Magnetocaloric effect in polycrystalline cobalt

Kh O Urinov, Kh A Jumanov, A M Khidirov, S Kh Urinov, J M Abdiyev, T A Jumaboyev and M R Eshmirzayev

Samarkand branch of Tashkent University of information technologies named after Mukhammad al-Khwarizmi, 47A Sh.Mirzo Street, Samarkand, 140100, Uzbekistan

E-mail: adkham1972@gmail.com

Abstract. The article discloses an experimental and theoretical study of the magnetocaloric effect in a uniaxial ferromagnetic crystal on the orientation phase transition. The proposed by authors method based on heat exchange in a layered structure, polycrystalline cobalt and a film of heat-sensitive material with metal-dielectric phase transition is promoted. The results of the experiment are made in accordance with the general expression for ferromagnets.

1. Introduction

The magnetocaloric effect (MCE) is the change in temperature of the magnetic sample by changing the external magnetic zero imposed on it. The cause of this effect is the change in the magnetic state of the substance and, consequently, its internal energy. MCE in paramagnetic materials has already found its wide application in the technique of cryogenic temperatures while the study of MCE and its practical application in ferro and ferrimagnets require further development.

Measurement of MCE in magnetically ordered substances can be carried out under two fundamentally different conditions:
- the magnetic field strength change without modification of its orientation in relation to the sample;
- the magnetic field rotation relatively to the selected direction in the sample;

In the first case- a change in exchange energy is typical for an isotropic sample and in the second case- a change is in the energy of magnetic anisotropy.

In recent years the prospects of creating new types of refrigeration machines using FEM in ferromagnets have been grounded [1]. This is primarily due to developments in the field of physics on a solid body.

One of the types of magnetic refrigeration machine is given in [2, 3]. The ferromagnetic working body moves cyclically between the receiver and the source of heat in a nonuniform magnetic field. In the zone of strong magnetic field, it is isothermally magnetized, isolated and generated heat is transferred to the receiver. In the zone of weak magnetic field due to demagnetization the body is cooled down and the heat is transferred to it from the source. The metal Gadolinium has been used as the working fluid. FEM in gadolinium reaches 14 K when the magnetic field \( H = 70 \) kE is turned on at Curie temperature 293 K. The use of gadolinium in the reciprocating machine provided a temperature gradient of 46 K.

It is relevant to investigate FEM under other magnetic phase transitions where sufficient cooling efficiency is possible in a relatively weak magnetic field. The latter includes magnetic orientation phase transitions associated with the changes in the orientation of the magnetic moment relative to the axes of the crystal when the temperature changes [4]. Taking it into account the processes of rotational
magnetization during the remagnetization moment can significantly change the nature of the MCE. Recently experiments have been carried out on study the MCE in orientational phase transitions in rare-earth magnets [5], exhibiting characteristic abnormalities. To predict the efficiency of magnetic cooling in the orientation phase transitions and to discuss the existing experimental results analytical calculation of MCE is necessary.

2. Theory
Consider the free energy density of a uniaxial ferromagnetic crystal placed in an external magnetic field of \( H \)

\[
f = k_1 \sin^2 \theta + k_2 \sin^4 \theta \quad MH \cos(\psi - \theta).
\]

(1)

Where \( k_1 \) and \( k_2 \) - the constant of the uniaxial magnetic anisotropy, \( M \) - the saturation magnetization, \( \psi \) and \( \theta \) - respectively the angles between the directions of the external magnetic field and the magnetization and the normal to the base plane.

Magnetization is of interest in two cases:

\[
\psi = \pi / 2, \quad \psi = 0.
\]

In the first case, the condition of minimum free energy density leads to two equations for the equilibrium magnetization orientation:

\[
\cos \theta = 0
\]

(2)

\[
2 k_1 \sin \theta + 4 k_2 \sin^3 \theta \quad MH = 0.
\]

(3)

Equation (2) describes the state of saturation, the equation (3) describes the change in magnetization when the magnetic field strength changes. The solutions to equation (3) are as follows:

\[
\sin \theta = p^{1/3} + q^{1/3},
\]

(4)

\[
p = \frac{MH}{8 k_2} + \sqrt{\left( \frac{k_1}{6 k_2} \right)^3 + \left( \frac{MH}{8 k_2} \right)^2},
\]

(5)

\[
q = \frac{MH}{8 k_2} \sqrt{\left( \frac{k_1}{6 k_2} \right)^3 + \left( \frac{MH}{8 k_2} \right)^2}.
\]

(6)

from the ratio \( \sin^3 \theta = 1 \) it is clear that the condition (2) is valid starting from the fields, greater than or equal \( H_k = 2k_1 / M \).

In the absence of a magnetic field two equilibrium magnetization orientations are possible:

\[
\sin \theta = 0, \quad k_1 / 2 k_2 \geq 0,
\]

(7)

\[
\sin \theta = \frac{k_1}{2 k_2}, \quad k_1 / 2 k_2 \leq 0.
\]

(8)

Conditions (8) correspond to the orientation phase transition [4]; this is the very situation we are interested in. It is clear from (5) and (6) that in this case should be \( k_1 \leq 0 \), \( k_2 > 0 \), i.e. here it is possible to consider only a second order phase transition.

The expression for the adiabatic temperature changes generally has the following form:
where \( C_A \) - heat, \( \alpha \) - the order parameter, \( A \) - conjugate field.

According to the model orientation phase transition [4] the order parameter for selecting we dare to conclude that the conjugate field is to be selected combination \( MH \).

For simplicity we neglect the contribution of the rotation processes in the heat capacity. In this case the expression for the adiabatic temperature change is given by:

\[
\Delta T = \frac{T}{c} H \int_{H_1}^{H} \frac{d\sin \theta}{dT} MdH ,
\]

where

\[
\frac{d\sin \theta}{dT} = \frac{H}{8k_2} \frac{dM}{dT} (p^{2/3} q^{2/3}) \frac{1}{2} \left( \frac{k_1}{6k_2} \right)^3 \left( \frac{MH}{8k_2} \right) ^{1/2} 
\]

\[
\left[ \frac{1}{2k_2} \left( \frac{k_1}{6k_2} \right)^2 \frac{dk_1}{dT} \frac{H}{4k_2} \left( \frac{MH}{8k_2} \right) \right] (p^{2/3} - q^{2/3})
\]

Here, to simplify the expression we neglect the dependence \( k_2 \) temperature. The initial field \( H_1 \) chosen from the condition

\[
\left( \frac{k_1}{6k_2} \right)^3 + \left( \frac{MH}{8k_2} \right) ^2 = 0
\]

\( dk_1 / dT = 10^{5} \text{ ergs/sm K}, \ k_2 = 10^{8} \text{ ergs/sm M} = 10^3 \ . \ T = 300 \text{ TO}, \ C = 10^7 \text{ ergs/sm K}, \ k_1 = -10^7 \text{ ergs/sm dM / dT} = -1 \text{ Gs/K}, \ \psi = \pi / 2 \ (1); \ 10^{-7}, -5, \ \pi / 2 \ (2); \ -10^7, -12, \ \pi / 2 \ (3); \ -1.8*10^7, -1, 0 \ (4); \ -1.8*10^7, -5, (5); \ 1.8*10^7, -12, 0 \ (6) \) according to (5) and (6).

The complete expression for the adiabatic temperature change is:

\[
\Delta T = \frac{T}{c} \left[ \frac{k_2}{M} \frac{dM}{dT} \left( p^{4/3} + q^{4/3} \right) \frac{dk_1}{dT} \left( p^{2/3} + q^{2/3} \right) + \frac{k_1}{3M} \frac{dM}{dT} \left( p^{2/3} + q^{2/3} \right) \right] (p^{2/3} + q^{2/3}).
\]

Consider FEM during magnetization normal to the base plane which in accordance with previous findings is the axis of hard magnetization. The conditions for the minimum free energy density here also lead to the control of two for the equilibrium orientation of the magnetization

\[
sin \theta = 0 ,
\]

\[
2k_1 \cos \theta + 4k_2 \sin^2 \theta \cos \theta + MH = 0
\]

Solution of equation (15) has the form

\[
\cos \theta = p^{1/3} + q^{1/3},
\]

where in this case

\[
p = \frac{MH}{8k_2} + \left( \frac{k_1 + 2k_2}{6k_2} \right)^3 + \left( \frac{MH}{8k_2} \right)^2
\]

\[
q = \frac{MH}{8k_2} + \left( \frac{k_1 + 2k_2}{6k_2} \right)^3 + \left( \frac{MH}{8k_2} \right)^2
\]
4. (18)

Linked to the order parameter field $\cos \theta$ there is also a combination of $MH$ and formal FEM calculation is carried out in a similar manner as in the previous case. Of course, the expression for the adiabatic temperature change is given by

$$\Delta T = \frac{k_2}{c} \left[ \frac{dM}{dT} \right] \left( p^{4/3} + q^{4/3} \right) + \frac{dk_1}{dT} \left( p^{2/3} + q^{2/3} \right) + \frac{k_2}{3M} \left[ \frac{dM}{dT} \right] \left( p^{2/3} + q^{2/3} \right) \left( p^{2/3} + q^{2/3} \right)$$

Figure 1 shows the field dependence of the FEM for different parameters appearing in (19).

As mentioned above, when a ratio of magnetic anisotropy constants $k_1 > 0$, $k_2 < 0$. MCE calculation is not possible, as in this case the orientation transition is a phase transition of the first kind. However, this case is practically more important because an abrupt behavior of the order parameter should result in accordance with (9) to a strong MCE. Such situation is possible in a class of barium hexaferrite, magnetic anisotropy is studied in [6]. The phase transition temperature is determined by the condition that free energy densities of the two phases and at an arbitrary orientation of the magnetic field is determined from the condition

$$MH \left( \sin \psi + \cos \psi \right) = k_1 + k_2$$

3. Sample preparation. Experimental Procedure

As an object of the study polycrystalline cobalt uniaxial crystal was chosen. As the temperature sensing element vanadium dioxide VO$_2$ film was used. Vanadium dioxide at a temperature of 340 K undergoes FPMD with a conductivity jump reaching four orders of [7,8]. VO$_2$ film deposition was carried out by pyrolysis vanadium acetylacetonate. To investigate the MCE in a uniaxial crystal of cobalt on the surface of the ferromagnet; to eliminate the effect of the shunt in the case of metal films VO$_2$ deposition was performed on the reverse side of the substrate. The film thickness was VO$_2$ 1000-5000Å.

The resulting laminated system placed in a thermostatic chamber inside which a flat oven, a thermocouple and inlets for the supply of electrical devices are mounted. The chamber was placed in the gap of the electromagnet; the magnetic field intensity is varied in the range of 2 ÷ 25 kE. VO$_2$ films. The resistivity was measured by two-probe method. Contacts to the samples were produced with the help of the conductive adhesive based on polyacrylic resin. For the present research to have a VO$_2$ film with conductivity jump about two orders of magnitude and temperature coefficient of resistance in the area FPMD - 3 kW/deg were sufficient.

It is found that the temperature change in the chamber when the magnetic field is turned on because of the possible magnetoresistive effect furnace heater wire is not shown in the experiment. The magnetoresistive effect in VO$_2$ films is also negligible. This enables uniquely associate a temperature change in a layered system, a uniaxial crystal of cobalt when the magnetic field changes with MCE in the last [9].

The experiment was performed as follows. At a fixed temperature, and a given angle $\Psi$ a magnetic field of a certain intensity and record changes of the electrical VO$_2$ film. Temperature Stabilization time was a few seconds, after that, due to nonadiabatic the temperature was slowly returned to its original value.

4. Results and discussion

Using the technique described we have observed and investigated the MCE in the uniaxial crystal of cobalt. The measurements were performed on a series of uniaxial crystal cobalt. In all cases we obtained qualitatively unambiguous results. The peculiarity of its effect is unexpectedly large value typical to
anisotropy and signs of variability in a specific range of angles and fields [10]. Figure 1 shows the field dependence of the FEM under different parameters appearing in (13).

![Figure 1](image1)

**Figure 1.** Field dependence of the MCE in a uniaxial ferromagnet.

![Figure 2](image2)

**Figure 2.** FEM depend on the magnetic field \( H \) at room temperature for polycrystalline cobalt. The observed picture is explained by the anomalous dependence of the temperature anisotropy.

In figure 2 it is shown that when the magnetic field is 18.4 kE the value is \( \Delta T = 0 \), i.e. at this temperature and this value field in a polycrystalline cobalt occurs no thermal changes due to the rotational operation of the magnetization vector \( M \).

### 5. Conclusion

As was mentioned above, when a ratio of magnetic anisotropy constants \( k_1 \leq 0, k_2 > 0 \) the MCE calculation is not possible, in this case the orientation transition is considered to be a phase transition of the first kind. However, this case is practically more important because an abrupt behavior of the order parameter should result in accordance with (9) to a strong MCE.

MCE in polycrystalline samples is caused by two mechanisms:

a) by a decrease in entropy in a magnetic field with exact correspondence to the above formula (3);
b) by contribution of the magnetization rotation processes in the individual crystallites.

When considering the MCE in magnetically ordered media we should take into account the processes of rotation of the magnetization vector which, in some cases, may play a dominant role in the adiabatic magnetization.

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