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ORDER, DISORDER, AND PHASE TRANSITIONS IN CONDENSED SYSTEMS

On the Theory of Spin Exchange Structures

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Abstract—All possible types of spin ordering manifested in spin–spin correlation functions are determined. It is shown that orbital magnetism must arise in certain cases. Some general characteristics of arbitrary spin structures predicted by macroscopic theory are examined, including energy associated with inhomogeneity, anisotropy, and energy in external fields. © *2005 Pleiades Publishing, Inc.*

1. INTRODUCTION

It was shown in [1] that spin ordering of special type can arise in condensed matter when exchange coupling is much stronger than relativistic effects. In this case, the average microscopic spin density

$$\mathbf{S}(\mathbf{r}) = \langle \hat{\mathbf{S}}(\mathbf{r}) \rangle, \tag{1}$$

vanishes, and spontaneous loss of spin rotation symmetry in the exchange Hamiltonian manifests itself by anisotropy of the spin–spin correlation function

$$S_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \langle \hat{S}_\alpha(\mathbf{r}_1)\hat{S}_\beta(\mathbf{r}_2) \rangle. \tag{2}$$

This state is not magnetic, because invariance under time reversal is preserved. However, many characteristics of the corresponding spin ordering are similar to those of normal double exchange magnets [2] (low-frequency spin waves, magnetic resonance, susceptibility, etc.).

In principle, more complicated states may exist in which spontaneous loss of spin exchange invariance and symmetry under time reversal is manifested only in multiple-spin correlation functions. The nonmagnetic phases for which only even-order correlation functions do not vanish are called spin nematics [1]. For example, in the case a nonzero triple-spin correlation function

$$S_{\alpha\beta\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \langle \hat{S}_\alpha(\mathbf{r}_1)\hat{S}_\beta(\mathbf{r}_2)\hat{S}_\gamma(\mathbf{r}_3) \rangle, \tag{3}$$

the corresponding state is magnetic, because it is not invariant under time reversal. Phases characterized by odd-time spin correlation functions are called tensor magnets [3, 4]. They substantially differ from both normal magnets and spin nematics. These phases always have a low spin density due to relativistic effects. Recently, several materials were found in which extremely weak spontaneous sublattice magnetization is observed. In [5], it was suggested to detect tensor magnetic ordering in these materials by measuring elastic neutron scattering in an external magnetic field.

In [1, 3, 4], examples of tensor ordering were discussed, but the properties of the spin order parameter under crystallographic group transformations were not analyzed. In [6], the Landau theory second-order phase transitions was applied to analyze spin nematic phases characterized by nonzero spin–spin correlation functions resulting from second-order phase transitions in crystals with tetragonal symmetry.

In this study, we determine all possible types of tensor spin ordering, relying on the general ideas of the theory of spin exchange symmetry [2]. As in the case of a normal magnet, this can be done without analyzing phase transitions. We also discuss some special properties of tensor spin ordering predicted by macroscopic theory.

2. EXCHANGE SYMMETRY

The overall symmetry of a spin state is determined by symmetries of three types: (1) a classical crystallographic symmetry; (2) its combination with invariance under spin-space rotations and time reversal (interpreted as spin-space inversion); and (3) invariance of both spin density (1) and all spin–spin correlation functions under spin rotations.

The spin symmetries of the last type obviously constitute a symmetry group equivalent to a point group [7]. We denote spin symmetry groups of this type by adding the superscript *s* to the symbols representing the corresponding space point groups. For example, $C^s_{\infty v}$, C^s_s, and E^s correspond to collinear, coplanar, and noncollinear noncoplanar magnets, respectively.

The construction of exchange symmetry groups for normal magnets is based on the following observation [2]. In the general case, microscopic spin density can be expressed as

$$\mathbf{S}(\mathbf{r}) = f^{(1)}_a \mathbf{a} + f^{(1)}_b \mathbf{b} + f^{(1)}_c \mathbf{c}, \tag{4}$$

where the mutually orthogonal unit vectors **a**, **b**, and **c** make up a basis in the spin space, i.e., change sign under time reversal. The parenthesized superscript of a real function f is the rank of the spin tensor under consideration. The spin density squared,

$$\mathbf{S}^2 = (f_a^{(1)})^2 + (f_b^{(1)})^2 + (f_c^{(1)})^2 \quad (5)$$

is invariant under both spin-space rotations and time reversal. As a state variable, it must be invariant under all transformations in the crystal symmetry group G.

In the case of a collinear magnet, the functions f are linearly dependent. For example, a basis can be selected in the spin space so that $f_\alpha^{(1)} = f_b^{(1)} = 0$, and the corresponding $f_c^{(1)}$ transforms under a one-dimensional representation. For a coplanar magnet, $f_c^{(1)}$ can be set to zero, and the corresponding linearly independent $f_a^{(1)}$ and $f_b^{(1)}$ transform under similar one-dimensional representations, or under different one-dimensional representations, or under a two-dimensional representation. The three linearly independent functions corresponding to a general noncollinear magnet transform under similar or different one-dimensional representations, or under a one-dimensional representation for one of them and a two-dimensional representation for the remaining two, or under a three-dimensional representation.

For magnets with $C_{\infty v}^s$, C_s^s, and E^s symmetries, a prescribed spin density defines the symmetry of the corresponding state, and no analysis of correlation functions is required.

However, in the case of minimal loss of the symmetry of the exchange Hamiltonian, when invariance under spin-space rotations is preserved and only invariance under time reversal is lost, the order parameter is the three-point correlation function

$$S_{\alpha\beta\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = f^{(3-)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)E_{\alpha\beta\gamma}, \quad (6)$$

The minus in the superscript of f refers to the antisymmetric part of the spin tensor, and

1 ???

The isotropic tensor $E_{\alpha\beta\gamma}$ is

$$E_{\alpha\beta\gamma} = a_\alpha b_\beta c_\gamma + b_\alpha c_\beta a_\gamma + c_\alpha a_\beta b_\gamma - b_\alpha a_\beta c_\gamma - a_\alpha c_\beta b_\gamma - c_\alpha b_\beta a_\gamma.$$

It differs from the Levi-Civita symbol $e_{\alpha\beta\gamma}$ by the factor

$$\nu = \mathbf{a} \cdot [\mathbf{b} \times \mathbf{c}], \quad (7)$$

which changes sign under time reversal. The invariance of convolutions $S_{\alpha\beta\gamma}S_{\alpha\beta\gamma}$ under the group G implies that $f^{(3-)}$ transforms only under a one-dimensional representation. The corresponding material is a scalar magnet [3]. Both exchange and magnetic symmetries of this state are determined by the symmetry of $\nu f^{(3-)}$. The corresponding magnetic crystal symmetry is obviously equivalent to the crystal group G.

Isotropic quantity (7) is also finite for noncollinear noncoplanar magnets, for which all functions f in spin density (1) are linearly independent. It is natural to call this quantity *magnetic chirality.* In [8], it was noted that domain walls of special kind can exist in such phases. States that differ by the sign of (7) cannot be transformed into one another by any spin-space rotation. Thus, the boundary between them has structure determined by exchange interactions and therefore has an atomic thickness, in contrast to the domain-wall thickness in normal magnets determined by competing exchange and relativistic effects.

Note also the following feature of chiral magnets. In normal double exchange magnets, the atomic orbital moments are quenched. Spin-orbit interaction results in a low orbital-moment density. However, when (7) does not vanish, orbital motion of electrons in a crystal must not be quenched even in an exchange approximation; i.e., phases of this kind are orbital magnets. It is clear that the orientations of orbital moments are tied to crystallographic axes.

The phase with the highest chiral spin symmetry $\mathbf{D}_{\infty h}^s$ is called *chiral spin nematic* [1] and is characterized by the anisotropic part of the spin–spin correlation function,

$$S_{\alpha\beta} = \frac{f_1^{(2)}}{\sqrt{6}}(3c_\alpha c_\beta - \delta_{\alpha\beta}), \quad (8)$$

where $f_1^{(2)}$ is a function of $\mathbf{r}_1$ and $\mathbf{r}_2$. By virtue of the invariance of the convolutions $S_{\alpha\beta}S_{\alpha\beta}$ and $S_{\alpha\beta}S_{\beta\gamma}S_{\alpha\beta}$ under the group G, the function $f_1^{(2)}$ is totally invariant (identity representation).

Tensor magnets with symmetry $\mathbf{D}_\infty^s$ are characterized by magnetic chirality (6) and spin–spin correlations (8) with $f^{(3-)}$ and $f_1^{(2)}$ that transform under the same or different one-dimensional representations.

The spin–spin correlation function for group $\mathbf{C}_{\infty h}^s$ magnets contains both (8) and

$$f_c^{(2-)}(a_\alpha b_\beta - b_\alpha a_\beta), \quad (9)$$

which is antisymmetric with respect to spin indices [9]. An analysis of the invariance of nonmagnetic spin convolutions shows that $f_1^{(2)}$ is again totally invariant,

while $f_c^{(2-)}$ transforms under a one-dimensional representation. In this case, the role of order parameter is played by the pseudovector, which is dual to the antisymmetric part of the spin–spin correlation function in the spin space,

$$\mathbf{P} = f_c^{(2-)}[\mathbf{a}\times\mathbf{b}]. \quad (10)$$

In addition to the spin–spin correlation function characterizing the case of $\mathbf{C}_\infty^s$ (with similar selection rules for *f*), the group $\mathbf{C}_{\infty h}^s$ admits the vector

$$\mathbf{S} = f_c^{(1)}\mathbf{c}, \quad (11)$$

where *f* transforms under a one-dimensional representation. This phase obviously has a magnetic chirality.

Let us define the orientation of the basis spin-space vectors as follows. Under the $\mathbf{T}^s$, $\mathbf{T}_d^s$, $\mathbf{T}_h^s$, $\mathbf{Y}^s$, and $\mathbf{Y}_h^s$ groups, the vectors **a**, **b**, and **c** are aligned with the three mutually orthogonal second-order axes; under the $\mathbf{O}^s$ and $\mathbf{O}_h^s$ groups, they are aligned with the fourth-order axes. Under the chiral spin groups, the vector **c** is aligned with the principal axis. Under the $\mathbf{D}_n^s$, $\mathbf{D}_{nh^s}$, and $\mathbf{D}_{nd}^s$ groups, the vector **a** is aligned with one of the U_2^s axes. Under the $\mathbf{C}_n^s$, $\mathbf{C}_{nh}^s$, and $\mathbf{S}_{2n}^s$ groups, the vector **a** is arbitrarily oriented. Under the $\mathbf{C}_i^s$ group, the entire basis is arbitrarily oriented.

Under the $\mathbf{C}_i^s$ group, when exchange symmetry is lost completely while invariance under time reversal holds, it is reasonable to consider the antisymmetric part of the spin–spin correlation function, whose general form is

$$S_{\alpha\beta}^{(-)} = (f_a^{(2-)}a_\gamma + f_b^{(2-)}b_\gamma + f_c^{(2-)}c_\gamma)E_{\alpha\beta\gamma}. \quad (12)$$

Note that $\mathbf{C}_i^s$ does not admit linear dependence between the functions *f*. Invariance of the convolution $S_{\alpha\beta}^{(-)}S_{\alpha\beta}^{(-)}$ implies that the sum

$$(f_a^{(2-)})^2 + (f_b^{(2-)})^2 + (f_c^{(2-)})^2$$

is invariant under group *G* transformations. Thus, the functions *f* transform under the representations selected by rules similar to those for magnets. However, the additional requirement of invariance of $S_{\alpha\beta}^{(-)}S_{\beta\gamma}^{(-)}S_{\alpha\gamma}^{(-)}$ implies that invariance of the product $f_a^{(2-)}f_b^{(2-)}f_c^{(2-)}$, which substantially reduces the number of admissible types of ordering.

The groups $\mathbf{C}_n^s$ and $\mathbf{C}_{nv}^s$ with $n > 1$ admit collinear magnetism (11). Under the $\mathbf{C}_n^s$ groups, spin ordering is characterized by magnetic chirality. Therefore, the spin–spin correlation function contains antisymmetric part (9). Under $\mathbf{C}_2^s$, the correlation function $S_{\alpha\beta}$ contains the terms

$$\frac{f_2^{(2)}}{\sqrt{2}}(a_\alpha a_\beta - b_\beta b_\beta) + \frac{f_3^{(2)}}{\sqrt{2}}(a_\alpha b_\beta + b_\alpha a_\beta). \quad (13)$$

An analysis of spin–spin convolutions shows that $f_2^{(2)}$ and $f_3^{(2)}$ transform either under identical or different one-dimensional representations or under a single two-dimensional one. Under $\mathbf{C}_{2v}^s$, (13) contains only one term, which transforms under the identity representation.

Representations under the $\mathbf{C}_n^s$ and $\mathbf{C}_{nv}^s$ groups with $n > 2$ are selected by rules similar to those for $n = 2$, but *n*-spin correlators are anisotropic. Instead of the pair of tensors in (13), rank *n* spin tensors must be used. They can be represented as

$$\{(a+ib)^n + (a-ib)^n\}, \quad i\{(a+ib)^n - (a-ib)^n\}.$$

Hereinafter, expressions in curly brackets imply obvious combinations of spin indices.

The $\mathbf{C}_{nh}^s$ phases differ from $\mathbf{C}_n^s$ phases only by the absence of magnetic vector (11).

Under the $\mathbf{S}_{2n}^s$ groups, the magnetic vector is also forbidden, but the spin–spin correlation function contains antisymmetric part (9). Axial anisotropy is associated with the correlation function of order $n + 3$. There exist the tensors $E_{\alpha\beta\gamma} * \{(a+ib)^n + (a-ib)^n\}$ and $iE_{\alpha\beta\gamma} * \{(a+ib)^n - (a-ib)^n\}$, where the asterisk denotes a tensor product. The corresponding amplitudes also admit one- and two-dimensional representations.

Under the $\mathbf{D}_n^s$ groups, the loss of invariance under time reversal implies the existence of nonzero triple-spin correlations (6).

Under $\mathbf{D}_2^s$, anisotropy in the spin space is described by the spin–spin correlation function

$$S_{\alpha\beta} = \frac{f_1^{(2)}}{\sqrt{6}}(3c_\alpha c_\beta - \delta_{\alpha\beta}) + \frac{f_2^{(2)}}{\sqrt{2}}(a_\alpha a_\beta - b_\alpha b_\beta). \quad (14)$$

The invariance of all possible spin convolutions implies that the functions $(f_1^{(2)})^2 + (f_2^{(2)})^2$ and $(f_1^{(2)})^3 + 3f_1^{(2)}(f_2^{(2)})^2$ must be invariant. Under any space group

G, $f_1^{(2)}$ transforms under the identity representation, and $f_2^{(2)}$ transforms under a one-dimensional representation. However, two-dimensional representations are also admissible. In particular, crystals of the rhombohedral and hexagonal systems admit representations with $\mathbf{k} = 0$, which keep invariant the polynomial

$$(f_1^{(2)})^3 - 3f_1^{(2)}(f_2^{(2)})^2 = \mathrm{Re}(f_1^{(2)} + if_2^{(2)})^3.$$

An example of such representation in any space group of crystal class C_3 is the representation under which the x and y vector components transform.

A simple analysis shows that the groups with higher order principal axes, as well as in tetrahedral groups, admit spin–spin correlation functions defined by a single tensor or two tensors of different rank whose amplitudes transform only under one-dimensional representations of G. The corresponding order parameter tensors are

$\mathbf{D}_n^s : E_{\alpha\beta\gamma}, \{(a+ib)^n + (a-ib)^n\}$

$\mathbf{D}_{nh}^s : \{(a+ib)^n + (a-ib)^n\}$

$\mathbf{D}_{nd}^s : E_{\alpha\beta\gamma} * \{(a+ib)^n + (a-ib)^n\}$

$\mathbf{T}^s : E_{\alpha\beta\gamma}, T_{\alpha\beta\gamma}$

$\mathbf{T}_d^s : T_{\alpha\beta\gamma}$

$\mathbf{T}_h^s : E_{\alpha\beta\gamma} * T_{\delta\eta\mu}$

Here, $T_{\alpha\beta\gamma}$ is the tetrahedral tensor

$$\{abc\} = a_\alpha b_\beta c_\gamma + b_\alpha c_\beta a_\gamma + c_\alpha a_\beta b_\gamma + b_\alpha a_\beta c_\gamma + a_\alpha c_\beta b_\gamma + c_\alpha b_\beta a_\gamma.$$

The octahedral group $\mathbf{O}^s$ of spin symmetry admits triple spin correlations (6). The amplitude $f^{(3-)}$ transforms under a one-dimensional representation. Anisotropy in the spin space corresponds to a four-spin correlation function of the form $f^{(4)}O_{\alpha\beta\gamma\delta}$, where $O_{\alpha\beta\gamma\delta}$ is the antisymmetric traceless tensor

$$O_{\alpha\beta\gamma\delta} = a_\alpha a_\beta a_\gamma a_\delta + b_\alpha b_\beta b_\gamma b_\delta + c_\alpha c_\beta c_\gamma c_\delta - \frac{1}{5}I^{(4)}_{\alpha\beta\gamma\delta}$$

with cubic symmetry. Here, $I^{(4)}$ is the spherically symmetric rank four tensor

$$I_{\alpha\beta\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}.$$

The amplitude $f^{(4)}$ must be symmetric under G, because the convolution $O_{\alpha\beta\gamma\delta}O_{\alpha\beta\mu\nu}O_{\gamma\delta\mu\nu}$ does not vanish.

Under the cubic $\mathbf{O}_h^s$ group, the order parameter is $O_{\alpha\beta\gamma\delta}$.

The icosahedral group $\mathbf{Y}^s$ admits triple-spin correlations (6), and spin-space anisotropy is associated with a six-spin correlation function of the form $f^{(6)}Y_{\alpha\beta\gamma\delta\eta\mu}$, where the tensor $\mathbf{Y}_h^s$ has the icosahedral symmetry. The symmetric traceless rank six tensor with icosahedral symmetry has the form

$$Y = \Big\{(c+\phi a)^6 + (c-\phi a)^6 + (a+\phi b)^6 + (a-\phi b)^6 + (b+\phi c)^6 + (b-\phi c)^6 - \frac{2(1+\phi^2)^3}{35}I^{(6)}\Big\},$$

where $\mathbf{c} + \phi\mathbf{a}$, $\mathbf{c} - \phi\mathbf{a}$, $\mathbf{a} + \phi\mathbf{b}$, $\mathbf{a} - \phi\mathbf{b}$, $\mathbf{b} + \phi\mathbf{c}$, and $\mathbf{b} - \phi\mathbf{c}$ are the position vectors of the six vertices of an icosahedron none of which is a diametrically opposite to another. The icosahedron is inserted in the standard manner in a cube with edges of length 2 aligned with the basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$. The number ϕ is $(\sqrt{5} - 1)/2$. The symmetric rank six tensor

$$I^{(6)}_{\alpha\beta\gamma\delta\eta\mu} = \delta_{\alpha\beta}I^{(4)}_{\gamma\delta\mu\nu} + \delta_{\alpha\gamma}I^{(4)}_{\beta\delta\mu\nu} + \delta_{\alpha\delta}I^{(4)}_{\beta\gamma\mu\nu} + \delta_{\alpha\mu}I^{(4)}_{\beta\gamma\delta\nu} + \delta_{\alpha\nu}I^{(4)}_{\beta\gamma\delta\mu}$$

is spherically symmetric.

Under both icosahedral spin groups, the function $f^{(6)}$ is invariant under G, because the convolution $Y_{\alpha\beta\gamma\delta\eta\mu}Y_{\alpha\beta\gamma\varepsilon\zeta\xi}Y_{\delta\eta\mu\varepsilon\zeta\xi}$ does not vanish.

Note that the tetrahedral, cubic, and icosahedral tensors are presented in different form in the theory of nonchiral nematic liquid crystals (e.g., see [9]).

3. LIFSCHITZ INVARIANTS

A homogeneous state of spin ordering is unstable if its symmetry admits Lifschitz invariants, which have the form of convolutions of polynomials of a_α, b_β, and c_γ with the spatial derivatives $\partial_i a_\alpha$, $\partial_i b_\beta$, and $\partial_i c_\gamma$. Since the convolution of two basis vectors is either 0 or 1, these invariants reduce to sums of terms of the form $\tilde{a}_\alpha \partial_i \tilde{b}_a$, where $\tilde{\mathbf{a}}$ and $\tilde{\mathbf{b}}$ are basis vectors.

Under an infinitesimal spin-space rotation to an angle $\delta\boldsymbol{\theta}$, an arbitrary vector $\tilde{\mathbf{a}}$ changes by

$$\delta\tilde{\mathbf{a}} = [\delta\boldsymbol{\theta} \times \tilde{\mathbf{a}}]. \quad (15)$$

Therefore, the part of energy that is linear in gradients reduces to $L_{i\alpha}\theta_{i\alpha}$, where the matrix $L_{i\alpha}$ is a vector in the orbital-momentum space and a pseudovector in the spin space, and

$$\theta_{i\alpha} = \frac{\delta\theta_\alpha}{dx_i}. \quad (16)$$

By analogy with elasticity theory, $\theta_{i\alpha}$ should be called angular distortion (or orientational strain). The distortion $\theta_{i\alpha}$ is a pseudovector in the spin space, because it is obvious from (15) that $\delta\boldsymbol{\theta}$ is a spin-space pseudovector (invariant under time reversal).

The matrix $L_{i\alpha}$ is a characteristic of a spin system. Since it is independent of spatial gradients, it must have the symmetry of a homogeneous spin state. It is obvious that $L_{i\alpha}$ does not vanish only under finite spin symmetry groups and only in the cases when the antisymmetric part of the spin–spin correlation function is admissible. Note also that the functions $f^{(2-)}$ transform under the vector representation of G.

4. ENERGY OF ORIENTATIONAL STRAIN

In any chiral spin phase with weakly nonuniform orientation of order parameter, the exchange energy has the standard form

$$\frac{1}{2}\Lambda_{ij}\partial_i\mathbf{c}\partial_j\mathbf{c}, \tag{17}$$

where the tensor Λ is invariant under G.

In the general case, the exchange energy is a quadratic function of the angles of spin-space rotation of the form

$$\frac{1}{2}\Lambda_{ij\alpha\beta}\theta_{i\alpha}\theta_{j\beta}, \tag{18}$$

where the tensor Λ is symmetric in the orbital-momentum space and antisymmetric in the spin space. It is obvious that Λ is analogous to $L_{i\alpha}$ in that it is invariant under the exchange symmetry group of the state in question.

Under the spin tetrahedral, cubic, and icosahedral symmetry groups, $\Lambda_{ij\alpha\beta}$ reduces to the simple form

$$\Lambda_{ij}^{(0)}\delta_{\alpha\beta}, \tag{19}$$

where G. The corresponding contribution is obviously contained in the energy associated with inhomogeneity of any spin ordering.

The chiral groups $\mathbf{D}_n^s$, $\mathbf{D}_{nh}^s$, and $\mathbf{D}_{nd}^s$ with $n > 2$ admit an additional term

$$\Lambda_{ij}^{(1)}c_\alpha c_\beta, \tag{20}$$

where the tensor $\Lambda_{ij}^{(1)}$ is also invariant under G. This is also true for $\mathbf{C}_n^s$, $\mathbf{C}_{nv}^s$, $\mathbf{C}_{nh}^s$, and $\mathbf{S}_{2n}^s$ with $n > 2$ when the n- or $(n + 3)$-spin correlation function is determined by a single function of coordinates that transforms under a one-dimensional representation of G.

In the remaining nonchiral spin orderings, as well as in noncollinear magnets [2], a special analysis is required to determine Λ in each particular case.

5. RELATIVISTIC ANISOTROPY EFFECTS

Relativistic spin-orbit and magnetic dipole–dipole effects result in dependence of the energy of a crystal on the orientation of spin structures relative to the crystallographic axes.

By analogy with the theory of second-order phase transitions, the laws of transformation of the functions f^n under elements of G should be extended to the spin vector and tensors. Then the role of order parameter in antiferromagnets will be played by antiferromagnetic unit vectors $\mathbf{l}_i$ [2]. Only when magnetization $\mathbf{M}$ is admissible, it should be treated as an order parameter instead of the unit vector $\mathbf{M}/|\mathbf{M}|$, because magnetization is contained in Maxwell's equations. In phases with tensor spin structures, the role of order parameters is played by tensors with amplitudes constant in space (see above). In particular, when correlation function (6) does not vanish, the order parameter can be defined as the unit chirality ν, which changes sign both under time reversal and under certain crystal transformations (in accordance with the law of transformation of $f^{(3-)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$).

In normal magnets, the energy associated with anisotropy can be expanded in terms of magnetic-vector components, with the fine structure constant as an expansion parameter. In collinear magnets, the first term in the expansion, e.g., for a uniaxial crystal, can be written as $\beta^{[2]}l_z^2$. The anisotropic coefficient $\beta^{[2}$ scales with α^2 times the volume density of exchange energy. Hereinafter, the superscript in brackets is the exponent of a power of the fine structure constant. The next term in the expansion for a uniaxial crystal is $\beta^{[4]}l_z^4$, where the coefficient $\beta^{[4]}$ has the order of α^4. Generally, the expansion of the energy of a collinear magnet contains only even powers n of components of the magnetic vector, and the corresponding coefficients scale with α^n. The energy of anisotropy of noncollinear coplanar magnets (spin structures with two vectors) has an analogous form. For noncollinear noncoplanar magnets, the energy may contain spin-orbit terms of special form. In particular, for the so-called disordered antiferromagnet, the role of order parameter is played by three spin vectors S_x^α, S_y^β, and S_z^γ, where the subscripts indicate that they transform under a vector representation in the orbital-momentum space. In addition to the standard relativistic terms

$$\beta_1^{[2]}(S_i^i)^2 + \beta_2^{[2]}S_i^kS_k^i, \tag{21}$$

(see [2]), we should also include the additional term

$$\beta_3^{[2]} \nu S_i^i. \quad (22)$$

On a microscopic level, this term is due to exchange and spin-orbit interactions, and scales with α^2, as do the terms in (21). Note that this anomalous term is obviously comparable to the standard ones (21) near the point of second-order transition to the paramagnetic state, when all components of the order parameter vanish.

These considerations suggest a general rule for the relativistic terms in the expansion in terms of an arbitrary spin order parameter: relativistic invariants with even and odd number n of spin indices scale with α^n and α^{n+1}, respectively.

Since all spin order parameters enumerated above are such that spin convolutions of their powers cannot yield anisotropic or nonchiral tensors of lower rank, anisotropy effects, as well as the orientational effects of magnetic and electric fields and uniform deformations of the crystal, are fully manifested only in relatively high order terms in the expansions in terms of the fine structure constant and external perturbation amplitudes.

Consider two examples: A $\mathbf{T}_d^s$ tetrahedral tensor magnet and an $\mathbf{O}_h^s$ cubic spin nematic in the exchange crystal class $\mathbf{D}_{2h}$.

In both cases, the first terms of the expansion of the anisotropy energy have the form $\beta_1 S_{zzzz} + \beta_2 S_{xxxx} + \beta_3 S_{yyyy} + \beta_4 S_{xxyy} + \beta_5 S_{yyzz} + \beta_6 S_{zzxx}$, where the cubically symmetric tensor S is $O_{\alpha\beta\gamma\delta}$ in the latter case and $S_{\alpha\beta\gamma\delta} = T_{\alpha\beta\mu} T_{\mu\gamma\delta}$ in the former. Note that the anisotropy arises in fourth-order terms in the fine structure constant (rather than in second-order terms, as in crystal class $\mathbf{D}_{2h}$ magnets).

In external magnetic field, the anisotropy of spin ordering corresponds to exchange-coupling terms proportional to $S_{\alpha\beta\gamma\delta} H_\alpha H_\beta H_\gamma H_\delta$ and in mixed exchange–relativistic terms

$$\eta_1 S_{\alpha\beta xx} H_\alpha H_\beta + \eta_2 S_{\alpha\beta yy} H_\alpha H_\beta + \eta_3 S_{\alpha\beta zz} H_\alpha H_\beta.$$

SPELL: 1. ???, 2. Lifschitz, 3. Mel'nikovskii—?

In the tetrahedral case, when f^3 transforms under the identity representation, energy contains anomalous terms: an exchange one proportional to $T_{\alpha\beta\gamma} H_\alpha H_\beta H_\gamma$ and exchange–relativistic one of the form

$$\zeta_1 T_{\alpha xx} H_\alpha + \zeta_2 T_{\alpha yy} H_\alpha + \zeta_3 T_{\alpha zz} H_\alpha.$$

As shown in [10], terms of this type can arise for noncollinear noncoplanar magnets.

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