

ON THE THEORY OF THE TEMPERATURE DEPENDENCE OF FERROMAGNETIC ANISOTROPY

E. A. TUROV and A. I. MITSEK

Institute for Metal Physics, Academy of Sciences, U.S.S.R.

Submitted to JETP editor May 30, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 1127-1132 (October, 1959)

We have used the phenomenological spin wave theory to evaluate the temperature dependence of the magnetic anisotropy free energy in ferromagnets in the low temperature region. It is shown that if we use the usual expressions for this free energy, the temperature dependence of the anisotropy constant of N -th order may depend substantially on the magnitude of the ratio at 0°K of the subsequent constants to the one given. The mixing of anisotropy constants of different orders in the equations for their temperature dependence disappears only when the anisotropy energy is written in the form of an expansion in homogeneous harmonic polynomials (in the direction cosines of the magnetization vector relative to the crystal axes). It then turns out that in the low temperature region the temperature dependence (1) of the anisotropy constants, established theoretically by Zener,¹ is only approximately valid.

1. In recent years there have appeared a number of theoretical papers¹⁻⁷ devoted to the evaluation of the temperature dependence of the constants of magnetic crystallographic anisotropy of ferromagnetic single crystals. The interest in this problem is enhanced, in particular, by the large part played by the magnetic anisotropy in ferromagnetic resonance phenomena.

Zener¹ developed a classical theory of the change with temperature of the anisotropy constants; this theory was independent of the type of binding between the magnetic atoms. He started from the assumption that one can separate off in the crystal a short-range order region of spins around each atom, inside which the local anisotropy constants are temperature independent. Assuming also that the distribution of the spin oscillations between such regions would be a random one, Zener obtained, after averaging the local anisotropy energy over all directions of the short-range order, the following result for the macroscopic anisotropy constant of N -th order*

$$K_N(T)/K_N(0) = [M(T)/M(0)]^{N(2N+1)}. \quad (1)$$

Here $K_N(T)$ and $K_N(0)$ are anisotropy constants and $M(T)$ and $M(0)$ the spontaneous magnetization at a temperature T and at the absolute zero,

*Since the anisotropy energy must be an even function of the magnetization M , it is convenient to define as the order of the constant not the degree of the invariant of the components of M which multiplies the constant, but one half of this degree. This we shall do throughout the whole of the paper.

respectively. Carr² has shown that one can obtain essentially the same result in the molecular-field approximation. It follows, in particular from Eq. (1), that for cubic crystals ($N = 2$) we have for the first anisotropy constant $K_2 \sim M^{10}$. This last relation was already obtained in 1936 by Akulov⁸ from theoretical considerations similar to Zener's.

The papers by Tyablikov and Gusev,³ Pal,⁴ Keffer,⁵ Kasuya,⁶ and Potapkov⁷ used spin-wave theory to discuss the temperature dependence of the anisotropy constants. The results of these papers also agreed approximately with Eq. (1) for the first and second anisotropy constants of uniaxial and cubic crystals. Experiments, however, did not confirm such a simple and universal temperature dependence of those constants K_N which are usually used for a theoretical analysis. The constants K_2 , for instance, change in a number of ferrites appreciably less with temperature than would follow from Eq. (1).^{*} On the other hand, K_2 for nickel increases appreciably faster with decreasing temperature than according to the "M¹⁰-law."

In the papers quoted,³⁻⁷ the authors use as a rule, various microscopic models, which are based upon a number of often very arbitrary assumptions about the interaction mechanism that leads to the ferromagnetic anisotropy, and also upon assumptions about the nominal value of the spontaneous

*It was thought for a long time that the $K_2 \sim M^{10}$ law was well satisfied for iron. Recent experimental work,⁹ however, led to a completely different result: $K_2 \sim M^4$ or M^5 .

magnetization at 0°K.* It is thus of interest to evaluate the temperature dependence of the magnetic anisotropy constants of ferromagnetics in the low-temperature region using the phenomenological spin-wave theory,¹⁰ which is based solely on symmetry considerations and is free from a number of restrictions inherent in the microscopic models. This calculation will be given in a general form which is independent of the type of symmetry of the crystal.

2. The phenomenological Hamiltonian of a ferromagnet can in the general case be written in the form¹⁰

$$\mathcal{H} = \int \mathcal{H}(\mathbf{r}) d\mathbf{r},$$

$$\mathcal{H}(\mathbf{r}) = A_{ij} \frac{\partial m_k}{\partial r_i} \frac{\partial m_k}{\partial r_j} + K_{n_1 n_2 n_3} m_x^{n_1} m_y^{n_2} m_z^{n_3} - \frac{1}{2} M_0^2 \mathbf{m} \nabla \int \frac{\text{div } \mathbf{m}(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} - M_0 \mathbf{m} \mathbf{H}. \quad (2)$$

Here $\mathbf{m}(\mathbf{r}) = \mathbf{M}(\mathbf{r})/M_0$ is the unit vector of the local magnetization; $i, j, k = x, y, z$; n_1, n_2, n_3 are integers such that $n_1 + n_2 + n_3 = 2N$ is an even number; repeated indices imply summation. The first term in (2) is that part of the exchange energy which is connected with the inhomogeneities of $\mathbf{m}(\mathbf{r})$ and is characterized by the parameters A_{ij} . The second term gives the energy of the magnetic crystallographic anisotropy written in the form of an expansion in increasing powers of the magnetization components; the set of non-vanishing anisotropy constants $K_{n_1 n_2 n_3}$ of order $N = \frac{1}{2}(n_1 + n_2 + n_3)$ (and also the number of different parameters A_{ij}) is determined by the crystal symmetry.† The third term describes the magnetostatic energy caused by the inhomogeneities of the magnetization and the last term, finally, is the energy of the ferromagnetic in an external field \mathbf{H} .

We choose a system of coordinates (ξ, η, ζ) with a ζ axis along the classical equilibrium (at 0°K) magnetization vector $\mathbf{m}_0 = \boldsymbol{\alpha}$. The components of $\boldsymbol{\alpha}$ in the x, y, z system will then be equal to $\alpha_x = \sin \theta \cos \varphi$, $\alpha_y = \sin \theta \sin \varphi$, and $\alpha_z = \cos \theta$, where θ and φ are respectively the polar and azimuthal angles of the vector $\boldsymbol{\alpha}$ with

*References 3 and 7 are least encumbered by these deficiencies.

† In view of the condition $m_x^2 + m_y^2 + m_z^2 \approx 1$, different invariants permitted by the symmetry turn out to be linearly dependent. We shall assume that the expansion given contains already only independent invariants. The choice of these invariants and of the constants K_N is, finally, not unique. One can, however, always perform the transformation from one set of constants to another one.

respect to the x, y, z axes. Restricting ourselves to the low-temperature case, we shall consider only small oscillations of the vector \mathbf{m} about the direction of $\boldsymbol{\alpha}$. These oscillations can be approximately expressed in terms of the Bose amplitudes $b_{\mathbf{r}}$ and $b_{\mathbf{r}}^\dagger$ using the relations¹⁰

$$m_\xi = (\mu/2M_0)^{1/2} (b_{\mathbf{r}} + b_{\mathbf{r}}^\dagger), \quad m_\eta = i(\mu/2M_0)^{1/2} (b_{\mathbf{r}} - b_{\mathbf{r}}^\dagger),$$

$$m_\zeta = 1 - \mu b_{\mathbf{r}}^\dagger b_{\mathbf{r}}/M_0, \quad (3)$$

where $\mu = g e \hbar / 2mc$ and g is the Landé factor.

The changeover from (3) to m_x, m_y , and m_z is through the transformation formulae

$$m_x = m_\xi \cos \theta \cos \varphi - m_\eta \sin \varphi + m_\zeta \sin \theta \cos \varphi,$$

$$m_y = m_\xi \cos \theta \sin \varphi + m_\eta \cos \varphi + m_\zeta \sin \theta \sin \varphi,$$

$$m_z = -m_\xi \sin \theta + m_\zeta \cos \theta. \quad (4)$$

Substituting (3) into (4) and after that into the Hamiltonian (2), and segregating the quadratic expression in the operators $b_{\mathbf{r}}$ and $b_{\mathbf{r}}^\dagger$, we obtain, after the usual transformations that bring this expression to diagonal form, the spectrum of the energy eigenvalues of the system

$$\mathcal{H} = \mathcal{H}_0 + \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} N_{\mathbf{k}}.$$

Here

$$\mathcal{H}_0 = K_{n_1 n_2 n_3} \alpha_x^{n_1} \alpha_y^{n_2} \alpha_z^{n_3} - M_0 (\boldsymbol{\alpha} \mathbf{H}) \quad (5)$$

gives us, after minimizing with respect to $\boldsymbol{\alpha}$, the ground state of the system;* $\varepsilon_{\mathbf{k}}$ is the energy of a spin wave with wave vector \mathbf{k} , and $N_{\mathbf{k}}$ the number of spin waves with that wave vector.

We shall restrict our considerations to the temperature range for which

$$\kappa T \gg 2\pi\mu M_0, \quad \mu K_N / M_0 \quad (6)$$

(κ is Boltzmann's constant); the energy of the spin waves that influence the thermodynamic behavior of the system can then approximately be written in the form

$$\varepsilon_{\mathbf{k}} = (\mu/M_0) \{ 2A_{ij} k_i k_j + M_0 (\boldsymbol{\alpha} \mathbf{H}) + 2\pi M_0^2 \sin^2 \theta_{\mathbf{k}} - \frac{1}{2} \sum_N [2N(2N+1) - \nabla_{\boldsymbol{\alpha}}^2] f_N(0) \}, \quad (7)$$

where $\theta_{\mathbf{k}}$ is the angle between the vectors \mathbf{k} and $\boldsymbol{\alpha}$, $\nabla_{\boldsymbol{\alpha}}^2$ is the Laplacian in terms of the variables $\alpha_x, \alpha_y, \alpha_z$, and $f_N(0)$ denotes the homogeneous polynomial of degree $2N$

*That is, the equilibrium orientation of the vector $\boldsymbol{\alpha}$, determined by the simultaneous action of the external field and the internal anisotropy forces.

$$f_N(0) = \sum_{(n_1+n_2+n_3=2N)} K_{n_1 n_2 n_3} \alpha_x^{n_1} \alpha_y^{n_2} \alpha_z^{n_3}. \quad (8)$$

The first term in (5), which is just the anisotropy energy at 0°K, can be rewritten in terms of $f_N(0)$ in the form

$$F_A(0) = \sum_N f_N(0). \quad (9)$$

The spin wave energy consists according to (7) of the following successive four parts: the exchange energy, the energy in the external magnetic field, the magnetostatic energy, and, finally, the energy connected with the internal magnetic-anisotropy forces. Condition (6) means in fact that our results will only be valid in that temperature range where the first (exchange) term in (7) is large compared to the third and fourth terms. We shall exclude these latter from our consideration of the region of very low temperatures, near absolute zero ($T \lesssim 0.1$ to 1°K).

Knowing the energy spectrum of the system (7) we can evaluate its thermodynamic potential

$$\Omega = \mathcal{H}_0 + \kappa T \sum_{\mathbf{k}} \ln(1 - e^{-\epsilon_{\mathbf{k}}/\kappa T}).$$

Separating in Ω the part that depends on the direction of α relative to the crystallographic axes, and taking Eq. (6) into account, we get, for sufficiently large external fields H so that there is saturation ($\alpha \cdot H \approx H$), the free energy of anisotropy at temperature T :

$$F_A(T) = \sum_N \left\{ 1 - \frac{\Delta M(T)}{2M_0} [2N(2N+1) - \nabla_{\alpha}^2] \right\} f_N(0). \quad (10)$$

In this formula we have expressed that part of the anisotropy free energy which depends on the temperature through the temperature variation of the magnetization $\Delta M(T) = M_0 - M(T)$, taking into account that

$$M(T) = -\partial\Omega/\partial H = M_0 - \mu \sum_{\mathbf{k}} (e^{\epsilon_{\mathbf{k}}/\kappa T} - 1)^{-1}.$$

3. Expression (10) for the free energy of magnetic anisotropy can be simplified considerably if the homogeneous polynomials f_N , in which F_A is expanded, satisfy the Laplace equation

$$\nabla_{\alpha}^2 f_N = 0,$$

i.e., are harmonic polynomials. In that case we have instead of (10)

$$F_A(T) = \sum_N f_N(T), \quad (9')$$

where

$$f_N(T) = f_N(0) [1 - (\Delta M/M_0) N(2N+1)]. \quad (11)$$

The temperature dependence of any anisotropy constant which is one of the expansion coefficients of the free energy of anisotropy in terms of invariants written in the form of homogeneous harmonic polynomials ("harmonic invariants") satisfies thus, according to (9), (9'), and (11), a general law which is independent of the type of the crystal symmetry and which is determined solely by the degree $2N$ of the corresponding polynomial f_N . Indeed, if

$$f_N = \sum_n K_N^{(n)} W_{N,n}(\alpha_x, \alpha_y, \alpha_z),$$

where $W_{N,n}(\alpha_x, \alpha_y, \alpha_z)$ are independent harmonic invariants* of degree $2N$, then

$$K_N^{(n)}(T) = K_N^{(n)}(0) [1 - N(2N+1) \Delta M/M_0], \quad (12)$$

or

$$(K_N^{(n)}(0) - K_N^{(n)}(T))/K_N^{(n)}(0) = P_N(M(0) - M(T))/M(0), \quad (13)$$

where $M(0) \equiv M_0$ and

$$P_N = N(2N+1). \quad (14)$$

This relation is approximately the same as Eq. (1) at low temperatures (i.e., for $\Delta M \ll M_0$), but with one reservation, namely that it must be applied to the constants in front of harmonic invariants.

Relation (13) remains formally the same in the case of the customary "non-harmonic" form of writing the anisotropy free energy. The coefficient P_N in it will, however, be essentially different: it will depend not only on the order N of the corresponding constant K_N , but also on the magnitude of the ratio at 0°K of the next constants to the one given. The coefficient P_N in Eq. (13) will, for instance, take on the following form for the case of the first constants in hexagonal ($N=1$) and in cubic ($N=2$) crystals, respectively, if one uses the standard form for the anisotropy energy¹¹

$$P_1 = 3 - \frac{6K_2(0) + \dots}{K_1(0)}, \quad P_2 = 10 - \frac{K_3(0) + 8K_4(0) + \dots}{K_2(0)}, \quad (15)$$

while if we use the harmonic expression for F_A we would have according to (14) $P_1 = 3$ and $P_2 = 10$.

*The index n is introduced for the case where the number of independent invariants of degree $2N$ is larger than 1.

It is well known that even at room temperature the first and second anisotropy constants in ferromagnets are often of the same order of magnitude (see Bozorth's book¹²), and with decreasing temperature the second constant usually increases faster than the first one.* There are also indications in the literature that constants of higher order are also by no means small compared with the first constants.¹⁴ This fact enables us to explain in principle why, for instance, for cubic crystals the following rule which follows from Eq. (1)

$$\Delta K_2(T)/K_2(0) = 10\Delta M(T)/M(0) \quad (16)$$

is not satisfied experimentally even in the low temperature region. It is clear from the second equation in (15) that in the case where F_A is written in the conventional way the numerical coefficient on the right hand side of (16) may be either less or more than 10, depending on the relative signs and on the ratio of the magnitudes at 0°K of the later constants and of the first constant.† The rule expressed by (16) needs only be satisfied when the anisotropy energy is analyzed using its harmonic representation.

4. We shall, in conclusion, give the general expansion of F_A in terms of harmonic invariants for cubic and uniaxial crystals.

For crystals of cubic symmetry we have (up to terms of the eighth power in the α_i)

$$\begin{aligned} F_A = & K_2[\alpha_x^4 + \alpha_y^4 + \alpha_z^4 - 1/3(\alpha_x^2\alpha_y^2 + \alpha_x^2\alpha_z^2 + \alpha_y^2\alpha_z^2)] \\ & + K_3[\alpha_x^6 + \alpha_y^6 + \alpha_z^6 - 15/2(\alpha_x^4\alpha_y^2 + \alpha_x^2\alpha_y^4 + \alpha_x^4\alpha_z^2 \\ & + \alpha_x^2\alpha_z^4 + \alpha_y^4\alpha_z^2 + \alpha_y^2\alpha_z^4) + 90\alpha_x^2\alpha_y^2\alpha_z^2] + K_4[\alpha_x^8 + \alpha_y^8 + \alpha_z^8 \\ & - 14(\alpha_x^6\alpha_y^2 + \alpha_x^2\alpha_y^6 + \alpha_x^6\alpha_z^2 + \alpha_x^2\alpha_z^6 + \alpha_y^6\alpha_z^2 + \alpha_y^2\alpha_z^6) \\ & + 35(\alpha_x^4\alpha_y^4 + \alpha_x^4\alpha_z^4 + \alpha_y^4\alpha_z^4)]. \end{aligned} \quad (17)$$

For uniaxial crystals we have (up to terms of the fourth power and not taking the anisotropy in the basal plane into account)

$$\begin{aligned} F_A = & K_1(\alpha_x^2 + \alpha_y^2 - 2\alpha_z^2) \\ & + K_2\left[(\alpha_x^2 + \alpha_y^2)^2 - 8(\alpha_x^2 + \alpha_y^2)\alpha_z^2 + \frac{8}{3}\alpha_z^4\right]. \end{aligned} \quad (18)$$

It is necessary to add to this last expression for the case of tetragonal crystals a term of the form

$$K_2'[\alpha_x^4 + \alpha_y^4 - 6\alpha_x^2\alpha_y^2], \quad (19)$$

which describes the anisotropy in the basal plane. The harmonic invariants of the fourth and sixth degree when the anisotropy in the basal plane is taken into account are, for instance, given for rhombohedral and hexagonal crystals by Landau and Lifshitz.¹⁵

The temperature dependence of the constants K_N entering into Eqs. (17) – (19) is described by the general Eq. (13). Since there is no mixing of constants of different order in this formula, we may expect the treatment of the experimental temperature dependence of the magnetic-anisotropy energy and of its theoretical analysis to be facilitated by precisely this formulation of F_A .

Accurate experimental studies of the temperature dependence of the anisotropy constants accompanied by a simultaneous measurement of the magnetization in order to verify the theoretical Eq. (13) would at this moment be of great importance, since they would enable us to verify the basic ideas and methods of contemporary ferromagnetic theory.

The authors express their deep gratitude to S. V. Vonsovskii for discussing the present paper and for valuable advice.

¹ C. Zener, Phys. Rev. **96**, 1335 (1954).

² W. J. Carr Jr., Phys. Rev. **109**, 1971 (1958).

³ S. V. Tyablikov, JETP **20**, 661 (1950); S. V. Tyablikov and A. A. Gusev, Физика металлов и металловедение (Physics of Metals and Metallurgy) **2**, 385 (1956).

⁴ L. Pal, Acta Phys. Hung. **3**, 287 (1954).

⁵ F. Keffer, Phys. Rev. **100**, 1692 (1955).

⁶ T. Kasuya, J. Phys. Soc. Japan **11**, 944 (1956).

⁷ N. A. Potapkov, Dokl. Akad. Nauk SSSR **118**, 269 (1958), Soviet Phys. - Doklady **3**, 89 (1958).

⁸ N. Akulov, Z. Physik **100**, 197 (1936); Ферромагнетизм (Ferromagnetism), M.-L., 1939.

⁹ C. D. Graham Jr., Phys. Rev. **112**, 1117 (1958).

¹⁰ E. A. Turov and V. G. Shavrov, Тр. Ин-та физики металлов АН СССР (Proc. Inst. Metals Acad. Sc. U.S.S.R.) No. 20, 101 (1958); Izv. Akad. Nauk SSSR, Ser. Fiz. **22**, 1168 (1958), Columbia Tech. Transl. p. 1158.

¹¹ S. V. Vonsovskii and Ya. S. Shur, Ферромагнетизм (Ferromagnetism), Gostekhizdat, 1948, pp. 268 and 272.

¹² R. Bozorth, Ferromagnetism (Russ. Transl.), IIL, 1956, p. 453 [Van Nastrand, N.Y. 1951].

¹³ H. Sato and B. S. Chandrasekhar, J. Phys. Chem. Solids **1**, 228 (1957).

*An indication that subsequent anisotropy constants might influence the temperature dependence of earlier ones was already given in Zener's paper¹ and also in references 2 and 13.

†It has already been shown that both these cases ($P_2 < 10$ and $P_2 > 10$) occur experimentally.

¹⁴ Kirenskii, Nosova, and Reshetnikova, *Izv. Akad. of Continuous Media*, Gostekhizdat, 1957, p. 200.
Nauk SSSR, Ser. Fiz. **21**, 1105 (1957), Columbia Tech.
Transl. p. 1093.

¹⁵ L. D. Landau and E. M. Lifshitz, *Электродинамика сплошных сред (Electrodynamics)*, Gostekhizdat, 1957, p. 218.
Translated by D. ter Haar

Vacuum Tubes (see Methods and Instruments)

Viscosity (see Liquids)

Wave Mechanics (see Quantum Mechanics)

Work Function (see Electrical Properties)

X-rays

Anomalous Heat Capacity and Nuclear Resonance in Crystalline Hydrogen in Connection with New Data

on Its Structure. S. S. Dukhin — 1054L.

Diffraction of X-rays by Polycrystalline Samples of Hydrogen Isotopes. V. S. Kogan, B. G. Lazarev, and R. F. Bulatova — 485.

Investigation of X-ray Spectra of Superconducting CuS.

I. B. Borovskii and I. A. Ovsyannikova — 1033L.

Optical Anisotropy of Atomic Nuclei. A. M. Baldin — 142.

ERRATA TO VOLUME 9

On page 868, column 1, item (e) should read:

(e). Ferromagnetic weak solid solutions. By way of an example, we consider the system Fe-Me with A2 lattice, where Me = Ti, V, Cr, Mn, Co, and Ni. For these the variation of the moment m with concentration c is

$$dm/dc = (Na)_{Me} \mp 0.642 \{ 8 (2.478 - R_{Me}) + 6 |2.861 - R_{Me}| \mp [8(2.478 - R_{Fe}) + 6(2.861 - R_{Fe})] \},$$

where the signs $-$ and $+$ pertain respectively to ferromagnetic and paramagnetic Me when in front of the curly brackets, and to metals of class 1 and 2 when in front of the square brackets. The first term and the square brackets are considered only for ferromagnetic Me. We then have $dm/dc = -3$ (-3.3) for Ti, -2.6 (-2.2) for V, -2.2 (-2.2) for Cr, -2 (-2) for Mn, 0.7 (0.6) for Ni, and 1.2 (1.2) for Co; the parentheses contain the experimental values.

ERRATA TO VOLUME 10

Page	Reads	Should Read
224, Ordinate of figure	10^{23}	10^{29}
228, Column 1, line 9 from top	3.6×10^{-2} mm/min	0.36 mm/min
228, Column 1, line 16 from top	0.5 mm/sec	0.05 mm/min
329, Third line of Eq. (23a)	$+ (1/4 \cosh r + \dots$	$+ 1/4 (\cosh r + \dots$
413, Table II, line 2 from bottom	$-0.0924 \pm$	$-1.0924 \pm$
413, Table II, line 3 from bottom	$+1.8730 \pm$	$+0.8370 \pm$
479, Fig. 7, right, 1st line	92 hr	9.2 hr
499, Second line of Eq. (1.8)	$+\tilde{k} \sin^2 \alpha / \omega_N^2 + \langle c^2 \tilde{k}^2 \dots$	$+\left(\tilde{k}/\omega_H\right)^2 \sin^2 \alpha \langle c^2 \tilde{k}^2 \dots$
648, Column 1, line 18 from top	18×80 mm	180×80 mm
804, First line of Eq. (17)	$-1/3 (\alpha_x^2 \alpha_y^2 + \dots$	$\dots - 3 (\alpha_x^2 \alpha_y^2 + \dots$
967, Column 1, line 11 from top	$\sigma(N', \pi) \approx 46(N', N')$	$\sigma(N', \pi) > \sigma(N', N')$
976, First line of Eq. (10)	$= \frac{e^2}{3r^2c^4}$	$= \frac{e^2}{3\hbar^2c^2}$
978, First line of Eq. (23)	$\left[\frac{(2\gamma^2 - 1)^2}{(\gamma^2 - 1) \sin^4(\theta/2)} \right]$	$\left[\frac{(2\gamma^2 - 1)^2}{(\gamma^2 - 1)^2 \sin^4(\theta/2)} \right]$