THEORY OF COLLINEAR METAMAGNETISM*

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Two-sublattice collinear Heisenberg metamagnets with uniaxial two-ion anisotropy are investigated by the renormalized high density expansion method. Formulas for both magnetization and the free energy are obtained, including Gaussian fluctuations of the self-consistent field as well as the scattering of spin waves on these fluctuations. When applied to the typical metamagnet $FeCl_2$ the theory yields the phase boundaries in better agreement with the experimental ones than other existing theories. Moreover, the isotherms of magnetization are obtained numerically for $FeCl_2$.

1. Introduction

It is well-known that a sufficiently strong external magnetic field destroys the antiferromagnetic ordering of a uniaxial, two-sublattice spin system. Provided the field is applied parallel to the preferred axis, there are two types of destruction of the antiferromagnetic structure (labelled A) [1–5]. One consists in the so called spin-flopping equivalent to the transition to the oblique phase (also termed the flop phase). The other is a direct transition to the phase P via abrupt reversal of opposite spins. The phase P, in which the physical difference between the sublattices vanishes, is commonly called "paramagnetic", but sometimes also "induced ferromagnetic" or even "ferromagnetic" [1, 3].

Antiferromagnets of the latter type i.e. exhibiting only the immediate transition from the phase A to P, are referred to as metamagnets [1, 6, 15].

In the present paper this term is used in a somewhat more limited sense, namely only to those antiferromagnets of which the magnetization (below certain temperature T_t) rises discontinuously with the field. The corresponding transitions line $H_{AP}(T)$ determines the boundary separating the regions A and P (equilibrium line). This boundary runs on up to the Nèel point T_N, but above T_t it corresponds to continuous transitions. Consequently, the temperature T_t has the significance of a point, where the order of the transi-

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tion [11–14] changes [11–25]. The possibility of the occurrence of such a point has been discussed for the first time by Landau [26] in 1937. The new interpretation proposed by Griffiths [27, 28] in 1970 elucidated the properties of T_t: it exhibits the tricriticality when the so called "staggered field" is taken into account as a third thermodynamical parameter (besides T and H). Thus, in the vicinity of T_t we are dealing with a critical region of a new kind (tricritical), a very interesting topic of study for the general theory of phase transitions. Let us mention other papers analysing tricritical phenomena in metamagnets: Hankey et al. [29, 30], Riedel [31, 32], Chang et al. [33, 34], Harbus et al. [35–37] and (using the Monte-Carlo method) Landau and Arora [38, 39] — all within the scaling hypothesis, Reatte [40] and Stauffer [41] within the droplet model and some other authors [42–45] applying the renormalization-group approach.

A satisfactory thermodynamical description of metamagnets has to comprise the phase diagram in the (T, H)-plane. In our case, the diagram consists of the single coexistence line $H_{AP}(T)$ accompanied along its first-order segment by two further lines: $H_A(T)$ and $H_P(T)$ which determine the range of metastable states i.e. the existence limits of the phases A and P respectively. The phase diagram has to cover the whole temperature interval up to T_N and the wide range of the external magnetic field up to the threshold field $H_s = H_{AP}(0)$ which can attain some hundreds of kilo-oersteds. That is the reason why all complete theoretical phase diagrams for metamagnets obtained up to now, have been calculated only in the molecular field approximation [18, 21–23, 46–50]. Unfortunately, each theory in this approximation gives results that are at most qualitatively correct [51, 21, 25]. Some better approximations are valid only within a narrow range of temperature; therefore, they have been used near T_N (high temperature expansion [36, 37], the Bethe-Peierls-Weiss method [19, 20] and the constant-coupling method [6, 15]) or near $T = 0$ (semiclassical method [52, 53]) only.

Thus, we see that the theory is still rather underdeveloped except for the immediate neighbourhood of the points: $T = 0$, $T = T_t$ and $T = T_N$.

The intention of the present paper is to develop the theory of Heisenberg metamagnets in such a way that the obtained phase diagram may be sufficiently accurate in the whole range of temperature. For this purpose we will use the high density expansion method, the most precise tool in the theory of magnetically ordered crystals. The renormalized version [64] of this method (see Section 3) yields good results in the whole range of temperature. Our numerical calculations, carried out to compare results with the experimental data, are based on the parameters corresponding to the best measured metamagnet, ferrous chloride $FeCl_2$, having a relatively simple magnetic structure [1, 21, 54—57]. Our work is restricted to the case of constant pressure, since variations of the latter do not affect the essential features of metamagnets [58–61].

2. The model adopted

As the well suited model of the $FeCl_2$-type of metamagnets we adopt that one in which the moments are strictly localized and coupled by the Heisenberg exchange interactions. To account for the crucial role of anisotropy in the metamagnetic phenomena [6, 52,

1], we provide the corresponding Hamiltonian with an Ising term (uniaxial two-ion anisotropy).

Consequently, the Hamiltonian for phase A, written in the two-sublattice notation, reads

$$\mathcal{H} = -\tfrac{1}{2}\sum_{f\neq f'}\sum_{\alpha\gamma} I_{11}^{\alpha\gamma}(f-f')S_f^{\alpha}S_{f'}^{\gamma} - \sum_{g\neq g'}\sum_{\alpha\gamma} I_{22}^{\alpha\gamma}(g-g')S_g^{\alpha}S_{g'}^{\gamma}$$
$$+ \sum_{f\neq g}\sum_{\alpha\gamma} I_{12}^{\alpha\gamma}(f-g)S_f^{\alpha}S_g^{\gamma} - \mu H(\sum_f S_f^z + \sum_g S_g^z) - \mu H_{st}(\sum_f S_f^z - \sum_g S_g^z), \tag{1}$$

where

$$\alpha\gamma = -+ \quad \text{or} \quad +- \quad \text{or} \quad zz \tag{2}$$

$$I_{11}^{\alpha\gamma} = I_{22}^{\alpha\gamma} = \begin{cases} \tfrac{1}{2}I_1 & \text{for } \alpha\gamma = -+, +- \\ I_1 + D_1 & \text{for } \alpha\gamma = zz \end{cases}$$
$$I_{12}^{\alpha\gamma} = I_{21}^{\alpha\gamma} = \begin{cases} \tfrac{1}{2}I_2 & \text{for } \alpha\gamma = -+, +- \\ I_2 + D_2 & \text{for } \alpha\gamma = zz \end{cases}. \tag{3}$$

The vectors f denote the positions of lattice sites in the first sublattice whereas g denote the same in the other. The symbol I_1 stands for the intra-sublattice exchange coupling parameter and is assumed to have the ferromagnetic sign, whereas the I_2 corresponds to the inter-sublattice coupling with the antiferromagnetic sign. The D_1 and D_2 are the coefficients of the two-ion anisotropy terms for the same sublattice and for different sublattices respectively. The symbol μ denotes the magnetic moment of one ion. Generally we also assume that the considered metamagnet sample is a bulk single-crystal being a single magnetic domain and great enough to neglect all surface effects.

To discuss the tricritical properties of the model adopted here, we have introduced the fictive[1] "staggered field" H_{st}, stabilizing the collinear antiferromagnetic ordering. It is defined as the derivative $H_{st} = -\partial G/\partial L$ of the thermodynamical potential G, where $L = \tfrac{1}{2}(M_1 - M_2)$ is the order parameter for the phase A (see [35]).

To construct a theory of sufficient generality and valid in a wide range of temperatures the thermodynamical perturbation method is used, as mentioned above. We have chosen that their modification, which (owing to the renormalization of the first three terms [64]) include[2] Gaussian fluctuations of the self-consistent field as well as the scattering of magnons of these fluctuations. The results obtained will be of better accuracy (in the whole range of temperature) than those of RPA II.

The precondition of all perturbation procedures is the proper decomposition of the Hamiltonian into "unperturbed" and "perturbed" summands:

$$\mathcal{H} = \mathcal{H}^0 + (\mathcal{H} - \mathcal{H}^0) = \mathcal{H}^0 + \mathcal{H}^1 \tag{4}$$

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[1] In some cases it is possible to ascribe a certain physical meaning to the "staggered field", see e.g. Blume [62, 63].

[2] In the present paper the upper index 0 always denotes the zero approximation, here identical with the molecular field approximation (MFA).

provided that $\mathcal{H}^0$ permits strict calculations and adequately describes the fundamental properties of the system. In the present paper we employ the decomposition introduced by Vaks et al. [65] and adapt it here to the two-sublattice systems.

$$\mathcal{H}^0 = \tfrac{1}{2} NB(\langle S_f^z\rangle^2 + \langle S_g^z\rangle^2) - NC\langle S_f^z\rangle\langle S_g^z\rangle - \frac{1}{\beta} y_1 \sum_f S_f^z - \frac{1}{\beta} y_2 \sum_g S_g^z, \tag{5}$$

$$\mathcal{H}^1 = -\tfrac{1}{2} \sum_{f\neq f'} \sum_{\alpha\gamma} I_{11}^{\alpha\gamma}(f-f')\delta S_f^\alpha \delta S_{f'}^\gamma - \tfrac{1}{2} \sum_{g\neq g'} \sum_{\alpha\gamma} I_{22}^{\alpha\gamma}(g-g')\delta S_g^\alpha \delta S_{g'}^\gamma + \sum_{f\neq g} \sum_{\alpha\gamma} I_{12}^{\alpha\gamma}(f-g)\delta S_f^\alpha \delta S_g^\gamma, \tag{6}$$

where the following symbols have been used

$$\delta S_f^\alpha = S_f^\alpha - \langle S_f^z\rangle \delta_{z,\alpha},$$

$$\delta S_g^\gamma = S_g^\gamma - \langle S_g^z\rangle \delta_{z,\gamma},$$

with

$$\delta_{z,\alpha} = \begin{cases} 1 & \text{if } \alpha = z \\ 0 & \text{if } \alpha \neq z, \end{cases}$$

and further

$$y_1 = \beta(\mu H + \mu H_{st} + B\langle S_f^z\rangle - C\langle S_g^z\rangle), \tag{7}$$

$$y_2 = \beta(\mu H - \mu H_{st} + B\langle S_g^z\rangle - C\langle S_f^z\rangle),$$

$$\beta = (k_B T)^{-1}, \quad NC = \sum_{f\neq g} I_{12}^{zz}, \quad NB = \sum_{f\neq f'} I_{11}^{zz}, \tag{8}$$

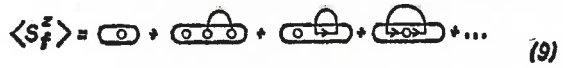
with N — the total number of ions in one sublattice. The $\langle S_f^z\rangle$ and $\langle S_g^z\rangle$ are two parameters yet to be determined from the minimization of the free energy.

3. The renormalized high density expansion

To obtain corrections of higher order we apply that variant of the thermodynamic perturbation approach which is known in the literature as the high density expansion method [66–71]. When used in the theory of strongly coupled magnetics, this method is based on the classification of Feynman diagrams with respect to powers of the parameter z^{-1} where z is the effective number of spins within the range of interactions of a given spin.

It is well-known that high density expansions become reasonable only when the deviations from the molecular field are not too large. For example, near the critical point

the fluctuations are large and consequently the expansion parameter z^{-1} cannot be treated more as a small quantity. To show this, let us calculate T_N. For this purpose we write the high density expansions for the sublattice magnetizations by having recourse to the diagrammatical notation introduced by Izyumov et al. [69–71]: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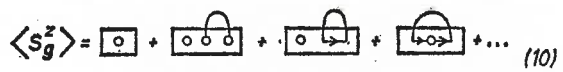

(10)

The value T_N we find from the condition: $\langle S_f^z \rangle = -\langle S_g^z \rangle \to 0$ when $H = 0$. Provided that $\langle S_f^z \rangle \ll 1$ we can rewrite Eq. (9) in the form

$$\langle S_f^z \rangle = \left[A(T) + \frac{1}{z} B(T) \right] \langle S_f^z \rangle + \frac{1}{z^2} [C(T) \ln \langle S_f^z \rangle + \ldots] + \ldots, \tag{11}$$

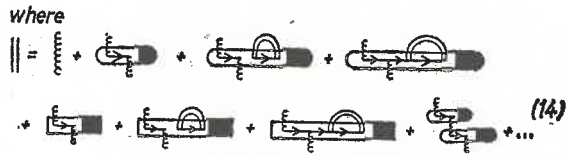
where A, B and C are some functions of temperature. It can be demonstrated that certain expressions in the z^{-2} term diverge logarithmically if $\langle S_f^z \rangle \to 0$ [65]. Thus, the Nèel temperature can be found only to an accuracy of the first approximation. Therefore, the high density expansion contains some terms which are divergent in the vicinity of the critical point although the expansion series ought to be convergent for physical reasons.

From the above we see that it is useless to take into account the further terms in the high density expansion when the temperature is near the critical points. There are, however, other ways to obtain more precise results, namely either by modifying the decomposition of the Hamiltonian (1) [72] or by appropriate renormalization of the first terms in Eqs. (9) and (10). The first way obviously improves only the results obtained by the zero order approximation [72]. The second one seems to be more efficient. Following the method of Ref. [64] we carry out the renormalization of diagrams to the first order of the expansions (9) and (10) in such a way that


(12)


, (13)

where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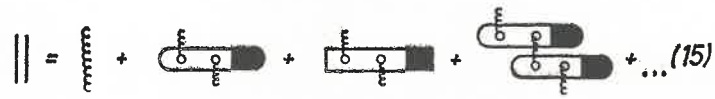
or


(15)

represents the renormalized transversal and longitudinal interaction lines, respectively. The blackened parts of the diagrams denote the infinite partial sums of the following diagrams:

(16)

(17)

Eqs. (12) and (13) have the following analytical form

$$\langle S_f^z\rangle = \bar{b}_1 + \frac{1}{N}\sum_k \left\{ n_1 - [1-\bar{b}_1' I_{11}^{+-}(k)] \left[\tfrac{1}{2}(n_+ + n_-) + \frac{(n_+ - n_-)(\varepsilon_1(k)-\varepsilon_2(k))}{2(\omega_+(k)-\omega_-(k))} \right] - \frac{(n_+ - n_-)\bar{b}_1'\bar{b}_2[I_{12}^{+-}(k)]^2}{\omega_+(k)-\omega_-(k)} \right\}, \tag{18}$$

$$\langle S_g^z\rangle = \bar{b}_2 + \frac{1}{N}\sum_k \left\{ n_2 - [1-\bar{b}_2' I_{22}^{+-}(k)] \left[\tfrac{1}{2}(n_+ + n_-) + \frac{(n_+ - n_-)(\varepsilon_1(k)-\varepsilon_2(k))}{2(\omega_+(k)-\omega_-(k))} \right] - \frac{(n_+ - n_-)\bar{b}_1\bar{b}_2'[I_{12}^{+-}(k)]^2}{\omega_+(k)-\omega_-(k)} \right\}, \tag{19}$$

where

$$n_{1,2} = (\exp y_{1,2} - 1)^{-1}, \tag{20}$$

$$n_\pm = [\exp(\beta\omega_\pm(k)) - 1]^{-1}, \tag{21}$$

$$\omega_\pm(k) = \tfrac{1}{2}\{\varepsilon_1(k)+\varepsilon_2(k) \pm \sqrt{[\varepsilon_1(k)-\varepsilon_2(k)]^2 + 4\langle S_f^z\rangle\langle S_g^z\rangle [I_{12}^{+-}(k)]^2}\}, \tag{22}$$

$$\varepsilon_{1,2}(k) = \beta^{\sigma_1} y_{1,2} - \langle S_{f,g}^z\rangle I_{11}^{-+}(k), \tag{23}$$

$$\bar{b}_{1,2}^{[n]} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-\tfrac{1}{2}\xi^2) b^{[n]}(y_{1,2} + \Delta y_{1,2}\xi) d\xi, \tag{24}$$

$$(\Delta y_{1,2})^2 = \frac{1}{N}\sum_k \frac{[1-\beta\bar{b}_{2,1}' I_{11}^{zz}(k)]\beta I_{11}^{zz}(k) + \beta^2 \bar{b}_{2,1}'[I_{12}^{zz}(k)]^2}{[1-\beta\bar{b}_1' I_{11}^{zz}(k)]\,[1-\beta\bar{b}_2' I_{11}^{zz}(k)] - \beta^2\bar{b}_1'\bar{b}_2'[I_{12}^{zz}(k)]^2} \tag{25}$$

and

$$b_{1,2}^{[n]} = \frac{d^n[SB_s(Sy_{1,2})]}{dy_{1,2}^n}, \tag{26}$$

where B_s is the Brillouin function.

We can also write in the above approximation the formula for the free energy of a metamagnetic:

$$F_A = \tfrac{1}{2} NB(\langle S_f^z\rangle^2 + \langle S_g^z\rangle^2) - NC\langle S_f^z\rangle \langle S_g^z\rangle - \frac{N}{\beta\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-\tfrac{1}{2}\xi^2) [\ln \phi_1(\xi)$$

$$+ \ln \phi_2(\xi)] d\xi + \tfrac{1}{2} \sum_k \ln |[1 - \beta \bar{b}_1' I_{11}^{zz}(k)] [1 - \beta \bar{b}_2' I_{11}^{zz}(k)]$$

$$- \beta^2 \bar{b}_1' \bar{b}_2' [I_{12}^{zz}(k)]^2| + \frac{N}{2\beta} [(\Delta y_1)^2 \bar{b}_1' + (\Delta y_2)^2 \bar{b}_2']$$

$$+ \frac{1}{\beta} \sum_k \{\ln |1 - \exp(-\beta\omega_+)| - \ln |1 - \exp(-y_1)|$$

$$+ \ln |1 - \exp(-\beta\omega_-)| - \ln |1 - \exp(-y_1)|\}, \qquad (27)$$

where

$$\phi_i(\xi) = \frac{\operatorname{sh}[(S+\frac{1}{2})(y_i + \xi \Delta y_i)]}{\operatorname{sh}[\frac{1}{2}(y_i + \xi \Delta y_i)]}.$$

Eqs. (12) and (13) involve those contributions to the sublattice magnetizations which result from the temperature-renormalized free spin waves, from the Gaussian fluctuations $\Delta y_{1,2}$ of the molecular field as well as from spin waves scattered on these fluctuations. Moreover, the above formulas have been derived without any assumptions as to the magnitude of Gaussian fluctuations. On these grounds one can presume tht Eqs. (18) and (19) describe more strictly the behaviour of the system in the critical region than Eqs. (9) and (10).

If the fluctuations are small, we can write

$$\bar{b}_{1,2} = b_{1,2} + \tfrac{1}{2} b_{1,2}'' \Delta y_{1,2} + \frac{1}{z^2}(0). \qquad (28)$$

In this case, Eqs. (18) and (19) go over into the formulas of RPA II i.e. into Eqs. (9) and (10).

Taking $H = 0$, $H_{st} = 0$, $y_1 = -y_2 \to 0$ and using Eq. (18) we find the implicit equation for the Nèel temperature T_N

$$\frac{k_B T_N}{B + C} = \left(\frac{\partial \langle S_f^z\rangle}{\partial y_1}\right)_{y_1 = 0}. \qquad (29)$$

4. The two-phase approach

To study the metamagnetic transitions we have to use the two-phase approach. In the case of metamagnets such an approach is even more consistent with the empirical facts than in the case of common antiferromagnets with an intermediate flop phase for which it

is often used [3, 73]. Then, we calculate separately both boundaries $H_A(T)$ and $H_P(T)$ which determine the range of existence of the antiferromagnetic and paramagnetic phases respectively. Moreover, from the equality of the free energies we find for $T < T_t$ the coexistence line $H_{AP}(T)$ (being the boundary of stability for both phases i.e. the thermodynamical equilibrium line). The phase P is defined as the one in which the difference between the sublattices vanishes. The free energy in the phase P calculated in the same approximation as for phase A can be expressed as ($H_{st} = 0$)

$$F_P = N(B-C)\langle S^z\rangle^2 - \frac{2N}{\beta\sqrt{2\pi}}\int_{-\infty}^{\infty}\exp\left(-\tfrac{1}{2}\xi\right)^2 \ln\phi(\xi)d\xi$$

$$+\sum_k \ln|1-\beta\bar{b}'(y)\,[I_{11}^{zz}(k)-I_{12}^{zz}(k)]| + \frac{N}{\beta}\,\bar{b}'(y)\,(\Delta y)^2$$

$$+\frac{2}{\beta}\sum_k \{\ln|1-\exp(-\beta\omega(k))| - \ln|1-\exp(-y)|\}, \tag{30}$$

where the magnetization $\langle S^z\rangle$ is described by the formula:

$$\langle S^z\rangle = \bar{b}(y) + \frac{1}{N}\sum_k \{n-[1-\bar{b}'(y)\,(I_{11}^{+-}(k)-I_{12}^{+-}(k))]n_k\} \tag{31}$$

with

$$n = (\exp y - 1)^{-1}, \quad n_k = [\exp(\beta\omega(k))-1]^{-1}, \tag{32}$$

$$\omega(k) = \beta^{-1}y - \langle S^z\rangle\,(I_{11}^{-+}(k)-I_{12}^{-+}(k)), \tag{33}$$

$$\bar{b}^{[n]}(y) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\exp\left(-\tfrac{1}{2}\xi^2\right)b^{[n]}(y+\xi\Delta y)d\xi \tag{34}$$

and

$$y = \beta[\mu H + (B-C)\langle S^z\rangle] \tag{35}$$

and the squared average of the molecular field fluctuations is

$$(\Delta y)^2 = \frac{1}{N}\sum_k \frac{\beta(I_{11}^{zz}(k)-I_{12}^{zz}(k))}{1-\beta\bar{b}'(y)\,(I_{11}^{zz}(k)-I_{12}^{zz}(k))}. \tag{36}$$

5. Some analytical results

The essential properties of metamagnets may be represented by the phase diagram in the plane of the parameters (T, H). To determine the main elements of this diagram we take, at first, the staggered field to be equal to zero. To obtain the coexistence line

$H_{AP}(T)$ for $T < T_t$ we require the free energies Eqs. (27) and (30) to be equal. In particular, for $T = 0$ the following relations are valid:

$$\bar{b}_1 = -\bar{b}_2 = b(y) = S,$$
$$\bar{b}'_1 = \bar{b}'_2 = \bar{b}'(y) = 0. \tag{37}$$

Thus we obtain the following expression for the threshold field:

$$H_s = H_s^0 + \frac{1}{2\mu N} \sum_k (\Delta k)^{-1} \{I_{11}^{+-}(k)\,[B+C] - [I_{11}^{+-}(k)]^2 + [I_{12}^{+-}(k)]^2\}, \tag{38}$$

with

$$H_s^0 = H_{AP}^0(T = 0) = \frac{1}{\mu} CS,$$
$$\Delta k = [(B+C-I_{11}^{+-}(k))^2 - (I_{12}^{-+}(k))^2]^{1/2}. \tag{39}$$

On the basis of Eq. (38) we state that the zero fluctuation cause the threshold field (i.e. the coordinate of the phase coexistence point for $T = 0$) to increase in comparison with the MFA. The boundaries of existence H_A and H_P are determined from the conditions of susceptibility divergence for $T \leqslant T_t$ and $H_{st} = 0$

$$\lim_{H \to H_A(T)} \frac{\partial}{\partial H} (\langle S_f^z \rangle + \langle S_g^z \rangle) = \infty \tag{40}$$

provided that $H < H_A(T)$ and

$$\lim_{H \to H_P(T)} \frac{\partial \langle S^z \rangle}{\partial H} = \infty \tag{41}$$

provided $H > H_P(T)$. Note that the quite analogous conditions using staggered susceptibility

$$\lim_{\substack{H \to H_A(T) \\ H_{st} \to 0}} \frac{\partial}{\partial H_{st}} (\langle S_f^z \rangle - \langle S_g^z \rangle) = \infty \tag{42}$$

provided $H < H_A(T)$, may be used alternatively to calculate the A–P boundary for $T > T_t$ where $H_{AP} = H_A = H_P$.

Ziman [74] has proved that the susceptibility becomes divergent when the energy of the lowest excitation (spin wave) vanishes. The same holds in the case of the renormalized energies of spin waves, depending on temperature [3, 73]. Thus in practice the conditions Eqs. (40–42) can be replaced by:

$$\omega_-(k_0, H_A(T)) = 0, \tag{43}$$
$$\omega(k'_0, H_P(T)) = 0, \tag{44}$$

$$\left(\frac{\partial \omega_-}{\partial k}\right)_{k=k_0} = 0, \quad \left(\frac{\partial^2 \omega_-}{\partial k^2}\right)_{k=k_0} > 0, \tag{45a}$$

$$\left(\frac{\partial \omega}{\partial k}\right)_{k=k_0'} = 0, \quad \left(\frac{\partial^2 \omega}{\partial k^2}\right)_{k=k_0'} > 0. \tag{45b}$$

Calculating k_0 and k_0' from Eqs. (45) and inserting them into Eqs. (43), (44) we obtain the boundaries of existence of the phases A and P:

$$H_A(T) = \frac{1}{2\mu}\{(C-d_1)(\langle S_f^z\rangle + \langle S_g^z\rangle)$$

$$+\sqrt{(C+d_1)^2(\langle S_f^z\rangle + \langle S_g^z\rangle)^2 + 4\langle S_f^z\rangle \langle S_g^z\rangle (C-d_2)^2}\} \tag{46}$$

and

$$H_P(T) = \frac{\langle S^z\rangle}{\mu}(2C-d_1-d_2), \tag{47}$$

where

$$Nd_1 = 2\sum_{f\neq f'} D_1(f-f'), \tag{48}$$

$$Nd_2 = 2\sum_{f\neq g} D_2(f-g). \tag{49}$$

For $T = 0$, equations (46) and (47) become:

$$H_A(T=0) = \frac{S}{\mu}\left\{\sqrt{(C+d_1)^2-(C-d_2)^2}\right.$$

$$\left. - \frac{(B-C)(B-d_1)}{\sqrt{(C+d_1)^2-(C-d_2)^2}}\left[\frac{1}{N}\sum_k (\Delta k)^{-1}(B+C-I_{11}^{+-}(k)-1)\right]\right\}, \tag{50}$$

$$H_P(T=0) = \frac{S}{\mu}(2C-d_1-d_2). \tag{51}$$

The zero-temperature equations given above are identical to those derived earlier by Turov and Irkhin [4], by minimizing the antiferromagnetic energy for $T = 0$.

The boundaries of existence of the phases A and P define the maximum range of the hysteresis loop ΔH. The observed breadth of the hysteresis loop, however, depends strongly on the rate of magnetic field variation, on the perfection of the sample and on some other factors [21]. When measuring the breadth of the hysteresis loop we are never sure if this is the maximum breadth because the measurements are performed in non-equilibrium states [75]. The obtained boundaries of existence of the phases A and P allow us to determine T_t and, moreover, to find a criterion of occurrence for the metamagnetism in the free

spin wave approximation i.e. for $T = 0$. Using the notion of the threshold field H_s this criterion can be formulated as follows: an antiferromagnetic is a metamagnetic when

$$H_P(T = 0) < H_s. \tag{52}$$

Note that the analogous relation for the phase A

$$H_A(T = 0) > H_s \tag{53}$$

is equivalent to the inequality (52). On inserting into Eq. (52) the explicit expressions for H_s and H_P we obtain

$$C \leqslant d_1 + d_2 + \frac{1}{2NS} \sum_k \Delta_k^{-1} \{ I_{11}^{+-}(k) (B + C - I_{11}^{+-}(k)) + [I_{12}^{+-}(k)]^2 \}. \tag{54}$$

If we neglect the intrasublattice coefficient d_1 as well as the term resulting from the zero vibrations, we get

$$C \leqslant d_2, \tag{55}$$

which is indentical to the well known criterion of Nèel [1, 52]. As can be seen, the generalized criterion (54) permits the occurrence of metamagnetism for slightly lower anisotropy than that predicted by Nèel [52].

The maximum breadth of a hysteresis loop is obviously given by

$$\Delta H(T) = H_A(T) - H_P(T). \tag{56}$$

Taking into consideration that at the tricritical point (T_t, H_t) the order of the transition changes, we obtain the following condition (for $T < T_t$)

$$\lim_{T \to T_t} \Delta H(T) = 0, \tag{57}$$

which can be used to determine the coordinates (T_t, H_t) after substituting (46) and (47). Another way to find H_t and T_t is to require the magnetization jump on the phase coexistence line to vanish

$$\lim_{T \to T_t} \Delta M = 0 \tag{58}$$

provided $T < T_t$, where

$$\Delta M = \langle S^z \rangle - \tfrac{1}{2} (\langle S_f^z \rangle + \langle S_g^z \rangle).$$

We now have to determine the further part of the coexistence line $H_{AP}(T)$ above the tricritical point. In practice one cannot use the equilibrium condition

$$F_A(T, H_{AP}(T)) = F_P(T, H_{AP}(T)) \tag{59}$$

because in this case the two free energies approach each other tangentially, so that the precise determination of their common point is impossible. Taking this into account we have

to find the required line from the condition that the difference between sublattices vanishes at the boundary of the P state.

$$\lim_{H \to H_{AP}} (\langle S_f^z \rangle - \langle S_g^z \rangle) = 0 \tag{60}$$

provided that $T > T_t$ and $H < H_{AP}(T)$.

6. *Magnetization and phase diagram*

To calculate other characteristics, namely the free energy and isotherms of magnetization, we have to apply numerical methods. For this purpose we specify the values of the spin and exchange parameter, choosing $C/B = 6.7$ for $S = 1/2$ which corresponds [21] to the data for $FeCl_2$ in the molecular field approximation. The choice of the anisotropy constants $d_1/C = 1.1$ and $d_2/C = 0.1$ fulfills criterion (54) and agrees roughly with the breadth of the hysteresis loop obtained by means of formula (56) from the results of Jacobs and Lawrence [21].

Anhydrous ferrous chloride $FeCl_2$, the best examined metamagnet, crystallizes in the rhombohedral system (lattice of the $CdCl_2$ type). Below $T_N = 23.5$ K the spins point

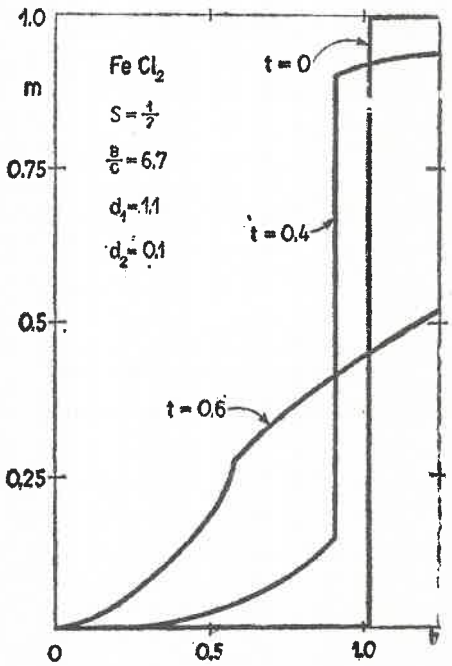


Fig. 1

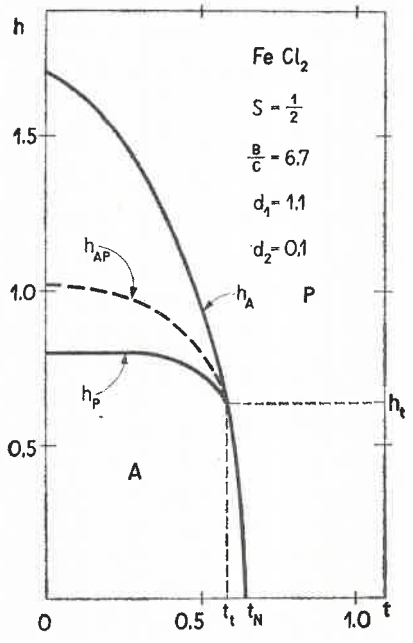


Fig. 2

Fig. 1. Isotherms of magnetization $m(h)$ plotted for $t = 0, 0.4, 0.6$. For the phase A, $m = \langle S_f^z \rangle + \langle S_g^z \rangle$; for the phase P, $m = 2\langle S^z \rangle$. Here $h = H/H_s^0$ and $t = T/T_N^0$, the upper index 0 denoting the zero approximation

Fig. 2. The phase diagram of $FeCl_2$ in the plane (t, h), obtained from the renormalized high-density expansion method

alternately parallel and antiparallel to the trigonal axis, constituting ferromagnetic planes perpendicular to this axis. The first stage of the numerical calculations was to calculate the magnetizations $\langle S_f^z\rangle^0$, $\langle S_g^z\rangle^0$ and $\langle S^z\rangle^0$, and the free energies F_A^0 and F_P^0 in the zero approximation as functions of the magnetic field and temperature. Next, we tried to solve the set of two complicated equations (18) and (19) describing the magnetization of the sublattices. They are, indeed, formally solvable without approximation, but in practice this requires an excessively long time on a digital computer. Beyond the vicinity of the critical points the deviations from the molecular field are small; therefore, one restricts the iterative procedure to the first step. At first we calculated for various temperatures the free energies from Eqs. (27) and (30) as functions of the magnetic field.

Two important values were found without any simplifications: the Nèel point T_N from Eq. (29) and the threshold field H_s from Eq. (38).

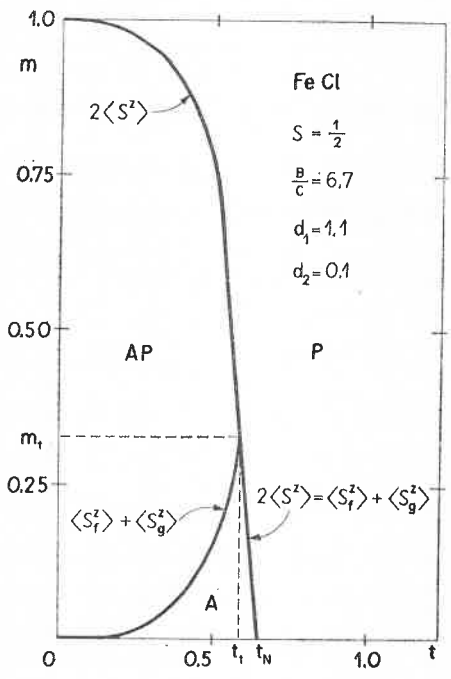


Fig. 3

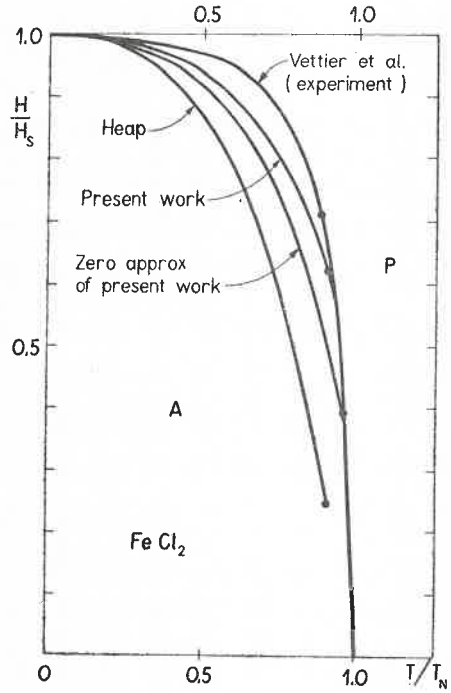


Fig. 4

Fig. 3. The phase diagram of $FeCl_2$ constructed in variables t and m (m taken along the line $h_{AP}(t)$). Symbol AP denotes the coexistence area

Fig. 4. Comparison of 4 phase diagrams for $FeCl_2$: *1* — Heap's result BPW [20], *2* — the present result H_{AP}^0/H_s^0, *3* — the present result H_{AP}/H_s, *4* — the experimental diagram by Vettier et al. [61]. Each result is reduced to its own H_s and T_N. The dots correspond to the tricritical points

Magnetization processes for several temperatures are shown in Fig. 1. The coexistence line of the phases A and P was determined from the conditions (59) and (60). Next, the existence boundary $H_P(T)$ was obtained from Eq. (47). Also, the tricritical point was found from Eq. (57).

The coexistence line is shown in Fig. 2, as well as the reduced boundaries of existence: $H_P(T)/H_s^0$ for the phase P and $H_A(T)/H_s^0$ for the phase A. In Fig. 3 the same phase diagram is plotted in other variables, namely magnetization and temperature. In Fig. 4, using a unified scale, we compare the experimental phase boundary for $FeCl_2$ with those obtained from different theories. The following results are shown: *1* and *2* — lines obtained from the zero and first approximation of this work, *3* — Heap's line [20] calculated by the Bethe-Peierls--Weiss (BPW) method, *4* — the line of Vettier et al. [61] obtained experimentally. The tricritical points are indicated in all 4 cases.

7. Conclusions

In order to describe the metamagnets more precisely than previous researchers using only effective field theories, we searched for a method which would be sufficiently exact in a wide regime of T and H. We have chosen the high density expansion and we improved its poor accuracy in the critical regions in the present work by renormalizing the graphs for the sublattice magnetization. The modified method, even in the first order step, has proved to yield a theory of metamagnetism more precise than the mean field approximation and even than the random phase approximation.

The (T, H) phase diagram obtained by this method shows, already in the zero approximation, a better agreement with the experimental boundaries than e.g. Heap's result [20]. Excellent evidence of the quality of our theory is provided by Fig. 4, where several stability boundaries are compared. Even more illustrative is the following confrontation of the reduced coordinates of the tricritical point:

	T_t/T_N	H_t/H_s
1. Heap [20] BPW method	0.92	0.25
2. The present work — zero approx.	0.95	0.39
3. The present work	0.91	0.62
4. Vettier et al. [61] experiment	0.89	0.72
5. Jacobs and Lawrence [21] experiment	0.87	0.74

Unfortunately, we are unable to compare the magnetization isotherms in Fig. 1 with experimental curves since all those available ones are uncorrected for demagnetization.

The criterion (54) determining the appearance of metamagnetism is slightly generalized with regard to the Nèel condition [1, 52] as it contains both uniaxial two-ion anisotropy constants: d_1 (intrasublattice) and d_2 (intersublattice) each being multiplied by the corresponding numbers of nearest neighbours. Contrary to Nèel's result, the intersublattice anisotropy d_1 is not necessary for the appearance of metamagnetism if only $d_2 \neq 0$. The third term in Eq. (54) resulting from the zero excitations contributes rather little to the quantitative role of the inequality derived.

The method presented in this paper seems to be efficient also in other problems of metamagnetism, such as pressure effects, the role of the single-ion anisotropy, and tricritical behaviour. Another example of its application is the $FeBr_2$-type of metamagnets showing unusual phase diagrams. For this case calculations by the present authors using the same method are now in an advanced stage.

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