FIELD-DEPENDENT PHASE TRANSITIONS OF UNIAXIAL FERROMAGNETS

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In the molecular field approximation (MFA), the thermodynamical properties of a ferromagnetic system described by a Hamiltonian bilinear in the spin operators are examined. It is shown that, discontinuities of the thermodynamical quantities lie on a "critical hyper-surface" in the space $\{\boldsymbol{M}, \boldsymbol{H}, T\}$. This leads, under specific conditions, to a field-dependent temperature of the second-order ferro-para phase transition. The latter result is consistent with recent experimental and theoretical investigations. The influence of the uniaxial anisotropy on this phenomenon is also discussed.

1. Introduction

As shown by recent experiments [1, 2], the second-order ferro-paramagnetic phase transition in ferromagnets is not necessarily destroyed upon application of an external magnetic field. According to theoretical investigations [3–9], such a phenomenon can occur in a uniaxial ferromagnet with the field perpendicular to the easy axis, vanishing in the case of other field directions.

The influence of the perpendicular field on the magnetization direction of a uniaxial ferromagnet seems to be well known and understood (see, *e. g.*, [10]). Below a critical value of the field, $H_c(T)$, there are two energetically equivalent directions of the magnetization which form the same angle with the field. Above this value, only the direction of the field is admissible for the magnetization. The papers [3÷6,9] show the existence of a second-order phase transition at the point $H_c(T)$, above which the magnetization assumes the direction of the external field. In other words, if we write the inverse relation, $T_c(H)$, the temperature of the second-order phase transition is field-dependent. It coincides with the ordinary (field-free) Curie temperature in the case $H = 0$.

For the Heisenberg model such results have been obtained upon the assumption of the exchange anisotropy [5, 6, 9]. From a purely physical point of view, however, it is rather obvious that the occurrence of this effect should not depend on the type and the origin of the

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anisotropy. This is also suggested by phenomenological considerations [3, 4, 8, 10], but a proof of this statement based on the Heisenberg model and MFA will be given in the present paper, where we do not specify the type of the uniaxial anisotropy (excluding, however, an anisotropy of crystal-field type). In our present formulation, the possibility of shifting of the transition temperature with the external field follows immediately from the equations of state for the anisotropic (uniaxial) ferromagnet. Furthermore, we extend here the considerations to the case of a ferromagnet with three mutually perpendicular inequivalent preferred directions and the field perpendicular to the magnetically easiest one, in which case a second-order phase transition should apparently occur as well, but with the transition temperature depending additionally on the field direction in the hard plane.

2. *Minimization of the model free energy*

Consider an arbitrary Hamiltonian bilinear in the spin operators,

$$\mathscr{H} = -\tfrac{1}{2}\sum_{f\neq g} A_{ij}^{fg} s_i^f s_j^g - \mu H_i \sum_f s_i^f, \tag{1}$$

where s_i^f is the spin operator of the i-component at the lattice site f, $A_{ij}^{fg} = A_{ji}^{fg} > 0$ is the interaction tensor, and H_i the components of the external magnetic field. We use the summation convention over repeated lower indices. A convenient approach to the problem in MFA is the application of Bogolyubov's variational principle [11]. In this formulation, the thermodynamical description of a system is obtained through the minimization of the so-called model free energy, F, which can be easily obtained [12, 6] for the Hamiltonian (1). Upon assuming

$$\sigma_i^f \equiv \langle s_i^f \rangle / s \equiv \sigma_i \tag{2}$$

(s is the maximum spin eigenvalue) and introducing reduced quantities, it reads

$$\varphi = -\frac{s+1}{3s}\tau \ln \frac{\operatorname{sh}\{(2s+1)\tilde{B}_s(\sigma)/2s\}}{\operatorname{sh}\{\tilde{B}_s(\sigma)/2s\}} +$$

$$+\frac{s+1}{3s}\tau\sigma\tilde{B}_s(\sigma) - h_i n_i \sigma - \tfrac{1}{2}\alpha_{ij} n_i n_j \sigma^2, \tag{3}$$

where

$$\varphi \equiv \frac{F}{Ns^2\Omega}, \quad \tau \equiv \frac{3kT}{s(s+1)\Omega}, \quad h_i \equiv \frac{\mu H_i}{s\Omega}, \quad n_i \equiv \frac{\sigma_i}{\sqrt{\sigma_i\sigma_i}} \equiv \frac{\sigma_i}{\sigma}, \tag{4}$$

$$\alpha_{jj} \equiv \Omega^{-1} \sum_g A_{ij}^{fg}, \quad \Omega \equiv \sum_g A_{ij}^{fg}\delta_{ij}, \tag{5}$$

N denotes the number of lattice sites, and $\tilde{B}_s(x)$ is the inverse function of

$$B_s(x) \equiv \frac{2s+1}{2s}\operatorname{cth}\frac{2s+1}{2s}x - \frac{1}{2s}\operatorname{cth}\frac{1}{2s}x. \tag{6}$$

In our case, the minimization procedure should be carried out with respect to the magnetization components σ_i, or the absolute value σ and the direction cosines n_i of the magnetization vector. In the latter case, the necessary conditions for an extremum of (3) lead to the equations

$$G_i(n_j, \sigma; h_j) \equiv \varepsilon_{ijk} n_j (h_k + \alpha_{kl} n_l \sigma) = 0$$

$$G_4(n_j) \equiv n_i n_i - 1 = 0$$

$$G_5(n_j, \sigma; h_j, \tau) \equiv \frac{s+1}{3s} \tau \tilde{B}_s(\sigma) - h_i n_i - \alpha_{ij} n_i n_j \sigma = 0, \tag{7}$$

where ε_{ijk} is the antisymmetric unit pseudotensor.

One can find effective solutions of (7) only in special cases, choosing appropriately the form of the tensor α_{ij} (or A_{ij}^{fg}) and the direction of the external field. However, the form of α_{ij} can also be simplified due to the symmetry of the lattice.

Let $\{x_i\}$ and $\{\tilde{x}_i\}$ be two Cartesian coordinate systems such that $\{\tilde{x}_i\} = U\{x_i\}$ where U is any transformation of the point group corresponding to the given crystal lattice, and assume that, *e. g.*, the x_3-coordinate axes of each reference frame coincide with the crystallographic axis of highest rotational symmetry. Then, it is obvious that for two fields, h_i and $\tilde{h}_i$, such that $h_i = \tilde{h}_i$ the respective solutions n_i and $\tilde{n}_i$ of Eqs (7) should be identical, which leads to the conlusion $\tilde{\alpha}_{ij} = \alpha_{ij}$ and, due to the invariance under the transformations U, to the result

$$\alpha_{ij} = \alpha_{11}\delta_{i1}\delta_{j1} + \alpha_{22}\delta_{i2}\delta_{j2} + \alpha_{33}\delta_{i3}\delta_{j3} \tag{8}$$

if the lattice has higher than monoclinic symmetry and the coordinate axes lie in the principal crystallographic directions.

The sufficient conditions for a minimum of (3) to exist can be analysed by the method presented in previous papers [12, 6], by examining the sign of the quadratic form

$$\begin{aligned} d^2\Phi = {} & [p(\sigma)\tilde{\alpha}_{11} + q(\sigma)\tilde{h}_1]\, d\sigma^2 + \sigma[(\tilde{\alpha}_{11} - \tilde{\alpha}_{22})\,\sigma - \tilde{h}_1]\, d\tilde{n}_2^2 + \\ & + \sigma[(\tilde{\alpha}_{11} - \tilde{\alpha}_{33})\,\sigma - \tilde{h}_1]\, d\tilde{n}_3^2 - 2[2\tilde{\alpha}_{12} + \tilde{h}_2]\, d\sigma\, d\tilde{n}_2 - \\ & - 2[2\tilde{\alpha}_{13}\sigma + \tilde{h}_3]\, d\sigma d\tilde{n}_3 - 2\sigma^2\tilde{\alpha}_{23}\, d\tilde{n}_2 d\tilde{n}_3 \\ \equiv {} & a_{ij} d\tilde{y}_i\, d\tilde{y}_i \end{aligned} \tag{9}$$

where

$$d\tilde{y}_1 = d\sigma, \; d\tilde{y}_2 = d\tilde{n}_2, \; d\tilde{y}_3 = d\tilde{n}_3 \tag{10}$$

$$\Phi = \varphi + \lambda n_i n_i \tag{11}$$

$$\tilde{n}_k = R_{ki} n_i, \; \tilde{h}_k = R_{ki} h_i, \; \tilde{\alpha}_{kl} = R_{ki} R_{lj} \alpha_{ij} \tag{12}$$

$$q(x) = \frac{1}{\tilde{B}_s(x)} \frac{d}{dx} \tilde{B}_s(x) > 0, \quad p(x) = xq'(x) - 1 > 0 \quad \text{for} \quad 0 < x < 1, \tag{13}$$

and the transformation matrix

$$(R_{ij}) = \begin{pmatrix} \sin\vartheta \sin\psi & \sin\vartheta & \cos\psi \cos\vartheta \\ -\cos\psi & \sin\psi & 0 \\ -\cos\vartheta \sin\psi & -\cos\vartheta \cos\psi & \sin\vartheta \end{pmatrix} \tag{14}$$

with the angles ϑ, ψ defined by

$$\begin{aligned} n_1 &= \sin\vartheta \sin\psi \\ n_2 &= \sin\vartheta \cos\psi \\ n_3 &= \cos\vartheta \end{aligned} \tag{15}$$

is chosen in such a way that $\tilde{n}_1 = 1$. In the formula (9), the Lagrange factor λ and the temperature τ have been eliminated by applying the necessary conditions (7) to Φ, *i. e.*, $\frac{\partial \Phi}{\partial n_i} = 0$ and $\frac{\partial \Phi}{\partial \sigma} = 0$, respectively. Making use of (12)–(15) and (7) for $a_{12} = a_{21}$ one can show that the coefficients $a_{ij} = a_{ji}$ of the quadratic form (9) for the diagonal tensor α_{ij}, Eq. (8), read

$$\begin{aligned} a_{11} &= p(\sigma)\, \alpha_{ij} n_i n_j + q(\sigma)\, h_i n_i \\ a_{22} &= \sigma^2 n^{-2} \{\varkappa_{12}(n_1^2 - n_2^2) + n_3^2(\alpha_{33} - \alpha_{ij} n_i n_j)\} + h_i n_i \sigma \\ a_{33} &= \sigma^2 n^{-2}(1 - 2n_3^2)\,(\alpha_{ij} n_i n_j - \alpha_{33}) + h_i n_i \sigma \\ a_{12} &= n_1 n_2 n^{-1}\, \varkappa_{12}\sigma, \quad \alpha_{23} = -n_1 n_2 n_3 n^{-2}\, \varkappa_{12}\sigma^2 \\ a_{13} &= n^{-1}\{n_3(h_1 n_1 + h_2 n_2) - h_3 n^2 + 2 n_3 \sigma(\varkappa_{13} n_1^2 + \varkappa_{23} n_2^2)\} \end{aligned} \tag{16}$$

where

$$n = (n_1^2 + n_2^2)^{1/2},$$

$$\varkappa_{11} = 0,\ \varkappa_{12} = \alpha_{11} - \alpha_{22},\ \varkappa_{13} = \alpha_{11} - \alpha_{33},\ \varkappa_{21} = \alpha_{22} - \alpha_{11} \dots \tag{17}$$

For the form (9) to be positive, the standard conditions are to be satisfied, such as the positiveness of the eigenvalues of the matrix a_{ij} or that of the principal minors of det a_{ij}. In this way, by assuming an exchange anisotropy, the cases $\alpha_{11} = \alpha_{22} \neq \alpha_{33}$ (easy axis or plane, depending on the sign of $\varkappa_{23} = \varkappa_{13}$) were considered previously [6] and shown to lead to a second-order phase transition[1] if the field is perpendicular to the easy axis (plane), and to no phase transition in the case of the parallel field (see, however, Footnote in Section 4). Our present analysis shows, moreover, the validity of these conclusions for an arbitrary (anisotropic) tensor A_{ij}^{fg} if only the lattice is of tetragonal, trigonal or hexagonal symmetry (a cubic lattice implies, of course, $\alpha_{11} = \alpha_{22} = \alpha_{33}$). The case of the orthorombic lattice ($\alpha_{11} \neq \alpha_{22} \neq \alpha_{33} \neq \alpha_{11}$) requires special consideration which will be given in Section 4.

3. *Thermodynamical description*

According to Bogolyubov's variational principle [11], the model free energy approximates from above the true free energy of the system under consideration. By inserting a solution of (7), which satisfies the conditions (16) and represents an absolute minimum of (3),

[1] There is an error in formula (19) in [6] (*Acta Phys. Polon.*) where a factor 2 has been omitted in the term proportional to P_{23}. Consequently, the determinants Δ in the sufficient conditions (31) and (53) in [6] should respectively read

$$\Delta = \gamma\Psi(\sigma)(|\varkappa|\sigma^2 - h_\perp^2|\varkappa|^{-1}) \tag{31}$$

$$\Delta = \gamma'\Psi(\sigma)(h_{||}^2|\varkappa|^{-1} - |\varkappa|\sigma^2) \tag{53}$$

into (3), one obtains the approximate free energy of a stable state of our system. (A relative minimum of (3) corresponds to a metastable state). Thus, if the solutions n_i and σ of (7) exist and meet the conditions (16), Eqs (7) can be considered an implicit form of the equations of state described by $n_i(h_j, \tau)$, $\sigma(h_j, \tau)$. The system (7) consists of five equations for four quantities to be determined; it can be easily noticed, however, that of the three functions G_i one is linearly dependent on the two others and, as the Jacobi matrix constructed of the derivatives of G_i, G_4, G_5 with respect to n_i and σ is of fourth rank, the system (7) is consistent. Therefore, in our further considerations we can restrict ourselves to four of the functions G_i, G_4, G_5, *e. g.*, G_μ where $\mu = 2, 3, 4, 5$.

If

$$\det \frac{\partial G_\mu}{\partial y_\nu} \neq 0 \tag{18}$$

where $\nu = 1, 2, 3, 4$ and y_ν is defined by $y_i = n_i$, $y_4 = \sigma$, it follows from the continuity of G_μ (and G_1) along with their first derivatives that the solutions of (7), $n_i(h_j, \tau)$, $\sigma(h_j, \tau)$, and their first derivatives with respect to h_j and τ are continuous (and Single-valued) functions. In other words, if $n_i(h_j, \tau)$, $\sigma(h_j, \tau)$ and/or their derivatives are discontinuous or multiple-valued), Eqs (7) are satisfied, too, and, instead of (18), the equation

$$\det \frac{\partial G_\mu}{\partial y_\nu} = 0 \tag{19}$$

holds. These equations, (7) and (19), represent a new set of five linearly independent equations for the four unknown functions $n_i(h_j, \tau)$, $\sigma(h_j, \tau)$ and lead therefore in this case to a relationship between the variables τ and h_j, say $\tau_c(h_j)$. This, in turn, leads to a "critical hyper-surface" $n_i^c(h_j)$, $\sigma_c(h_j)$ and one can easily show that the point of a second-order phase transition in a uniaxial ferromagnet [6] lies on it.

In the opposite case, when the conditions (16) and (18) for a set of the solutions $n_i(h_j, \tau)$ $\sigma(h_j, \tau)$ of (7) are met, other thermodynamical quantities (for a stable or metastable state) can be obtained from (3). Thus, by differentiation of (3) with respect to τ or h_i one has the entropy (in the units of Nk gas constant)

$$S = \ln \frac{\operatorname{sh}\{(2s+1)\tilde{B}_s(\sigma)/2s\}}{\operatorname{sh}\{\tilde{B}_s(\sigma)/2s\}} - \sigma \tilde{B}_s(\sigma), \tag{20}$$

the specific heat at constant field

$$C = \tilde{B}_s(\sigma) \frac{\partial \sigma}{\partial \tau}, \tag{21}$$

and the isothermal susceptibility tensor

$$\chi_{ij} = n_i \frac{\partial \sigma}{\partial h_j} + \sigma \frac{\partial n_i}{\partial h_j}. \tag{22}$$

(In the latter formula, terms containing second derivatives and those non-linear in the first ones vanish because of (7)). Since $n_i(h_j, \tau)$, $\sigma(h_j, \tau)$ and the respective derivatives of these functions are continuous, φ, S, C and χ_{ij} are also continuous. Hence, discontinuities of σ_i

and/or S (corresponding to a minimum of the free energy) can occur in the case of (19) or at the stability boundary ($d^2\Phi = 0$). If the stable values of σ_i and S are continuous functions of h_j, τ, the existence of a second-order phase transition requires any of the first derivatives of n_i or σ to be discontinuous on the critical hyper-surface (see, *e. g.*, the results of [5, 6]).

4. *Second-order phase transition in the case of three inequivalent magnetically preferred directions* ($\alpha_{11} \neq \alpha_{22} \neq \alpha_{33} \neq \alpha_{11}$, $h_3 = 0$)

As an example of the general considerations of the preceding Sections, consider the case of the orthorombic lattice when (8) applies and one of the field components, assume h_3, is equal to zero. Then, from (7) two kinds of solutions are obtained such that $n_3 \neq 0$, and another with $n_3 = 0$. For the first one we obtain

$$n_1 = h_1/\varkappa_{31}\sigma, \quad n_2 = h_2/\varkappa_{32}\sigma, \quad n_3 = \pm(1 - n^2 - n_2^2)^{1/2}$$

$$\frac{s+1}{3s}\tau\tilde{B}_s(\sigma) = \alpha_{33}\sigma \tag{23}$$

whereas in the latter case n_1, n_2 and σ satisfy the system of equations

$$h_2 n_1 - h_1 n_2 + \varkappa_{21} n_2 n_1 \sigma = 0$$

$$n_1^2 + n_2^2 - 1 = 0$$

$$-\frac{s+1}{3s}\tau\tilde{B}_s(\sigma) + h_1 n_1 + h_2 n_2 + \alpha_{11} n_1^2 \sigma + \alpha_{22} n_2^2 \sigma = 0. \tag{24}$$

The solutions (23) are real if

$$\beta \equiv (\beta_1^2 + \beta_2^2)^{1/2} \leqslant \sigma \leqslant 1 \tag{25}$$

where

$$\beta_1 = h_1/\varkappa_{31}, \quad \beta_2 = h_2/\varkappa_{32}. \tag{26}$$

This implies the solution (23) to be restricted to the temperature interval

$$0 \leqslant \tau \leqslant \tau_c \equiv 3s\alpha_{33}\beta/(s+1)\,\tilde{B}_s(\sigma) \tag{27}$$

and, if $h_1 > 0$, $h_2 > 0$, the direction cosines to be confined to the intervals

$$\beta_1/\beta \geqslant n_1 \geqslant \beta, \quad \beta_2/\beta \geqslant n_2 \geqslant \beta$$

$$|n_3| \leqslant (1 - \beta^2)^{1/2}. \tag{28}$$

Among the solutions of (24) there is one which is determined for $0 \leqslant \tau < \infty$, $0 < h_1, h_2 < \infty$. If $\varkappa_{21} > 0$, it satisfies the conditions

$$0 < n_1 < h_1/h, \quad 0 < h_2/h < n_2, \quad 0 < \sigma \leqslant 1$$

$$h \equiv (h_1^2 + h_2^2)^{1/2}. \tag{29}$$

Besides, there can exist additional solutions of (24), which divide into two groups. If $h_1 > 0$, $h_2 > 0$ and $\varkappa_{21} > 0$, for one group the direction cosines n_1, n_2 are confined to the intervals

$$-h_1/h < n_1 < 0, \quad -1 < n_2 < -h_2/h, \tag{30}$$

and these solutions are admissible for

$$h_1 n_1 + h_2 n_2 + \alpha_{11} n_1^2 \sigma + \alpha_{22} n_2^2 \sigma \geqslant 0 \tag{31}$$

if negative temperatures are to be avoided. The remaining solutions, for which

$$n_1 > 0, \quad n_2 < 0 \tag{32}$$

can occur for sufficiently low values of $h_1/\varkappa_{21}\sigma > 0$, $h_2/\varkappa_{21}\,\sigma > 0$ (see, *e. g.*, the analysis of an analogous equation to (24) for the magnetization directions in a uniaxial ferromagnet given in [10]).

It is easy to notice that the solutions (23) and one of (24) (namely, (29) for $h_1 > 0$, $h_2 > 0$) coincide if

$$n_1 \equiv n_1^c = \beta_1/\beta, \quad n_2 \equiv n_2^c = \beta_2/\beta, \quad n_3 = n_3^c = 0$$

$$\sigma \equiv \sigma_c = \beta, \quad \tau = \tau_c. \tag{33}$$

On the other hand, one can show Eq. (33) to represent the explicit from of the critical hyper--surface (19) for the case $h_3 = 0$. Let us assume $h_1 > 0$, $h_2 > 0$; then, according to the preceding Section, a phase transition will occur on the hyper-surface (33) if (*i*) in the neighbourhood of the hyper-surface (33) the solutions (23) and/or (29) of (24) (for $\tau > \tau_c$, $\sigma < \beta$ or $0 < \tau < \infty$, $0 < \sigma < 1$) satisfy the conditions for the absolute minimum of the free energy (3); (*ii*) there exist discontinuities of the second derivatives of φ with respect to τ and/or h_1, h_2 on this surface for the solutions which satisfy the condition (*i*).

Making use of (16), (17) one can prove that, if $\varkappa_{31} > 0$, $\varkappa_{32} > 0$, the solutions (23) satisfy the sufficient conditions for a minimum of the free energy (3) in the whole region (25), (27), (28) (with the exception of the boundary points $\tau = 0$, $\tau = \tau_c$). From (17), for the solutions of (24) ($n_3 = 0$) we have $a_{13} = a_{23} = 0$, and for (29) moreover $a_{11} > 0$. In this case, the conditions for a minimum of the free energy reduce to

$$a_{11}a_{22} - a_{12}^2 > 0$$

$$a_{33}/\sigma = \sigma(\alpha_{11}n_1^2 + \alpha_{22}n_2^2 - \alpha_{33}) + h_1 n_1 + h_2 n_2 > 0. \tag{34}$$

One can easily check that $a_{33} = 0$ for (33), and that the form of a_{33} ensures the positiveness of (34) for sufficiently high fields. However, the question arises whether (33) is the only point at which $a_{33} = 0$. According to (24), a_{33} does not depend explicitly on the temperature and is a function of σ, h_1, h_2 only (and the parameters $\alpha_{11}, \alpha_{22}, \alpha_{33}$). The dependence of a_{33}/σ on σ is shown in Fig. 1 for different values of h_1, h_2.

It follows from Fig. 1 that $a_{33} > 0$ for $\sigma < \beta(\tau > \tau_c)$ and $a_{33} < 0$ for $\sigma > \beta(\tau < \tau_c)$ if $\beta < 1$. In the case $\beta > 1$, we have $a_{33} > 0$ for $0 < \sigma < 1$ ($0 \leqslant \tau < \infty$, $0 < h_1$, $h_2 < \infty$).

This indicates the absence of the minimum for the state (29) if $\sigma > \beta$ ($\tau < \tau_c$). If these results (based on numerical tests) are valid for arbitrary $\alpha_{11}, \alpha_{22}, \alpha_{33}$, and the solution (29) of (24) is the absolute minimum of the free energy (3), the state with $n_3 \neq 0$, (23), occurs at low temperatures and fields ($\tau < \tau_c, \beta < 1$), and the state with $n_3 = 0$, (24), (29), for higher values of these parameters ($\tau > \tau_c, \beta < 1$). If $\beta > 1$, the only admissible state is (24). As the solutions (23) and (29) of (24) coincide for (33), the continuity of the free energy (3)

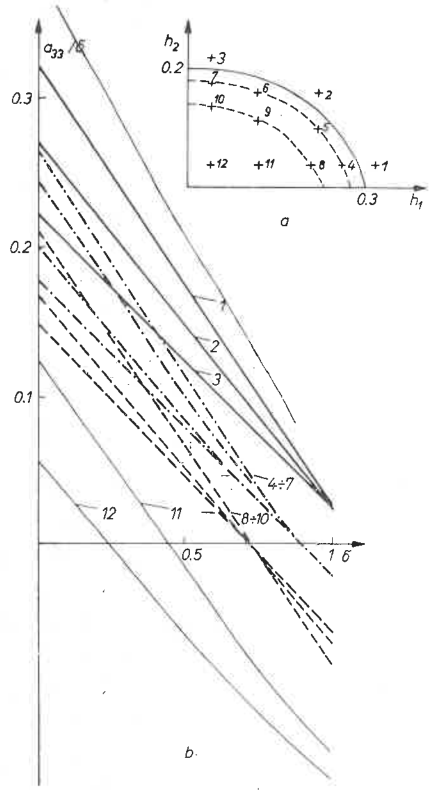

Fig. 1a, b. Area 1a of the possible phase transition (restricted by the solid line — the curve $(h_1 \varkappa_{31})^2 + (h_2 \varkappa_{32})^2 = 1$) in the (h_1, h_2) plane for $\alpha_{11} = 0.2, \alpha_{22} = 0.3, \alpha_{33} = 0.5$. The daggers denote the field values for which the curves for the solution (29) of Eqs (24) in 1b are plotted

and the entropy (20) is ensured if $\beta < 1$. For $\beta > 1$, when the solution (29) of (24) is the only possible state, a discontinuity of n_i, σ and/or of the derivatives of these functions could occur for (33), on the ground that the solutions of (7) and/or of their derivatives may be discontinuous for (19). However, the same method which was used in showing the possible existence of discontinuities of the solutions of (7) for the case (19) in the previous Section, permits now to prove that there are no discontinuities for the solutions $n_1(h_1, h_2, \tau)$, $n_2(h_1, h_2, \tau)$, $\sigma(h_1, h_2, \tau)$ (and their first and second derivatives with respect to h_1, h_2, τ) of (24) for (33). Thus, if $\beta > 1$, $h_1 > 0$, $h_2 > 0$ and $\alpha_{33} > \alpha_{22} > \alpha_{11}$ ($\varkappa_{31} > 0$, $\varkappa_{32} > 0$, $\varkappa_{21} > 0$), the state (24), (29) without any phase transition should occur in our system, since the specific heat (21) and the components of the susceptibility tensor (22) are continuous functions of τ and h_1, h_2. On the other hand, the existence of a second-order phase transition in the case $\beta < 1$ is quite obvious, as

$$\frac{\partial n_3}{\partial \tau} \neq 0, \qquad \frac{\partial n_3}{\partial h_{1,2}} \neq 0$$

$$\lim_{\tau \to \tau_c - 0} \frac{\partial n_3}{\partial \tau} = \mp\infty, \quad \lim_{\tau \to \tau_c - 0} \frac{\partial n_3}{\partial h_{1,2}} = \mp\infty \tag{35}$$

for (23), whilst

$$n_3 = \frac{\partial h_3}{\partial \tau} = \left.\frac{\partial n_3}{\partial \tau}\right|_{\tau_c+0} = \frac{\partial n_3}{\partial h_{1,2}} = \left.\frac{\partial n_3}{\partial h_{1,2}}\right|_{\tau_c+0} = 0 \tag{36}$$

for (24) which, according to (21), (22), suffices for the existence of a second-order phase transition for (33).

Incidentally, this phase transition manifests itself also through the discontinuity of the derivatives of the other two direction cosines, and the magnitude of the magnetization as well, with respect to field components and temperature. Namely, for (23) on the critical hyper-surface (33) these derivatives read

$$\left.\frac{\partial n_1}{\partial \tau}\right|_{\tau_c-0} = \frac{s+1}{3s}\,\frac{\beta_1 \tilde{B}_s(\beta)}{\beta^2 p(\beta)}, \qquad \left.\frac{\partial n_2}{\partial \tau}\right|_{\tau_c-0} = \frac{s+1}{3s}\,\frac{\beta_2 \tilde{B}_s(\beta)}{\beta^2 p(\beta)}$$

$$\left.\frac{\partial \sigma}{\partial \tau}\right|_{\tau_c-0} = -\frac{s+1}{3s}\,\frac{\tilde{B}_s(\beta)}{\beta^2 p(\beta)}. \tag{37}$$

$$\frac{\partial n_1}{\partial h_1} = \frac{1}{\varkappa_{31}\beta}, \qquad \frac{\partial n_1}{\partial h_2} = \left.\frac{\partial n_1}{\partial h_2}\right|_{\tau_c-0} = 0$$

$$\frac{\partial n_2}{\partial h_1} = \left.\frac{\partial n_2}{\partial h_1}\right|_{\tau_c-0} = 0, \qquad \left.\frac{\partial n_2}{\partial h_2}\right|_{\tau_c-0} = \frac{1}{\varkappa_{32}\beta}$$

$$\frac{\partial \sigma}{\partial h_{1,2}} = \left.\frac{\partial \sigma}{\partial h_{1,2}}\right|_{\tau 0-0} = 0 \tag{38}$$

where the function $p(\beta)$ in (37) is defined by (13). For (24), the respective derivatives of n_1, n_2, σ can be obtained as solutions of the three (independent) systems of linear equations

$$\begin{pmatrix} h_2 + \varkappa_{21} n_2 \sigma, & -h_1 + \varkappa_{21} n_1 \sigma, & \varkappa_{21} n_1 n_2 \\ n_1 \quad , & n_2 \quad , & n_3 \\ h_1 + 2\alpha_{11} n_1 \sigma, & h_2 + 2\alpha_{22} n_2 \sigma, & \Lambda \end{pmatrix} \begin{pmatrix} \dfrac{\partial n_1}{\partial \xi_\nu} \\ \dfrac{\partial n_2}{\partial \xi_\nu} \\ \dfrac{\partial n_2}{\partial n_\nu} \end{pmatrix} = \begin{pmatrix} \eta_\nu \\ 0 \\ \varrho_\nu \end{pmatrix} \tag{39}$$

where $\nu = 1, 2, 3$, $\Lambda = \alpha_{11}n_1^2+\alpha_{22}n_2^2-(s+1)\,\tau\tilde{B}_s'(\sigma)/3s$ and

$$\begin{aligned} &\xi_1 = h_1 \quad && \eta_1 = n_2 \quad && \varrho_1 = n_1 \\ &\xi_2 = h_2 \quad && \eta_2 = n_1 \quad && \varrho_2 = n_2 \\ &\xi_3 = h_3 \quad && \eta_3 = 0 \quad && \varrho_3 = (s+1)\,\tilde{B}_s(\sigma)/3s. \end{aligned} \tag{40}$$

One can show that (37) and (38) do not satisfy these equations for the case (33), and that there exist solutions of (39) for (33) such that each derivative of n_1, n_2, σ with respect to h_1, h_2, τ differs from those given in (37), (38).

The above results elucidate the behaviour of the magnetization in the case $\alpha_{33} > \alpha_{22} > \alpha_{11}$ and for a field $h_3 = 0$, $h_1 \neq 0$, $h_2 \neq 0$. For (24), the magnitude of the magnetization depends on h_1, h_2, τ, whereas for (23) solely on the temperature, being the same (in the limits of MFA) as in the field-free case. When introducing spherical coordinates (15), we have $\vartheta = \vartheta(\tau, h_1, h_2)$, $\psi = \psi(h_1, h_2)$, for the phase (23) while $\varphi = \pi/2$; $\psi = \psi(\tau, h_1, h_2)$ for (24). Furthermore, for (24), (29) it can be proved that

$$\begin{gathered} \psi(\tau, h_1, h_2) \neq \psi_h \\ \lim_{\tau\to\infty} \psi(\tau, h_1, h_2) = \lim_{h\to\infty} \psi(\tau, h_1, h_2) = \psi_h \end{gathered} \tag{41}$$

where ψ_h is the azimuthal angle of the external magnetic field. From that, the behaviour of the magnetization is rather clear. For sufficiently low fields ($\beta < 1$) and temperatures ($\tau < \tau_c$), the magnetization vector declines from the easiest direction x_3 in such a way that the magnitude of the magnetization remains the same as in the field-free case at that temperature, the angle ψ depending solely on the strength and the direction of the external field, and ϑ on both the field and the temperature. When raising the temperature and/or the field strength, the projection of the magnetization on the easiest axis decreases, vanishing at $\tau_c(h_1, h_2)$. The new phase (24) is continued above this point; the magnetization magnitude begins now to depend on the field components, the angle ψ on the temperature, coinciding with that of the field, ψ_h, in the limit case $\tau \to \infty$ and/or $h \to \infty$.

If the external field is not perpendicular to the easiest magnetization axis, a numerical analysis of the whole problem is necessary. It seems however that, much like in the uniaxial case [5–9], the existence of a field component parallel to the easiest axis destroys the second-order phase transition in the system.

For $h_1 \neq 0$, $h_2 = 0$, $h_3 = 0$ or $h_2 \neq 0$, $h_1 = 0$, $h_3 = 0$, the solutions of (7) can be found immediately from (23), (24). Let us assume $h_1 \neq 0$. Then, according to (23) and (24), four magnetization directions are admissible: two along the axis x_1 (parallel or antiparallel to the field) and two others in the planes (x_1, x_2), (x_1, x_3), being real for

$$|h_1| \leqslant |\varkappa_{12}|, \quad |h_2| \leqslant |\varkappa_{13}|, \tag{42}$$

respectively. If $\varkappa_{12} > 0$, $\varkappa_{13} > 0$ (easiest axis along x_1), the solution with the magnetization parallel to the field satisfies the conditions for the absolute minimum of the free energy for $-\infty < \tau < \infty$, $-\infty < h_1 < \infty$; the one with the magnetization antiparallel to the field is a relative minimum in a certain field and temperature interval[2], and the remaining two do not correspond to a minimum. For the field perpendicular to the easiest axis ($h_1 \neq 0$, $\varkappa_{13} < 0$ or $\varkappa_{12} < 0$), the solution for which the magnetization lies in the plane spanned by the easiest axis and the field satisfies the conditions for a minimum in the field interval (42) if $0 < \tau < \tau_c(h_1)$. Above $\tau_c(h_1)$ the magnetization is parallel to the field. If the conditions (42) are not fulfilled, the latter is the minimum in the whole temperature region. The remaining solutions never satisfy the minimum conditions. As in the uniaxial case [6], a second-order phase transition occurs at $\tau_c(h_1)$ if the conditions (42) are met.

5. *Concluding remarks*

A characteristic feature of second-order phase transitions is the change of a symmetry on passing the phase boundary. Our results indicate clearly a relationship between the magnetic symmetry of the ferromagnetic lattice and the direction of the external magnetic field, which plays an important role in magnetic phenomena and phase transitions. There is a basic difference, for instance, between the case when the field lies along a main crystallographic direction (an axis of our coordinate system) and that when its direction is arbitrary in the hardest plane, for the case $\alpha_{11} \neq \alpha_{22} \neq \alpha_{33} \neq \alpha_{11}$ Section 4). Namely, in the latter case the magnetization is usually not parallel to the field direction upon passing to the paramagnetic phase (cp. Eq. (41)). Moreover, one sees that it is not the type of the anisotropic interaction but the lattice symmetry as such which is responsible for this effect.

One should be careful when applying our method to pseudodipolar interactions in the hexagonal dense-packed lattice, which leads to magnetic isotropy if there is no lattice deformation along the six-fold axis from the ideal configuration [13]. This, of course, does not contradict the conclusion (8) (where $\alpha_{11} = \alpha_{22} = \alpha_{33}$ follows only for cubic lattices), which is a result of symmetry with respect to point groups (it does not distinguish between the simple and dense-packed hexagonal lattice).

Intra-atomic interactions (crystal-field anisotropy) have been excluded from our considerations, as the model free energy (3) assumes in that case a much more complicated form (see, *e. g.*, [14, 5]), which causes additional, purely mathematical difficulties. Their influence on the described effects, however, seems to be much the same as that of other uniaxial anisotropy forms, for these interactions (assumed, *e. g.*, in the x_3-direction) cause the constant α_{33} to depend merely on the absolute value of the magnetization (but not on its direction) [5]. Hence, the form of the last equation of (7), describing the dependence $\sigma(\tau)$, can be changed, while the remaining ones, $G_i = G_4 = 0$, describing the magnetization direction and being essential for the problem, remain unchanged. Incidentally, the equations $G_i = G_4 = 0$ which do not include the temperature explicitly should apperently be valid in a much wider temperature region than the MFA itself (cp., *e. g.*, [9]), according to the rule noticed in [15].

[2] The reversal of the field direction along the easiest axis leads to an inversion of the magnetization direction, which occurs in the field interval $|h_1| < |h_{1t}(\tau)|$ where h_{1t} can be determined like in [6]. From the dynamical point of view, the system undergoes a first-order phase transition within this interval for $0 < \tau < \tau_c(0)$ (where $\tau_c(0)$ is the ordinary Curie point), since the first derivative of φ with respect to the field component h_1, namely σ_1, changes its sign. (Note, however, that the entropy (21) is continuous if this phase transition occurs for $h_1 = 0$.)

The Hamiltonian (1) does not exclude long-range dipolar interactions. However, the assumptions (2), (5) actually restrict the considerations to infinite samples (or finite ones with periodic boundary conditions). None the less, it is known from experiment [16, 17] and micromagnetic considerations [18, 19] and [20], that the assumption (2) is even in that case a reasonable approximation for an ellipsoidal sample of sufficiently small size. Thus, if we assume the validity of (2), (5) for such a ferromagnetic sample with dipolar interactions included and apply the symmetry conditions of Section 2, we obtain (8) and $\alpha_{11}=\alpha_{22} \neq\alpha_{23}$ for an ellipsoid of revolution (with x_3 as the revolution axis). On the other hand, phenomenological considerations concerning the thermodynamical behaviour of an ellipsoid uniformly magnetized in an external magnetic field lead to the model free energy (3) with α_{ij} proportional to the demagnetizing factors.

In the case of nonuniform magnetization, the assumption (2) is clearly no longer valid. However, the results obtained in [3] show that in this case, too, second-order magnetic phase transition can occur in the presence of an external magnetic field.

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