Orientational phase transitions in anisotropic rare-earth magnets at low temperatures

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Abstract. Orientational phase transitions are investigated within the Heisenberg model with single-site anisotropy. The temperature dependence of the cone angle is calculated within the spin-wave theory. The role of the quantum renormalizations of anisotropy constants is discussed. A comparison with the experimental data on the cone-plane orientational transition in holmium is performed.

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1. Introduction

The old problem of magnetic structure of rare-earth metals and their compounds is still a subject of experimental and theoretical investigations. These substances have complicated phase diagrams and demonstrate a number of orientational phase transitions. In particular, such transitions take place in the orthoferrites and practically important intermetallic compounds $\text{RCO}_5$ (R=Pr,Nd,Tb,Dy,Ho), see, e.g., Ref. [1]. Qualitative explanation of these transitions has been obtained many years ago within the Heisenberg model with inclusion of magnetic anisotropy [2]. In a number of systems, lattice (magnetoelastic) effects are important. The standard description is usually performed within mean-field approaches. However, quantitative comparison with experimental data requires a more detailed treatment.

Provided that the orientational transition temperature is low (in comparison with the magnetic ordering point), spin-wave theory is applicable [2]. In the simplest case of the second-order anisotropy the magnetization lies either along the easy axis or in the easy plane. Inclusion of higher-order anisotropy constants can lead to cone phases where magnetization makes the angle $\theta$ with the $z$-axis. The case $\theta = \pi/2$ was considered in Refs. [3, 4, 5, 6] where the temperature renormalization of anisotropy constants and the spin-wave spectrum in Tb and Dy within the standard spin-wave theory were calculated.

In the present paper we consider the cone phase with arbitrary $0 \leq \theta \leq \pi/2$. The situation here is analogous to that for the field-induced orientational phase transitions, e.g., in the transverse-field Ising model (see Ref.[7] and references therein). Unlike the latter model, one can expect that at low enough temperatures and small value of anisotropy the spin-wave theory is applicable for an arbitrary relation between anisotropy parameters, not only close to the orientational phase transition. Even for the second-order easy-plane anisotropy, the Holstein-Primakoff representation for spin operators used in Refs. [3, 4, 5] leads to so-called kinematical inconsistencies because of incorrect treating on-site kinematical relations. To avoid this difficulty, we use the technique of spin coherent states. Our approach is to some extent similar to the operator approach used in Ref. [4], but gives a possibility to treat more simply higher-order anisotropy constants, as well as to calculate higher-order terms of $1/S$-expansion.

The anisotropic Heisenberg model used is formulated in Sect 2. In Sect 3 we develop a special form of the $1/S$-expansion which gives a possibility to take into account exactly on-site kinematical relations. In Sect 4 we treat the cone-plane transition owing to the temperature dependence of the cone angle $\theta$ and discuss experimental data on the rare earth metals.
2. The model and mean-field approximation

We start from the Hamiltonian of the Heisenberg model with inclusion of single-site anisotropy

\[ H = -\frac{J}{2} \sum_{\langle ij \rangle} S_i S_j + B_2^0 \sum_i (O_2^0)_i + B_4^0 \sum_i (O_4^0)_i \]  

where \( J > 0 \) is the exchange parameter,

\[ O_2^0 = 3(S^z)^2 - S(S + 1) \]
\[ O_4^0 = 35(S^z)^4 - 30S(S + 1)(S^z)^2 + 25(S^z)^2 + 3S^2(S + 1)^2 - 6S(S + 1) \]

are the irreducible tensor operators of second and fourth order, \( B_{2m}^l \) are the corresponding anisotropy constants.

Up to unimportant constant we can rewrite the Hamiltonian (1) in the form

\[ H = -\frac{J}{2} \sum_{\langle ij \rangle} S_i S_j + D \sum_i (S_z^i)^2 + D' \sum_i (S_z^i)^4 \]  

where

\[ D = 3B_2^0 - [30S(S + 1) - 25]B_4^0 \]
\[ D' = 35B_4^0 \]

For \( D, D' > 0 \) spins of magnetic ions lie in the easy plane \( xy \), while for \( D, D' < 0 \) we have the easy axis \( z \). For \( D > 0, D' < 0 \) a first-order transition takes place between the easy plane (which is favored by second-order anisotropy) and easy axis (which is favoured by large \(|D'|\)). We consider only the case \( D < 0, D' > 0 \) where the cone phase occurs at intermediate values of \( D/(2D'S^2) \), so that spin orientation direction makes the angle \( \theta \) with the \( z \)-axis and the orientational phase transitions are of the second order. This is the case for Gd and also for Ho, Er in low-temperature phases.

In the phenomenological approach it is supposed (see, e.g., Refs. [1, 2])

\[ F = F_{\text{is}} + D(T)(S \cos \theta)^2 + D'(T)(S \cos \theta)^4 \]  

where \( F_{\text{is}} \) is the isotropic (\( \theta \)-independent) part of the free energy. Then we obtain by minimization of \( F \)

\[ \cos^2 \theta(T) = -\frac{D(T)}{2D'(T)S^2} \]  

so that at the point where \( D(T) = 0 \) the spins become directed in the \( xy \) plane while at \(|D(T)| \geq 2D'(T)S^2\) they are aligned along the \( z \)-axis. The temperature dependence of \( D(T) \) is supposed to have the form

\[ D(T) = 2D'S^2(T_1 - T)/(T_2 - T_1) \]
with $D'(T) > 0$. Thus at $T = T_1$ the transition from the easy-plane to cone structure takes place, while at $T = T_2$ the transition from the cone to easy-axis structure occurs. At the same time, Zener’s result for the temperature dependence of anisotropy constants in an axially symmetric state with $\theta = 0$ has the form

$$B_0^l(T) = B_0^l M^{(l+1)/2}$$

(8)

where $M = \langle \tilde{S}^z \rangle / S$ is the relative magnetization, and $D(T)$, $D'(T)$ are determined by the same relations (4) with $B_0^l \rightarrow B_0^l(T)$. As pointed in Refs. [3, 4, 5, 6], the temperature dependences of anisotropy constants have a more complicated form for the cone structures with $\theta > 0$ (in fact, only the case $\theta = \pi/2$ is discussed in Refs. [3, 4, 5, 6]).

A systematic way of calculating temperature dependences of anisotropy constants is the 1/$S$-expansion which is considered in the next section.

3. The 1/$S$-expansion of the partition function

The 1/$S$-expansion developed here is slightly different from the standard scheme of 1/$S$-expansion [3, 4, 6] since it gives a possibility to take into account exactly the kinematical relations between powers of spin operators on each site. We use the coherent state approach (see, e.g., Ref. [9]) to write down the partition function in the form

$$Z = \int D\pi \exp \left\{ iS \int_0^{\beta} d\tau (1 - \cos \theta) \frac{\partial \varphi}{\partial \tau} - \langle \pi | \mathcal{H} | \pi \rangle \right\}$$

(9)

where $\pi$ is the unit-length vector, $\vartheta$ and $\varphi$ are its polar and azimuthal angles respectively, $|\pi\rangle = \exp(i\vartheta S^y + i\varphi S^z) |S\rangle$ are the coherent states ($S^z | S\rangle = S | S\rangle$). To construct the 1/$S$-expansion we rotate the coordinate system around the $y$-axis through the angle $\theta$. The Hamiltonian (4) takes the form

$$\mathcal{H} = -\frac{J}{2} \sum_{(ij)} S_i S_j$$

$$+ \sum_i \sum_{l,m,m'=-l} B_i^m \frac{(l+m)!(l-|m'|)!}{(l-m)!(l+|m'|)!} A_i^m |d_{mm'}(\theta)(\tilde{O}[^{m'}|_{i})$$

where $d_{mm'}(\theta)$ are the Wigner matrices of the rotation group irreducible representation,

$$A_i^m = \frac{(l-m)!}{(l+[m] - 1)!!} \frac{1}{K_l^m}$$

(11)

$([m] = m$ for $m$ even and $[m] = m + 1$ for $m$ odd), for $l \leq 4$ we have $K_l^m = 1$, and the tilde sign here and hereafter is referred to the rotated coordinate system. Since the partition function (9) is invariant under rotation of the states $|\pi\rangle$, it is
convenient to use the coherent states defined in the same coordinate system, i.e.,
\[ |\tilde{\pi}\rangle = \exp(i\vartheta \tilde{S}^y + i\varphi \tilde{S}^z)|\tilde{S}\rangle = S|\tilde{S}\rangle. \]
The advantage of using the coherent states is the simple form of the averages of the tensor operators \(^{(2)}\) over \(|\tilde{\pi}\rangle\).

By direct calculation we obtain
\[ \langle \tilde{\pi}|O^m_l|\tilde{\pi}\rangle = S_l A^m_l P^m_l (\cos \vartheta) \cos m \varphi \] (12)
where \(P^m_l(x)\) are the associated Legendre polynomials, the factors \(S_l = S(S-1)/2\)...\([S-(l-1)/2]\) take into account properly the kinematical relations on each site. In particular, the second-order anisotropy term vanishes for \(S = 1/2\), and the fourth-order for \(S = 1/2, 1, 3/2\), as it should be (unlike the results of boson representations in Refs.\(^{[3, 5, 6]}\)).

Using (12) we obtain for the case \(B^m_l = B^0_l \delta_{m0}\) under consideration the result
\[ \langle \tilde{\pi}|H|\tilde{\pi}\rangle = -\frac{JS^2}{2} \sum_{ij} \tilde{\pi}_i \tilde{\pi}_j \] (13)
\[ + \sum_i \sum_{l=2,4} \sum_{m=-l}^l S_l B^0_l A^0_l (l-|m|)! P^{|m|}_l (\cos \theta) P^{|m|}_l (\cos \varphi) \cos m \varphi \]
Further calculations are performed in the same line as in Ref. \(^{[7]}\). Representing \(\cos \vartheta = \sqrt{1 - \sin^2 \vartheta}\) and expanding in \(\sin \vartheta\) we obtain the \(1/S\)-expansion of the partition function. It should be stressed that we retain the factors \(S_i\), as well as \(S\)-dependences in (4), non-expanded. By performing decouplings, terms of third order are reduced to linear ones, and terms of fourth order to quadratic ones. The requirement of absence of \(\sin \vartheta\)-linear terms leads to the result for the cone angle \(\theta\)
\[ \cos^2 \theta = \frac{3}{7} \left[ 1 - X + Y - \frac{B^0_2 S_2}{10 B^0_4 S_4} \left( 1 - \frac{7}{2S} + 6X + Y \right) \right] \] (14)
where
\[ X = \langle \pi^2_{x_i} \rangle \equiv \langle \sin^2 \vartheta \cos^2 \varphi \rangle = \sum_q \frac{J_0 - J_q}{2E_q} \frac{E_q}{\coth E_q/2T}, \]
\[ Y = \langle \pi^2_{y_i} \rangle \equiv \langle \sin^2 \vartheta \sin^2 \varphi \rangle = \sum_q \frac{J_0 - J_q + \Delta_0/S}{2E_q} \frac{E_q}{\coth E_q/2T}, \] (15)
and the “bare” magnon spectrum reads
\[ E_q = S \sqrt{(J_0 - J_q)(J_0 - J_q + \Delta_0/S)}, \]
\[ \Delta_0 = 2 \left[ 3B^0_2 S_2 \cos 2\theta - 10B^0_4 S_4 (28 \cos^4 \theta - 27 \cos^2 \theta + 3) \right], \]
\(\Delta_0\) being the energy gap. The corrections in (14) can be collected into powers in the same way as in Refs.\(^{[10, 11]}\) to obtain the correct description of thermodynamics at not too low temperatures. (In the presence of higher-order anisotropy this is essential since
the coefficients at \(X, Y\) increase as \(\sim l^2/2\) with anisotropy order.) Then we have

\[
\cos^2 \theta = \frac{3}{7} \frac{Z_X}{Z_Y} \left[ 1 - \frac{1}{10} \frac{B_0^2(T)S_2}{B_4^0(T)S_4} \right]
\]

where

\[
B_0^0(T) = Z_X^2 Z_Y B_2^0, \quad B_4^0(T) = Z_X Z_Y B_4^0
\]

are the temperature-renormalized anisotropy constants,

\[
Z_X = 1 + \frac{1}{2S} - X, \quad Z_Y = 1 + \frac{1}{2S} - Y
\]

The relations (18) extend the results of Refs. (3, 4, 5, 6) to the case where spins make a non-zero angle with the \(z\)-axis. The renormalized gap has the form

\[
\Delta = 6 \cos^2 \theta B_0^0 S_2 - 20 B_4^0 S_4 \left[ 3(1 - 7X) - 3 \cos^2 \theta \left( 9 - 56X - 7Y \right) \right]
\]

\[
+ 28 \cos^4 \theta \left( 1 - 6X - \tilde{Y} \right) \right] - 196 \sin^2 \theta \cos^2 \theta
\]

\[
\times \sum_{k,\omega_n} \left[ \frac{3B_2^0 S_2 (J_0 - J_k) - 10 B_4^0 (S_4/S) \Delta_0 \cos^2 \theta}{\omega_n^2 + S^2 (J_0 - J_k)(J_0 - J_k + \Delta_0/S) \right]^2
\]

(20)

\[
\Delta = 6 \cos^2 \theta B_0^0 S_2 - 20 B_4^0 S_4 \left[ 3(1 - 7X) - 3 \cos^2 \theta \left( 9 - 56X - 7Y \right) \right]
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+ 28 \cos^4 \theta \left( 1 - 6X - \tilde{Y} \right) \right] - 196 \sin^2 \theta \cos^2 \theta
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\[
\times \sum_{k,\omega_n} \left[ \frac{3B_2^0 S_2 (J_0 - J_k) - 10 B_4^0 (S_4/S) \Delta_0 \cos^2 \theta}{\omega_n^2 + S^2 (J_0 - J_k)(J_0 - J_k + \Delta_0/S) \right]^2
\]

(20)

where \(\tilde{X} = X - 1/(2S), \quad \tilde{Y} = Y - 1/(2S)\). After introducing the temperature-renormalized second- and fourth order anisotropy parameters \(D(T)\) and \(D'(T)\),

\[
D(T) S^2 = 3B_2^0(T) S_2 - 30 B_4^0(T) S_4,
\]

\[
D'(T) S^4 = 35 B_4^0(T) S_4 (Z_Y/Z_X),
\]

the expression for \(\cos \theta\) coincides with that of the phenomenological theory (3). Collecting again corrections in (20) into powers, we obtain for the renormalized gap in the notations (21) the expression

\[
\Delta = 2D(T) S^2 \cos 2\theta + 2D'(T) S^4 \cos^4 \theta + 6D'(T) S^4 \sin^2 \theta \cos^2 \theta
\]

\[
- 196 \sin^2 \theta \cos^2 \theta \sum_{k,\omega_n} \left[ \frac{3B_2^0 S_2 (J_0 - J_k) - 10 B_4^0 (S_4/S) \Delta_0 \cos^2 \theta}{\omega_n^2 + S^2 (J_0 - J_k)(J_0 - J_k + \Delta_0/S) \right]^2
\]

(22)

which also coincides with that obtained in the phenomenological theory except for the last term. Note that at \(\theta > 0\) the renormalizations (21) are present even at \(T = 0\), which should be taken into account when treating experimental data.

4. Orientational phase transitions

Now we can pass to description of possible orientational phase transitions. Consider first the case of a small enough constant \(B_4^0\) (or, equivalently, \(D'\)), so that \(\cos^2 \theta(0)\) is
close to unity. Then $\cos^2 \theta(T)$ increases with temperature and there occurs a transition to the easy-axis phase at the point determined by

$$\frac{3 Z_X}{7 Z_Y} \left[ 1 - \frac{B_2^0(T)}{10 B_4^0(T)} S_2 \right] = 1$$

(23)

In the opposite case of a large enough $B_4^0$, $\cos^2 \theta(0)$ is small, and $\cos^2 \theta(T)$ decreases with temperature, so that at the point where

$$B_2^0(T) S_2 = 10 B_4^0(T) S_4$$

(24)
a phase transition to the easy-plane phase occurs. Thus one can expect that there exists the critical value $\theta_c$: for $\theta_0 = \theta(0) < \theta_c$ we have a decrease of $\theta(T)$ with $T$ and the phase transition from cone to easy-axis phase, while for $\pi/2 > \theta_0 > \theta_c$ we have an increase of $\theta(T)$ with $T$ and the phase transition from cone to easy-plane phase. The numerical computations for the simple cubic lattice (see Fig.1) yield $\theta_c \simeq 50^\circ$. Fig.2 shows the corresponding temperature dependences of the anisotropy constants $D(T), D'(T)$. For simplicity, $J_q$ is taken for the simple cubic lattice.

The phase transitions described by Eqs. (23) and (24) are analogous to those in the phenomenological theory of Ref. [1] that occur at $D(T) = 0$ and $D(T) = -2D'(T)S^2$, respectively. However, unlike the phenomenological approach, microscopical consideration leads to either cone to easy-axis or cone to easy-plane transition with increasing temperature, depending on the zero-temperature value of $\theta$. At the same time, the transition from the easy-plane to easy-axis structure (through the intermediate cone phase) cannot be explained by purely magnetic renormalizations of anisotropy constants.

The result (14) gives the mean-field values of the critical exponents (e.g., $\beta = 1/2$) for both the ground-state and temperature orientational phase transitions. Unlike the systems discussed in Ref. [7], the system under consideration has the dynamical critical exponent $z = 2$ (i.e., single excitation mode with nearly quadratic dispersion is present). Thus the upper critical dimensionality for the ground-state QPT is $d^+_c = 4 - z = 2$. In this respect, the system is analogous to $XY$ model in the transverse magnetic field [12]. A characteristic feature of such systems is the mean-field behavior of critical exponents both above and below the critical dimensionality. For (hypothetical) systems with $d = 2$ logarithmic corrections to ground-state properties near QPT are present (see, e.g., Ref. [13]). At the same time, the upper critical dimensionality for the temperature phase transition is $d^+_c = 4$, and at $d < d^+_c$ the temperature-transition critical exponents differ from their mean-field values.

Now we discuss the experimental situation. In Gd (see, e.g., Refs. [2, 14]) the orientational phase transition from cone-phase to easy-axis phase is observed at $T_c = 240$K. The temperature dependence of the cone angle at $T < T_c$ (and also of magnetic anisotropy constants) is non-monotonous, unlike the results obtained in Sect
This complicated situation is connected with the absence of orbital momentum and smallness of anisotropy in gadolinium.

In holmium the low-temperature phase is conical spiral one, the angle of the cone changing from \( \approx 80^\circ \) to \( 90^\circ \) in the temperature interval \( 0 - 20 K \). The spiral angle makes up about \( 30^\circ \). Since the sixth-order anisotropy is important, we use the Hamiltonian

\[
\mathcal{H}_{\text{Ho}} = \mathcal{H} + B_0^6 \sum_i (O_6^0)_i + B_0^6 \sum_i (O_6^i)
\]  

(25)

The hcp lattice is not of a Bravais type. However, if we neglect the optical mode (which is possible at \( T \ll T_N = 133 K \)) one can put (see, e.g., Ref. [2])

\[
J_q = 2J \left[ \cos q_z + 2 \cos(q_x/2) \cos(\sqrt{3}q_y/2) \right] + 2J' \cos q_z \left[ \exp(iq_y/\sqrt{3}) + 2 \cos q_z \exp(-iq_y/2\sqrt{3}) \right]
\]  

(26)

The parameters of the Hamiltonian were taken from Ref. [13]: \( J = 0.65K \), \( J' = 0.6J \), \( B_2^0 = 0.35K \), \( B_4^0 = 0 \), \( B_6^0 = -1.1 \cdot 10^{-5}K \), \( B_6^0 = 1.07 \cdot 10^{-4}K \) (note that our value of \( B_2^0 \) includes also renormalization due to dipolar anisotropy). For simplicity, we restrict ourselves to a collinear magnetic structure (this is justified by that the spiral angle in the rare earths is small, especially at low temperatures). The calculations with the Hamiltonian (25) are completely analogous to those in the previous Section. Calculated dependence of the cone angle is compared with the result of the mean-field approximation and experimental data in Fig.3. One can see that our results improve somewhat those of the mean-field theory where the temperature dependence of the anisotropy constants is given by (8).

To conclude, we have formulated a consistent spin-wave approach to description of thermodynamic properties of anisotropic magnets at low temperatures. The renormalizations of the anisotropy constants and spin-wave spectrum for an arbitrary cone angle are calculated. This gives a possibility to describe the orientational phase transition between the cone and plane phases.

We are grateful to J.Jensen for comments concerning the experimental situation in holmium.

Figure captions

Fig.1. The theoretical temperature dependences of the cone angle \( \theta(T) \) for \( S = 7/2 \) and different values of second-order anisotropy: \( D/J = 0.004; 0.005; 0.006 \) from upper to lower curve. The value of \( D'/J \) is \( 3.7 \cdot 10^{-4} \).

Fig.2. The temperature dependences of the anisotropy constants \( D(T), D'(T) \) corresponding to Fig.1.

Fig.3. Calculated dependences of the cone angle in the mean-field approximation (short-dashed line) and renormalized spin-wave theory (RSWT, long-dashed line) as compared with experimental points for holmium (Refs. [2, 16]).
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\[ D(T) S^4 \quad \text{line of phase transition to plane} \]

\[ D(T) S^4 \quad \text{line of phase transition to axis} \]

\[ D, \theta_0 = 61^\circ \]

\[ D, \theta_0 = 45^\circ \]

\[ D, \theta_0 = 29^\circ \]
