

FOUR-ION ANISOTROPY AS SOURCE OF SPONTANEOUS METAMAGNETISM*

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A new mechanism leading to spontaneous metamagnetism is proposed in the form of a model Hamiltonian involving the four-ion anisotropic term besides the common Heisenberg coupling. Calculations carried out in the molecular field approximation lead to an unambiguously metamagnetic nature (like Mn_3GaC) of the magnetization and phase diagram obtained from this model. Moreover, a simplified form of the model Hamiltonian is presented, easier in calculations but nonetheless exhibiting typical metamagnetic behaviour. Finally, a substitute operator with temperature dependent coefficient is proposed instead of the anisotropic term. The resulting pseudo-Hamiltonian appears to be a very efficient tool for preliminary thermodynamical calculations, giving also good agreement with the typical features of the temperature-induced metamagnetism.

1. Introduction

The term "metamagnetism" is employed for two distinct categories of sharp phase changes between antiferromagnetic and ferromagnetic (or the appreciably saturated paramagnetic) ordering. The first category comprises the field-induced transitions observed in considerably anisotropic collinear antiferromagnets. In 1939, this phenomenon was named "metamagnetism" by Becquerel [1]. In 1956, the same name has been used by Néel [2, 3] to denote another category of magnetic changes. These transitions occur in the absence of an external magnetic field when the temperature varies. To distinguish the two categories, we introduce the name "spontaneous metamagnetism" for the latter one.

Let us label the collinear antiferromagnetic phase as A and the ferromagnetic one as F. In this paper, we shall be dealing with a two-sublattice spin system exhibiting the $A \rightarrow F$ transition with increasing temperature, as observed in Mn_3GaC or in $FeRh$. The old hypothesis hitherto put forward to explain this phenomenon [7] is that of Kittel [6],

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assuming the inversion of inter-sublattice exchange interactions. However, there exists yet another theory of spontaneous metamagnetism due to Néel (see [2] or [3]) in 1956, but it leads to $F \rightarrow A$ transitions only and is thus unable to explain the phase changes which are the topic of our study.

The purpose of the present paper is to show that spontaneous metamagnetism can be described completely without applying the inversion hypothesis. Our alternative theory assumes a model Hamiltonian, involving a uniaxial four-ions anisotropy term besides the common Heisenberg coupling. Hereafter, we shall demonstrate that our model shows all the features of spontaneous metamagnetism known from experiment.

In addition to the $(H-T)$ phase diagram and other characteristics of a metamagnet, we obtain some further results. Among others, the proposed model enables one to elucidate Smart's [4] supposition of the linear dependence of the Weiss coefficient on temperature. It turns out to be a particular approximation of our model. Moreover, we shall derive a simplified model, very useful for the rapid investigation of spontaneous metamagnetism. As a special case, a pseudo-Hamiltonian containing the temperature-dependent coefficients will be proposed, extremely convenient for the thermodynamical treatment of magnetic phase transitions.

2. The model Hamiltonian

For the two-sublattice spin system we propose a Hamiltonian consisting of the following two terms:

$$\mathcal{H} = \mathcal{H}' + \mathcal{H}'', \quad (1)$$

\mathcal{H}' being an isotropic Heisenberg Hamiltonian with Zeeman term added (the applied field H being aligned along the z -axis),

$$\mathcal{H}' = -\frac{1}{2} \sum_{f,f'}^* J_{ff'} \mathbf{S}_f \cdot \mathbf{S}_{f'} - \frac{1}{2} \sum_{g,g'}^* J_{gg'} \mathbf{S}_g \cdot \mathbf{S}_{g'} - \sum_{f,g}^* J_{fg} \mathbf{S}_f \cdot \mathbf{S}_g - g\mu_B H \left(\sum_f S_f^z + \sum_g S_g^z \right) \quad (2)$$

and \mathcal{H}'' — the anisotropic term privileging the z -axis:

$$\mathcal{H}'' = \frac{1}{2} \sum_{f,g,f',g''}^{**} D_{fgf'g''} S_f^z S_g^z S_{f'}^z S_{g''}^z + \frac{1}{2} \sum_{g,f,g',g''}^{**} D_{gfg'g''} S_g^z S_f^z S_{g'}^z S_{g''}^z. \quad (3)$$

Here, the symbols f, f' and f'' denote the position vectors of sites belonging to the sublattice I, whereas g, g' and g'' denote the same within the sublattice II. Summation \sum^* runs, as usual, over all pairs of sites. Summation \sum^{**} is taken only over such sets of four sites, where three sites are nearest neighbours of the fourth one.

The Heisenberg part is assumed to involve ferromagnetic coupling only. Such Hamiltonian is not by itself able to stabilize the antiferromagnetic state in any temperature interval, not even at absolute zero.

The term given by Eq. (3) expresses a four-ions type of anisotropic coupling, written in a form suited to the two-sublattice system. It prefers the z -axis, depends on the change of sign of the magnetization of one of two sublattices and agrees with the symmetry of

spin system. As a product of spin operators, this term ensures the stronger dependence of its average $\langle \mathcal{H}'' \rangle$ on temperature than that of $\langle \mathcal{H}' \rangle$.

The term (3) can also be treated as a term of the power expansion of general spin Hamiltonian [8]. For the case of one-sublattice systems we obtain the four-spin interactions considered by Oitmaa [9].

In Section 3 we search for the behaviour of the complete model given by (1), whereas in Sections 4 and 5 the properties of two slightly altered Hamiltonians, simplified with respect to (1), are studied. An approximate approach has to be used throughout and the preliminary step always consists in the decomposition of the Hamiltonian into an "unperturbed" and a "perturbed" part:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1. \quad (4)$$

Most of our calculations are carried out on the level of the molecular field approximation, to be denoted hereafter as MFA.

3. Behaviour of the original model within the MFA

(a) Decomposition of the Hamiltonian

To investigate the properties of our model in its original form specified by Eqs. (2) and (3) within the MFA, we decompose the Hamiltonian (1) as follows:

$$\begin{aligned} \mathcal{H}_0 = & \frac{1}{2} NB(M_I^2 + M_{II}^2) + NAM_I M_{II} - \frac{3}{2} NDM_I M_{II}(M_I^2 + M_{II}^2) \\ & - \frac{1}{\beta} Y_I \sum_f S_f^z - \frac{1}{\beta} Y_{II} \sum_{II} S_{II}^z, \end{aligned} \quad (5)$$

$$\begin{aligned} \mathcal{H}_1 = & -\frac{1}{2} \sum^* J_{ff'} (\delta S_f^z \delta S_{f'}^z + S_f^- S_{f'}^+) - \frac{1}{2} \sum^* J_{gg'} (\delta S_g^z \delta S_{g'}^z + S_g^- S_{g'}^+) \\ & - \sum^* J_{fg} [\delta S_f^z \delta S_g^z + \frac{1}{2} (S_g^+ S_f^- + S_f^- S_g^+)] \\ & + \frac{1}{2} \sum^{**} D_{fgf'f''} [\delta S_f^z \delta S_g^z \delta S_{f'}^z \delta S_{f''}^z + M_{II} \delta S_f^z \delta S_{f'}^z \delta S_{f''}^z] \\ & + (M_I \delta S_g^z + M_I M_{II}) (\delta S_f^z \delta S_{f'}^z + \delta S_{f'}^- \delta S_{f''}^z + \delta S_{f''}^- \delta S_f^z) \\ & + M_I^2 \delta S_g^z (\delta S_f^z + \delta S_{f'}^z + \delta S_{f''}^z) + \frac{1}{2} \sum^{**} D_{gg'g''} [\delta S_g^z \delta S_{g'}^z \delta S_{g''}^z] \\ & + M_I \delta S_g^z \delta S_{g'}^z \delta S_{g''}^z + (M_{II} \delta S_f^z + M_I M_{II}) (\delta S_g^z \delta S_{g'}^z + \delta S_{g'}^- \delta S_{g''}^z \\ & + \delta S_{g''}^- \delta S_g^z) + M_{II}^2 \delta S_f^z (\delta S_g^z + \delta S_{g'}^z + \delta S_{g''}^z). \end{aligned} \quad (6)$$

When writing the above Hamiltonians, the following symbols have been introduced

$$NB = \sum^* J_{ff'} = \sum^* J_{gg'}, \quad (7)$$

$$NA = \sum^* J_{fg}, \quad (8)$$

$$ND = \sum^{**} D_{fgf'f''} = \sum^{**} D_{gg'g''}, \quad (9)$$

with: N — the number of sites in one sublattice, M_I, M_{II} — some parameters yet to be determined

$$Y_I = \beta[g\mu_B H + BM_I + AM_{II} - \frac{1}{2} DM_{II}(3M_I^2 + M_{II}^2)], \quad (10a)$$

$$Y_{II} = \beta[g\mu_B H + BM_{II} + AM_I - \frac{1}{2} DM_I(3M_{II}^2 + M_I^2)], \quad (10b)$$

$$\beta^{-1} = kT, \quad \delta S_f^z = S_f^z - M_I, \quad \delta S_g^z = S_g^z - M_{II}. \quad (11)$$

The differences (11) may well be referred to as magnetization fluctuation operators, since the parameters M_I and M_{II} will turn out to be the average magnetization per ion in the sublattice I and II, respectively. Thus, checking the term H_1 within MFA, we omit the fluctuations themselves.

(b) Free energy and magnetization

Using the formula

$$F = -\frac{1}{\beta} \ln \text{Sp} e^{-\beta \mathcal{H}_0} \quad (12)$$

we now calculate the free energy within MFA. Introducing the following reduced magnitudes:

$$\begin{aligned} n &= \frac{B}{A}, & d &= \frac{Ds^2}{A}, & f &= \frac{F}{NkT_c}, \\ t &= \frac{T}{T_c}, & h &= \frac{g\mu_B H}{A}, & x &= \frac{M_I}{s}, & y &= \frac{M_{II}}{s} \end{aligned} \quad (13)$$

we obtain

$$\begin{aligned} f &= \frac{3s}{2(s+1)(n+1)} [n(x^2 + y^2) + 2xy - 3dxy(x^2 + y^2)] \\ &\quad - t \left[\ln \frac{\sinh(s + \frac{1}{2})y_I}{\sinh \frac{1}{2} y_I} + \ln \frac{\sinh(s + \frac{1}{2})y_{II}}{\sinh \frac{1}{2} y_{II}} \right], \end{aligned} \quad (14)$$

where:

$$y_I = \frac{3}{s+1} \frac{1}{t(n+1)} [h + nx + y - \frac{1}{2} y(3x^2 + y^2)d], \quad (15)$$

$$y_{II} = \frac{3}{s+1} \frac{1}{t(n+1)} [h + ny + x - \frac{1}{2} x(3y^2 + x^2)d]. \quad (16)$$

The parameters M_I and M_{II} can be determined from the following conditions:

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = 0 \quad (17)$$

and are found to be equal to

$$x = \mathcal{B}(y_I), \quad (18)$$

$$y = \mathcal{B}(y_{II}), \quad (19)$$

where \mathcal{B} denotes the Brillouin function. With regard to Eqs. (15) and (16), we recognize Eqs. (18) and (19) as the simultaneous implicit equations for the sublattice magnetizations M_I and M_{II} within MFA.

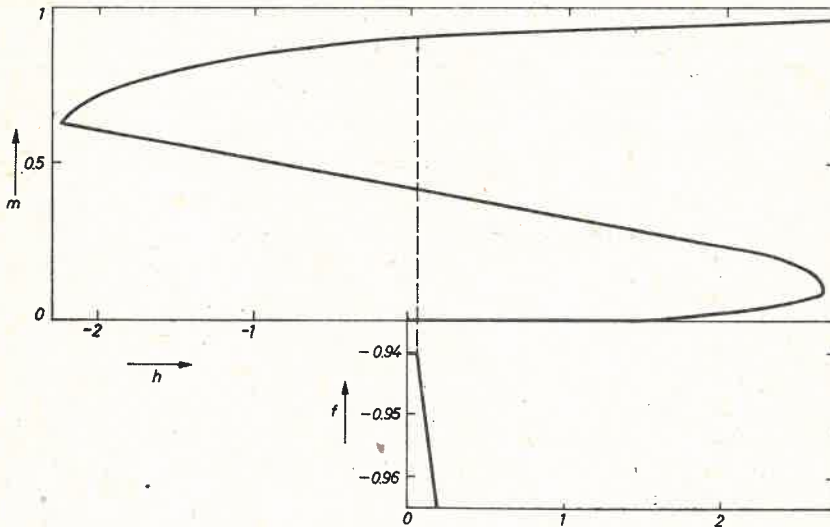


Fig. 1. Magnetization process $m(h)$, shown together with the diagram of free energy $f(h)$, calculated for $t = 0.5$, $d = 1.2$, $n = 10$ and $s = 1/2$

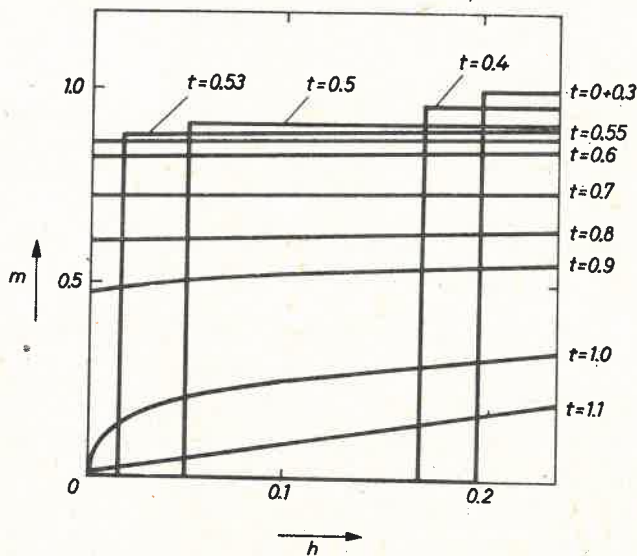


Fig. 2. Isotherms of magnetization, plotted for different values of t with metastable and unstable parts deleted (parameter values — as in Fig. 1)

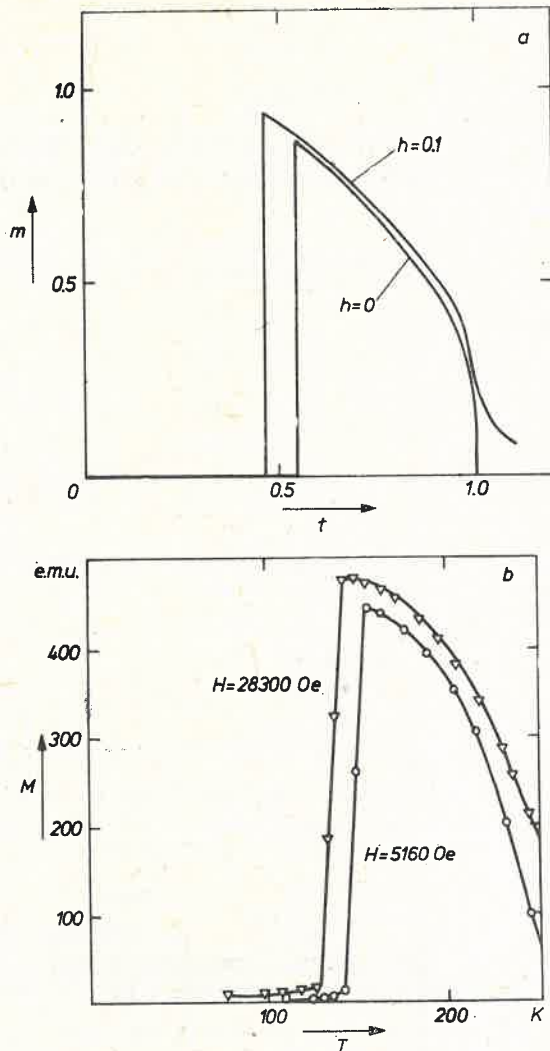


Fig. 3. Isoagres of magnetization (a) calculated for $h = 0$ and $h = 0.1$, (b) measured by Guillot [5] for $H = 5160$ Oe and $H = 28300$ Oe

We use them to evaluate numerically some isotherms and isoagres (i. e. the curves at constant field) of magnetization, choosing the case $s = 1/2$ for simplicity and taking $d = 1.2$ and $n = 10$. To determine with accuracy the metastable parts of a given magnetization curve, we find from Eq. (14) the intersection point of free energies f_A and f_B , as shown at the double Fig. 1. The isotherms $m(h)$ for several values of t are constructed in such a way and plotted in Fig. 2, the metastable as well as unphysical sections being discarded. Some isoagres, corresponding to the $h = 0$ and $h = 0.1$, are shown in Fig. 3a; they exhibit the behaviour typical for spontaneous metamagnetics as known e.g. from measurements [5] made on Mn_3GaC (Fig. 3b).

(c) Phase diagram

To visualize the essential metamagnetic features of our model, we plot the phase diagram in the (T, H) -plane. All transition points are found from the intersection of the free energy curves $f_A(h)$ and $f_P(h)$ plotted at constant values of t .

The phase diagram obtained (Fig. 4) occupies the quadrant $T > 0, H > 0$. The ferromagnetic phase reduces merely to the interval (T_M, T_c) on the T -axis. Along the boundary bordering the A-phase we find the first order transition. This line starts with the point

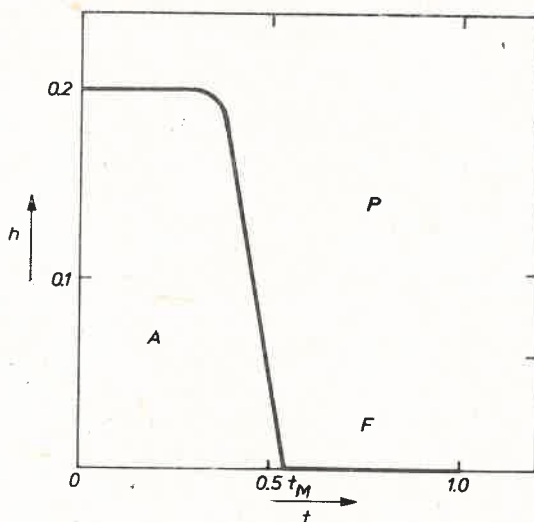


Fig. 4. Phase diagram in the (T, H) -plane, calculated from the formulas of Chapter 3

$(T_M, 0)$ and goes a long way rectilinearly with decreasing temperature. Just the same run of the A-P line has been found experimentally by Guillot in the case of Mn_3GaC [5]. At about $T = 2T_M/3$, the A-P boundary in our phase diagram becomes curved and goes next horizontally up to the H -axis, obeying themselves the third law of thermodynamics.

At $t = 0$, we get from (18) and (19) the strict expression for the threshold field:

$$h_t = -1 + d. \quad (20)$$

In the vicinity of zero temperature, however, we derive from Eq. (14) the approximate formula

$$h_{AP} \approx x[x^2(4-3x)d+x-2], \quad (21)$$

assuming $|x| \approx |y| \approx 1$ and taking into account that, practically, $\ln(2 \cosh z) = z$ holds when $z \gg 1$.

The area lying beyond the A and F phases (commonly regarded as paramagnetic) is denoted by the symbol P in Fig. 4. No intermediate (e. g. oblique) phase occurs within our model, therefore, the boundary $h_{AP}(t)$ is identical with the transition line between the phases A and P.

4. Simplified model and its properties within the MFA

(a) Derivation and decomposition^{*}

As a consequence of the four-operator nature of the part \mathcal{H}'' of our Hamiltonian, we have to calculate in any approximation better than MFA the highly inconvenient four-spin correlation functions. We shall prove below that the Hamiltonian \mathcal{H}'' can be simplified in such a manner that only two-spin correlation functions can occur in further calculations.

We decompose the term \mathcal{H}'' into two summands:

$$\mathcal{H}'' = \tilde{\mathcal{H}}'' + V \quad (22)$$

provided the second summand is sufficiently small so that it can be neglected. From among the many possible ways of decomposition, we propose here the following procedure:

$$\tilde{\mathcal{H}}'' = \frac{1}{2} \sum^{**} D_{fgf'f''} \langle S_f^z S_{f''}^z \rangle S_f^z S_g^z + \frac{1}{2} \sum^{**} D_{gf'g''} \langle S_g^z S_{g''}^z \rangle S_f^z S_g^z, \quad (23)$$

$$V = \frac{1}{2} \sum^{**} D_{fgf'f''} S_f^z S_g^z (S_f^z S_{f''}^z - \langle S_f^z S_{f''}^z \rangle) + \frac{1}{2} \sum^{**} D_{gf'g''} S_f^z S_g^z (S_g^z S_{g''}^z - \langle S_g^z S_{g''}^z \rangle). \quad (24)$$

The above decomposition fulfills the required inequality $\langle V \rangle \ll \langle \tilde{\mathcal{H}}'' \rangle$. Introducing the notation

$$\sum_{f',f''}^{**} D_{fgf'f''} = \sum_{g',g''}^{**} D_{gf'g''} = D_{fg} \quad (25)$$

we rewrite Eq. (23) in the form

$$\tilde{\mathcal{H}}'' = \frac{1}{2} \sum^* D_{fg} s^2 (u_I + u_{II}) S_f^z S_g^z, \quad (26)$$

where $s^2 u_I$ and $s^2 u_{II}$ are the correlation functions $\langle S_i^z S_j^z \rangle$ for the I and II sublattice respectively, assumed to be independent of site.

Instead of the complete Hamiltonian (1), we have to consider the simplified operator

$$\tilde{\mathcal{H}} = \mathcal{H}' + \tilde{\mathcal{H}}''. \quad (27)$$

Below we give some results which may be obtained from Eq. (27).

(b) Free energy and magnetization

Let us derive the free energy formulae for the Hamiltonian (27) in MFA. To do this, we split (27) into two summands

$$\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_0 + \tilde{\mathcal{H}}_1 \quad (28)$$

choosing

$$\begin{aligned} \tilde{\mathcal{H}}_1 = & -\frac{1}{2} \sum^* J_{ff'} (\delta S_f^z \delta S_{f'}^z + S_f^- S_{f'}^+) - \frac{1}{2} \sum^* J_{gg'} (\delta S_g^z \delta S_{g'}^z + S_g^- S_{g'}^+) \\ & - \sum^* J_{fg} (\delta S_f^z \delta S_g^z + \frac{1}{2} S_f^- S_g^+ + \frac{1}{2} S_g^- S_f^+) + \frac{1}{2} \sum^* D_{fg} s^2 (u_I + u_{II}) \delta S_f^z \delta S_g^z. \end{aligned} \quad (29)$$

The part $\tilde{\mathcal{H}}_1$ now involves all operators S^+ , S^- and δS^z , which ensures the MFA (see Section 3). The remaining part is then equal to

$$\begin{aligned} \tilde{\mathcal{H}}_0 = & \frac{1}{2} B(M_I^2 + M_{II}^2) + AM_I M_{II} - \frac{1}{2} Ds^2 M_I M_{II} (u_I + u_{II}) \\ & - \frac{1}{\beta} \tilde{Y}_I \sum_f S_f^z - \frac{1}{\beta} \tilde{Y}_{II} \sum_g S_g^z. \end{aligned} \quad (30)$$

Inserting $\tilde{\mathcal{H}}_0$ into the formula (12), we obtain the free energy in the MFA:

$$\begin{aligned} \tilde{f} = & \frac{3s}{2(s+1)} \frac{1}{n+1} \{n(x^2 + y^2) + xy[2 - d(u_I + u_{II})]\} \\ & - t \left[\ln \frac{\sinh(s + \frac{1}{2})\tilde{y}_I}{\sinh \frac{1}{2}\tilde{y}_I} + \ln \frac{\sinh(s + \frac{1}{2})\tilde{y}_{II}}{\sinh \frac{1}{2}\tilde{y}_{II}} \right], \end{aligned} \quad (31)$$

where

$$\tilde{y}_I = \frac{3}{s+1} \frac{1}{t(n+1)} [h + nx + y - \frac{1}{2} y(u_I + u_{II})d], \quad (32)$$

$$\tilde{y}_{II} = \frac{3}{s+1} \frac{1}{t(n+1)} [h + ny + x - \frac{1}{2} x(u_I + u_{II})d]. \quad (33)$$

Imposing the stationary conditions

$$\frac{\partial \tilde{f}}{\partial \tilde{y}_I} = \frac{\partial \tilde{f}}{\partial \tilde{y}_{II}} = 0 \quad (34)$$

we obtain the following implicit equations:

$$x = \mathcal{B}(\tilde{y}_I), \quad (35)$$

$$y = \mathcal{B}(\tilde{y}_{II}). \quad (36)$$

Together with (33) and (32), Eqs. (35) and (36) obviously represent simultaneous equations for the sublattice magnetizations. Preliminary numerical calculations at constant h yield the temperature dependence of the total magnetization $m = \frac{1}{2}(x+y)$ in a form quite similar to that obtained in Section 3.

(c) Threshold field and transition point

Equating both free energies $\tilde{f}_A(h)$ and $\tilde{f}_B(h)$ at $h = 0$ we get the same formula for the threshold field as in Section 3:

$$h_t = -1 + d. \quad (37)$$

Taking $|x| \approx |y| \approx 1$, we find the following equation of the A-P boundary in the vicinity of absolute zero:

$$h_{AP}(t) = x(2-x) \left[\frac{1}{2} (u_I + u_{II})d - 1 \right] \quad (38)$$

the transition field h_{AP} depending indirectly on temperature via $x(t)$, $u_I(t)$ and $u_{II}(t)$.

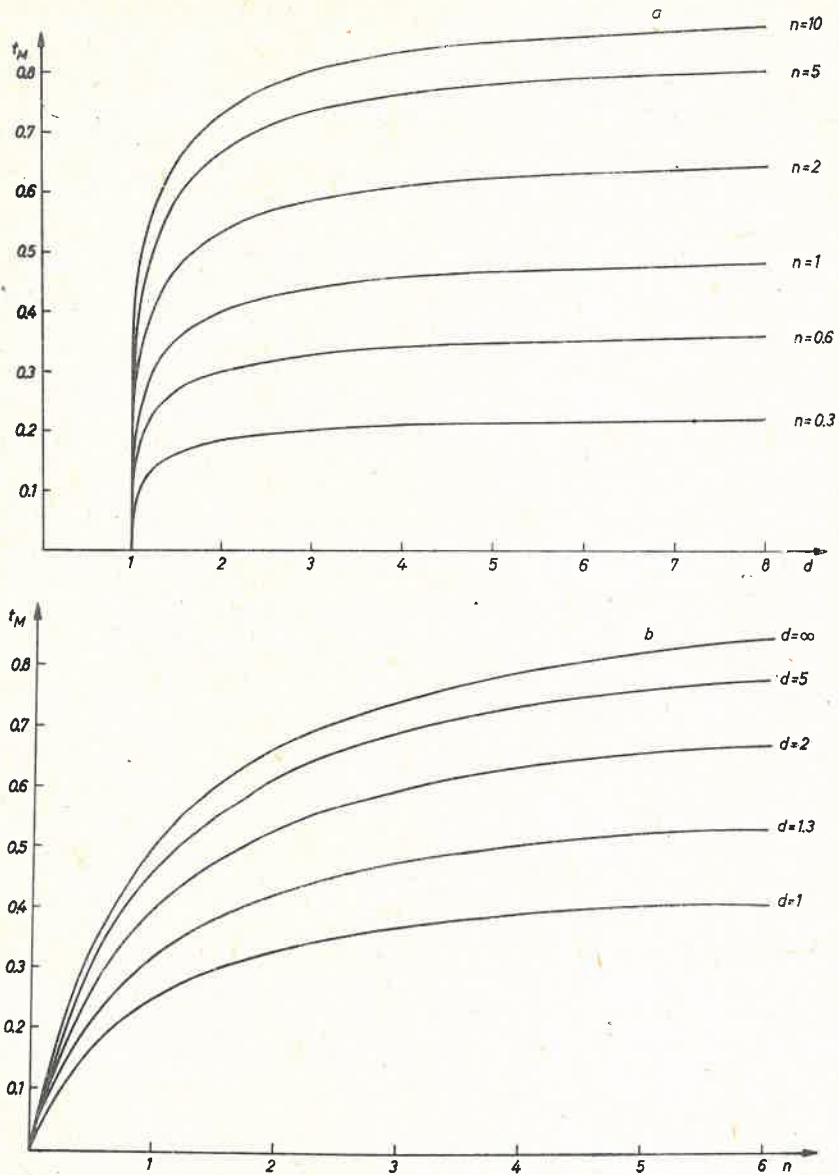


Fig. 5. Metamagnetic transition temperature t_M , plotted: (a) as a function of d , (b) as a function of n , according to Eq. (42)

Let us now determine the point t_M of spontaneous (i. e. for $h = 0$) transition. In this case we have $u_1 = u_2 = u$ and in the antiferromagnetic phase $y = -x$ strictly. Thus, from Eqs (32) and (33), two simple equations result. At $t = t_M$ they go over into two identical ferromagnetic equations, because the effective interlattice interaction vanishes:

$$1 - du(t_M) = 0. \quad (39)$$

Within MFA, the spins are uncorrelated and therefore $u = x^2$. Thus, we obtain for t_M the equation

$$1 - x^2 d = 0, \quad (40)$$

where $x(t_M)$ fulfils the relation:

$$x(t_M) = \operatorname{tgh} \frac{nx(t_M)}{(n+1)t_M}. \quad (41)$$

By (40) and (41), we get:

$$t_M = \frac{n}{n+1} \frac{w}{\operatorname{artgh} w}, \quad (42)$$

with $w^{-2} = d$. Some typical curves of $t_M(d)$ at $n = \text{const}$ as well as $t_M(n)$ at $d = \text{const}$ are plotted in Fig. 5. They characterize well the dependence of the transition point t_M on the parameters d and n of a given sample.

(d) Connections with Smart's hypothesis

The simplified Hamiltonian $\tilde{\mathcal{H}}$ enables one to understand the nature of Smart's hypothesis [4], which assumes a linear dependence of the molecular-field coefficient on temperature.

Within MFA we have

$$u_I + u_{II} = x^2 + y^2. \quad (43)$$

In a weak external field, the sublattice magnetizations are almost equal: $x^2 \approx y^2$. For temperatures of the order of magnitude of the Curie point, molecular field theory yields:

$$x^2 \approx \alpha(1-t) \quad (44)$$

where

$$\alpha = \frac{10}{3} \frac{(s+1)^2}{(s+1)^2 + s^2}$$

and, consequently, we have

$$(u_I + u_{II}) = 2\alpha(1-t). \quad (45)$$

We now insert this expression into Eqs (35) and (36) and obtain the following interlattice Weiss coefficient

$$1 - \alpha d(1-t) \quad (46)$$

which corresponds to the hypothesis of Smart. We see from the above derivation that Smart's hypothesis is the better the nearer we are to T_c .

5. Further simplification: the pseudo-Hamiltonian

(a) Motivation

With the aim to find an efficient tool for rapid calculations, we search for some further simplification of our model Hamiltonian. It appears that the role of an appropriate substitute for the Hamiltonian \mathcal{H}'' can be played by the operator

$$G = \sum_{f,g}^* D_{fg} s^2 \alpha (1-t) S_f^z S_g^z, \quad (47)$$

where D_{fg} is a constant coefficient. Namely, we shall show in the present Section that the operator G when inserted instead of \mathcal{H}'' into the free energy formula gives the same expression as that which results from Eq. (31) if the approximation (44) is used. Therefore, we can treat the operator $\mathcal{H}' + G$ as some kind of temperature-dependent pseudo-Hamiltonian which is very convenient in the thermodynamical description of spontaneous metamagnetism.

(b) Free energy and magnetization

Substituting the pseudo-Hamiltonian $\mathcal{H}' + G$ into Eq. (12) we get the following expression for the free energy:

$$f = \frac{3s}{s+1} \frac{1}{n+1} \left\{ \frac{n}{2} (x^2 + y^2) + xy [1 - \alpha d (1-t)] \right\} - t \left[\ln \frac{\sinh(s + \frac{1}{2}) \eta_{\text{I}}}{\sinh \frac{1}{2} \eta_{\text{I}}} + \ln \frac{\sinh(s + \frac{1}{2}) \eta_{\text{II}}}{\sinh \frac{1}{2} \eta_{\text{II}}} \right], \quad (48)$$

where:

$$\eta_{\text{I}} = \frac{3}{s+1} \frac{1}{t(n+1)} \{h + nx + y [1 - \alpha(1-t)d]\},$$

$$\eta_{\text{II}} = \frac{3}{s+1} \frac{1}{t(n+1)} \{h + ny + x [1 - \alpha(1-t)d]\}. \quad (49)$$

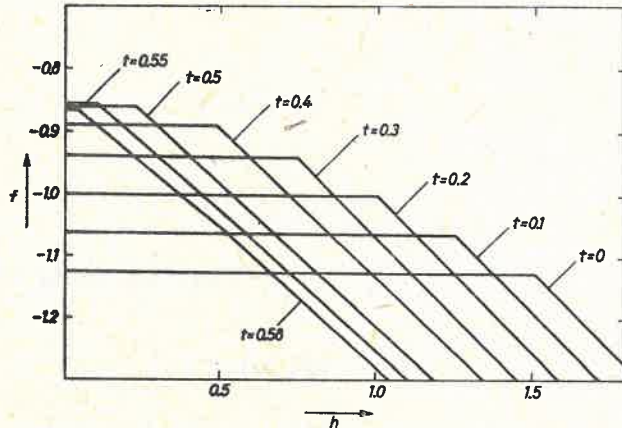


Fig. 6. The free energy $f(h)$, calculated within the simplification (47) for several temperatures ($n = 3$, $ad = 2.5$, metastable parts omitted)

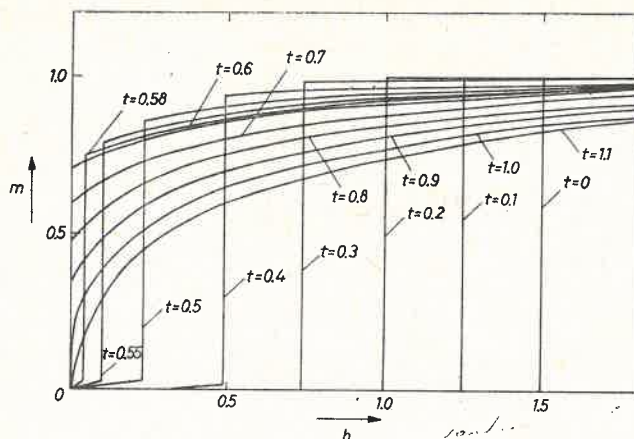


Fig. 7. Isotherms of magnetization, plotted for the same values of temperature as in Fig. 6 ($n = 3$, $ad = 2.5$) as well as for $t = 0.6, 0.7, 0.8, 0.9, 1.0$ and 1.1

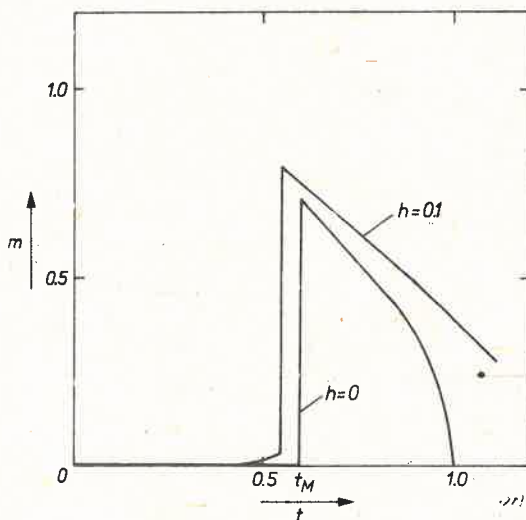


Fig. 8. Isoagres of magnetization, for $h = 0$ and $h = 0.1$

The state of equilibrium is found in the standard way from the stationary conditions, and we obtain the simultaneous equations for the sublattice magnetization:

$$x = \mathcal{B}(\eta_I); \quad y = \mathcal{B}(\eta_{II}). \quad (50)$$

Now, using Eqs (49) and (50) and taking $s = 1/2$ for simplicity, we calculate the isotherms of magnetization $m(h)$ for the chosen values $d = 0.83$ and $n = 3$ in quite the same way as in Section 3. They are shown in Fig. 7. The transition field values are determined directly from break-points of the free energy (see, for example, Fig. 6 plotted according to Eq. (48) when ignoring metastability).

Next, the isotherms obtained permit the construction of the isoagres $m(t)$, plotted in Fig. 8 for three different values of h . The isoagres, like the isotherms, exhibit behaviour typical for spontaneous metamagnetics.

(c) Phase diagram

Plotting many isothermal curves of the free energy $f(h)$ like those of Fig. 6 we obtain graphically the transition points. In this way the entire H - T phase diagram is determined as shown in Fig. 9.

Two most important points of this diagram can be expressed algebraically. First, the threshold field, determined as usually by equating $f_A = f_P$ at $t = 0$. It appears to have

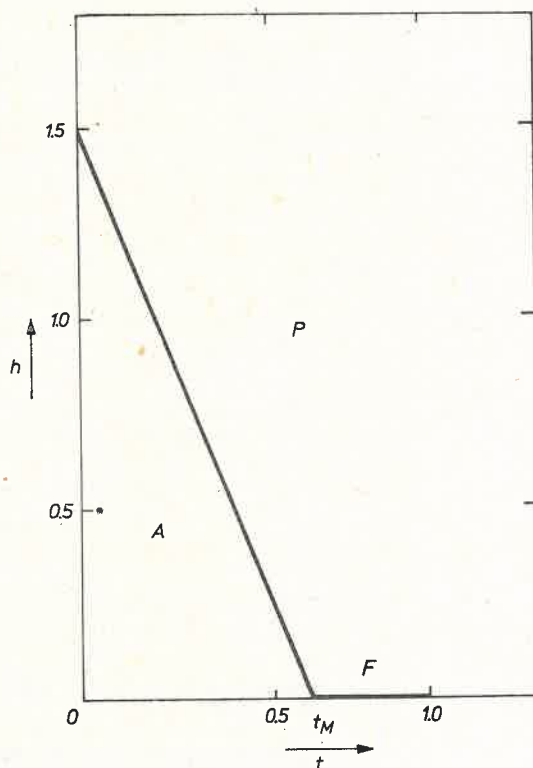


Fig. 9. Phase diagram in the (T, H) plane, calculated on the simplification (47)

the value $h_t = \alpha d - 1$. Second, the spontaneous transition temperature t_M , derived from the vanishing of the inter-sublattice coefficient in Eqs (49) for the case $h = 0$ and $x = -y$. It is found to depend solely on d :

$$t_M = 1 - \frac{1}{\alpha d}. \quad (51)$$

For low temperatures, we easily derive the equation of the AP boundary:

$$h_{\text{AP}} = x(2-x) [\alpha(1-t)d - 1]. \quad (52)$$

Within the region where $x \approx 1$ holds, Eq. (52) describes obviously a straight line with the slope

$$\frac{dh_{\text{AP}}}{dt} = -\alpha d. \quad (53)$$

In contrast to Fig. 4, the prominent slope at $T = 0$ due to the approximation (44) disagrees with the third law.

The validity of the approximation $x \approx 1$ reaches very far in practice. For instance for the case $d = 0.83$ and $n = 3$, the boundary in Fig. 9 is rectilinear up to $(1/2)T_c$. Near T_M this line exhibits a slight curvature. This discrepancy against Fig. 4 does not exceed the accuracy of measurements made up today.

6. Conclusions

(a) Properties of the original Hamiltonian

As follows from Section 3, the addition of the four-ion anisotropic term (3) to the common Heisenberg ferromagnetic exchange is sufficient to stabilize the antiferromagnetic state at low temperatures and leads by itself to the spontaneous A \rightarrow F change of state at some temperature T_M . The isotherms (Fig. 2) as well as the isoagres of magnetization (Fig. 3) provide further evidence of metamagnetic behaviour of the model proposed in the present paper. The most instructive summary of the essential features is given by the (T, H) phase diagram (Fig. 3). Note that the entire A-P boundary is of the first order.

Although the present results have been obtained in the mean-field approximation and for some chosen values of the coupling parameters, they manifest unambiguously all the typical features of spontaneous metamagnetism. In other words, our model describes a new mechanism creating the temperature-induced A \rightarrow F transitions, free of any further phenomenological assumptions such as Kittel's exchange inversion hypothesis.

Obviously, the parameters D of our model, similarly to the exchange integrals in the Heisenberg term, are also the phenomenological constants. For this reason, no attempt will be made to fit the theoretical results quantitatively to the experimental ones, since the data are as yet insufficient.

(b) Remarks as to the simplified Hamiltonian

In Section 4, we have introduced the simplified version of the proposed Hamiltonian with the aim to avoid the four-spin correlation functions occurring inevitably in all calculations (except within MFA) based on the original form (3). The quality of a theory starting with \mathcal{H} depends, of course, on the manner in which one approximates the two-spin correlation functions occurring there. Tentative calculations carried out within the MFA show very good conformity to the results of the Section 3. It seems that the simplification

$\tilde{\mathcal{H}}$ may be used in many cases to predict the behaviour of metamagnetism originating in the mechanism proposed here.

The simplest assumption approximating the correlation functions in the whole interval $(0, T_c)$ is their proportionality to $T_c - T$. Just this assumption leads immediately to Smart's hypothesis.

By having recourse to Eqs (13) let us rewrite the threshold field (20) in terms of the original parameter characterizing a given substance:

$$H_t = \frac{1}{g\mu_B} (Ds^2 - A). \quad (54)$$

The occurrence of spontaneous metamagnetism (or $T_M > 0$) is possible only if $H_t > 0$. In this way we obtain a simple condition for the existence of the temperature-induced transition to ferromagnetism within our model:

$$D > As^{-2}. \quad (55)$$

The inequality (55) is merely a necessary condition, deduced from the zero temperature properties. That is why it does not involve the intra-sublattice coupling B , which plays no role at $T = 0$.

The formula (42) for the transition temperature permits the detailed discussion of the coupling parameters for a given t_M . It shows, moreover, that a further necessary condition for the occurrence of metamagnetism, namely $T_M < T_c$, is always fulfilled within our model on account of $|t_M| < 1$ for every case (see also Fig. 5). Also the Eq. (42) requires $B > 0$ since otherwise $T_M = 0$.

(c) Comments on the pseudo-Hamiltonian simplification

On accepting the simplification proposed in Section 5, a very efficient operator $\mathcal{H}' + G$ is gained at the expense of the loss of its true Hamiltonian nature. It replaces successfully the original Hamiltonian in all thermodynamical theories.

The operator G may be regarded as deriving from $\tilde{\mathcal{H}}''$, since direct substitution of the approximation (45) into $\tilde{\mathcal{H}}''$ gives precisely G . Thus, the adoption of G is closely related to Smart's hypothesis. The violation of the third law of thermodynamics within this simplified model is due to the approximation (45) which is a rather inappropriate one for low temperatures.

(d) Various remarks

Contrary to the theories using only the Heisenberg model modified by the exchange inversion assumption, all calculations based on the proposed model Hamiltonian permit the study of both the critical as well as the high-temperature properties of a spontaneous metamagnets.

It is perhaps worth while noting that the condition (55) imposed on the constant D responsible for the contribution of the anisotropic term is formally of a form analogous to the condition necessary for the occurrence of field-induced metamagnetism: $K^2 > AM^2$,

where K is the common anisotropy constant and M — the saturation moment of a sublattice. Thus, magnetic anisotropy plays a very similar role in both categories of metamagnetic phenomena.

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