Magnetocaloric effect in thin magnetic films $\gamma$-Fe2O3

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Abstract. In this paper, we studied the thermal properties of thin films associated with significant difficulties caused by their small volume. Nevertheless, this problem provides undoubted interest, since calorimetric studies can provide useful information about the thermometric properties of films, phase transformations in them. The problem can be solved by using materials phase transition the metal-insulator in thermal contact with the sample as heat-sensitive elements of the films. The theory of the magnetocaloric effect in uniaxial and polycrystalline ferromagnets taking into account the rotation of magnetization is presented. The issues of creation of new refrigerating machines using the magnetocaloric effect are discussed. The magnetocaloric effect in magnetically ordered single crystals is studied taking into account the processes of magnetization rotation. An expression for the magnetocaloric effect in a ferromagnetic polycrystal is obtained, which well describes the experimental results.

Introduction

The study of thermomagnetic phenomena in magnets is one of the directions in the field of physics of magnetic phenomena. Under thermomagnetic phenomena is understood as a set of effects arising under the action of the magnetic field $\vec{H}$, when there is a heat flux of some density and the transformation of energy (both reversible and irreversible) magnetization into heat is realized[1]. The magnetocaloric effect (MCE) belongs to the class of reversible thermomagnetic phenomena.

The magnetocaloric effect is understood as the temperature of the magnet under the action of an external field. As a rule, in conditions of thermal magnetization increases the temperature, and the demagnetization - downwards. In principle, thermo magnetic energy devices phenomenon characteristic of all magnetic materials (para, ferro, antiferromagnetic materials), although the magnetocaloric effect is particularly large in ferromagnetic materials and paramagnetic materials[2].

Experimental study of thermal properties of thin films is associated with significant difficulties caused by their small volume. However, this problem provides great interest, since the calorimetric studies can provide useful information on the thermometric properties of the films, phase transformations in them, etc. the Problem can be solved by the use as thermosensitive elements of the films of materials with phase transition the metal - insulator (PTMI) being in thermal contact with the studied sample. Planar execution of the test film and the sensing element provides maximum heat transfer between the layers, and a strong change in the electrical conductivity of the films in the PTMI allows high sensitivity to record temperature changes. In this paper, we investigated the MCE in thin magnetic films. The PTMI in magnetically ordered crystals consists in temperature change at adiabatic change of an external magnetic field [3,4]. As will be shown below film geometry, the state of the surface and the nature of the magnetic anisotropy affect the appearance of MCE in thin magnetic films.

2. Magnetocaloric effect in thin magnetic films in the model of uniform rotation of magnetization

Consider MCE in thin magnetic films in a model of uniform rotation. The density of the free energy of the film, placed in an external magnetic field of intensity $H$, can be represented as:
\[ f = f_0 + K\sin^2\theta - MH \cos(\psi - \theta) \]  

where \( f_0 \) – the density of the free energy does not depend on magnetic state; \( K \)– constants of magnetic anisotropy of the film including anisotropy of the form and induced magnetic anisotropy if they are present in the sample; \( M \)- the magnetization of the film; \( \psi \)- and \( \theta \)- accordingly, the angles between the selected direction and the directions of the magnetic field and magnetization vectors [5,6].

The value of MCE is determined by the slope of the isentrope

\[ S = -\frac{df}{dT} \]

Using (1) and the condition of equilibrium of magnetization we obtain

\[ \frac{df}{d\theta} = K\sin 2\theta - MH \sin(\psi - \theta) = 0 \]

we can show that

\[ \frac{\partial S}{\partial T} = \frac{\partial S_0}{\partial T} + 2 \frac{\partial \theta}{\partial T} \left[ \frac{\partial M}{\partial T} \sin 2\theta - \frac{\partial M}{\partial T} H \sin(\psi - \theta) \right] + \left( \frac{\partial \theta}{\partial T} \right)^2 \left[ 2K\sin 2\theta + MH \cos(\psi - \theta) \right] \]

Considering the temperature change at MCE to be small, we can limit ourselves to the linear decomposition of magnetization and the constant of magnetic anisotropy in temperature [7]. Derivatives of \( \theta \) angles by temperature and field are found from the equilibrium condition \( \frac{df}{d\theta} = 0 \).

In the absence of magnetic anisotropy \( (K=0, \psi=0) \) expressions (6) go to the known for isotropic ferromagnet [8,9]. Depending on the ratio between the temperature behavior of magnetization and the magnetic anisotropy constant, the first term b (6) provides heating or cooling of the film. Note that in the absence of induced magnetic anisotropy \( (K=2\pi M^2) \) it is always negative.

\[ 2K\cos 2\theta + MH \cos(\psi - \theta) = \frac{d^2f}{d\theta^2} \geq 0 \]

In this case, in particular \( C_H = C_0 \) for illustration in Figure 1. presents the angular dependence of the FE film with \( K=2\pi M^2, H=4\pi M \).

![Figure 1. Anisotropy magnetocaloric effect in thin magnetic films in the model of uniform rotation of magnetization, K=2πM², H=4πM.](image)

3. **Sample preparation. Experimental technique**

As objects of study were selected ferrimagnetic film of Nickel metal and ferrimagnetic insulator \( \gamma \)-Fe2O3. Thickness of samples was 1000 – 3000 A. Monocrystalline film \( \gamma \)-Fe2O3 received by the method
of chemical transport reactions of substrates of magnesium oxide, the thickness of the substrates is 0.3 mm. as the temperature sensing element used the film of vanadium dioxide VO2. Vanadium dioxide at a temperature of 340 K and undergoes PTMI with a jump of conductance reaching four orders of magnitude [10]. Deposition of VO2 films was carried out by pyrolysis of vanadium acetylacetonate. To study FE in the films γ-Fe2O3 the VO2 deposition was carried out directly on the surface of the ferromagnetic; to eliminate the shunt effect in the case of metal films deposition of VO2 was performed on the opposite side of the substrate. The thickness of VO2 films was 1000 - 5000A.

The resulting layered systems were placed in a thermostatic chamber, inside which a flat furnace, thermocouple, inputs for electrical and power devices were mounted. The chamber was located in the gap of the electromagnet, the magnetic field strength of which varied within 2-20kE. Electrical resistance of VO2 films was measured by two-probe method. Contacts to the samples were made using conductive glue based on polyacrylic resin. For the present work it was sufficient to have VO2 films with a jump in conductivity of about two orders and a temperature coefficient of resistance near PTMI – 3 kΩ/ deg.

It is established that the temperature change in the chamber when the magnetic field is turned on due to the possible magnetoresistive effect of the wire heater of the furnace is not manifested in the experiment. The magnetoresistive effect in VO2 films is negligible. This makes it possible to uniquely associate the temperature change in the layered system containing the magnetic film with the change of the magnetic field and the MCE in the latter.

The experiment was conducted as follows. At a fixed temperature and a given angle ψ, the magnetic field of a certain intensity was switched on and the change in the electrical resistance of the VO2 film was recorded. The temperature setting time was a few seconds, after that, due to nonadiabaticity, the temperature slowly returned to its original value.

4. Results and discussion

Using the described technique, we detected and investigated FEM in Nickel and γ-Fe2O3. Measurements were made on a series of films. In all cases, qualitatively unambiguous results are obtained. The peculiarity of the effect is its unexpectedly large value, characteristic, anisotropy and alternating signs in a certain area of angles and fields. For Figure 2 shows the angular dependence of MCE in the film γ-Fe2O3 thickness of 3000 A in a magnetic field of 5.3 kE. A characteristic feature of the effect in this case are two additional maxima ΔT, indicating the contribution of magnetic crystallographic anisotropy to the MCE, the first constant of which in γ-Fe2O3 is negative [5].

![Figure 2](image)

**Figure 2.** The angular dependence of the magnetocaloric effect in the film γ-Fe2O3 film thickness of 3000 A, the magnetic field of 5.3 kE

As in the case of film it is cooling with increasing tension, isentrope MCE ≈ - 2.4·10^{-5} deg/E.
From the comparison of the calculated and experimental results it can be seen that the model of homogeneous rotation qualitatively explains the data. This refers to the anisotropy of the effect and its alternating sign.

5. Conclusion
In this work, we first conducted a pilot study of the finite element method in thin magnetic films. This was facilitated by the method proposed by the authors, based on heat exchange in a layered structure containing the investigated film and a film of a thermo sensitive material with PTMI. The measurements were conducted on films of Nickel and $\gamma$-Fe2O3, showed that a decisive role in the manifestation of MCE plays the character of magnetization of the films. The proposal of the authors with a significant contribution to the MCE of surface magnetic anisotropy does not contradict the results of the experiment.

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