A Heisenberg Ferromagnet With Biquadratic and Dipol-octupol Interactions

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A Heisenberg $S = 3/2$ ferromagnet with isotropic biquadratic exchange and dipole-octupol coupling is discussed. The conditions for the exact ferromagnetic ground state are derived. The thermodynamical behaviour in the molecular field approximation is discussed. Collective excitation spectra and the $1/z$ correction to the free energy are found.

I. Introduction

Hamiltonians with higher order couplings play an important role in the description of magnetic compounds. These couplings are important in such substances as: MnAs, UO_2, UP, TbSb, rare earth vanadates and phosphates.

The origin of such couplings may be of a different nature: superexchange interactions, magnetostriction, phonon exchange between ions, description in terms of the lowest-lying levels [1]. In some cases, the higher order couplings can be larger than the bilinear ones. Such terms have been taken into account in numerous papers [2], [3], [4], [5]. The main stress however is laid on quadrupolar biquadratic exchange interactions.

Tôru Moriya [6], extending the theory of superexchange interaction to include spin-orbit coupling, gets in the fourth order of perturbation theory an effective spin Hamiltonian in which, in addition to biquadratic exchange there appears a term linear in one spin variable and of the third order in the other. This term is as important as the biquadratic one. Such an interaction is not trivial for $S \geqq 3/2$.

The dipole-octupol interaction was introduced first by Bleaney in [7] for the description of the hyperfine structure of Γ_8 ions in cubic symmetry.

We will consider a more general, spin preserving form of the dipole-octupol interaction:

$$\sum_{ij} V_{ij}(S_i S_j)(S_j \bar{\zeta}_i)(S_j \bar{\zeta}_j). \tag{1.1}$$

$\bar{\zeta}$ is a constant vector. The last two factors in (1.1) are equivalent to $(S_j^z)^2$. As can be seen it is a dipole-octupol interaction of an easy axis type.

II. Ground State

The system of localized spins we assume to be described by the Hamiltonian

$$\begin{aligned} H = & -g u H^z \sum_i S_i^z - (1/2) \sum_{ij} I_1^{ij} S_i S_j \\ & - (1/2) \sum_{ij} I_2^{ij} (S_i S_j)^2 \qquad (2.1) \\ & - (1/2) \sum_{ij} I_3^{ij} (S_i S_j)(S_j \bar{\zeta})(S_j \zeta) = \sum_{ij} H_{ij}. \end{aligned}$$

The first term reflects the interaction of the system with the external magnetic field, the second and third are Heisenberg and biquadratic exchanges, respectively, the last is dipol-octupol coupling. We should note that the second and third terms in [1] have full rotational symmetry, so the ferromagnetic ground state requires $I_3 > 0$. In the other case easy plane ordering will be favorized.

Making no further assumptions about the magnitudes of the coupling parameters we shall try to extablish the relations between them through the conditions under which the system is ground state ferromagnetic. We shall follow the procedure given in [4].

Let us consider a pair of the nearest neighbours, since

$$S_i \cdot S_j = (1/2) S_\mathrm{T}(S_\mathrm{T} + 1) - S(S+1). \tag{2.2}$$

S_T = total spin of any pair of the nearest neighbours, S = one site spin. The expectation value u of $S_i \cdot S_j$ varies from $-S(S+1)$ to S^2 ($S_\mathrm{T} = 2S$).

Let us consider two situations:

$$\begin{aligned} & u > 0 \quad \text{then} \\ & u S(S+1) \geqq E[S_i S_j (S_j^z)^2] \geqq (1/4) u, \end{aligned} \tag{2.3}$$

and

$$\begin{aligned} & u < 0 \quad \text{then} \\ & u S(S+1) \leqq E[S_i S_j (S_j^z)^2] \leqq (1/4) u, \end{aligned} \tag{2.4}$$

where $E[x]$ is the expectation value of x.

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With these relations, the expectation value of H_{ij} can be written as

$$\begin{aligned} &-(1/2)\,I_1^{ij}u-(1/2)\,I_2^{ij}u^2\\ &-(1/2)\,I_3^{ij}u\,(1/4)\,. \end{aligned} \tag{2.5}$$

The ferromagnetic ground state minimizes the expectation value of (2.5) if:

$$\begin{aligned} &-\frac{1}{2S^2}\left(I_3^{ij}S(S+1)+I_1^{ij}\right)\leqq I_2^{ij};\\ &I_3^{ij}S(S+1)+I_1^{ij}\geqq 0\,. \end{aligned} \tag{2.6, 7}$$

If the conditions (2.6, 7) are fulfilled then the system is ground state ferromagnetic. The conditions (2.6) are sufficient but not necessary.

III. Thermodynamical Behaviour

In the following, we shall limit ourselves to the $S=3/2$ case in the ferromagnetic ground state. With the help of the generalized molecular field approximation (MFA), see [4], we calculate the free energy of the system.

We choose a trial density matrix ϱ_t, which satisfies the following conditions:

a) It is factorized.
b) It is translationally invariant.
c) It is invariant under rotations around the "Z" axis.

For details see [4].

Minimizing the free energy of the system in MFA with respect to all variational parameters, we get the form of t the free energy in MFA as

$$\begin{aligned} F_0=U-T\cdot S=\operatorname{Tr}\{\varrho_t\cdot H\}\\ -T\cdot S\{\varrho_t\}\,. \end{aligned} \tag{3.1}$$

With the trial density matrix ϱ_t fulfilling the assumptions a—c we get the expression for the free energy per spin

$$\begin{aligned} U=&-(1/2)\,(I_1-(1/2)\,I_2)\,m^2\\ &-(1/2)\,I_2((1/2)\,(15/4-x)^2+x^2)\\ &-(1/2)\,I_3\,m\,w\,, \end{aligned} \tag{3.2}$$

where

$$\begin{aligned} &I_\alpha=\sum_i I_\alpha^{ij}\,,\quad m=\langle S^z\rangle\,,\\ &x=\langle (S^z)^2\rangle=(1/3)\,S(S+1)+y\,,\\ &w=\langle (S^z)^3\rangle\,. \end{aligned} \tag{3.3}$$

The three order parameters m, x, w are only those which should be considered; the other ones can be expressed in MFA by those three. MFA analysis of a system with octupolar ordering, arising, however, from the other type of interaction, has been done by Sivardiere in [8].

The entropy may be written as

$$S_0=-\sum_{m_{si}}p_{m_{si}}\ln(p_{m_{si}})\,. \tag{3.4}$$

m_{si} are the eigenvalues of S^z, $p_{m_{si}}$ are the probabilities that the state with $S=m_{si}$ is occupied.

$$\begin{aligned} &m=\sum_{m_{si}}p_{m_{si}}m_{si}\,,\quad x=\sum_{m_{si}}p_{m_{si}}(m_{si})^2\,,\\ &w=\sum_{m_{si}}p_{m_{si}}(m_{si})^3\,,\quad \sum_{m_{si}}p_{m_{si}}=1\,. \end{aligned} \tag{3.5}$$

The $p_{m_{si}}$ are given by the following equations:

$$\begin{aligned} p_{3/2}=p_4&=(12x-3-2m+8w)/48\,, \quad (3.6)\\ p_{-3/2}=p_1&=(12x-3+2m-8w)/48\,,\\ p_{1/2}=p_2&=(27-12x-24w+54m)/48\,,\\ p_{-1/2}=p_3&=(27-12x+24w-54m)/48\,. \end{aligned}$$

Minimizing (3.1) with respect to m, x, w, we get

$$\begin{aligned} \partial F_0/\partial m=&-(I_1-(1/2)\,I_2)\,m-(1/2)\,I_3w\\ &+(1/24)\,T\ln(p_1/p_4)\\ &+(9/8)\,T\ln(p_2/p_3)=0\,,\\ \partial F_0/\partial x=&-(1/2)\,I_2(3x-15/4)\\ &+(1/4)\,T\ln(p_1p_4/p_2p_3)=0\,,\\ \partial F_0/\partial w=&-(1/2)\,I_3w+(1/6)\,T\ln(p_4/p_1)\\ &+(1/2)\,T\ln(p_3/p_2)=0\,. \end{aligned} \tag{3.7}$$

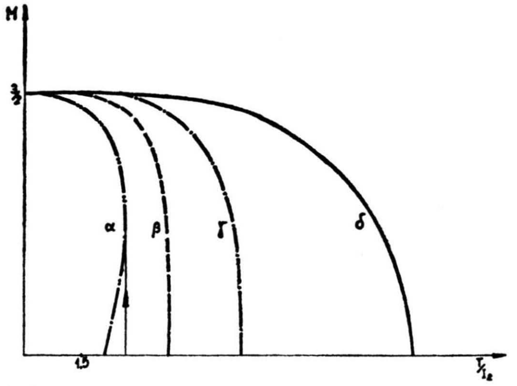
Any group (m, x, w) of solutions of (3.7) is associated with a different phase. The spin system at any temperature chooses the phase which has the lowest free energy.

In the region where only $x\neq 0$, a solution of (3.7) takes the form

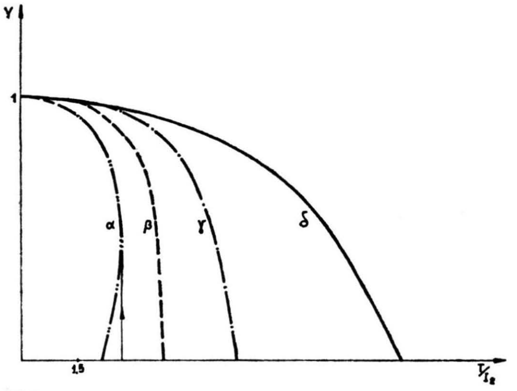
$$x_1=5/4\quad\text{and}\quad x_2=\tanh((3/2)\,I_2y)+5/4\,. \tag{3.8}$$

The solutions of (3.7) are plotted in Figures 1a—1c. From (3.7) it results that a phase with $m=0$ x, $w\neq 0$ cannot be relized, i.e. octupolar ordering appears at the Curie temperature. The disordered phase is stable for $T>\max\{T_1, T_2, T_3\}$, where

$$\begin{aligned} T_1&=(-B+(B^2+I_3^2A)^{1/2})/2A\,,\\ B&=-(82/18)\,I_3-(10/9)\,(2I_1-I_2)\,,\\ T_2&=(3/2)\,I_2\,,\quad T_3=(36/730)\,(2I_1-I_2)\,,\\ A&=16/9\,. \end{aligned} \tag{3.9}$$



1 a)



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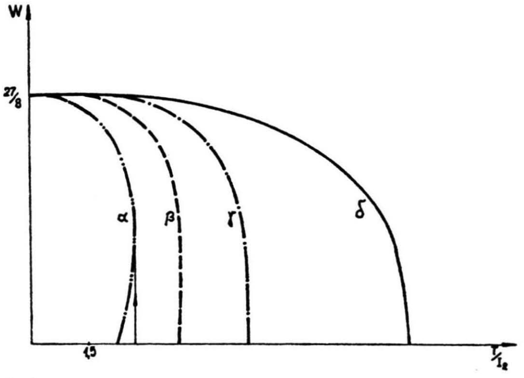

1 c)

Figs. 1a—1c. Temperature dependence of order the parameters m, y, w for various values of parameters $(I_1/I_2, I_3/I_2)$ α: (0.8, 0.8), β: (1, 2), γ: (2.5, 1), δ: (5, 1).

If $T_2 > T_1$, T_3, the half ordered phase ($m = w = 0$, $x \neq 5/4$) can appear. The phase diagrams for a few values of coupling parameters are plotted in Figure 1d. For $I_1/I_2 < 1.5$ quadrupolar ordering with $m = 0$ can be realized.

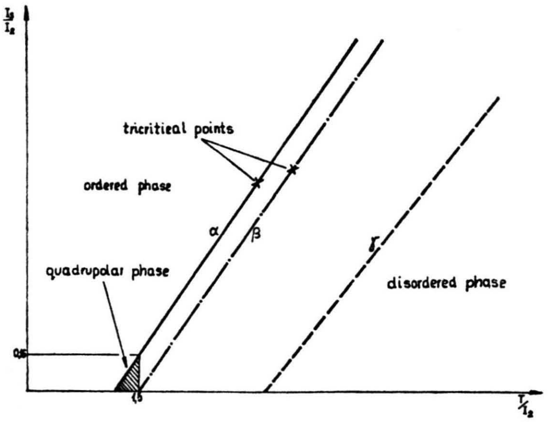

Fig. 1d. Phase diagrams in the I_3/I_2, T/I_2 plane for various values of the ratio I_1/I_2, $\alpha = 1.3$, $\beta = 1.5$, $\gamma = 3.0$.

IV. Elementary Excitations

Let us write the Hamiltonian (2.1) in the form

$$H = H_0 + H_{\text{int}} + E_0 , \tag{4.1}$$

where H_0 is the MFA Hamiltonian

$$\begin{aligned} H_0 = &- y_1 \sum_i S_i^z - y_2 \sum_i (S_i^z)^2 \\ &- y_3 \sum_i (S_i^z)^3 , \end{aligned} \tag{4.2}$$

$$\begin{aligned} &y_1 = g u H^z + (I_1 - (1/2) I_2) m + (1/2) I_3 w , \\ &y_2 = (3/2) I_2 y, y_3 = (1/2) I_3 m . \end{aligned} \tag{4.3}$$

H_{int} describes the effective interaction between ions. When we use the Racah operators, it takes the form

$$\begin{aligned} H_{\text{int}} = &- (1/4) \sum_{ij} (I_1^{ij} - I_2^{ij} \cdot 1/2)(S_i^z S_j^z + S_i^- S_j^+) \\ &- (1/8) \sum_{ij} I_2^{ij} (L_{21}^i L_{2-1}^j + L_{22}^i L_{2-2}^j) \\ &- (3/4) \sum_{ij} I_2^{ij} (S_i^z S_j^z)^2 \\ &- (1/8) \sum_{ij} I_3^{ij} (S_i^z (S_j^z)^3 + (S_i^z)^3 S_j^z) \\ &- (1/8) \sum_{ij} I_3^{ij} (S_i^+ L_{3-1}^j + S_i^- L_{31}^j) \\ &+ \text{c.c} = \sum_{ij\alpha\beta\gamma\delta} V_{ij}^{\alpha\beta\gamma\delta} L_{\alpha\beta}^i L_\gamma^j \delta , \end{aligned} \tag{4.4}$$

where

$$\begin{aligned} &\tilde{S}^z = S^z - \langle S^z \rangle , \quad (\tilde{S}^z)^2 = (S^z)^2 - \langle (S^z)^2 \rangle , \\ &(\tilde{S}^z)^3 = (S^z)^3 - \langle (S^z)^3 \rangle , \\ &L_{21} = S^+ S^z + S^z S^+ , \quad L_{22} = (S^+)^2 , \\ &L_{31} = (S^z)^2 S^+ + S^+ (S^z)^2 . \end{aligned} \tag{4.5}$$

Green's functions of the Racah operaters are defined as

$$K_0^{\alpha\beta\gamma\delta}(\omega) = \int_0^\beta e^{-i\omega\tau} \{\langle T L^i_{\alpha\beta} L^j_{\gamma\delta}(\tau)\rangle_0 - \langle L_{\alpha\beta}\rangle_0 \langle L_{\gamma\delta}\rangle_0\} \, d\tau \,, \tag{4.6}$$

where T is time ordering operator. With the help of these Greens functions we can write down the equation for energies of elementary excitations. For details see [9].

$$\det |\hat{1} - \hat{V}\hat{K}_0| = 0 \,. \tag{4.7}$$

$\hat{V}$ and $\hat{K}$ are given by (4.4) and (4.6), respectively. The elements of this matrix are numbered by multiindices $(\alpha\beta)$, $(\gamma\delta)$. The magnon solutions of (4.7) are equivalent to solutions of the equation

$$(i\omega)^3 + B(i\omega)^2 + C i\omega + D = 0 \tag{4.8}$$

with coefficients B, C, D given in Appendix I. The energies of quadrupolar $\Delta S^z = 2$ excitations are given by formulae

$$\varepsilon_{4,5} = (1/2)(A_1 \pm \sqrt{A_1^2 - 4A_2}) \,, \tag{4.9}$$

$$\begin{aligned} A_1 &= E_1 + E_2 - E_3 - E_4 \\ &\quad - (1/8)\, I_2(k)(\varphi_4 + \varphi_5) \,, \\ A_2 &= (E_1 - E_3)(E_2 - E_4) \\ &\quad - (1/8)\, I_2(k)[\varphi_4(E_1 - E_3) \\ &\quad + \varphi_5(E_2 - E_4)] \,, \end{aligned} \tag{4.10}$$

where the E_i are eigenvalues of (4.2). The φ_i are given in Appendix I. The solutions of (4.7) are plotted in Figure 2.

The $1/z$ (z-number of effectively interacting ions) correction to the free energy is given by the expression

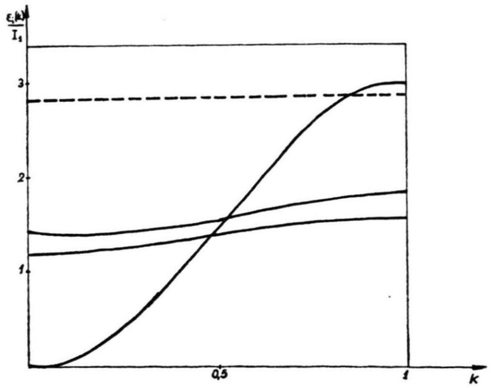

Fig. 2. Collective spectra for the sc lattice along the 001 direction calculated from (4.7) for $I_1/I_2 = 10$, $I_3/I_2 = 0.5$.

$$F = T/N \sum_k \ln \frac{\prod_{i=1}^{5} \exp(-\beta\varepsilon_i) - 1}{\prod_{i=1}^{5} \exp(-\beta E_i) - 1} + T/N \sum_k \ln(\det |1 - \bar{V}\bar{K}|) \,. \tag{4.11}$$

The E_i are given by (AI.2). $\bar{V}$ and $\bar{K}$ are 11×11 matrices with elements defined by (4.4) and (4.6), respectively.

Summary

The higher interactions bring about that multipolar order parameters must be considered. From (3.7) it appears that octupolar ordering appears together with the dipolar one. Quadrupolar ordering may appear before the dipolar one if the respective transition temperature is higher than the Curie temperature, which depends the on relations between the coupling parameters.

In the $1/z$ approximation the collective excitation spectra of ferromagnet are found, similary as the $1/z$ correction to the free energy. Three of the elementary excitations are transitions with $S^z = 1$, the other two are quadrons. The quadrupolar mode is almost of constant energy similary as in the $S = 1$ case (see e.g. [10]). The dependence of the energy of the spectra on the coupling parameters is presented in the Appendix.

Appendix I

Let's define first auxilary values

$$\begin{aligned} \varphi_i &= \frac{1}{Q_0}[\exp(-\beta E_i) - \exp(-\beta E_{i+1})] \,, \\ i &= 1, 2, 3 \,, \\ \varphi_i &= \frac{1}{Q_0}[\exp(-\beta E_i) - \exp(-\beta E_{i+2})] \,, \\ i &= 1, 2 \,, \end{aligned} \tag{AI.1}$$

$$Q_0 = \operatorname{Tr} e^{-\beta H_0} \,, \quad \tilde{E}_i = E_i - E_{i+1} \,, \quad i = 1, 2, 3 \,, \tag{AI.2}$$

$$\begin{aligned} \bar{x}_1 &= (1/4)[35/8\, I_3(k) - I_1(k) + (1/2)\, I_2(k)] \,, \\ \bar{x}_2 &= x_1 - I_3(k) \,, \\ \bar{x}_3 &= (1/8)[(I_1(k) - (1/8)\, I_2(k))\, I_3(k) - (I_1(k) \\ &\quad - (1/2)\, I_2(k))\, I_2(k)] \,, \\ \bar{x}_4 &= (1/8)\, I_2(k) \\ &\quad \cdot [(35/8)\, I_3(k) - (I_1(k) - (1/2)\, I_2(k)] \,, \\ x_5 &= (1/4)\, I_1(k)\, I_2(k)\, I_3(k) \,. \end{aligned} \tag{AI.3}$$

Using these values we can write the coefficients in (4.8). E_i are the eigenvalues of (4.2).

$$B = \tilde{E}_1 + \tilde{E}_2 + \tilde{E}_3 + \bar{x}_1 \varphi_1 (\tilde{E}_2 + \tilde{E}_3) + \bar{x}_2 \varphi_2 , \tag{AI.4}$$

$$C = \tilde{E}_1 \tilde{E}_2 + \tilde{E}_1 \tilde{E}_3 + \tilde{E}_2 \tilde{E}_3 + \bar{x}_1 \varphi_1 (\tilde{E}_2 + \tilde{E}_3) + \bar{x}_2 \varphi_2 (\tilde{E}_1 + \tilde{E}_3) + \bar{x}_3 \varphi_3 (\tilde{E}_1 + \tilde{E}_2) + \bar{x}_3 \varphi_1 \varphi_2 + \bar{x}_4 \varphi_1 \varphi_3 + \bar{x}_3 \varphi_2 \varphi_3 , \tag{AI.5}$$

$$D = \tilde{E}_1 \tilde{E}_2 \tilde{E}_3 + \bar{x}_1 \varphi_1 \tilde{E}_2 \tilde{E}_3 + \bar{x}_2 \varphi_2 \tilde{E}_1 \tilde{E}_3 + \bar{x}_1 \varphi_3 \tilde{E}_1 \tilde{E}_2 + \bar{x}_3 \varphi_2 \varphi_3 \tilde{E}_3 + \bar{x}_4 \varphi_2 \varphi_3 \tilde{E}_2 + \bar{x}_3 \varphi_2 \varphi_3 \tilde{E}_1 + \bar{x}_5 \varphi_1 \varphi_2 \varphi_3 . \tag{AI.6}$$

Acknowledgements

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