

SYMMETRY CONDITIONS IMPOSED ON THE HAMILTONIAN OF  
BILINEAR SPIN INTERACTIONS IN CRYSTALS

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A method of constructing the Hamiltonian of bilinear interactions between magnetic point pairs in the most general form permitted by a crystallographic symmetry is proposed. Considerations are presented for an arbitrary space group and arbitrary ordering of magnetic points. As an example, interactions between nearest neighbours in the hcp lattice are discussed and, in particular, a form of anti-symmetric interactions is derived.

*1. Introduction*

To describe the properties of magnetic crystals in which un-paired electrons occur on inner atomic shells, the generalized Heisenberg model [1] can be used. In this model, the real crystal is replaced by a lattice of magnetic moments ("spins") localized at its sites and mutually interacting pairwise. The interaction is rendered analytically by a spin Hamiltonian constructed, in general, as a quadratic form of spin operators attached to the sites and involving phenomenological force parameters, which have to be determined from an appropriate theory of microscopic interactions in the crystal. Because of the high complexity of these interactions, such parameters have not hitherto been determined *a priori*, neither has their order of magnitude been correctly predicted. In this situation data of magnetic measurements as well as of neutron magnetic scattering experiments are usually explained on the base of some assumed spin Hamiltonian, and the force constants are determined from the condition of optimal adjustment of the experimental data to the theory based on this Hamiltonian.

It is usually assumed that an essential role belongs only to interactions between rather near neighbours. With respect to the crystal symmetry, the number of independent force parameters is then small and it is worth while to attempt to determine all of them from the experimental data without any further model simplifications. In the present paper, a general

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method of determining the interaction parameters permitted by a crystal symmetry is proposed. To this aim, we shall give a receipt for constructing the most general form of the Hamiltonian in the bilinear interaction approximation permitted by the crystal space group symmetry assuming a prescribed ordering of magnetic points in the chemical unit cell. The Hamiltonian can be used as a tool in analyzing experimental data with the purpose of determining essential magnetic interactions.

In Section 2, we shall establish a convention for labelling points and pairs of points in a crystal permitting the full use of group theory methods. In further Sections, we shall formulate analytically a condition for the invariance of the Hamiltonian with respect to the space group operators and, moreover, shall introduce a general form of its invariant expansion. Finally we shall consider, as an example, the hcp lattice.

## 2. Convention of labelling pairs of sites in a crystal

Let  $G$  be the space group of the crystal. We denote its elements as

$$g = \{R[\mathbf{r}]|\mathbf{t}+\mathbf{n}\} \quad (1)$$

where  $R[\mathbf{r}]$  is a rotation or a rotation-inversion with a fixed point  $\mathbf{r}$ ;  $\mathbf{t}$  is a non-integer translation related with  $R$  and dependent upon  $\mathbf{r}$ ;  $\mathbf{n} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$  is an integer translation,  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  stand for the basic vectors, and  $n_1, n_2, n_3$  are arbitrary integers. The elements  $g \in G$  are products of the rotations  $R[\mathbf{r}]$  and the translations  $\mathbf{t}+\mathbf{n}$ , the rotation having to be performed first. The set  $\{R_1, \dots, R_{n_F}\} = F$  forms a point group, referred to as the crystallographic class. The set of all points obtained from an arbitrary lattice site by way of all integer translations contained in the space group is termed a chemical sublattice, whereas the set of all chemical sublattices obtained with the aid of arbitrary elements  $g \in G$  is termed a simple crystal [2]. A real crystal consists of at least one simple crystal. Thus, an arbitrary crystal site is determined by a vector  $\mathbf{r}_{w\mathbf{n}}$ , where the index  $w$  labels the simple crystals,  $v = 1, 2, \dots, q_w$  extending over crystallographically equivalent chemical sublattices, whereas  $\mathbf{n}$  stands for the Wigner-Seitz unit cells. The set of all elements of a space group  $G$  which do not change the position of the site  $w\mathbf{n}$  *i. e.* elements of the form

$$R_\lambda^U = \{R_\lambda[\mathbf{r}_{w\mathbf{n}}]|0\}, \quad \lambda = 1, 2, \dots, n_w \quad (2)$$

is a point group of this site denoted as  $U[w\mathbf{n}]$ . The group  $F$  can be treated as the sum of left cosets of the group  $U[w\mathbf{n}]$ :

$$F \sim \bigcup_{v=1}^{q_w} R_v^{\mathcal{A}} U[w\mathbf{n}] \quad (3)$$

where  $R_v^{\mathcal{A}}$  is an element of the space group carrying over a site  $w\mathbf{n}$  into a site  $v\mathbf{n}$ , *i. e.*

$$\{R_v^{\mathcal{A}}|\alpha\}\mathbf{r}_{w\mathbf{n}} = \mathbf{r}_{v\mathbf{n}}. \quad (4)$$

The sum in Eq. (3) is dealt with as a sum of sets, whereas the symbol  $\sim$  means a one-to-one equivalence which goes over into an equality when translations are neglected (*i. e.* at  $g \rightarrow R$ ). Obviously, the set  $\{R_v^{\mathcal{N}}\}$  is not uniquely determined by (4). One such set is arbitrarily chosen with the limitation that  $R_1^{\mathcal{N}} = E$  where  $E$  is the unit element. For an arbitrary simple crystal one obtains

$$n_w q_w = n_F. \quad (5)$$

For  $n_w = 1$  site positions in a simple crystal are termed general positions, whereas in the remaining cases we speak of distinct special positions.

For our further considerations it seems useful to introduce the notion of coordination sphere. The  $l$ -th coordination sphere of a site  $w\mathbf{n}$ , to be referred to as the central site, is the set of all sites equally distant from it:

$$|\mathbf{r}_{w'\mathbf{v}'\mathbf{n}'} - \mathbf{r}_{w\mathbf{v}\mathbf{n}}| = r_l, \quad l = 1, 2, \dots \quad (6)$$

with

$$r_{l+1} > r_l. \quad (7)$$

Obviously, if the set  $\{w' \mathbf{v}' \mathbf{n}'\}$  is a coordination sphere of a site  $w\mathbf{n}$  then, by (4), the set

$$\mathbf{r}_{w'\mathbf{v}'\mathbf{n}'} = \{R_v^{\mathcal{N}} | \alpha\} \mathbf{r}_{w\mathbf{v}\mathbf{n}} \quad (8)$$

is a coordination sphere of a site  $w\mathbf{v}\mathbf{n}$ . Sites of a coordination sphere of a site  $w\mathbf{v}\mathbf{n}$  will be labelled by means of certain elements of the point group of the central site  $U[w\mathbf{v}\mathbf{n}]$ . Elements of this group transform arbitrary sites of an arbitrary coordination sphere  $l$  into sites of the same coordination sphere. Let us define a simple sphere as a set of sites in which an arbitrary site can be carried over into other arbitrary sites of this set by means of the operations  $R_\lambda^U \in U[w\mathbf{v}\mathbf{n}]$ . The notion of the simple sphere is analogous to that of the simple crystal. Cases when one coordination sphere contains more than one simple sphere are rather rare and can be eliminated by a slight change of the mutual position of two distinct simple crystals without changing the numbers  $q_w$  for  $w \neq w'$ , or by a slight change of the Bravais lattice parameters without a change of the space group for  $w = w'$ . Sometimes, however, this difficulty cannot be eliminated without transgressing the crystal symmetry (*e.g.* the eighth coordination sphere of the simple cubic lattice consists of two simple spheres). Distinct simple spheres contained in one coordination sphere will be labelled by an index  $v$ .

Let us take into consideration the  $v$ -th simple sphere belonging to the  $l$ -th coordination sphere of the central site  $w\mathbf{n}$ . Site positions of this sphere are determined by  $\varrho_{lv}^{w\mathbf{1}\mathbf{n}}$ ,  $\kappa = 1, 2, \dots, Z_{lv}^w$ . Let us furthermore introduce the group

$$U[w\mathbf{1}\mathbf{n}/lv] = U[w\mathbf{1}\mathbf{n}] \cap U[lv] \quad (9)$$

where the symbol  $\cap$  denotes an intersection of sets *i.e.* a common part of sets. It can be one of the groups  $C_{nv}$  or one of their subgroups. The group  $U[w\mathbf{1}\mathbf{n}]$  can be written as a sum of left cosets of the group  $U[w\mathbf{1}\mathbf{n}/lv]$ :

$$U[w\mathbf{1}\mathbf{n}] = U_\kappa R_\kappa^K U[w\mathbf{1}\mathbf{n}/lv] \quad (10)$$

with (see: Fig. 1)

$$\{R_n^{\mathcal{K}}|\alpha\} \varrho_{lv1}^{w1n} = \varrho_{lvx}^{w1n} \quad (11)$$

$$\{R_\eta^{U'}|\alpha\} \varrho_{lv1}^{w1n} = \varrho_{lv1}^{w1n} \quad \eta = 1, 2, \dots, n_w/lv \quad (12)$$

$$n_w/lv Z_{lv}^w = n_w. \quad (13)$$

We choose arbitrarily a set  $\mathcal{K}[w1n/lv]$  of elements  $R_n^{\mathcal{K}}$  with the limitation that  $R_1^{\mathcal{K}} = E$ . As seen,

$$U[w1n/lvx] = R_n^{\mathcal{K}} U[w1n/lv1] (R_n^{\mathcal{K}})^{-1}. \quad (14)$$

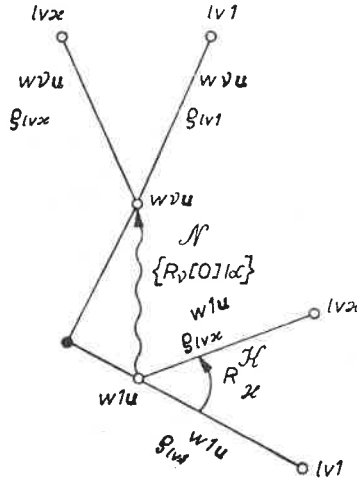


Fig. 1. Labelling pairs of sites in a crystal

The labelling of sites of the coordination sphere of the site  $wv\mathbf{n}$  is determined by the elements of the set  $\mathcal{K}[w1n/lv1]$  (see: Fig. 1) in accordance with the formula:

$$\{R_v^{\mathcal{N}}|\alpha\} \varrho_{lvx}^{w1n} = \varrho_{lvx}^{wv\mathbf{n}}. \quad (15)$$

This is obviously an equivalent of Eq. (4).

Evidently,

$$U[wv\mathbf{n}] = R_v^{\mathcal{N}} U[w1\mathbf{n}] (R_v^{\mathcal{N}})^{-1} \quad (16)$$

and

$$U[wv\mathbf{n}/lvx] = R_v^{\mathcal{N}} U[w1\mathbf{n}/lvx] (R_v^{\mathcal{N}})^{-1}. \quad (17)$$

An arbitrary element  $R_n \in F$  can be written uniquely in the form

$$R_n = R_v^{\mathcal{N}} R_n^{\mathcal{K}} R_\eta^{U'}, \quad R_v^{\mathcal{N}} \in \mathcal{N}_w, \quad R_n^{\mathcal{K}} \in \mathcal{K}[w1n/lv1], \\ R_\eta^{U'} \in U[w1n/lv1]. \quad (18)$$

Thus, Eqs (11), (12) and (15) fully determine the action of the rotation elements of the space group on pairs of sites. We have

$$\{R_n|\alpha\} \varrho_{lvx}^{wv\mathbf{n}} = \{R_n|\alpha\} \{R_v^{\mathcal{N}}|\alpha'\} \{R_n^{\mathcal{K}}|\alpha''\} \varrho_{lv1}^{w1n} \\ = \{R_v^{\mathcal{N}}|\alpha_1\} \{R_n^{\mathcal{K}}|\alpha_2\} \{R_\eta^{U'}|\alpha_3\} \varrho_{lv1}^{w1n} = \varrho_{lvx}^{wv'\mathbf{n}} \quad (19)$$

The action of translations on pairs of sites is given simply by

$$\{E|\mathbf{n}\}Q_{l\nu\kappa}^{w\nu\mathbf{n}} = Q_{l\nu\kappa}^{w\nu\mathbf{n}+\mathbf{n}'} \quad (20)$$

We thus have determined the rules for the labelling of site pairs of a crystal lattice by means certain subsets of the space group  $G$  as well as the action of an arbitrary element  $g \in G$  on these pairs.

### 3. Condition for invariance of the Hamiltonian with respect to the symmetry operations of the space group

The Hamiltonian of bilinear spin interactions can be written in general as:

$$H = \sum_{w\nu\mathbf{n}} \sum_{l\nu\kappa} \sum_{\alpha,\alpha'} Q_{w\nu\mathbf{n}; l\nu\kappa}^{\alpha\alpha'} S_{w\nu\mathbf{n}}^{\alpha} S_{w\nu\mathbf{n}; l\nu\kappa}^{\alpha'} \quad (21)$$

where

$$\begin{aligned} a &= 0, \pm 1 \\ S^{\pm 1} &= \mp \frac{1}{\sqrt{2}} (S^x \mp iS^y) \\ S^0 &= S^z \end{aligned} \quad (22)$$

are the spin operator components of appropriate sites, whereas the tensor coefficients  $Q$  are force parameters. Let us consider the limitations imposed on the expansion (21) by the lattice symmetry.

Consider the operator vector field:

$$S(\mathbf{r}) = \sum_{w\nu\mathbf{n}} \sum_{\alpha} e_{\alpha} S_{w\nu\mathbf{n}}^{\alpha} \delta(\mathbf{r} - \mathbf{r}_{w\nu\mathbf{n}}) \quad (23)$$

where  $e_{\pm 1} = \mp 1/\sqrt{2}(e_x \pm ie_y)$ ,  $e_0 = e_z$ ;  $e_x, e_y, e_z$  are unit axial vectors in the Cartesian system;  $\delta(\mathbf{r})$  is Dirac's delta function. Under an arbitrary  $g \in G$ , this field transforms according to the formula:

$$\begin{aligned} T(g)S(\mathbf{r}) &= gS(g^{-1}\mathbf{r}) \\ &= \sum_{\alpha,\alpha'} \sigma^{\alpha\alpha'}(g) e_{\alpha'} \sum_{w\nu\mathbf{n}} S_{w\nu\mathbf{n}}^{\alpha} \delta(g^{-1}\mathbf{r} - \mathbf{r}_{w\nu\mathbf{n}}) \end{aligned} \quad (24)$$

where  $\sigma^{\alpha\alpha'}(g)$  are matrix elements of the axial vector representation in the basis  $e_{\alpha}$ . The relation (24) defines the representation  $T$  of the group  $G$  in the space  $L$ , spanned by the basis  $e_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{w\nu\mathbf{n}})$ . As seen, the space  $L$  can be treated as the tensor product of two spaces

$$L = \mathcal{A} \otimes \mathcal{A} \quad (25)$$

where  $\mathcal{A}$  is the space spanned by the normalized, orthogonal functions:

$$\delta_{w\nu\mathbf{n}}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_{w\nu\mathbf{n}}) \quad (26)$$

whereas  $\mathcal{A}$  is defined by the basis  $e_{\alpha}$ ,  $\alpha = 0, \pm 1$ . Respectively, the representation  $T$  is a simple product

$$T = P \otimes \sigma \quad (27)$$

where  $P$  is the representation acting in the space  $\mathcal{A}$  defined as

$$P(g)\delta_{wv\mathbf{n}}(\mathbf{r}) = \delta_{wv\mathbf{n}}(g^{-1}\mathbf{r}) = \delta_{g[wv\mathbf{n}]}(\mathbf{r}) \quad (28)$$

whereas  $\sigma$  is the usual axial vector representation acting in the space  $\mathcal{A}$ . It should be noted that, in accordance with (23) and (24), the operators  $S_{wv\mathbf{n}}^z$  play the role of coordinates in the space  $L$ .

An arbitrary quadratic form in the shape of Eq. (21) transforms according to the representation  $T^{(2)}$ . It can be said that this representation acts in the space,

$$L^{(2)} = L \otimes L' \quad (29)$$

where

$$L' = \mathcal{A}' \otimes \mathcal{A}' \quad (30)$$

is the space corresponding to sites of coordination spheres. The condition for the invariance of the Hamiltonian with respect to the symmetry operations is thus equivalent to the requirement that the expansion (21) shall be an element of the subspace  $L_0^{(2)} \subset L^{(2)}$  transforming according to the unit representation of the group  $G$ . Our problem reduces to finding all the linear independent invariants of the space group in  $L_0^{(2)}$  i.e. to finding a basis in  $L_0^{(2)}$ .

#### 4. Decomposition of $L^{(2)}$ into irreducible subspaces and a classification of the invariants

Let us rewrite Eq. (29) in the following form:

$$L^{(2)} = (\mathcal{A} \otimes \mathcal{A}') \otimes (\mathcal{A} \otimes \mathcal{A}'). \quad (31)$$

To find a basis in  $L_0^{(2)}$ , we first have to determine irreducible bases in the distinct spaces occurring in the product (31). In order to render the procedure more clear, we shall carry it out in three steps: (a) — a decomposition of the positional space  $(\mathcal{A} \otimes \mathcal{A}')$  into subspaces irreducible with respect to the crystal space group; (b) — a decomposition of the space of free spin vectors  $(\mathcal{A} \otimes \mathcal{A}')$  according to the irreducible representations conjugate to the representations of the positional space; (c) — a classification of the invariants in  $L^{(2)}$ .

##### (a) Decomposition of the space $\mathcal{A} \otimes \mathcal{A}'$

It is readily noted that, an account of the condition for the invariance with respect to translations, it is sufficient for determining  $L_0^{(2)}$  to consider only a subspace  $\Psi \subset \mathcal{A} \otimes \mathcal{A}'$  described by the basis

$$\varphi_{\nu\kappa}^{wv} \begin{bmatrix} \nu \\ \kappa \end{bmatrix} = \sum_{\mathbf{n}} \delta_{wv\mathbf{n}}(\mathbf{r}) \delta_{\nu\kappa}^{wv\mathbf{n}}(\mathbf{r}')$$

where

$$\delta_{\nu\kappa}^{wv\mathbf{n}}(\mathbf{r}) = \delta[\mathbf{r} - (\mathbf{r}_{\nu\kappa} - \mathbf{r}_{wv\mathbf{n}})]. \quad (32)$$

In accordance with (28), the representation  $P$  can be defined by acting on the indices of the basis functions instead of acting on their argument and therefore we shall henceforth not

consider their dependence on  $\mathbf{r}$ . The action of the representation  $P^{(2)}$  on the elements (32) is given by

$$P^{(2)}(g)\varphi_{lv}^w \begin{bmatrix} \nu \\ \kappa \end{bmatrix} \equiv P^{(2)}(\{R|\mathbf{t}+\mathbf{n}\})\varphi_{lv}^w \begin{bmatrix} \nu \\ \kappa \end{bmatrix} = \varphi_{lv}^w \begin{bmatrix} R_\nu \\ R_\kappa \end{bmatrix}. \quad (33)$$

It results that the representation  $P^{(2)}(g)$  in the space  $\Psi$  is determined only by the rotational elements  $R$ . Hence, instead of a representation of the space group  $G$  in the space  $\mathcal{A} \otimes \mathcal{A}'$ , we shall consider only some representation of the crystal class  $F$  in the space defined by (33).

The space  $\Psi$  decomposes in a natural way into subspaces invariant under  $P^{(2)}$  according to the formula:

$$\Psi = \sum_{wlv} \oplus \Psi_{lv}^w \quad (34)$$

where  $\Psi_{lv}^w$  is a subspace with elements of the basis (32) having fixed  $w, l, v$ . Each subspace  $\Psi_{lv}^w$  can be further decomposed into subspaces irreducible with respect to the group  $F$ . The decomposition is given by:

$$\Psi_{lv}^w = \sum_{\gamma} \sum_{\vartheta} \oplus \Psi_{lv}^{\gamma\vartheta} \quad (35)$$

$$P_{lv}^{(2)w} = \sum_{\gamma} m_{\gamma}^{wlv} \tau^{(\gamma)} \quad (36)$$

where  $\tau^{(\gamma)}$  is the  $\gamma$ -th irreducible representation of the group  $F$ ;

$\vartheta = 1, 2, \dots, m_{\gamma}^{wlv}$  labels the irreducible subspaces transforming according to the representation  $\tau^{(\gamma)}$ ;

$P_{lv}^{(2)w}$  is the representation of the group  $F$  induced by  $P^{(2)}$  in the space  $\Psi_{lv}^w$ ,

$$m_{\gamma}^{wlv} = \frac{1}{n_F} \sum_{\pi=1}^{n_F} \chi_{\gamma}^*(R_{\pi}) \chi_{wlv}(R_{\pi}) \quad (37)$$

$\chi_{\gamma}(R_{\pi})$  is the character of the irreducible representation  $\gamma$ ;  $\chi_{wlv}(R_{\pi})$  is the character of the representation  $P_{lv}^{(2)w}$ . It is easily shown that the character  $\chi_{wlv}(R_{\pi})$  is equal to the number of the vectors  $\varrho_{lv\kappa}^{w\nu\mathbf{n}}$  which, at fixed  $w, \mathbf{n}, l, v$ , do not change their positions under the operator  $R_{\pi}$ . The bases of the irreducible representations in the spaces  $\Psi_{lv}^{\gamma\vartheta}$  can be written in the following form:

$$\Phi_{lv\mu}^{\gamma\vartheta} = \sum_{\nu, \kappa} Y_{lv\mu}^{\gamma\vartheta} \begin{bmatrix} \nu \\ \kappa \end{bmatrix} \varphi_{lv}^w \begin{bmatrix} \nu \\ \kappa \end{bmatrix} \quad (38)$$

where  $Y_{lv\mu}^{\gamma\vartheta}$  are expansion coefficients, whereas  $\mu$  labels the basis functions. These coefficients can be determined by means of the well-known projection procedure (see: e.g. [3]), by the operators:

$$\hat{\Phi}_{lv\mu}^{\gamma\vartheta} = \frac{s_{\gamma}}{n_F} \sum_{\pi} \tau_{\mu 1}^{(\gamma)*}(R_{\pi}) P_{lv}^{(2)w}(R_{\pi}) \quad (39)$$

where  $s_\gamma$  is the dimension of the irreducible representation  $\tau^{(\gamma)}$ , whereas  $\tau_{\mu\mu'}^{(\gamma)}$  are matrix elements of the representation. The basis (32) is real, and therefore we can choose the irreducible bases (38) in such a way that

$$(\Phi_{\nu\mu}^{w\gamma\delta})^* = \begin{cases} \Phi_{\nu\mu}^{w\tilde{\gamma}\delta} & \text{for complex } \tau^{(\gamma)} \\ \Phi_{\nu\mu}^{w\gamma\delta} & \text{for real } \tau^{(\gamma)} \end{cases} \quad (40)$$

where  $\tilde{\gamma}$  is the index of the representation conjugate to the representation  $\tau^{(\gamma)}$ .

(b) Decomposition of the space  $\Delta \otimes \Delta'$

When decomposing the space  $\Delta \otimes \Delta'$  into irreducible subspaces, one can first consider the representation  $D_1^+$  of the full orthogonal group  $O(3) \otimes I$ , instead of the representation  $\sigma$  of the point group  $F$ . The group  $F$  is a subgroup of  $O(3) \otimes I$ . The space  $\Delta \otimes \Delta'$  splits into subspaces irreducible with respect to  $O(3) \otimes I$  according to the formula:

$$\Delta \otimes \Delta' = \Delta^{(2)} \oplus \Delta^{(1)} \oplus \Delta^{(0)} \quad (41)$$

where  $\Delta^{(A)}$ ,  $A = 0, 1, 2$  transforms according to the representation  $D_A^+$  of the group  $O(3) \otimes J$ . The bases  $f_\beta^A$ ,  $\beta = -A, \dots, A$  in the spaces  $\Delta^{(A)}$  can be written, in general, as follows:

$$f_\beta^A = \sum_{\alpha+\alpha'=\beta} d_{\beta,\alpha\alpha'}^A e_\alpha e_{\alpha'} \quad (42)$$

In our further calculations we shall assume the following forms:

$$f_0^0 = \frac{1}{\sqrt{3}} (e_{-1}e'_1 - e_0e'_0 + e_1e'_{-1}) \quad (42a)$$

$$f_0^1 = \frac{1}{\sqrt{2}} (e_1e'_{-1} - e_{-1}e'_1) \quad (42b)$$

$$f_{\pm 1}^1 = \mp \frac{1}{\sqrt{2}} (e_0e'_{\pm 1} - e_{\pm 1}e'_0) \quad (42c)$$

$$f_0^2 = \frac{1}{\sqrt{2} \cdot 3} (e_{-1}e'_1 + e_1e'_{-1} + 2e_0e'_0) \quad (42d)$$

$$f_{\pm 1}^2 = \frac{1}{\sqrt{2}} (e_{\pm 1}e'_0 + e_0e'_{\pm 1}) \quad (42e)$$

$$f_{\pm 2}^2 = e_{\pm 1}e'_{\pm 1} \quad (42f)$$

The spaces  $\Delta^{(1)}$  and  $\Delta^{(2)}$  are in general reducible with respect to the group  $F$ . The decomposition into irreducible subspaces can be written in this case as follows:

$$\Delta^A = \sum_{\tilde{\gamma}\tilde{\delta}} \oplus \Delta_{\tilde{\gamma}\tilde{\delta}}^{(A)} \quad (43)$$

where  $\tilde{\delta} = 1, 2, \dots, m_\gamma^A$  labels the irreducible subspaces transforming according to the



irreducible representation conjugate to  $\tau^{(\gamma)}$  (due to the realness of the representation  $D_1^+$  one obtains  $m_\gamma^A = m_\gamma^A$ ). Bases in these subspaces can be written as:

$$B_\beta^{(A)\tilde{\gamma}\tilde{\delta}} = \sum_{\beta=-A}^A b_\beta^{(A)\tilde{\gamma}\tilde{\delta}} f_\beta^A. \quad (44)$$

The expansion coefficients  $b^{(A)\tilde{\gamma}\tilde{\delta}}_\mu$  are obtained in the projection procedure by means of the operators:

$$\hat{B}_\mu^{\tilde{\gamma}} = \frac{s_\gamma}{n_F} \sum_{\pi=1}^{n_F} \tau_{\mu 1}^{(\gamma)}(R_\pi) \sigma(R_\pi). \quad (45)$$

The formula (45) differs from (39) by the non-conjugateness of  $\tau_{\mu 1}^{(\gamma)}$ , as results by projecting on the conjugate representations. Hence, the basis functions (44) are contravariant to  $\Phi_{l\nu\mu}^{w\gamma\tilde{\delta}}$ . Due to the realness of the representation  $\sigma$ , the values  $B^{(A)\tilde{\gamma}\tilde{\delta}}_\mu$  satisfy relations analogous to (40).

### c) Classification of the invariants of spin pairs

From group representation theory, one obtains that the vectors

$$M_{wl\nu}^{(A)\gamma\tilde{\delta}} = \sum_\mu B^{(A)\tilde{\gamma}\tilde{\delta}}_\mu \Phi_{l\nu\mu}^{w\gamma\tilde{\delta}} = inv \quad (46)$$

form a basis in the space  $L^{(2)}$ . All the searched spin invariants are linear combinations of the expressions:

$$I_{wl\nu}^{(A)\gamma\tilde{\delta}} = \sum_{\mu=1}^{s_\gamma} \sum_{\nu=1}^{q_w} \sum_{\kappa=1}^{Z_{l\nu}^w} \sum_{\beta=-A}^A \sum_{\alpha,\alpha'=-1}^A Y_{l\nu\mu}^{*w\gamma\tilde{\delta}} d_{b,\alpha\alpha'}^{*A} b_\beta^{*(A)\tilde{\gamma}\tilde{\delta}} \sum_n S_{w\nu n}^\alpha S_{l\nu n}^{\alpha'}. \quad (47)$$

All distinct  $I$ 's given by (47) are linearly independent, and thus the indices  $A, w, l, \nu, \gamma, \tilde{\delta}(\gamma, w, l, \nu), \tilde{\delta}(\gamma)$  can be used for a complete classification of the invariants. Moreover, one has to keep in mind that, if  $\tilde{\delta} = 0$  or  $\tilde{\delta} = 0$ , then  $I \equiv 0$ .

The problem of finding all invariants constructed from spin operator components of pairs of crystal-sites is equivalent to decomposing the direct quadratic product of the axial vector space  $\Delta \otimes \Delta'$  into subspaces irreducible with respect to the crystallographic class  $F$  and finding the irreducible bases in subspaces of the considered spaces  $\Psi_{l\nu}^w$  transforming according to those representations of the group  $F$  which are contained in the direct quadratic product of the vector representation. Once we know these decompositions, we construct the required invariants according to the formula (47).

## 5. Possible forms of the spin Hamiltonian

The spin Hamiltonian has to be a Hermitian operator, constructed from the invariants (47) and real constants playing the role of phenomenological parameters. Since to the mutually conjugate basis elements (46) there correspond according to (40) mutually hermi-

tian-adjoint spin invariants (47), the general form of our Hamiltonian is

$$H = \sum' Q_{wlv}^{(A)\gamma\vartheta\tilde{\vartheta}} I_{wlv}^{(A)\gamma\vartheta\tilde{\vartheta}} + \sum'' Q_{wlv}^{(A)\gamma\vartheta\tilde{\vartheta}} (I_{wlv}^{(A)\gamma\vartheta\tilde{\vartheta}} + I_{wlv}^{(A)\tilde{\gamma}\vartheta\tilde{\vartheta}}) \quad (48)$$

where summation is over the set of indices:  $\{A, \gamma, \vartheta, \tilde{\vartheta}, w, l, v\}$  whereas the sum  $\Sigma'$  extends over the real representations and  $\Sigma''$  over the complex ones. The values  $Q$  are phenomenological parameters allowed by the symmetry which, for a specific material, have to be determined by adjustment to the experimental data. These quantities are accessible to interpretation within the framework of microscopic theories of magnetism for the crystal under consideration. The maximum number of parameters related with a given coordination sphere amounts to

$$N_{lv}^w = \left( \sum' m_{\gamma}^P + \frac{1}{2} \sum'' m_{\gamma}^P \right) \sum_A m_{\gamma}^A. \quad (49)$$

Let us now consider some particular cases of the Hamiltonian (48). For  $A = 0$ , strictly one invariant corresponds to every space  $\Psi_{lv}^w$ :

$$\Phi_{lv}^{w1} = (Z_{lv}^w)^{-1/2} \sum_{\nu, \kappa} \varphi_{lv}^{w[\nu]} \quad (50)$$

The appropriate invariant of the spin operators

$$I_{wlv}^{(0)} = \sum_n \sum_{\nu, \kappa} S_{w\nu n} \cdot S_{lv\kappa} \quad (51)$$

describes the normal isotropic interaction attributed mainly to exchange forces. As seen, the "exchange integral"  $Q_{wlv}^{(0)1}$  can depend on the type of interacting sites and their distances as well as on the crystallographic positions of chemically equivalent and equidistant pairs of interacting sites. Such interaction is allowed by symmetry in arbitrary crystals, between arbitrary pairs of sites.

For the case  $A = 1$ , we have so-called Dzyaloshinsky–Moriya antisymmetric interaction *i.e.* interaction described by the Hamiltonian

$$H_{DM} = \sum_{\substack{w\nu n \\ lv\kappa}} D_{lv\kappa}^{w\nu} \cdot (S_{w\nu n} \times S_{lv\kappa}). \quad (52)$$

Such interaction, for a given space  $\Psi_{lv}^w$ , is possible only if the decomposition of  $P_{lv}^w$  into irreducible representations of the group  $F$  contains representations occurring simultaneously in the axial vector representation. Thus, the symmetry imposes limitations on the occurrence of this interaction as well as on the direction of the vector parameter  $D$ .

The case  $A = 2$  contains various anisotropic symmetric interactions *i.e.* interactions described by traceless tensors of the second order. A particular case consists in the so-called dipolar or pseudodipolar interaction, of the form

$$\hat{H}_{\text{dip}} = \sum_{\substack{w\nu n \\ lv\kappa}} \theta_{lv\kappa}^{w\nu} \left[ S_{w\nu n} \cdot S_{lv\kappa} - \frac{3}{|\rho_{lv\kappa}^{w\nu}|^2} (S_{w\nu n} \cdot \rho_{lv\kappa}^{w\nu}) (S_{lv\kappa} \cdot \rho_{lv\kappa}^{w\nu}) \right]. \quad (53)$$

Sometimes, in describing the properties of magnetics one assumes, following Van Vleck [4], a model in which the energy of the symmetric anisotropic interactions is given in the bilinear approximation entirely by (53). However, from the procedure used in obtaining the Hamiltonian, it is seen that the anisotropic terms can possess a structure different from that of (53) and, moreover, that the complete description of the anisotropy requires the introduction of a larger number of parameters. It is to be hoped that sufficiently precise neutronographic and magnetic measurements will permit to individuate distinct forms of the anisotropy and to determine the values of the corresponding parameters.

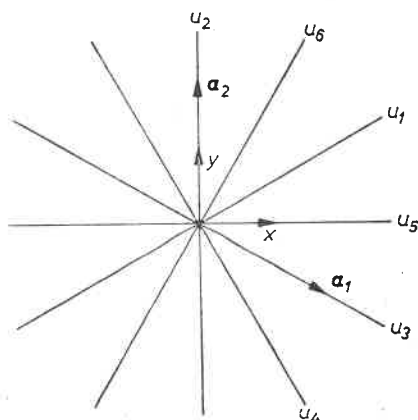


Fig. 2. Ordering of the horizontal two-fold axes of the group  $D_{6h}$

The literature often introduces phenomenologically a so-called monaxial anisotropy, described by

$$H_{un} = \sum_{\substack{wv\kappa \\ l\nu\kappa}} K_{lv\kappa}^{wv} S_{wv\kappa}^z S_{l\nu\kappa}^z \quad (54)$$

being a superposition of the cases  $A = 0$  and  $A = 2$ . When one assumes that  $K$  does not depend on  $\nu, \kappa$ , this interaction corresponds to a vector (50) in the space  $\Psi_{lv}^w$  and  $S_{wv\kappa}^z S_{l\nu\kappa}^z$  has to transform according to the unit representation of the group  $F$ . This is possible for point groups with a distinguished axis  $z$  *i.e.* for all crystallographical groups except the cubic ones.

### 6. An example: the hcp lattice

To illustrate the method we shall now obtain all possible interactions between pairs of nearest neighbours for the hcp lattice. This lattice obviously forms a simple crystal and, thus, the index  $w$  can be omitted. In this case we have in the Schoenflies notation:

$$F = D_{6h}, \quad \mathcal{N} = \{E, C_6\}, \quad U[1, \mathbf{n}] = U[2, \mathbf{n}] = D_{3h} \quad (55)$$

where the indices  $\nu = 1, 2$  correspond to sublattices  $A$  and  $B$ , respectively. The last two equalities of (55) now have the meaning of an isomorphism. The first coordination sphere

of any site consists of two simple spheres (we consider the hcp lattice as a lattice with ideal ratio  $c/a$ ); the sphere  $v = 1$  consists of sites of the same sublattice as the central site, whereas the sphere  $v = 2$  consists of sites of the other sublattice. Fig. 2 shows the chosen ordering of two-fold horizontal axes of the group  $D_{6h}$ , whereas Fig. 3 shows the manner of labelling the sites of the first coordination sphere according to the convention described in Sec. 2. The sets  $U[v/1v\kappa]$  and  $\mathcal{K}[v/1v\kappa]$  are given by

$$\begin{aligned} U(1/1, 1, 1) &= \{E, \sigma_n\}, \\ U(1/1, 2, 1) &= \{E, \sigma_5\}, \\ \mathcal{K}[1/1, 1, 1] &= \{E, C_3, C_3^2, u_4, u_5, u_6\} \\ \mathcal{K}[1/1, 2, 1] &= \{E, C_3, C_3^2, \sigma_h, S_3, S_3^{-1}\} \end{aligned} \quad (56)$$

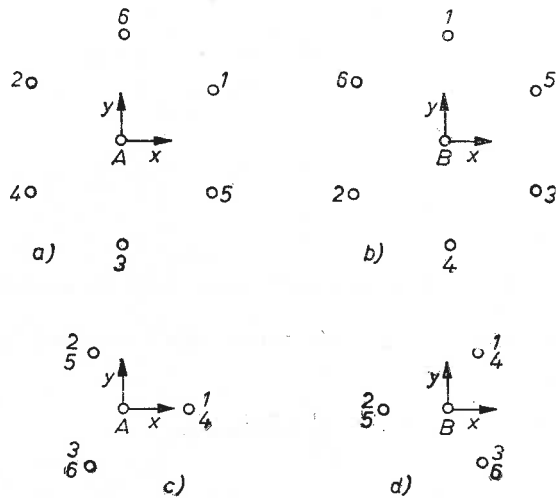


Fig. 3. Labelling the sites of the first coordination sphere a)  $v = 1, v = 1$ , b)  $v = 1, v = 2$ , c)  $v = 2, v = 1$  d)  $v = 2, v = 2$ . In the cases a) and b) the central site is situated in the plane of sites of the sphere; whereas in the cases c) and d) at half the distance between the planes 123 ( $z > 0$ ) and 456 ( $z < 0$ )

The decomposition of respective representations into irreducible representations of the group  $D_{6h}$  is of the following form (compare: (36) and (43)):

$$\begin{aligned} D_0^+ &= \Gamma_0^+ \\ D_1^+ &= \Gamma_2^+ \oplus \Gamma_5^+ \\ D_2^+ &= \Gamma_1^+ \oplus \Gamma_5^+ \oplus \Gamma_6^+ \\ P_{11} &= \Gamma_1^+ \oplus \Gamma_2^+ \oplus 2\Gamma_6^+ \oplus \Gamma_3^- \oplus \Gamma_4^- \oplus 2\Gamma_5^- \\ P_{12} &= \Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_5^+ \oplus \Gamma_6^+ \oplus \Gamma_2^- \oplus \Gamma_4^- \oplus \Gamma_5^- \oplus \Gamma_6^- \end{aligned} \quad (57)$$

TABLE I

Bases of irreducible representations in the space  $\Psi_{11}$  of the hcp lattice (unnormalized)  $\omega = \exp(i\pi/3)$ 

$\begin{matrix} \varphi \\ \gamma \vartheta \\ \mu \end{matrix} \begin{matrix} \nu \\ \kappa \end{matrix}$	1	1	1	1	1	1	2	2	2	2	2	2
	1	2	3	4	5	6	1	2	3	4	5	6
1,1 1	1	1	1	1	1	1	1	1	1	1	1	1
2,1 1	1	1	1	-1	-1	-1	1	1	1	-1	1	-1
6,1 -1	1	$-\omega$	$\omega^2$	0	0	0	$\omega^2$	1	$-\omega$	0	0	0
6,1 +1	0	0	0	$-\omega$	1	$\omega^2$	0	0	0	$\omega^2$	$-\omega$	1
6,2 -1	0	0	0	1	$-\omega$	$\omega^2$	0	0	0	$\omega^2$	1	$-\omega$
6,2 +1	$-\omega$	1	$\omega^2$	0	0	0	$\omega^2$	$-\omega$	1	0	0	0

TABLE II

Bases of irreducible representations in the space  $\Psi_{12}$  of the hcp lattice (unnormalized)

$\begin{matrix} \varphi \\ \gamma \vartheta \\ \mu \end{matrix} \begin{matrix} \nu \\ \kappa \end{matrix}$	1	1	1	1	1	1	2	2	2	2	2	2
	1	2	3	4	5	6	1	2	3	4	5	6
1,1 1	1	1	1	1	1	1	1	1	1	1	1	1
5,1 -1	1	$\omega^2$	$-\omega$	-1	$-\omega^2$	$+\omega$	$+\omega$	-1	$-\omega^2$	$-\omega$	-1	$\omega^2$
5,1 1	1	$-\omega$	$\omega^2$	-1	$\omega$	$-\omega^2$	$-\omega^2$	-1	$\omega$	$\omega^2$	1	$-\omega$
6,1 -1	1	$\omega^2$	$-\omega$	1	$\omega^2$	$-\omega$	$-\omega$	1	$\omega^2$	$-\omega$	1	$\omega^2$
6,1 1	1	$-\omega$	$\omega^2$	1	$-\omega$	$\omega^2$	$\omega^2$	1	$-\omega$	$\omega^2$	1	$-\omega$

where the notations of irreducible representations are those of the Tables of Koster *et al.* [5]. The bases (45) of irreducible representations in the spaces  $\mathcal{A}^{(A)}$  can be chosen in the form:

$$\begin{aligned}
 B^{(0)1+} &= f_0^0 \\
 B^{(1)2+} &= f_0^1; B_{\mp 1}^{(1)5+} = -f_{\pm 1}^1 \\
 B^{(2)1+} &= f_0^2; B_{\mp 1}^{(2)5+} = -f_{\pm 1}^2; B_{\mp 1}^{(2)6+} = f_{\pm 2}^2
 \end{aligned} \tag{58}$$

whereas the bases in the spaces  $\Psi_{11}$  and  $\Psi_{12}$  contravariant with respect to the bases (58), are determined by the coefficients  $Y$  (38) shown respectively in Tables I and II.\* Resorting

\* The bases determined in this way are not real; this leads to a constant complex factor in (47) which can be omitted.

to these Tables as well as to Eqs (57), (58) and (42), the particular invariants (47) can be easily obtained. We shall not adduce here the specific forms of all these invariants as this would require too much printing space.

As an example, we shall consider in more detail the invariant relating to the space  $\Psi_{12}^{5+} \otimes \Delta_{5+}^{(1)}$ , i.e.  $A = 1, \gamma = 5+, l = 1, v = 2$ . It can be written concisely as:

$$\begin{aligned}
 I_{1,2}^{(1)5+} \sim \sum_n \left\{ & [-S_1^x S_1^z + S_1^z S_1^y] - [S_1^{\alpha'} \rightarrow S_4^{\alpha'}] - [S_1^{\alpha} \rightarrow S_2^{\alpha}, S_1^{\alpha'} \rightarrow S_2^{\alpha'}] + \right. \\
 & + \left[ \frac{\sqrt{3}}{2} (S_1^x S_2^z - S_1^z S_2^x) + \frac{1}{2} (S_1^y S_2^z - S_1^z S_2^y) \right] - \\
 & - [S_2^{\alpha} \rightarrow S_5^{\alpha}] - [S_1^{\alpha} \rightarrow S_2^{\alpha}, S_2^{\alpha'} \rightarrow S_3^{\alpha'}] + [S_1^{\alpha} \rightarrow S_2^{\alpha}, S_2^{\alpha'} \rightarrow S_6^{\alpha'}] + \\
 & + \left[ -\frac{\sqrt{3}}{2} (S_1^x S_3^z - S_1^z S_3^x) + \frac{1}{2} (S_1^y S_3^z - S_1^z S_3^y) \right] - \\
 & \left. - [S_3^{\alpha'} \rightarrow S_6^{\alpha'}] + [S_1^{\alpha} \rightarrow S_2^{\alpha}, S_3^{\alpha'} \rightarrow S_4^{\alpha'}] - [S_1^{\alpha} \rightarrow S_2^{\alpha}, S_3^{\alpha'} \rightarrow S_4^{\alpha'}] \right\} \quad (59)
 \end{aligned}$$

where, for abbreviation, we have put  $S_n^{\alpha} \rightarrow S_{1,2,\kappa}^{\alpha} \rightarrow S_n^{\alpha} S_{\kappa}^{\alpha'}$ . This invariant describes the Dzyaloshinsky-Moriya antisymmetric interaction between nearest neighbours belonging to the two sublattices. On comparing (59) with (52), we conclude that

$$D_{1,2,\kappa}^{\nu} = D \xi(\nu, \kappa) (1 - e_z e_{\kappa}) \cdot \varrho_{1,2,\kappa}^{\nu n} \quad (60)$$

where,  $D$  is an arbitrary real constant;  $\xi(\nu, \kappa) = \mp 1$  is a phase factor defined by (59). A similar discussion for  $\Psi_{11}^{2+} \oplus \Delta_{2+}^{(1)}$  leads to the following result:

$$D_{1,1,\kappa}^{\nu} = D' \xi'(\nu, \kappa) e_{\kappa}. \quad (61)$$

As seen, the Dzyaloshinsky-Moriya vector for interaction between nearest neighbours of the same sublattice is parallel, but in the case of distinct sublattices, perpendicular to the hexagonal axis.

The invariants related with  $\Psi_{11}^{1+} \otimes \Delta^{(0)}$  and with  $\Psi_{21}^{1+} \otimes \Delta^{(0)}$  describe isotropic interaction of the form (51). It should be noted that the right "exchange integrals"  $J_{11}$  and  $J_{21}$  can differ even in the case when the distances between the respective sites are equal. Finally, the invariant related to  $\Psi_{11}^{6+,1} \otimes \Delta_{6+}^{(2)}$ ,  $\Psi_{11}^{6+,2} \otimes \Delta_{6+}^{(2)}$ ,  $\Psi_{11}^{1+} \otimes \Delta_{1+}^{(2)}$ ,  $\Psi_{12}^{1+} \otimes \Delta_{1+}^{(2)}$ ,  $\Psi_{12}^{5+} \otimes \Delta_{5+}^{(2)}$ ,  $\Psi_{12}^{6+} \otimes \Delta_{6+}^{(2)}$  describe symmetric anisotropy couplings.

In the example considered here, the number of linearly independent invariants, according to (49), amounts to:

$$N_{11} = 5, N_{12} = 5, N_1 = N_{11} + N_{12} = 10. \quad (62)$$

Thus, in order to obtain the complete description of the interactions, one has to determine ten independent force constants. In general, interactions between pairs of sites in the hcp lattice are treated in the bilinear approximation with the aid of three parameters: the isotropic exchange integrals  $J_{11}$  and  $J_{12}$ , as well as a single monaxial anisotropy constant. Such

a treatment amounts to neglecting the antisymmetric interactions as well as to an arbitrary simplification of the form of the symmetric anisotropy interactions. Thus, in heavy rare earth metals which crystallize in the hcp structure and exhibit strong, and moreover highly complicated magnetic anisotropies (see: *e.g.* [6]), none of these parameters seems *a priori* negligible.

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