd} . \\ \rho &= 0.97 + 1.9\ \eta \text{ for Y} . \\ \rho &= 0.77 + 0.74\,\eta \text{ for Tb-compound} . \end{aligned} \tag{5.18}$$

5.4 NUMERICAL EXAMPLE. — In arbitrary units we have put $J = B_I = a = -1$, $J' = \frac{1}{2}$ and $j_c = -\frac{1}{4}$ (neglecting b and C_I), say $\rho = +1$; $\eta = \frac{1}{4}$ and $\zeta = -\frac{1}{2}$. We obtain $\psi_I = 0$; $\psi_{II} = 217°$ and $q_3 = 103°$. These values have been used for drawing the schematic magnetic structure of figure 2.

To summarize, there is negative exchange between the manganese atoms $Mn_I(1)$ and $Mn_I(2)$ (B_I), between $Mn_{II}(5)$ in $\frac{1}{2}$, 0, z and $Mn_{II}(6)$ in $\frac{1}{2}$, 0, $\bar{z}$ (J) and between $Mn_I(1)$ and $Mn_{II}(5)$ (a), B_I, J and a being of comparable strength. There is a positive interaction J' between $Mn_{II}(5)$ and $Mn_{II}(6^+)$ in $\frac{1}{2}$, 0, $1-z$ ($z \simeq 0.24$). A non negligible super-superexchange in the Mn_{II} chains along c must be assumed to explain Buisson's [2] powder data.

The physical interpretation of the orthogonality relations ($\mathbf{S}_i.\mathbf{S}_j = S_i S_j \cos\theta_{ij}$ with $\theta_{ij} = \pm \pi/2$; cf. (2.11) and (3.9)) is the absence of any coupling, the corresponding matrix elements η_{ij} being zero.

5.5 REMARK. — One may question if other weak interactions are not more effective than the super-superexchange j_c through a distance of ~ 5.7 Å. We have indeed investigated the interaction via the magnetic path $Mn_I(1)$-O_{II}-$Mn_{II}(6^+)$ (or also $Mn_I(1)$-O_{III}-O_{II}-$Mn_{II}(6^+)$) where the point 6^+ is in $\frac{1}{2}$, 0, $1-z$. Here the distances $Mn_I(1)$-O_{II} and O_{II}-$Mn_{II}(6^+)$ are 3.53 Å and 1.95 Å respectively in $NdMn_2O_5$; these three atoms are aligned with a Mn_I-Mn_{II} distance of 5.48 Å, smaller than c. The effect is the addition to $\lambda_I + \lambda_{II}$ of a term of the form $p \cos(q - \psi_{II})$. Neglecting j_c, (3.14e) would be replaced by

$$p \sin(q - \psi_{II}) + J' \sin(q - 2\psi_{II}) = 0 . \tag{5.19}$$

The local stability condition (eliminating p) is seen to be

$$J' \sin\psi_{II} / \sin(q - \psi_{II}) > 0 . \tag{5.20}$$

With Buisson's datae [2] $\sin\psi_{II}$ and $\sin(q - \psi_{II})$ are both negative so that the condition $J' > 0$ is not modified.

We have also investigated the magnetic path $Mn_I(1)$-O-$Mn_{II}(8^+)$ where point 8^+ is in 0, $-\frac{1}{2}$, $1-z$. This interaction gives rise to a term of the same form as above.

6. **Negligible anisotropy in the rare earth system.** — PHASE RELATIONS. — We consider the rare earth system as being weakly coupled to the Mn-system and completely neglect RE-RE interactions. The form of the interaction matrix is now, the lower index III referring to the RE system

$$(\eta) = \begin{pmatrix} \eta_{I\text{-}I} & \eta_{I\text{-}II} & \eta_{I\text{-}III} \\ \eta_{II\text{-}I} & \eta_{II\text{-}II} & \eta_{II\text{-}III} \\ \eta_{III\text{-}I} & \eta_{III\text{-}II} & \eta_{III\text{-}III} \end{pmatrix} . \tag{6.1}$$

Taking only into account RE-Mn interactions at distances smaller than 3.4 Å, the interaction matrices $\eta_{III\text{-}I}$ and $\eta_{III\text{-}II}$ are as follows for the propagation vector $[\frac{1}{2}\ 0\ \tau]$:

$$\eta_{III\text{-}I} = \begin{array}{c} \\ 9 \\ 10 \\ 11 \\ 12 \end{array} \begin{array}{c} \begin{array}{cccc} 1 & 2 & 3 & 4 \end{array} \\ \begin{pmatrix} 0 & \gamma' & 0 & 0 \\ \gamma' & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma' \\ 0 & 0 & \gamma' & 0 \end{pmatrix} \end{array} ;$$

$$\eta_{III\text{-}II} = \begin{array}{c} \begin{array}{cccc} 5 & 6 & 7 & 8 \end{array} \\ \begin{pmatrix} \alpha & \alpha' & \beta & \beta' \\ -\alpha & -\alpha' & \beta & \beta' \\ \beta & \beta' & \alpha & \alpha' \\ \beta & \beta' & -\alpha & -\alpha' \end{pmatrix} \end{array} . \tag{6.2}$$

Here we have used the abbreviations

$$\left.\begin{aligned} \alpha = J_{III\text{-}II}(9.5) ; \quad \beta = J_{III\text{-}II}(9.7) ; \\ \gamma = J_{III\text{-}I}(9.2) ; \quad \alpha' = \alpha\sigma ; \quad \beta' = \beta\sigma ; \\ \gamma' = \gamma(1+\sigma) ; \quad \sigma = \exp -iq_3 \end{aligned}\right\} . \tag{6.3}$$

The distances are

$$\begin{aligned} d(9.5) &= 3.35 \text{ Å} ; \quad d(9.7) = 3.32 \text{ Å} ; \\ d(9.2) &= 3.3 \text{ Å} \quad \text{for } HoMn_2O_5 . \end{aligned}$$

The matrices $\eta_{I\text{-}III}$ and $\eta_{II\text{-}III}$ are the conjugate transposes of $\eta_{III\text{-}I}$ and $\eta_{III\text{-}II}$ respectively. In (6.3) the roman subscripts refer to the systems and the numbers in the parenthesis to the pairs of reference atoms.

We shall be concerned here with two extreme cases :

a) The one ion anisotropy of the rare earth is negligible.

b) The one ion anisotropy of the rare earth is very high (part 7).

Isotropic case. — In the isotropic case $\eta_{III\text{-}III}$ would have a form analogous to $\eta_{I\text{-}I}$ (2.3) ; for the time being we shall neglect $\eta_{III\text{-}III}$.

The last four equations of the matrix system (1.11), belonging to the root λ_{III}, when brought to a form analogous to (2.6), will obey the symbolic relation (6.4) [completing (2.7) and (3.17)] :

$$(9') = (10')^* = (11')^* = (12') . \tag{6.4}$$

The phase relations are found to be

$$Q_9 = Q_{III}; \qquad Q_{10} = -\sigma Q_{III}^*;$$
$$Q_{11} = -i\sigma Q_{III}^*; \quad Q_{12} = iQ_{III} \tag{6.5a}$$

or explicitely

$$\psi_9 = \psi_{III}; \qquad \psi_{10} = -\psi_{III} + \pi + q_3;$$
$$\psi_{11} = -\psi_{III} + \frac{\pi}{2} + q_3; \quad \psi_{12} = \psi_{III} + \frac{\pi}{2}. \tag{6.5b}$$

One recognizes the orthogonality relations

$$Q_{12} = iQ_9; \qquad Q_{11} = iQ_{10} \tag{6.6}$$

analogous to the relations (2.11) of the Mn_I-system.

Thus in the isotropic case the eq. (3.12) are to be completed by

$$\begin{aligned} \boldsymbol{\sigma}_9 &= \mathbf{u}\cos\psi_{III} + \mathbf{v}\sin\psi_{III};\\ \boldsymbol{\sigma}_{10} &= -\mathbf{u}\cos(\psi_{III} - q_3) + \mathbf{v}\sin(\psi_{III} - q_3)\\ \boldsymbol{\sigma}_{11} &= \mathbf{u}\sin(\psi_{III} - q_3) + \mathbf{v}\cos(\psi_{III} - q_3);\\ \boldsymbol{\sigma}_{12} &= \mathbf{u}\sin\psi_{III} - \mathbf{v}\cos\psi_{III}. \end{aligned} \tag{6.7}$$

Remark. — The reader may check that for the points 10^- at $\bar{x}\,\bar{y}\,\frac{1}{2}$ and 11^- at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2}$

$$Q_{10^-} = -Q_{III}^*; \quad Q_{11^-} = -iQ_{III}^* \tag{6.8}$$

and

$$\begin{aligned} \boldsymbol{\sigma}_{10^-} &= -\mathbf{u}\sin\psi_{III} + \mathbf{v}\cos\psi_{III};\\ \boldsymbol{\sigma}_{11^-} &= \mathbf{u}\sin\psi_{III} + \mathbf{v}\cos\psi_{III}. \end{aligned} \tag{6.9}$$

The points 10^- and 11^- are at the distance $-c$ from the corresponding reference points 10 and 11. For the spins at points 9, 10^-, 11^-, 12 one has exactly the same expressions as for those in points 1, 2, 3, 4 with ψ_{III} replacing ψ_I (cf. (3.12)).

The phases φ_j ($j = 9, 10, 11, 12$) used in the structure factor calculations and related to the ψ_j by (4.14) with $z_j = \frac{1}{2}$, can be expressed in terms of φ_{III}

$$\begin{aligned} \varphi_{III} &= \varphi_9 = \psi_{III} - \pi\tau; \quad \varphi_{10} = \pi - \varphi_{III};\\ \varphi_{11} &= \frac{\pi}{2} - \varphi_{III}; \qquad \varphi_{12} = \varphi_{III} - \frac{\pi}{2}. \end{aligned} \tag{6.10}$$

Thus the contributions of RE and of Mn_I to the structure factor will have the same form (cf. (3.1*b*), and (4.17)).

The eq. (9′) of the matrix-system will split into a real part giving λ_{III} (6.11) and an imaginary part which represents the equilibrium condition of the magnetic energy for ψ_{III} (6.13) :

$$\lambda_{III} = \lambda_{III\text{-}I} + \lambda_{III\text{-}II}; \tag{6.11}$$

with

$$\left.\begin{aligned} \lambda_{III\text{-}I} &= -\gamma[\cos(\psi_{III} + \psi_I) + \\ &\quad + \cos(\psi_{III} + \psi_I - q_3)],\\ \lambda_{III\text{-}II} &= \alpha[\cos(\psi_{III} - \psi_{II}) + \\ &\quad + \cos(\psi_{III} + \psi_{II} - q_3)]\\ &\quad + \beta[\sin(\psi_{III} - \psi_{II})\\ &\quad + \sin(\psi_{III} + \psi_{II} - q_3)] \end{aligned}\right\} \tag{6.12}$$

$$-\frac{\partial\lambda_{III}}{\partial\psi_{III}} = 0. \tag{6.13}$$

Of course the values of λ_I (3.14*a*) and λ_{II} (3.14*b*) as well as the equilibrium conditions (3.14*c*, *d*, *e*) will be modified too. One obtains with obvious notations

$$\left.\begin{aligned} \lambda_I &= \lambda_{I\text{-}I} + \lambda_{I\text{-}II} + \lambda_{I\text{-}III}\\ \lambda_{II} &= \lambda_{II\text{-}I} + \lambda_{II\text{-}II} + \lambda_{II\text{-}III} \end{aligned}\right\} \tag{6.14}$$

with

$$\left.\begin{aligned} \lambda_{I\text{-}II} &= \lambda_{II\text{-}I} = 2(a\cos\psi_I + b\sin\psi_I)\cos\psi_{II}\\ \lambda_{III\text{-}I} &= \lambda_{I\text{-}III}; \quad \lambda_{III\text{-}II} = \lambda_{II\text{-}III} \end{aligned}\right\} \tag{6.15}$$

and, for short,

$$\left.\begin{aligned} \text{2 L.H.S. (3.14}c\text{)} - \frac{\partial\lambda_{III}}{\partial\psi_I} &= 0 \quad a)\\ \text{2 L.H.S. (3.14}d\text{)} - \frac{\partial\lambda_{III}}{\partial\psi_{II}} &= 0 \quad b)\\ \text{L.H.S. (3.14}e\text{)} - \frac{\partial\lambda_{III}}{\partial q_3} &= 0 \quad c) \end{aligned}\right\} \tag{6.16}$$

as the reader may check with the help of (6.12) and the eq. (1′) and (5′) of the matrix-system.

At first sight it seems to be a formidable task to estimate nine exchange integrals (neglecting C_I), say B_I, J, J', j_c, a and b for the Mn system and α, β, γ for the Mn-RE interactions. Actually we have available three equilibrium conditions (3.14*c*, *d*, *e*) corresponding to the experimental datae of ψ_I, ψ_{II} and q_3 of the Mn-system before RE orders, *plus* four equilibrium conditions ((6.13) and (6.16*a*, *b*, *c*)) corresponding to the variates Ψ_I, Ψ_{II}, Ψ_{III} and q_3 once the RE ordering has set in. Thus seven exchange integrals can be expressed as linear functions of the two ones left over. Furthermore the positivity of λ_I, λ_{II}, λ_{III} will restrict the parameter space. We postpone the discussion after having dealt with the anisotropic case.

7. **High one ion anisotropy in the rare earth system.** — Here we shall be concerned with the extreme case of RE-moments still coupled to the Mn-system by isotropic forces, but constrained to fixed directions by high anisotropy forces.

When one ion and exchange anisotropy are present the hamiltonian (1.1) and the relation (1.2) are to be replaced by

$$H = -2\sum \mathbf{S}_i.\vec{\mathbf{J}}_{ij}.\mathbf{S}_j \tag{7.1}$$

and

$$\lambda_i \mathbf{S}_i = \sum_j \vec{\vec{\mathbf{J}}}_{ij} . \mathbf{S}_j \qquad (7.2)$$

where $\vec{\vec{\mathbf{J}}}_{ij}$ is a dyadic. In the present case where only isotropic exchange and one ion anisotropy for RE will be considered, we put

$$\vec{\vec{\mathbf{J}}}_{ij} = J_{ij} \vec{\vec{\mathbf{I}}} \qquad \text{for} \quad i \neq j$$

$$\vec{\vec{\mathbf{J}}}_{jj} = a_{1j}(\mathbf{x}, \mathbf{x} - \mathbf{y}, \mathbf{y}) + a_{2j}(\mathbf{x}, \mathbf{y} + \mathbf{y}, \mathbf{x}) \qquad (7.3)$$

$$\text{for} \quad j = 9, 10, 11, 12 .$$

Here $\vec{\vec{\mathbf{I}}}$ is the dyadic identity and $\vec{\vec{\mathbf{J}}}_{jj}$ represents the one ion anisotropy tensor which is traceless ($\vec{\vec{\mathbf{J}}}_{jj}$ scalar = 0) and symmetric in the x, y plane. One shows easily (see appendix A) that

$$a_{1j} = K \cos 2\beta_j ; \quad a_{2j} = K \sin 2\beta_j \qquad (7.4)$$

with

$$\begin{aligned} \beta_j &= \beta_9 \qquad \text{for} \quad j = 9, 10 ; \\ \beta_j &= -\beta_9 \quad \text{for} \quad j = 11, 12 . \end{aligned} \qquad (7.5)$$

Here β_j is the easy direction defined by the unit vector $\mathbf{n}_j$

$$\mathbf{n}_j = \mathbf{x} \cos \beta_j + \mathbf{y} \sin \beta_j . \qquad (7.6)$$

For the anisotropy energy $W_{an}(\mathbf{S}_i)$ of the spin $\mathbf{S}_i$ one gets the classical result

$$W_{an}(\mathbf{S}_i) = -\mathbf{S}_i . \mathbf{J}_{ii} . \mathbf{S}_i = -KS_i^2 . \qquad (7.7)$$

In the case of a very high anisotropy on the site j, the spin $\mathbf{S}_j$ of phase ψ_j in the direction $\mathbf{n}_j$ will be defined by

$$\mathbf{S}_j = S_{j0}(\mathbf{x} \cos \psi_j + \mathbf{y} \sin \psi_j) . \mathbf{n}_j, \mathbf{n}_j . \qquad (7.8)$$

Here $\mathbf{n}_j, \mathbf{n}_j$ is a unilinear dyadic formed with $\mathbf{n}_j$ (7.6).

Absorbing again the (maximum) spin length S_{j0} in the exchange constants we define

$$\boldsymbol{\sigma}_j = \frac{\mathbf{S}_j}{S_{j0}} = \mathbf{Q}_j + \mathbf{Q}_j^* \qquad (7.9)$$

with

$$\mathbf{Q}_j = Q_j \frac{\mathbf{x} + i\mathbf{y}}{2} \cdot \mathbf{n}_j, \mathbf{n}_j \quad (j = 9, \ldots, 12) . \qquad (7.10)$$

Note that $\boldsymbol{\sigma}$ (7.9) is no longer a unit vector, but its length depends on a phase. For instance

$$\begin{aligned} \boldsymbol{\sigma}_9 &= \cos(\psi_9 - \beta_9)\, \mathbf{n}_9 ; \\ \mathbf{Q}_9 &= \tfrac{1}{2} \exp -i(\psi_9 - \beta_9)\, \mathbf{n}_9 . \end{aligned} \qquad (7.11)$$

Note also that $|Q_j|^2$ is phase independent, as well in the helical as in the oscillating case.

In the present case $\eta_{III\text{-}III}$ is the diagonal matrix formed with the $\vec{\vec{\mathbf{J}}}_{jj}$ (7.3). Explicitely the ninth equation of the matrix system (1.11) will be

$$(\vec{\vec{\mathbf{J}}}_9 - \lambda_{III} \vec{\vec{\mathbf{I}}}) . \mathbf{Q}_9 + \sum_{j=1}^{8} \eta_{9j} \mathbf{Q}_j = 0 . \qquad (7.12)$$

Projecting this equation on $\mathbf{n}_9$ one finds

$$\left[(K - \lambda_{III}) Q_9 + \sum_{j=1}^{8} \eta_{9j} Q_j \right] \frac{\mathbf{x} + i\mathbf{y}}{2} \cdot \mathbf{n}_9 = 0 . \qquad (7.13)$$

In other words, factorizing a common factor $\mathbf{n}_9 . (\mathbf{x} + i\mathbf{y})$ one finds the *same phase factors Q_j and phase relations as in the isotropic* case. Thus λ_{III} will still be given by (6.12), but augmented by K and the condition (6.13) on ψ_{III} will be the same. In the same way the fifth equation of the matrix system will be (cf. (3.13))

$$-\lambda_{II} \mathbf{Q}_5 + \sum_{j=1}^{12} \eta_{5j} \mathbf{Q}_j = 0 . \qquad (7.14)$$

The multiplication by $\mathbf{Q}_5^*$ will give rise to

$$-\lambda_{II} + \left(\sum_{Mn} \eta_{5j} Q_j + \tfrac{1}{2} \sum_{RE} \eta_{5j} Q_j \right) Q_5^* = 0 . \qquad (7.15)$$

The phase relations are still seen to be conserved. The oscillating spin system will be given by $\boldsymbol{\sigma}_{j\,\text{isotrope}} . (\mathbf{n}_j, \mathbf{n}_j)$, say by

$$\begin{aligned} \boldsymbol{\sigma}_9 &= \cos(\psi_{III} - \beta_0)\, \mathbf{n}(\beta_0) ; \\ \boldsymbol{\sigma}_{10} &= -\cos(\psi_{III} + \beta_0 - q_3)\, \mathbf{n}(\beta_0) ; \\ \boldsymbol{\sigma}_{11} &= \sin(\psi_{III} - \beta_0 - q_3)\, \mathbf{n}(-\beta_0) ; \\ \boldsymbol{\sigma}_{12} &= -\sin(\psi_{III} + \beta_0)\, \mathbf{n}(-\beta_0) . \end{aligned} \qquad (7.16)$$

The oscillating spin order is obtained by projecting the helical spin order onto the anisotropy directions.

The only new feature which comes in is the occurrence of the factor $\frac{1}{2}$ before the summation on the Mn-RE interactions in (7.15). The consequence is that in the anisotropic case one shall have

$$\begin{aligned} \lambda_{I\text{-}an} &= (\lambda_{I\text{-}I} + \lambda_{I\text{-}II} + \tfrac{1}{2} \lambda_{I\text{-}III})_{is} \\ \lambda_{II\text{-}an} &= (\lambda_{II\text{-}I} + \lambda_{II\text{-}II} + \tfrac{1}{2} \lambda_{II\text{-}III})_{is} \\ \lambda_{III\text{-}an} &= \lambda_{III\text{-}is} + K . \end{aligned} \qquad (7.17)$$

Also the equilibrium conditions will hold with the only difference that in (6.16) λ_{III} is to be replaced by $\frac{1}{2} \lambda_{III}$. This also holds for the RE-contribution to the magnetic energy. One has to recall indeed that the spins $\boldsymbol{\sigma}_j$ (RE) (see (7.9)) are not unitary and that

$$\overline{(\boldsymbol{\sigma}_j(RE))^2} = \overline{\cos^2(\psi_j - \beta_j)} = \tfrac{1}{2} . \qquad (7.18)$$

From

$$\lambda_{III\,an}\, \boldsymbol{\sigma}_i(RE) = \vec{\vec{\mathbf{J}}}_{ii} . \boldsymbol{\sigma}_i(RE) + \sum_j \mathbf{J}_{ij} . \boldsymbol{\sigma}_j(Mn) \qquad (7.19)$$

one has for the magnetic exchange energy between Mn and RE

$$-2\sum_{ij}\boldsymbol{\sigma}_i(\mathrm{RE}).J_{ij}\,\boldsymbol{\sigma}_j(\mathrm{Mn}) = \\ = -2\sum_i(\lambda_{\mathrm{III\,an}}-K)\cos^2(\psi_i-\beta_i)\,. \quad (7.20)$$

Thus the magnetic energy in the anisotropic case is

$$W = -2(\lambda_{\mathrm{I}}+\lambda_{\mathrm{II}}+\tfrac{1}{2}\lambda_{\mathrm{III}})_{\mathrm{an}} \\ = -2(\lambda_{\mathrm{I\text{-}I}}+\lambda_{\mathrm{II\text{-}II}}+2\lambda_{\mathrm{I\text{-}II}}+\lambda_{\mathrm{I\text{-}III}}+\lambda_{\mathrm{II\text{-}III}}+\tfrac{1}{2}K)\,. \quad (7.21)$$

In the isotropic case one has

$$W = -2[\lambda_{\mathrm{I\text{-}I}}+\lambda_{\mathrm{II\text{-}II}}+ \\ +2(\lambda_{\mathrm{I\text{-}II}}+\lambda_{\mathrm{I\text{-}III}}+\lambda_{\mathrm{II\text{-}III}})]_{\mathrm{is}}\,. \quad (7.22)$$

7.1 Remark on intensities. — The magnetic structure factor may be brought to the following form in the sinusoidal case

$$F(\mathbf{h}^{\pm}) = 2\,i(\mathbf{u}\pm i\mathbf{v}).(-1)^L(1-(1)^H).\{\cdots\}\,S_{\mathrm{III}}\,f_{\mathrm{III}}$$

with

$$\{\cdots\}=\mathbf{n},\mathbf{n}\sin[2\pi(Hx'+Ky)\mp\varphi_9]\pm(-1)^{K+(H+1)/2}\times \\ \times\,\mathbf{n}',\mathbf{n}'\sin[2\pi(Hx-Ky)\mp\varphi_9]\,. \quad (7.23)$$

Here $\mathbf{n}$ is the unit vector (7.6) with $\beta_j=\beta_9$ and $\mathbf{n}'$ with $\beta_j=-\beta_9$. The expression above transforms to the helical case (compare with (4.17)) when replacing $\mathbf{n}$, $\mathbf{n}$ and $\mathbf{n}'$, $\mathbf{n}'$ by the identity operator.

7.2 Discussion. — Buisson [10] finds a better intensity agreement with a helical than with a sinusoidal RE-ordering for $NdMn_2O_5$. Using his datae reproduced in tables IV and V, we shall neglect in a first approximation the small parameters α, β, γ of the Nd-Mn coupling and solve the four eq. (3.14*c*, *d*) and (6.16*a*, *b*) for the exchange parameters J, J', a and b in terms of $B_{\mathrm{I}}=J_{\mathrm{I}}$ (1.2). The solution (neglecting C_{I}) is

$$J=5.81\,B_{\mathrm{I}};\quad a=3.72\,B_{\mathrm{I}};\quad b=B_{\mathrm{I}};\quad J'=0.58\,B_{\mathrm{I}}.$$

Note that these equations do not depend on super-superexchange. This approach to the problem gives at least a feeling for the magnitude of the exchange integrals which follows here the sequence

$$|J|>|a|>|b|>|J'|$$

with $|J'|$ about ten times smaller than $|J|$. When the values above are inserted into eq. (4.3) one finds $\mathrm{tg}\,2\psi_{\mathrm{I}}=0.4$ which corresponds to $\psi_{\mathrm{I}}=10.9^{\circ}$ and provides a check for the internal consistency of the procedure.

We have also set up the system of seven eq. ((3.14*c*, *d*, *e*), (6.13) and (6.16*a*, *b*, *c*)) in order to express the seven exchange parameters B_{I}, J, J', j_c, α, β, γ as linear functions of a and b with the result

$$J = 1.43\,a+0.34\,b;\quad J'=0.13\,a+0.04\,b;$$
$$j_c=-1.2\,J';\quad \beta=0.094\,a+0.136\,b;$$
$$\gamma=-0.330\,a+0.743\,b;\quad \alpha=-0.32\,\gamma;$$
$$B_{\mathrm{I}}=-1.01\,a+4.77\,b\,.$$

Note that here again J' is small with respect to J and negative. We find numerically

$$\lambda_{\mathrm{III}}=-0.065\,\gamma+1.74\,\beta$$

and may conjecture from the strength of the coefficients that the coupling with the Mn_{I}-system (γ) is much weaker than with the Mn_{II}-system. Writing $\gamma=0$, one finds $\alpha=0$, $a/b=2.19$ and the following set

$$J=1.58\,a;\quad J'=0.15\,a;\quad j_c=-0.18\,a;$$
$$B_{\mathrm{I}}=1.17\,a;\quad B=-0.03\,a;\quad J'/J=0.095\,.$$

Thus the Mn_{II}-Nd interaction is about 2 % of the strongest Mn_{II}-Mn_{II} interaction J, but amounts to about 20 % of the weak Mn_{II}-Mn_{II} interaction J'. The sequence is $|J|>|B_{\mathrm{I}}|>|a|>|b|>|J'|$.

The same procedure applied to the sinusoidal ordering of Tb and Er, using the datae of Tables IV and V shows again that J' is small and negative. Thus in the results obtained so far, there is at least qualitatively a common feature, the smallness of J' when compared to J. $|J'|<|J|$ is of course expected from our qualitative discussion of competing exchange interactions versus distance. Actually a non zero J' is needed to propagate the three dimensional order. The smallness of J' may explain the very low ordering temperature of $DyMn_2O_5$ [17] ($T_{\mathrm{N}}=8$ K).

Other qualitative statements are that the RE-Mn coupling parameter β is found to be positive for Nd and negative for Tb and Er (α is positive for Tb and Er).

One must remind however that in powder diagrams many satellites cannot be resolved and/or are obscured by nuclear peaks. Buisson's data [2, 10] are not precise enough for making quantitative statements. In fact the negativity of J' is not compatible with $J'\sin 2\psi_{\mathrm{II}}>0$ and $\sin 2\psi_{\mathrm{II}}>0$; also

Table V

Rare Earth Ordering (after Buisson [10])

	ψ_{I}	ψ_{II}	ψ_{III}	β_9	q
$Nd_{\mathrm{hél}}$	10°	223.7°	344°	—	146.9°
Tb_{sin}	18°	187.5°	168.1°	− 17°	110.2°
Er_{sin}	30°	196.8°	181.6°	− 5°	88.9°

$\delta^2 W/\delta\psi_I^2 > 0$ is not obeyed for RE = Nd, Er; $\delta^2 W/\delta q^2 > 0$ is not obeyed for RE = Nd, Er with the data [10].

The drawing of figure 4 compares the turn angles of the Mn_{II} spin system before [2] and after [10] Nd ordering according to Buisson (cf. Tables IV and V). Although the variation of q can be measured with confidence from a powder diagram, one may have doubts on the variation of ψ_{II}. Indeed if only

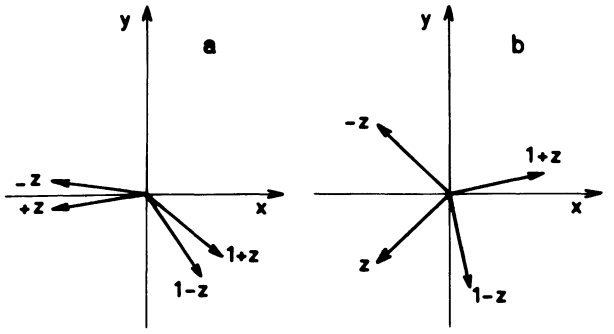

FIG. 4. — Order of Mn^{4+} spins in $NdMn_2O_5$: *a*) before Nd ordering; *b*) after Nd ordering. The angles with the x-axis are $-\psi_{II}$, $+\psi_{II}$, $q-\psi_{II}$, $q+\psi_{II}$ for the points at heights $-z$, $+z$, $1-z$, $1+z$ respectively.

the Mn_{II} system is markedly affected by the Nd-ordering, one finds neglecting γ

$$\lambda_{III} = 2\cos(\tfrac{1}{2}q_3 - \psi_{II})\,[\alpha\cos(\psi_{III} - \tfrac{1}{2}q_3) + \beta\sin(\psi_{III} - \tfrac{1}{2}q_3)] \quad (7.24)$$

and from (6.13)

$$\frac{\delta\lambda_{III}}{\delta q_3} = -\frac{1}{2}\frac{\delta\lambda_{III}}{\delta\psi_{II}}. \quad (7.25)$$

Thus if q_3 increases in the ordering process from 131.4° to 146.9° by $\delta q = 15.5°$, ψ_{II} should decrease, for $\delta\psi_{II} = -\frac{1}{2}\delta q = -8°$ which is contrary to Buisson's data.

We hope that more reliable datae will be made available by single crystal studies.

For completeness we show in figure 5 a schematic drawing of a helical order of RE spins with $\psi_{III} = 0$ (dashed arrows) and of a sinusoidal order given by the projection of the helical spins onto the anisotropy directions **n** for spins 9 and 10, **n**′ for spins 11 and 12 ($\beta_9 = 30°$).

7.3 REMARK ON ANISOTROPY. — The oscillating spin behaviour indicates that in the low symmetry site of the mirror m in the Kramers ion Er is in a doublet state far from excited states; for the non Kramers ion Tb we may expect a decomposition into

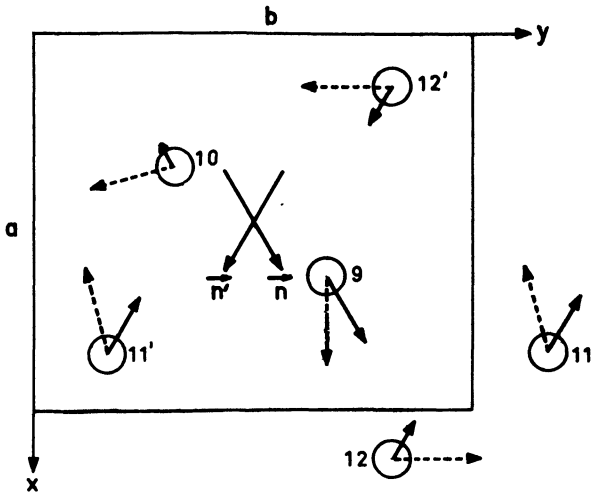

FIG. 5. — Schematic order of RE-spins. Helical order : dashed arrows. The anisotropy directions **n** for spins 9 and 10, **n** for spins 11 ans 12 are indicated at the centre of the figure.

singlet states, the ground state being formed by a pseudo-doublet of two singlet states of small separation, far away from excited states. In these cases a very high anisotropy of the g tensor is associated with Kramers ions (Er) while the non Kramers ions (Tb) show an Ising-like behaviour [11, 12]. For Nd we may suppose an inverted behaviour of the level system with respect to Er (Nd has three f electrons, Er has three f holes) so that many excited crystal field states mix in Nd to form a ground state of small magnetic anisotropy in the x-y plane.

For non Kramers ions the sinusoidal structure is perfectly stable until $T = 0$ in principle, as no entropy is associated with singlet ground states. For Kramers ions a *squaring up* should be expected at sufficiently low temperatures with a change of the intensities of the existing satellites and with the appearance of new, higher order satellites. However at very low temperatures, RE-RE interactions may become significant and give rise to new features.

8. **Connection with group theory.** — (REPRESENTATION ANALYSIS). — In earlier writings [13, 14] we have defined $\mathbf{S}_k$ *components of spins* by

$$\mathbf{S}(\mathbf{r}_j) = \mathbf{S}_k + \mathbf{S}_k^* = \mathbf{S}_k + \mathbf{S}_{-k} \quad (8.1)$$

with

$$\mathbf{S}_k(\mathbf{r}_j) = \tfrac{1}{2}(\mathbf{u} - i\mathbf{v})\,S\exp i\psi_j \quad (8.2)$$

and

$$\psi_j = 2\pi\mathbf{k}.\mathbf{r}_j + \varphi_j. \quad (8.3)$$

Here φ_j is constant on a given Bravais-lattice j. The $\mathbf{S}_k$-components transform like Bloch-waves in a lattice translation $\Delta\mathbf{R}$. Indeed

$$\mathbf{S}_k(\mathbf{r}_j + \Delta\mathbf{R}) = \exp(2\pi i\mathbf{k}.\Delta\mathbf{R})\,\mathbf{S}_k(\mathbf{r}_j). \quad (8.4)$$

By comparing (8.2) with the definition of $\mathbf{Q}_k$ (1.14) it is seen that

$$\mathbf{S}_k = \mathbf{Q}_k^* ; \qquad \mathbf{q} = 2\pi\mathbf{k} . \tag{8.5}$$

This simple relation (8.5) connects the (microscopic) matrix method [1] to the (macroscopic) group theoretical method, called representations analysis [14, 15]. It also shows what is meant by *equivalent points* [1] in the strict sense; in the helical and sinusoidal case, *equivalent points* are those which are related by symmetry operations of the space group G_k of the wave-vector $\mathbf{k}$.

8.1 SPACE GROUP G_k. — $\mathbf{k} = [\frac{1}{2}\ 0\ \tau]$ is invariant (modulo a vector $\mathbf{K}$ of the reciprocal lattice) under the operations of mirror-planes m_x and m_y perpendicular to the x-and y-axes respectively and under a rotation 2_z. Consequently the space group of $\mathbf{k}$ is $G_k = Pba2$. Taking as generators the glide plane $\mathbf{b}$ in $\frac{1}{4}\,yz$ and the twofold axis $\mathbf{2_z}$ in 00 z, one has

$$\mathbf{b} = (m_x \mid \tfrac{1}{2}\tfrac{1}{2}\ 0) ; \qquad \mathbf{2_z} = (\mathbf{2_z} \mid 000) \tag{8.6}$$

$$\mathbf{b2_z} = (\varepsilon \mid 110)\,\mathbf{2_z}\,\mathbf{b} . \tag{8.7a}$$

Thus for the case of the present wave vector $\mathbf{k} = [\frac{1}{2}\ 0\ \tau]$ $\mathbf{b}$ and $\mathbf{2_z}$ do not commute

$$\mathbf{b2_z} = -\,\mathbf{2_z}\,\mathbf{b} . \tag{8.7b}$$

One shows easily that

$$\mathbf{b}^2 = \mathbf{2_z^2} = \hat{\mathbf{1}} ; \qquad (\mathbf{b2_z})^2 = \mathbf{a}^2 = -\,\hat{\mathbf{1}} . \tag{8.8}$$

By a simple identification method [15, 16] one finds the matrices of the two-dimensional irreducible representation Γ of the wave vector group G_k, given in the table VI. (An equivalent irreducible representation is obtained by interchanging the matrix representatives of $\mathbf{b}$ and $\mathbf{2_z}$.) In the same table VI we have summarized the transformations properties of the $\mathbf{k}$-components of the spins $\mathbf{S}_1(\mathrm{Mn_I})$ and $\mathbf{S}_5(\mathrm{Mn_{II}})$ under the four group operations ε (identity), $\mathbf{b}$, $\mathbf{2_z}$ and $\mathbf{b2_z}$. The $\mathbf{k}$-components of $\mathbf{S}_9$(RE) transform in the same way as those of $\mathbf{S}_1(\mathrm{Mn_I})$, RE and $\mathrm{Mn_I}$ having the same site symmetry. We have omitted the z-components not needed here.

TABLE VI

Representation of the G_k group and transformation properties

Γ :	ε	$\mathbf{b}$	$\mathbf{2_z}$	$(\mathbf{b2_z})$
	$\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$	$\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$	$\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$	$\begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix}$
	$S_{1x;k}$	$S_{3x;k}$	$-\,S_{2x;k}$	$-\,S_{4x;k}$
	$S_{1y;k}$	$-\,S_{3y;k}$	$-\,S_{2y;k}$	$S_{4y;k}$
	$S_{5x;k}$	$S_{7x;k}$	$S_{5x;k}$	$S_{7x;k}$
	$S_{5y;k}$	$-\,S_{7y;k}$	$S_{5y;k}$	$-\,S_{7y;k}$

8.2 $\mathrm{Mn_I}$-SPINS. — We consider first the η_{I}-matrix (2.3) of the $\mathrm{Mn_I}$ case. If we call (A) (B) and (C) the 4×4 matrices formed by the coefficients of A, B and C respectively like (C) (8-9) for instance

$$(C) = \begin{pmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & -1\\ 1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\end{pmatrix} \text{ and so on} \tag{8.9}$$

one finds

$$(B)\,(C) = -\,(C)\,(B) . \tag{8.10}$$

Actually (B) is a permutation matrix realizing the following substitutions : $1 \to 2$; $2 \to 1$; $3 \to 4$; $4 \to 3$. Thus (B) is a representative of $\mathbf{2_z}$. In the same way (C) is a representative of $\mathbf{b}$ and (A) of the identity ε. One also checks

$$(B)^2 = (C)^2 = \mathbf{1} ; \qquad (BC)^2 = -\,\mathbf{1} . \tag{8.11}$$

Thus the matrices (A) (B) (C) and (BC) form a reducible representation of the group G_k. Consequently the *eigenvectors of the matrix* η $(\mathrm{Mn_I})$ *must be normal modes of* G_k.

8.2.1 *Basis vectors.* — In fact the demonstration of say, the orthogonality relations (2.11) is rather tricky. With the help of the matrices $D(\mathbf{T})$ and the transformations $\mathbf{T}S_{1\alpha;k}$ of table VI we first construct the basis vectors $\psi^{(\Gamma)}_{ij;\alpha}$ by the projection operator method

$$\psi^{(\Gamma)}_{ij;\alpha} = \sum_{T} D^{(\Gamma)}_{ij}(\mathbf{T})\,\mathbf{T}S_{1\alpha;k} ;$$
$$\alpha = x, y ; \quad \mathbf{T} = \varepsilon, \mathbf{b}, \mathbf{2_z}, \mathbf{b2_z} . \tag{8.12}$$

One gets from (8.5), (8.12) and table VI

$$V_{1x}\begin{cases}\psi_{11;x} = S_{1x;k} - S_{2x;k} = (Q_1 - Q_2)^*_x\\ \psi_{21;x} = (Q_3 - Q_4)^*_x\end{cases}$$

$$V_{1y}\begin{cases}\psi_{11;y} = (Q_1 - Q_2)^*_y = -\,i(Q_1 - Q_2)^*_x\\ \qquad\qquad\qquad\quad = -\,i\psi_{11;x}\\ \psi_{21;y} = (-\,Q_3 + Q_4)^*_y = i(Q_3 - Q_4)^*_x\\ \qquad\qquad\qquad\quad = i\psi_{21;x}\end{cases}$$

$$V_{2x}\begin{cases}\psi_{12;x} = (Q_3 + Q_4)^*_x\\ \psi_{22;x} = (Q_1 + Q_2)^*_x\end{cases}$$

$$V_{2y}\begin{cases}\psi_{12;y} = -\,(Q_3 + Q_4)^*_y = i\psi_{12;x}\\ \psi_{22;y} = (Q_1 + Q_2)^*_y = -\,i\psi_{22;x} .\end{cases} \tag{8.13}$$

Here we have used the conditions (see also (1.14) with $\mathbf{u} = \mathbf{x}$ and $\mathbf{v} = \mathbf{y}$)

$$Q_{jy} = iQ_{jx} . \tag{8.14}$$

8.2.2 *Invariants.* — We now investigate the invariants formed by pair multiplication of the vectors $V_{j\alpha}$ (8.13). For instance

$$V_{1x}\,V_{2x}^{*} = \psi_{11;x}\,\psi_{12;x}^{*} + \psi_{21;x}\,\psi_{22;x}^{*}$$
$$V_{1y}\,V_{2y}^{*} = \psi_{11;y}\,\psi_{12;y}^{*} + \psi_{21;y}\,\psi_{22;y}^{*} = -\,V_{1x}\,V_{2x}^{*}\,. \qquad (8.15a)$$

Thus incidentally

$$V_{1x}\,V_{2x}^{*} + V_{1y}\,V_{2y}^{*} = 0\,. \qquad (8.15b)$$

More particularly, using (8.13) and (8.14)

$$V_{1x}\,V_{1y}^{*} = i(|\,\psi_{11;x}\,|^2 - |\,\psi_{21;x}\,|^2) \qquad (8.16)$$

should be an invariant; but actually, operating with the glide plane **b**

$$\mathbf{b}(|\,\psi_{11;x}\,|^2 - |\,\psi_{21;x}\,|^2) = (|\,\psi_{21;x}\,|^2 - |\,\psi_{11;x}\,|^2)\,. \qquad (8.17)$$

Thus one must have

$$V_{1x}\,V_{1y}^{*} = 0 \quad \text{and} \quad |\,\psi_{11;x}\,|^2 = |\,\psi_{21;x}\,|^2\,. \qquad (8.18a)$$

One shows in the same way

$$V_{2x}\,V_{2y}^{*} = 0 \quad \text{and} \quad |\,\psi_{12;x}\,|^2 = |\,\psi_{22;x}\,|^2 \qquad (8.18b)$$
$$V_{1x}\,V_{2y}^{*} = V_{2x}^{*}\,V_{1y} = 0\,. \qquad (8.18c)$$

The three last relations are written explicitely and omitting the subscript x :

$$\left.\begin{aligned} |\,Q_1 \pm Q_2\,|^2 &= |\,Q_3 \pm Q_4\,|^2 \\ (Q_1 - Q_2)^{*}\,(Q_3 + Q_4) &= \\ &= (Q_1 + Q_2)\,(Q_3 - Q_4)^{*} \end{aligned}\right\}. \qquad (8.19)$$

It is an easy matter for the reader to check that the eq. (8.19) are compatible with $|\,Q_j\,| = 1$ and with the orthogonality relations (2.11) or (2.16). We postpone to the appendix B the proof that the orthogonality relations are the only solutions compatible with the matrix η_{I} and the system (8.19).

8.2.3 *Remark.* — One may question the mathematical reason of the *zero invariants* (8.15*b*) (8.18 *a*, *b*, *c*). Theoretically one has in the Mn_{I} case four spins in the x, y-plane, having eight components and giving rise to four basis vectors of dimension two, thus having altogether also eight components. One must remind however the existence of the four relations (8.14) in the S_k- (or Q_k-) formalism. Hence the basis vectors are not independant and the relations (8.14) imply the *zero invariants.*

8.3 Mn_{II}-SPINS. — One finds the basis vectors

$$V_{1x}\begin{cases}\psi_{11;x} = Q_{5x}^{*};\\ \psi_{21;x} = Q_{7x}^{*}\end{cases}\quad V_{1y}\begin{cases}\psi_{11;y} = -\,iQ_{5x}^{*}\\ \psi_{21;y} = \;\;iQ_{7x}^{*}\end{cases}. \qquad (8.20)$$

The vectors V_{2x} and V_{2y} are identically zero. The invariant $V_{1x}\,V_{1y}^{*}$ is again zero by the same reasoning as above and gives rise to the trivial identity

$$|\,Q_5\,|^2 = |\,Q_7\,|^2\,.$$

A more interesting relation is obtained by studying

$$V_{1x}(\mathrm{Mn_I})\,V_{1y}^{*}(\mathrm{Mn_{II}}) = (Q_1 - Q_2)_x^{*}\,(Q_5 - iQ_7)_y = i[-\,\psi_{11;x}(\mathrm{Mn_I})\,\psi_{11;x}^{*}(\mathrm{Mn_{II}}) + \psi_{21;x}(\mathrm{Mn_I})\,\psi_{21;x}^{*}(\mathrm{Mn_{II}})]\,. \qquad (8.21)$$

The transformation by **b** shows this mixed invariant to be zero, implying $Q_5 = iQ_7$. This orthogonality relation here appears as being due to the coupling of the Mn_{II} to the Mn_{I}-system. The second orthogonality relation (3.9) is demonstrated in the same way.

8.4 RE-SPINS. — 8.4.1 *Helical case.* — The reasoning is the same as for Mn_{I}, the lower indices 9, 10, 11, 12, replacing the indices 1, 2, 3, 4. Thus the phase relations (6.6) are demonstrated as those of Mn_{I}.

8.4.2 *Sinusoidal case.* — One can show (see appendix C) that the basis vectors can be written

$$\vec{\boldsymbol{\psi}}_{ij;\alpha} = \mathbf{n},\,\mathbf{n}\psi_{ij;\alpha}\,, \qquad (8.22)$$

where the $\psi_{ij;\alpha}$ are the basis vectors of the helical case. Thus the phase relations between the Q_j of the helical case are conserved.

APPENDIX A

The anisotropy tensor. — The anisotropy energy of the ion i is

$$W_{\mathrm{an}}^{i} = -\,\mathbf{S}_i.\vec{\mathbf{J}}_{ii}.\mathbf{S}_i = -\,S_i^2(a_{1i}\cos 2\beta_i + a_{2i}\sin 2\beta_i)\,. \qquad (A.1)$$

The constants a_{1i} and a_{2i} are determined by the requirement of a minimum of W_{an}^{i}. Thus

$$a_{2i}/a_{1i} = \mathrm{tg}\,2\beta_i \qquad (A.2)$$

wherefrom follows (7.4), K being an anisotropy constant.

We consider the transformation of $\vec{\mathbf{J}}_9$ under the operations $\mathbf{2_z}$ and **b** (glide plane) of the wave vector group G_k. The rotation $\mathbf{2_z}$ transports point 9 to point 10 and leaves $\vec{\mathbf{J}}_9$ invariant. Thus

$$\vec{\mathbf{J}}_9 = \vec{\mathbf{J}}_{10}\,. \qquad (A.3)$$

The plane b transports point 9 to point 11, changes $\mathbf{x}$ to $-\,\mathbf{x}$ and consequently $\vec{\mathbf{J}}_9$ to

$$\vec{\mathbf{J}}_{11} = a_1(\mathbf{x},\,\mathbf{x}-\mathbf{y},\,\mathbf{y}) - a_2(\mathbf{x},\,\mathbf{y}+\mathbf{y},\,\mathbf{x}) = \vec{\mathbf{J}}_{12} \qquad (A.4)$$

so that the easy direction for the moments 11 and 12 is $-\,\beta_9$.

APPENDIX B

The orthogonality proof. — *a*) Let us try the substitution (B.1) in (8.19)

$$Q_3 = \alpha Q_2 ; \qquad Q_4 = \beta Q_1 \tag{B.1}$$

with

$$| \alpha |^2 = | \beta |^2 = 1 .$$

By identifications of coefficients one gets

$$\alpha\beta^* = \alpha^* \beta = 1 ; \qquad \alpha + \alpha^* = 0$$

and

$$\alpha = \beta = \pm i . \tag{B.2}$$

Thus the orthogonality relations (2.11) (2.16) are compatible with group theory.

b) Let us try the substitution (B.3) in (8.19)

$$Q_3 = \alpha Q_1 ; \qquad Q_4 = \beta Q_2 . \tag{B.3}$$

One now finds

$$\alpha = \beta = \alpha^* = \pm 1 . \tag{B.4}$$

Returning back to the matrix η_1 (2.3) it is seen that

$$Q_3 = + Q_1 = \cos \frac{v}{2} ; \quad Q_4 = + Q_2 = \sin \frac{v}{2} \tag{B.5}$$

is solution for the root λ^+ (2.19) where v is defined by (cf. (2.13))

$$v = \frac{\pi}{2} - \varphi . \tag{B.6}$$

(B.5) shows that here $| Q_1 | \neq | Q_2 |$. Thus this solution is at least incomplete.

The other possibility to be investigated is

$$- Q_3 = Q_1 = \sin \frac{v}{2} ; \quad - Q_4 = Q_2 = \cos \frac{v}{2} \tag{B.7}$$

which is still solution for λ^+. One may now construct a complete solution, satisfying $| Q_j | = 1$ with for instance the components in (B.5) along Ox and those under (B.7) along Oy, as visualized in the following scheme :

Spins	1	2	3	4
x-components	$\cos \frac{v}{2}$	$\sin \frac{v}{2}$	$\cos \frac{v}{2}$	$\sin \frac{v}{2}$
y-components	$\sin \frac{v}{2}$	$\cos \frac{v}{2}$	$- \sin \frac{v}{2}$	$- \cos \frac{v}{2}$.

(B.8)

The eigenvector (Q_1, Q_2, Q_3, Q_4) is now $(Q_1, - iQ_1^*, Q_1^*, iQ_1)$ with $Q_1 = \exp i \frac{v}{2}$. One recognizes again the orthogonality relations (2.11).

c) We have also studied the most general type of linear substitutions (B.9) in (8.19)

$$Q_3 = \alpha Q_2 + \gamma Q_1 ; \quad Q_4 = \beta Q_1 + \delta Q_2 \tag{B.9}$$

with the following result, after some lengthy calculations

$$Q_3 = \cos \mu Q_1 + i \sin \mu Q_2 ;$$
$$Q_4 = i \sin \mu Q_1 + \cos \mu Q_2 . \tag{B.10}$$

However the requirement of $| Q_j | = 1$ introduces the condition $\sin \mu \cos \mu = 0$ with two types of solutions, either $\cos \mu = 0$ and $\sin \mu = \pm 1$ or $\sin \mu = 0$ and $\cos \mu = \pm 1$, already discussed under *a*) and *b*) respectively.

APPENDIX C

Sinusoidal case. — We shall show that the phase factors Q_j are still the same as in the isotropic case. We define

$$\vec{\vec{\mathbf{Q}}}_{jx} = \tfrac{1}{2} S\mathbf{n}_j, \mathbf{n}_j Q_j ; \quad \vec{\vec{\mathbf{Q}}}_{jy} = i\vec{\vec{\mathbf{Q}}}_{jx} \tag{C.1}$$

so that

$$\mathbf{S}_j = \vec{\vec{\mathbf{Q}}}_{jx} . \mathbf{x} + \vec{\vec{\mathbf{Q}}}_{jy} . \mathbf{y} + \text{complex conjugate} . \tag{C.2}$$

Split the dyadic $\vec{\vec{\mathbf{N}}}$ (C.3) into two parts

$$\vec{\vec{\mathbf{N}}} = \mathbf{n}, \mathbf{n} = \vec{\vec{\mathbf{N}}}_0 + \vec{\vec{\mathbf{N}}}_1 \tag{C.3}$$

$$\vec{\vec{\mathbf{N}}}_0 = \mathbf{x}, \mathbf{x} \cos^2 \beta_9 + \mathbf{y}, \mathbf{y} \sin^2 \beta_9$$
$$\vec{\vec{\mathbf{N}}}_1 = (\mathbf{x}, \mathbf{y} + \mathbf{y}, \mathbf{x}) \sin \beta_9 \cos \beta_9 . \tag{C.4}$$

$\vec{\vec{\mathbf{N}}}_0$ transforms according to the representation Γ_x^2 or Γ_y^2, i. e. according to the identity representation Γ_0 and $\vec{\vec{\mathbf{N}}}_1$ according to the representation $\Gamma_x \times \Gamma_y = \Gamma_z$ of the following group table VII (associated with $\mathbf{k} = 000$).

Thus $\vec{\vec{\mathbf{N}}}_0 Q_{j\alpha}$ ($\alpha = x, y$) transforms according to Γ (Table VI) and $\vec{\vec{\mathbf{N}}}_1 Q_{j\alpha}$ according to $\Gamma_z \times \Gamma$ so that

$$D^{\Gamma_z \Gamma}(T) = \chi^{\Gamma_z}(T) D^{\Gamma}(T) . \tag{C.5}$$

Note that the matrices of $\Gamma_z \times \Gamma$ still satisfy the multiplication rules of G_k so that $\Gamma_z \times \Gamma$ is equivalent to Γ.

TABLE VII

Representations of Pba2 ($\mathbf{k} = 0$)

	ε	$\mathbf{b}$	$\mathbf{2_z}$	$\mathbf{b2_z}$
Γ_0	1	1	1	1
Γ_z	1	− 1	1	− 1
Γ_x	1	− 1	− 1	1
Γ_y	1	1	− 1	− 1

The application of the projection operator formula (8.12) gives

$$\vec{\vec{\psi}}_{ij;\alpha} = \vec{\vec{N}}_0 \sum_T D^{\Gamma}_{ij}(T)\, TQ_{j\alpha} + \sum_T D^{\Gamma}_{ij}(T)\, \chi^{\Gamma z}(T)\, T(\vec{\vec{N}}_1\, Q_{j\alpha}) . \quad (C.6)$$

Actually

$$T(\vec{\vec{N}}_1\, Q_{j\alpha}) = \chi^{\Gamma z}(T)\, \vec{\vec{N}}_1\, TQ_{j\alpha}\,; \quad (\chi^{\Gamma z}(T))^2 = 1 \quad (C.7)$$

so that finally

$$\vec{\vec{\psi}}_{ij;\alpha} = \vec{\vec{N}}\psi_{ij;\alpha} \quad (C.8)$$

where the $\psi_{ij;\alpha}$ are the basis vectors of the helical case.

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