MAGNETOCALORIC EFFECT IN THE RANGE OF THE LOW-TEMPERATURE TRANSFORMATION OF MAGNETITE

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The temperature dependence of the reversible magnetocaloric effect was studied on magnetic single crystals between 80 and 290°K. Two minima have been discovered and are attributed to a change in the anisotropic properties of the crystal. The effect of the conditions of cooling of the magnetite on the magnitude of the magnetocaloric effect has been studied. An irreversible change of the temperature in a relatively narrow temperature range (95 − 115°K) has also been detected.

INTRODUCTION

AS is well known, magnetite (Fe_3O_4) has a cubic structure of the inverted-spinel type. At temperatures close to 110°K, a transformation takes place in magnetite and leads to a sharp anomalous change in its electric,[1-3] magnetic,[3,4] galvano- and thermomagnetic,[5,6] and also thermal[7] properties. As a result of this transformation, the magnetic symmetry also changes from cubic to uniaxial.[8] Lee[8] has shown that if the single crystal of magnetite is cooled in a sufficiently strong magnetic field, then one of the axes of the cube, closest to the direction of the external field, becomes the direction of easy magnetization or the symmetry axis at temperatures below the transformation temperature. On going through the transformation region, the magnetization in weak fields changes radically, while the saturation magnetization remains practically unchanged.

The nature of this low-temperature transformation of magnetite is still not fully explained. Verwey et al.[1] have shown that the transformation is due to the ordering of divalent and trivalent iron ions over the octahedral lattice sites. This ordering is due to the change in the structure, in which the crystal symmetry goes from cubic at temperatures above the transformation into orthorhombic.[9] Bickford[10] investigated the temperature dependence of the anisotropic constant of a single crystal of magnetite, starting with room temperatures and below, and found that the anisotropy constant increases sharply in the region of the low-temperature transformation. As follows from the theory,[11] in the temperature region where the anisotropy constant of the crystal experiences a sharp change with tempera-

ture, one can expect a large reversible magnetocaloric effect in the region of the rotation fields. On the other hand, an investigation of the magnetocaloric effect permits a qualitative study of the behavior of the anisotropic constant.

The purpose of this investigation was to ascertain the singularities in the behavior of the magnetocaloric effect in the region of the low-temperature transformation of magnetite, and also to investigate qualitatively the temperature dependence of the first anisotropic constant in this temperature region.

As is well known, adiabatic magnetization is always accompanied by a change in the temperature of the magnetized body, the value of which can in general be represented in the form

$$\Delta T = \Delta T_1 + \Delta T_2 + \Delta T_3 + \Delta T_4, \qquad (1)$$

where ΔT_1, ΔT_2, and ΔT_3 are the changes in temperature due respectively to the reversible processes of displacement, rotation, and true magnetization, while ΔT_4 is the temperature change due to all other irreversible processes. The contribution made by each term in (1) depends, in particular, on the temperature and on the applied magnetic field. In the region of sufficiently low temperature ($T \ll \Theta_f$, where Θ_f is the Curie temperature), the value of ΔT_3 is relatively small for magnets in which the susceptibility of the para process tends to zero as $T \to 0$°K. In the region of rotation fields $H < H_s$ (H_s is the saturation field), in the absence of irreversible processes, the main contribution to ΔT is made by ΔT_2, i.e., the change in temperature is determined essentially by the magnetic energy of the crystallographic anisotropy.

It follows from the work of Akulov et al.[11] that in this case ΔT is connected with the derivative of the

anisotropy constants with respect to the tempera-
ture, $\partial K/\partial T$, by the following relation (we discard
terms containing $\partial^2 K/\partial T^2$ and derivatives of higher
order):

$$\Delta T = - (T/C_{pI})(\partial K/\partial T)_H \Delta \sum_{i \neq j} \alpha_i^2 \alpha_j^2, \qquad (2)$$

where C_{pI} is the specific heat at constant p and
magnetization I, while α_i and α_j are the direction
cosines of the spontaneous magnetization relative
to the cubic axes of the crystal. We can thus assume
that, subject to several conditions, the experimen-
tally-measured magnetocaloric effect ΔT is essen-
tially determined by (2), and that the magnitude of
the effect is a function of both the temperature and
the intensity of the applied magnetic field. If the
measurements are carried out at constant fields,
the value of ΔT is proportional to the derivative
$\partial K/\partial T$ for the corresponding temperature, and this
makes possible a qualitative investigation of the
temperature variation of the anisotropy constant.

MEASUREMENT SETUP AND PROCEDURE

We investigated two natural single crystals of
magnetite of different stoichiometric composition.
The samples were in the form of spheres, 9.50 ±
0.5 (sample 1) and 10.64 ± 0.2 (sample 2) mm
in diameter. The measurements of the magnetocal-
oric effect for sample 1 was with a potentiometer
circuit of sensitivity 5×10^{-8} v/mm, corresponding
to a change of 3×10^{-3} deg in the sample tempera-
ture. Sample 2 was investigated with the aid of
another potentiometer circuit, including a dc photo-
electron-optical amplifier (type FÉOU-18) and a
ÉPP-09 automatic recorder. The sensitivity of the
second setup was 10^{-8} v/mm, corresponding to a
temperature change of approximately 1×10^{-3} deg.
The measuring element was a copper-constantan
thermocouple, soldered to the surface of sample 1
or inserted inside sample 2. To reduce heat losses,
the thermocouple wires were made of the smallest
diameter possible without allowing the wire resist-
ance to decrease greatly the sensitivity of the
apparatus.

The sample was placed inside a silvered Dewar
vessel 20 mm in diameter, the open end of which
was immersed in a second Dewar of larger diam-
eter.[6] The sample temperature was varied by
means of a bifilar heating coil located inside the
inverted Dewar. The coil was fed with alternating
current through a ferroresonant voltage stabilizer.
A cryostat of this kind maintains the temperature
stable within ± 10^{-3} deg over a time sufficient to
perform a measurement cycle.

The experimental difficulties with measuring
small values of adiabatic temperature changes in
ferromagnetic semiconductors of low thermal con-
ductivity have been described, in particular, by
Clark and Sucksmith.[12] In our procedure these
difficulties were coped with by measuring ΔT in
several samples with different thermocouple loca-
tions, by choosing thermocouple wires of different
thickness, and also by using a Dewar with reflect-
ing walls.

After the equilibrium temperature of the sample
was established, the electromagnet was turned on
and the change in the sample temperature was de-
termined from the deflection of the galvanometer.
After 20 minutes, the sample again assumed its
initial temperature and the electromagnet was
turned off. A temperature change in the opposite
direction was then observed. The absolute changes
in the sample temperature due to turning the
magnetic field on and off were equal, within the
limits of experimental accuracy, and their average
was taken as the value of the magnetocaloric effect
ΔT. To eliminate the ballistic overshoot of the
galvanometer coil, a compensating coil with a small
number of turns was connected in the thermocouple
circuit.

The same procedure was used to investigate the
temperature dependence of the magnetocaloric
effect in both samples. The sample was first de-
magnetized at room temperature and then cooled to
the boiling temperature of liquid nitrogen in the
absence of a magnetic field. The temperature de-
pendence of the magnitude of the effect was investi-
gated as the sample was heated. This was followed
by an investigation of the influence of conditions of
cooling in a magnetic field of different intensity on
the magnitude of the effect. The sample, previously
demagnetized at room temperature, was cooled in
a magnetic field of given intensity H_0 to the boiling
temperature of liquid nitrogen, and then the tem-
perature was raised to a value somewhat lower than
the transformation temperature. The dependence
of the magnitude of the effect ΔT on the intensity
of the magnetic field was plotted in the transforma-
tion region, the measurement being started with the
lowest value of the field and terminated with the
largest. The sample was then heated to room tem-
perature, demagnetized, and cooled in a magnetic
field of different intensity.

We know that magnetite displays a jump in mag-
netization in weak magnetic fields, and consequently
this effect must be investigated in fields strong
enough to produce saturation. Our measurements
of the temperature dependence of the magnetization
I of the investigated specimens in the interval

from 85 to 125°K have shown that a plot of I(T) measured in a field of 15,000 oe, no longer has a jump. The direction of the magnetic field in all the measurements coincided with the crystallographic [111] direction of the single crystal. The absolute error in the measurements of ΔT did not exceed 2×10^{-3} deg in the entire temperature interval.

MEASUREMENT RESULTS AND THEIR DISCUSSION

Figure 1 shows the temperature dependence of the magnetocaloric effect ΔT for samples 1 and 2.

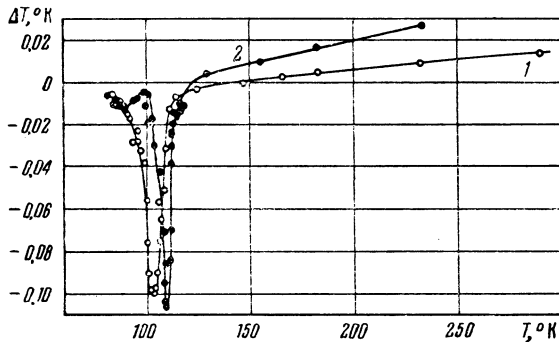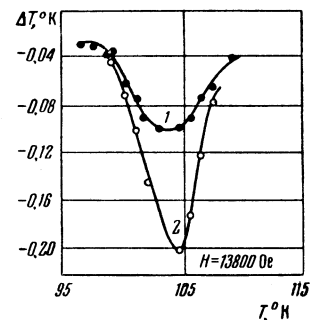
FIG. 1. Temperature dependence of the magnetocaloric effect for samples 1 (curve 1) (H = 13,800 oe) and 2 (curve 2) (H = 17,000 oe).

Both curves show the course of heating of samples first demagnetized at room temperature and then cooled to 80°K in the absence of a magnetic field. The curves for samples 1 and 2 were obtained in magnetic fields of 13,800 and 17,000 oe, respectively. As can be seen from the figure, a reversible temperature change of opposite sign takes place at low temperatures, i.e., the sample temperature decreases as the field is turned on. The effect vanishes at T = 125°K for sample 2 and T = 145°K for sample 1. Further increase in the temperature makes the effect positive. A striking fact is the presence of a sharp minimum of the curve at T = 104° for sample 1 ($|ΔT|_{max}$ = 0.100°) and at T = 110°K for sample 2 ($|ΔT|_{max}$ = 0.105).

It must be noted that a "first measurement effect" is observed in the region of the minimum of the curves. If the specimen was kept at the measurement temperature in the absence of a magnetic field for approximately 20 minutes, the first turning on of the magnetic field led to an irreversible reduction in the temperature, the value of which was approximately double that obtained in the subsequent applications of the magnetic field. In all the subsequent applications, the magnitude of the magnetocaloric effect was always reproducible and fully reversible. The results of the measurements of the

reversible change in temperature and of the "first-measurement effect" are shown in Fig. 2 for sample 1, cooled in the absence of a magnetic field. The same phenomenon was observed also for sample 2, but in the vicinity of 110°K. As can be seen from Fig. 2, the "first-measurement effect" (curve 2) reaches a minimum in the vicinity of 105°K, as does the reversible change in the temperature (curve 1). At this temperature the difference between these curves reaches a maximum value. On both sides of the minimum, the curves tend to come together and the "first-measurement effect" practically disappears at 95° and 115°K.

FIG. 2. Temperature dependence of the reversible magnetocaloric effect for sample 1 (curve 1) in the vicinity of the temperatures where the 'first-measurement effect" is observed (curve 2).

The dependence of the magnitude of the effect ΔT on the intensity of the magnetic field is shown for sample 2 in Fig. 3 (the curves were taken at T = 109.6°K). As can be seen from Fig. 3, in weak fields (up to 3,000 oe) the magnetocaloric effect is positive. The magnitude of this effect is relatively small (on the order of 0.01°) and reaches a maximum at the weakest field (to 1,000 oe), vanishing at approximately 3,000 oe. Above 3,000 oe, the effect is negative and increases with increasing field. Curve 2 of Fig. 3 shows the influence of cooling the sample on the magnitude of the effect.

FIG. 3. Dependence of the magnetocaloric effect ΔT on the intensity of the magnetic field H for sample 2 at T = 109.6°K; curve 1 – sample cooled in the absence of magnetic field; curve 2 – sample cooled at H = 17,000 oe.
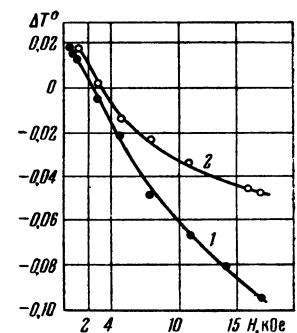
The sample was cooled to a temperature below that of the magnetic transformation in a field H_0 = 17,000 oe (parallel to the [111] crystal axis). As can be seen from a comparison of curves 1 and 2, cooling in a magnetic field reduces the effect substantially,

without influencing the dependence of the effect on the field. Cooling the sample in a magnetic field of lower intensity leads to analogous curves, located between curves 1 and 2. It must be indicated that as the sample is cooled in a magnetic field, the "first-measurement effect" is retained; all that is observed is a reduction in both the reversible and irreversible effects. The relation between the magnitudes of these effects remains the same. The value of ΔT for sample 1 depends analogously on H and on the method of cooling the sample with and without a field.

The reversible negative temperature change shown in Fig. 1 is undoubtedly connected in the main with the rotation processes. In this temperature region the para process has a relatively small influence. It makes a contribution on the order of $+ 0.01°$, as estimated with the aid of the values of C_p and I_s taken from references 7 and 10. With increasing temperature, the influence of the para process increases relative to the rotation processes, as a result of which the magnetocaloric effect reverses sign and becomes positive. The presence of a sharp minimum on the temperature-dependence curves of the magnetocaloric effect is connected with the low-temperature transformation of magnetite, at which the crystallographic symmetry of the lattice changes. The curve taken for sample 2 has still another minimum, near 90°K, which is much smaller in magnitude than the first. No second minimum was observed for sample 1, (possibly because of the lower sensitivity of measuring apparatus), but a sufficient dispersion of the experimental curves was observed in the vicinity of 90°K. In the same temperature region, as already indicated,[6] one observes anomalies of the electric, galvanomagnetic, and thermomagnetic properties. We cannot exclude the possibility that the magnetite experiences a transformation, which has not yet been investigated, in this temperature region.

It seems to us that an unequivocal explanation of the difference between curves 1 and 2 of Fig. 2 is at present still impossible. We can only assume that the irreversible effect (curve 2) is connected with the occurrence of an orthorhombic structure in the magnetite. Narovskaya[13] has shown that the irreversible thermal losses, in the region of the magnetite transformation and below, may be due to a shift of the c axis of the orthorhombic crystal from its initial direction to a direction along the edge of the cube closest to the direction of the applied field. However, we did not observe this effect at temperatures below 95°K.

The character of the dependence of ΔT on the intensity of the magnetic field (Fig. 3) can be appar-

ently attributed to a shift in the predominance of certain magnetization processes over others. At fields from 0 to 3,000 oe, where the effect is positive, the main contribution should be made by the irreversible displacements of the domain boundaries. It is possible here to correlate our measurements with the results of Bryukhatov,[14] who has shown, by measuring the magnetic moments in a rotating magnetic field, that in magnetite the hysteresis losses have a maximum at $H \approx 1,000$ oe and vanish at $H \approx 3,000$ oe. In fields of 3,000 oe and above, rotation processes predominate and lead to a reversible change in the temperature (except for the first measurement) with a negative sign. In this range of fields, the magnitude of the effect is in the first approximation linear in H^{-1}. The indicated character of the connection between ΔT and H indicates that the contribution of the displacement processes prevails over those of true magnetization, for according to theory, the magnetocaloric effect due to the para process should depend linearly on the intensity of the magnetic field in the region of low temperatures. In particular, as shown by Ivanovskiĭ,[15] the magnetocaloric effect for crystals with hexagonal symmetry depends linearly on H^{-1} in the range of rotation fields.

The influence of prior cooling of the sample in a magnetic field on the magnitude of the effect, shown in Fig. 3, can be apparently explained by the fact that cooling in a strong magnetic field leads to the appearance of an easy-magnetization axis, while cooling without a field makes the magnetite magnetically harder. The occurrence of an easy-magnetization axis causes the processes of rotation and orientation of the spontaneous magnetization along this axis to be accompanied by much smaller changes in the crystal temperature.

By using relation (2), it is possible to explain the temperature variation of the derivative of the anisotropy constant K and thereby obtain a qualitative idea of its variation with temperature. As was shown by Bickford,[10] only the first term (K_1) of the series expansion of the anisotropy energy need be considered, owing to the smallness of the remaining terms compared with K_1. The corresponding results for sample 2 are shown in Fig. 4, where the values of the specific heat are those given by Millar.[7]

It is seen from the figure that the derivative of the anisotropy constant with respect to temperature reaches its maximum value in the transformation region (110°K), and experiences thereby a sharp variation with temperature in a relatively small temperature interval (on the order of 15°). In the temperature region below the transformation point,
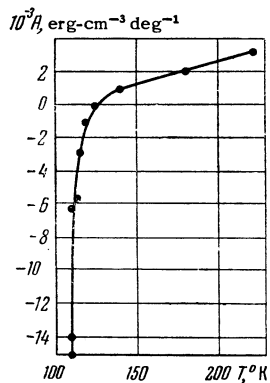
$10^{-3} A$, erg-cm^{-3} deg^{-1}

FIG. 4. Temperature dependence of the derivative of the anisotropy constant for sample 2.

$$A = (\partial K_1/\partial T)\Delta \sum_{i \neq j} \alpha_i \, \alpha_j^2$$

the crystal lattice of the magnetite has no longer a cubic but a rhombohedral symmetry, and here it is necessary to take into account[16] the presence of several anisotropy constants, which are nearly equal in order of magnitude.

[1] E. J. Verwey and J. H. de Boer, Rec. trav. Chim. 55, 531 (1936); E. J. Verwey and P. W. Haayman, Physica 8, 979 (1941); Verwey, Haayman, and Romeijn, J. Chem. Phys. 15, 181 (1947).

[2] E. J. Verwey, Nature 144, 327 (1939); T. Okamura and Y. Torizuca, Sci. Rep. Res. Inst. Tohoku Univ. 2, 352 (1950).

[3] C. A. Domenicali, Phys. Rev. 78, 458 (1950).

[4] P. Weiss and R. Forrer, Ann. Phys. 12, 279 (1929); Williams, Bozorth, and Goertz, Phys. Rev. 91, 1107 (1953); H. J. Williams and R. M. Bozorth, Revs. Modern Phys. 25, 79 (1953).

[5] P. A. Khalileev, Sov. Phys. 7, 108 (1953); A. A. Samokhvalov and I. G. Fakidov, Физика металлов и металловедение(Phys. of Metals and Metallography) 4, 249 (1957) amd 8, 694 (1959).

[6] A. A. Samokhvalov and I. G. Fakidov, Физика металлов и металловедение (Phys. of Metals and Metallography) 7, 465 (1959), and 9, 31 (1960); T. D. Zotov, ibid. 7, 906 (1959), 8, 639 (1959), and 9, 49 (1960).

[7] R. W. Millar, J. Amer. Chem. Soc. 51, 215 (1929).

[8] C. H. Li, Phys. Rev. 40, 1002 (1932).

[9] S. C. Abrahams and B. A. Calhoun, Acta Crystallogr. 8, 257 (1955).

[10] L. R. Bickford, Phys. Rev. 78, 449 (1950).

[11] N. S. Akulov and L. V. Kirenskiĭ, J. Phys. (U.S.S.R.) 3, 31 (1940); K. P. Belov, Упругие, тепловые и электрические явления в ферромагнетиках (Elastic, Thermal, and Electric Phenomena in Ferromagnets), Gostekhizdat, 1957.

[12] C. Clark and W. Sucksmith, Proc. Roy. Soc. 225, 147 (1954).

[13] N. P. Narovskaya, Кристаллография (Crystallography), 3, 346 (1958), Soviet Phys. —Crystallography 3, 348 (1958).

. [14] N. L. Bryukhatov, Izv. Akad. Nauk SSSR, Ser. Fiz. 21, 1268 (1957), Columbia Tech. Transl. p. 1257.

[15] V. I. Ivanovskiĭ, op. cit. ref. 6, 7, 29 (1959).

[16] B. A. Calhoun, Phys. Rev. 94, 1577 (1954).