SOVIET PHYSICS JETP VOLUME 24, NUMBER 4 APRIL, 1967

CONCERNING THE TEMPERATURE DEPENDENCE OF THE MAGNETIC ANISOTROPY CONSTANTS OF FERROMAGNETS AND FERRITES

A. I. DROKIN and L. I. SLOBODSKOĬ

Physics Institute, Siberian Division, Academy of Sciences, U.S.S.R.

Submitted to JETP editor April 30, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) **51**, 1023–1029 (October, 1966)

The Turov-Mitsek formula for the temperature dependence of the magnetic anisotropy constants derived on the basis of the phenomenological spin-wave theory is verified experimentally. The formula is found to be in satisfactory agreement with the experiments at low temperatures ($\Delta M \ll M_0$) for iron, nickel, manganese, and magnesium-manganese ferrite single crystals and for lithium pentaferrites. An investigation of the temperature course of the first magnetic anisotropy constant near the Curie point performed on various ferrite-spinel single crystals shows that the linear dependence of $K_1(T)$ predicted on the basis of thermodynamic considerations by Vonsovskiĭ is true only for ferrites which are stable with respect to thermal and thermomagnetic treatment.

1. INTRODUCTION

ONE of the basic questions in the theory of ferro- and ferrimagnetism and in the practical search for new magnetic materials is the problem of the anisotropy of the physical properties, its dependence on the structure of solid solutions, the temperature, the magnetic field, etc. This refers in the first instance to the anisotropy of the magnetic properties. The latter, along with other forms of anisotropy, has a large effect on the processes of the technical magnetization of ferromagnets and ferrites. A large number of theoretical and experimental papers have therefore been devoted to the temperature dependence of the magnetic anisotropy constants of ferromagnets and ferrites. Classical[1, 2] and quantum mechanical calculations of the $K_1(T)$ dependences have been carried out. The majority of these describes the temperature dependence of the magnetic anisotropy constants as a function of changes in the spontaneous magnetization in the low-temperature region.

Classical calculations, as well as calculations based on the application of the spin-wave method to dipole and quadrupole models, lead in the case of cubic crystals to the "tenth-power" law, i.e., they indicate that the first magnetic anisotropy constant in the region of low temperatures should vary as the tenth power of the saturation magnetization. However, experiments show that, for example, in iron the anisotropy constant changes with a lower power,[3] and in nickel with a considerably higher power.[4]

Bryukhatov and Kirenskiĭ[5] have found an empirical formula for the $K_1(T)$ dependence for iron and nickel. It turned out that the experimental points fit well a curve constructed according to this formula, not only in the case of iron and nickel, but in the case of many ferromagnets and ferrites, both at low temperatures and at rather high temperatures, up to one third of the Curie temperature Θ. The empirical formula of Bryukhatov and Kirenskiĭ does not contain the spontaneous magnetization. Attempts have been made to justify this formula theoretically.[6]

Recently Turov and Mitsek[7] calculated the temperature dependence of the magnetic anisotropy constants on the basis of a phenomenological spin-wave theory free of model considerations. This theory extends also to ferrites.[8] It is of interest to check this theory experimentally.

So far there are no calculations of the temperature dependence of the magnetic anisotropy constants at intermediate temperatures. For temperatures close to the Curie point one can assume from thermodynamic considerations that the dependence $K_1(T)$ should be linear.[9] This also requires experimental verification.

Two problems are solved in this work: we check experimentally the theory of Turov and Mitsek and the behavior of the magnetic anisotropy constant near the Curie point in certain single crystals of ferromagnets and ferrites with a cubic lattice.

2. THE TEMPERATURE DEPENDENCE OF THE FIRST MAGNETIC ANISOTROPY CONSTANT AT LOW TEMPERATURES IN NICKEL, IRON, AND CERTAIN SINGLE-CRYSTAL FERRITES WITH THE SPINEL STRUCTURE

Turov and Mitsek[7, 8] obtained on the basis of the phenomenological theory of spin waves the following temperature dependence of the magnetic anisotropy constants:

$$\frac{\bar{K}_N^{(n)}(0)-\bar{K}_N^{(n)}(T)}{\bar{K}_N^{(n)}(0)}=N(2N+1)\frac{M(0)-M(T)}{M(0)}. \quad (1)$$

Here K is the magnetic anisotropy constant, N is its order, the bar over K and the superscript (n) indicate that in the formula for the free energy of the anisotropy the constants appear in front of the harmonic invariants that are homogeneous harmonic polynomials, and M is the magnitude of the spontaneous magnetization. The temperature is indicated in parentheses: (0)–0°K and (T)–T°K.

In the classical calculation of Zener[2] the temperature dependence of the magnetic anisotropy constants was described by the formula

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

Here $K_N(T)$ and $K_N(0)$ are the anisotropy constants at the temperature of the measurement T and at 0°K, expressed in the traditional form when the free energy of the anisotropy is written as by Akulov.[1] At low temperatures (for $\Delta M \ll M_0$) relations (1) and (2) coincide provided one stipulates that they must be applied to the constants that appear in the free energy formula in front of the harmonic polynomials. For the first magnetic anisotropy constant of cubic crystals N = 2.

A direct measurement of the magnetic anisotropy constant near absolute zero is very complicated. One can, however, check indirectly that the formulas of Turov and Mitsek (1) agree with experiment. For iron and nickel,[5, 10] and also for simple spinel-structure ferrites that are stable against thermal and thermomagnetic processing[11-13] the empirical law of Bryukhatov and Kirenskiĭ[5] is well satisfied for a broad range of temperatures (from liquid nitrogen temperatures up to $^1/_3\Theta$):

$$K = K_0 e^{-\alpha T^2}. \quad (3)$$

Here K is the value of the first magnetic anisotropy constant at a temperature T, K_0 is its value at 0°K, and α is a constant for the given material.

If the extrapolation to absolute zero is reliable with careful measurement of the anisotropy constants, then at low temperatures ($\Delta M \ll M_0$) the curves of the temperature variation of the magnetic anisotropy constants obtained from the formula of Turov and Mitsek (1) and the corresponding curves of the empirical formula (3) should coincide provided we stipulate that they should be applied to the constants which appear in front of the harmonic invariants. However, even this is unnecessary if we consider the dependence of K/K_0 on T, since the higher-order constants for the investigated materials are small and the ratios K/K_0 and $\bar{K}^{(n)}(T)/\bar{K}^{(n)}(0)$ will be close. If this is the case, then the corresponding dependences K/K_0 and $\bar{K}^{(n)}(T)/\bar{K}^{(n)}(0)$ on T should be very close to each other and should coincide with the experimental data as one approaches liquid nitrogen temperatures.

In order to eliminate from the Turov and Mitsek formula the ratios $[M(0) - M(T)]/M(0)$ [which we shall write in the form $(M_0 - M)/M_0$] we used the known formulas for the temperature dependence of the spontaneous magnetization which correspond satisfactorily with experiment:

a) The Bloch formula[14]

$$M = M_0[1 - \beta(T / \Theta)^{3/2}], \quad (4)$$

β = 0.1174, and Θ is the Curie temperature.

b) The Frenkel-Heisenberg formula[15-16]

$$\frac{M}{M_0} = \text{th}\left(\frac{M}{M_0} \Big/ \frac{T}{\Theta}\right). \quad (5)^*$$

If we use the formulas of Vonsovskiĭ and Seidov[17] for $M(T)/M_0$, then the latter should also agree with experiment, because for the magnetization the "quadratic" and "three-halves" laws are difficult to distinguish experimentally.

Formula (1) reduces (when N = 2) to the following form:

$$\bar{K} / \bar{K}_0 = -9 + 10M / M_0. \quad (6)$$

eliminating M/M_0 from (4) and (6), we obtain

$$\bar{K} / \bar{K}_0 = 1 - 10\beta(T / \Theta)^{3/2}. \quad (7)$$

Making use of the approximate formula,

$$\text{th}\, x \approx 1 - 1 / (x + 1), \quad (8)$$

one can reduce (5) to the following form:

$$M / M_0 \approx 1 - T / \Theta. \quad (9)$$

Consequently,

$$M / M_0 \approx 1 - 2 / (e^{2(\Theta/T-1)} + 1). \quad (10)$$

Eliminating M/M_0 from (6) and (10), we obtain

$$\frac{\bar{K}}{\bar{K}_0} \approx 1 - \frac{10}{(\Theta/T)^2 - \Theta/T + 1}. \quad (11)$$

*th ≡ tanh.

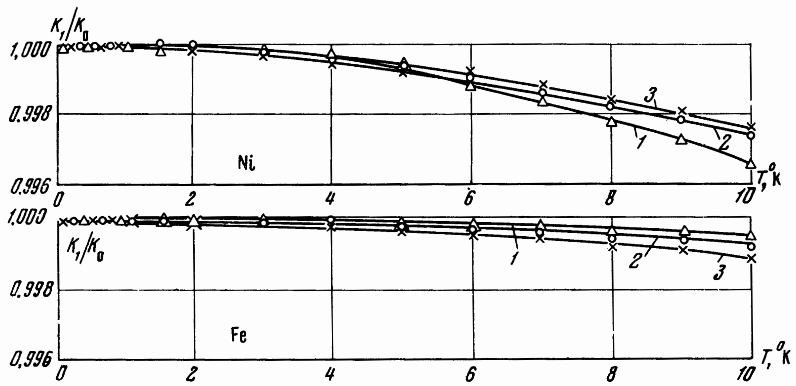

FIG. 1. Plots of the dependence of K_1/K_0 on T for nickel and iron calculated according to: 1 – the formula of Bryukhatov and Kirenskiĭ, 2 and 3 – the formula of Turov and Mitsek, using the Frenkel-Heisenberg and the Bloch equations to eliminate M/M_0 from it.

We used (3), (7), and (11) to plot K/K_0 vs. T for nickel at low temperatures according to the data of Kirenskiĭ [10] and Puzeĭ [4] ($\alpha = 0.000034$ deg^{-2}; $K_0 = -105 \times 10^4$ erg/cm^3; $\Theta = 621°$ K) and for iron according to the data of Kirenskiĭ [10] ($\alpha = 0.000003$ deg^{-2}; $K_0 = 26.3 \times 10^4$ erg/cm^3; $\Theta = 1043°$ K). These plots are shown in Fig. 1. It is seen from the plots that curves corresponding to formulas (3), (7), and (11) agree well with each other up to 5° K and differ inappreciably at 10° K. Curve 2, obtained from the Frenkel-Heisenberg formula (5), lies between curves (3) and (1) obtained from the Bloch (4) and Bryukhatov-Kirenskiĭ (3) formulas. At liquid-nitrogen temperatures curves 2 and 1 are closer to the experimental points.

Analogous graphs (Fig. 2) were plotted for the ferrite single crystals of the composition $Li_{0.48}Fe_{2.25}O_4$ [13] which we investigated ($\alpha = 0.000004$ deg^{-2}; $K_0 = -10.4 \times 10^4$ erg/cm^3; $\Theta = 943°$ K), $MnFe_2O_4$ [11] ($\alpha = 0.000029$ deg^{-2}; $K_0 = -17 \times 10^4$ erg/cm^3; $\Theta = 573°$ K), and $Mg_{0.5}Mn_{0.5}Fe_2O_4$ [12] ($\alpha = 0.000032$ deg^{-2}; $K_0 = -20.7 \times 10^4$ erg/cm^3; $\Theta = 733°$ K).

We note that in these instances, too, the curve plotted with the aid of the Frenkel-Heisenberg formula lies between the curves plotted with the aid of the formulas of Bloch and Bryukhatov and Kirenskiĭ. On approaching liquid-nitrogen temperatures the plots of K_1/K_0 vs. T (1 and 2) approach the experimental points closely for all the investigated ferrite single crystals.

It can thus be assumed that for the materials being considered, the theory of Turov and Mitsek is, with the admitted approximations, in satisfactory agreement with experiment. The largest deviations of the curves are apparently explained by the effect of high-order constants on the values of the ratios K/K_0 and $\bar{K}/\bar{K}_0$. We note that no such check can be made in the case of ferrites that are easily affected by thermal and thermomagnetic processing. The Bryukhatov-Kirenskiĭ law is also not satisfied for these ferrites. This is obviously explained by the change in the degree of reversibility of these ferrites on cooling from high temperatures. For materials which have appreciable second magnetic anisotropy constants one must allow in the calculations for the effect of these constants. [8]

3. TEMPERATURE VARIATION OF THE MAGNETIC ANISOTROPY CONSTANTS IN CERTAIN SINGLE-CRYSTAL FERRITES WITH THE SPINEL STRUCTURE ON APPROACHING THE CURIE POINT

On the basis of general thermodynamic calculations, Vonsovskiĭ [18] obtained for the temperature dependence of the spontaneous magnetization near the Curie point the following formula:

$$\left(\frac{\sigma_s}{\sigma_0}\right)^2 = \frac{a_\Theta'}{2b}(\Theta - T). \qquad (12)$$

Here σ_S is the value of the specific saturation magnetization at a temperature T, σ_0 is its value at 0° K, Θ is the Curie temperature, a'_Θ and b are constants. We note that this formula is valid

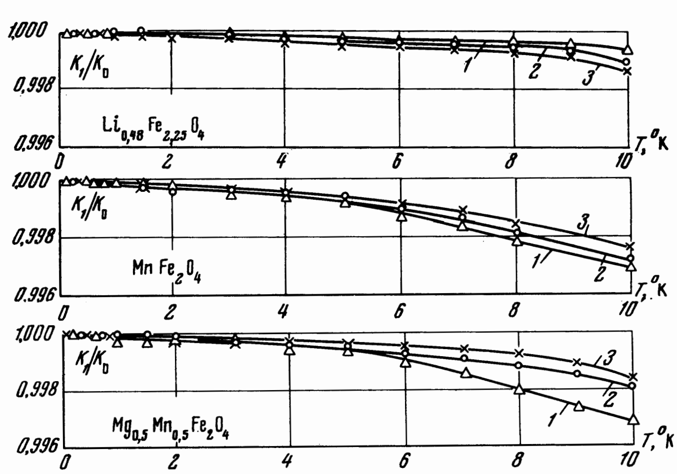

FIG. 2. The same as in Fig. 1 for lithium pentaferrite, and for for manganese and magnesium-manganese ferrites.

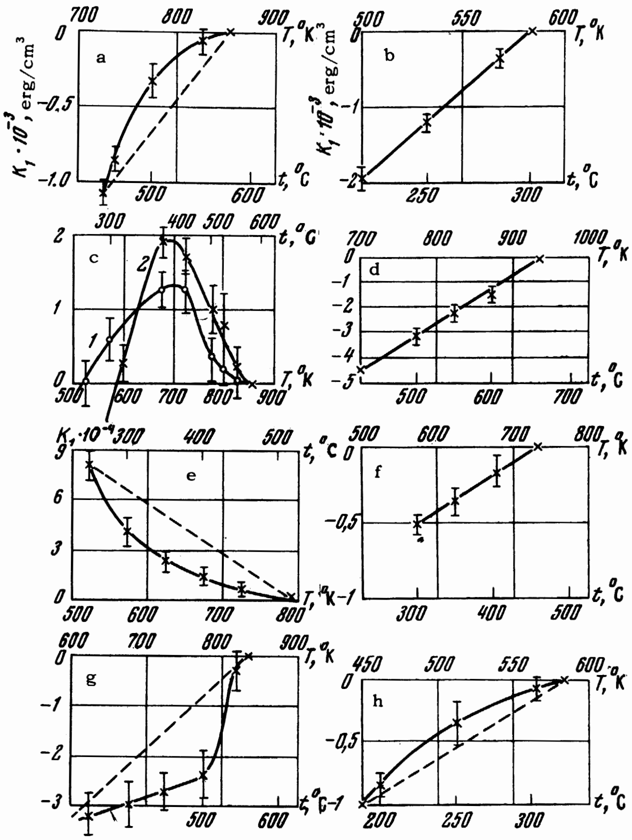

FIG. 3. The $K_1(T)$ dependence of single crystals of ferrites on approaching the Currie point: a – $FeOFe_2O_3$, b – $MnFe_2O_4$, c – nickel ferrites; curve 1 – sample No. 1 and curve 2 – sample No. 3, d – $Li_3O(Fe_2O_3)_5$, e – $CoFe_2O_4$, f – $Mg_{0.5}Mn_{0.5}Fe_2O_4$, g – $Ni_{0.71}Co_{0.03}Fe^{2+}_{0.2}Fe^{3+}_{2.04}O_4$, h – $Y_3Fe_5O_{12}$.

for small values of the parameter σ_S/σ_0, except in the immediate vicinity of the Curie point where the expansion of the thermodynamic potential in powers of the small parameter σ_S/σ_0 is incorrect.

By expanding the anisotropy energy near the Curie point in a series of even powers of σ and with account of (12), Vonsovskiĭ obtained the formula

$$(K_1)_{T\to\Theta} = C'(\Theta - T), \qquad (13)$$

where Θ is the Curie temperature, and C' is a constant which is independent of the temperature. It follows from (13) that the $K_1(T)$ dependence should be linear on approaching the Curie point. We carried out an experiment to check the validity of this relation. The magnetic anisotropy constant was determined by the torque method described in the literature.[19] The objects of the investigations were single-crystal spheres of the following compositions: $FeOFe_2O_3$; $MnFe_2O_4$; nickel-iron ferrites, sample No. 1–$Ni_{0.54}Fe^{2+}_{0.46}Fe_2O_4$, sample No. 2–$Ni_{0.64}Fe^{2+}_{0.36}Fe_2O_4$, and sample No. 3–$Ni_{0.72}Fe^{2+}_{0.28}Fe_2O_4$; $Li_3O(Fe_2O_3)_5$; $Co_{0.94}Fe^{2+}_{0.12}Fe^{3+}_{1.96}O_4$; $Mg_{0.5}Mn_{0.5}Fe_2O_4$; $Ni_{0.71}Co_{0.03}Fe^{2+}_{0.2}Fe^{3+}_{2.04}O_4$ and $Y_3Fe_5O_{12}$–yttrium iron garnet.

A number of experimental difficulties had to be overcome in the measurement of the torques at high temperatures. On the one hand, one had to increase the sensitivity of the torque magnetometer by using thin steel wires, on the other hand one had to resort to damping. The thermal insulation of the torque magnetometer had to be improved, thermally stable glue had to be used for fastening of the samples, thermally stable materials had to be used for the sphere holder, etc. The measurements for various ferrites were carried out at various sensitivities of the setup. The error limits of the measurements are indicated on the graphs of Fig. 3 which describe the $K_1(T)$ dependence of the investigated single crystals. From these it can be seen that the dependence is linear for curves b, d, f, h and is not linear for curves a, c, e, and g.

It has been established that ferrites for which the $K_1(T)$ dependence is linear near the Curie point are extremely stable against various types of heat treatment and magnetic annealing. At the same time, ferrites which are easily affected by such treatment do not exhibit a linear $K_1(T)$ dependence on approaching the Curie point.

[1] N. S. Akulov, Z. Physik **100**, 197 (1936); Ferromagnetizm (Ferromagnetism), Gostekhizdat, 1939.

[2] C. Zener, Phys. Rev. **96**, 5, 1335 (1954).

[3] C. D. Graham, Jr., Phys. Rev. **112**, 1117 (1958).

[4] I. M. Puzeĭ, Ferromagnetic Anisotropy and the Problem of High-permeability Alloys, doctoral dissertation, Central Scientific Research Institute of Ferrous Metallurgy, 1962.

[5] N. L. Bryukhatov and L. V. Kirenskiĭ, JETP **8**, 198 (1938).

[6] S. Sato and Y. Tino, J. Phys. et Rad. **17**, 5 (1956).

[7] E. A. Turov and A. I. Mitsek, JETP **37**, 1127 (1959), Soviet Phys. JETP **10**, 801 (1960).

[8] E. A. Turov and A. I. Mitsek, in: Ferrity (Ferrites), AN BSSR, 1960.

[9] S. V. Vonsovskiĭ and Ya. S. Shur, Ferromagnetizm (Ferromagnetism), Gostekhizdat, 1948.

[10] L. V. Kirenskiĭ, Investigation of the Energy Anisotropy of Ferromagnets, doctoral dissertation, Krasnoyarsk State Pedagogical Institute, 1950.

[11] L. V. Kirenskiĭ, A. I. Drokin, V. D. Dylgerov, N. I. Sudakov, and E. K. Zagirova, Izv. AN SSSR, ser. fiz. **25**, 1472 (1961), transl., Bull. Acad. Sc. Phys. Ser. p. 1488.

[12] A. I. Drokin, V. D. Dylgerov, N. I. Sudakov, and E. K. Zagirova, Izv. SO AN SSSR, ser. tekhn. nauk, **2**, No. 1, 99 (1963).

[13] A. I. Drokin, N. I. Sudakov, S. Sh. Gendelev, and V. K. Yanitskiĭ, FTT (in press).

[14] F. Bloch, Z. Physik **61**, 206 (1930).

[15] Ya. G. Frenkel, Z. Physik **49**, 619 (1928).

[16] W. Heisenberg, Z. Physik **49**, 619 (1928).

[17] S. V. Vonsovskiĭ and Yu. M. Seidov, Izv. AN SSSR, ser. fiz. **18**, 319 (1954), transl., Bull. Acad. Sc. Phys. Ser. p. 14.

[18] S. V. Vonsovskiĭ, Izv. AN SSSR, ser. fiz. **11**, 485 (1947).

[19] A. I. Drokin, N. I. Sudakov, S. Sh. Gendelev, E. M. Kondrat'ev, and L. I. Ryabinkina, Izv. vuzov, Fizika, No. 5, 162 (1965).

Translated by Z. Barnea
121