COMPLEX BEHAVIOR OF MAGNETIZATION AND MAGNETOCALORIC EFFECT IN LOW MAGNETIC FIELD IN THE VICINITY OF MAGNETIC PHASE TRANSITIONS

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ABSTRACT

As it has been recently theoretically shown by Kuz’min (2008) the nature of behavior of magnetic properties at the second-order magnetic phase transitions in low magnetic filed has unpredictable character. An approximate equation of state was proposed for ferromagnets, with a particular reference to magnetic refrigerants such as gadolinium. The displacement of the maximum in the specific heat under an applied magnetic field was demonstrated to be nonmonotonic: the maximum shifts toward lower temperatures in a weak field but toward higher temperatures in a strong field. In present work the possible behavior of the magnetization \( M(H, T) \) and magnetocaloric effect (MCE) \( \Delta T(H, T) \) in the vicinity of magnetic phase transitions is discussed. A simple model allowing calculation of magnetization peak value in the MCE maximum point is developed from the general principles of thermodynamics. Also the relationship between the behavior of the temperature-dependent heat capacity at constant pressure in different magnetic fields and the MCE in low magnetic systems is investigated. It is shown that the two are directly related to each other, and if the maximum value of the heat capacity at second order magnetic phase transition in ferromagnet is shifted to low temperature region in magnetic field up to 24 kOe, it can be expected that maximum MCE value changes its location with shift to high temperature region. The influence of the magnetic field on the heat capacity is discussed.

1. INTRODUCTION

The magnetocaloric effect (MCE) is generally recognized as the heating or the cooling of magnetic solids in a varying dc magnetic field. It was discovered by Warburg (1881) and, over the years, the nature and the behavior of the MCE as a function of temperature and magnetic-field change were the subjects of many experimental and theoretical studies. The MCE fundamentals are developed quite well. Nevertheless, even today advanced research on this magnetothermal phenomenon remains important from both basic and practical perspectives. The fundamental significance of the MCE arises from its intimate relationship with both magnetism and thermodynamics of solids. This warrants further basic experimental and theoretical studies to bring about a more complete understanding of the thermal behavior of magnetic solids as functions of both temperature and magnetic-field change. The applied importance of the MCE is easily appreciated from the fact that for many years it has been used successfully to reach ultra-low temperatures in a research environment (Giauque and MacDougall, 1933). Furthermore, recent technological advancements (Zimm et al., 1998) strongly suggest that in the near future the MCE may become the keystone for an energy efficient and environmentally safe near-room-temperature solid-state refrigeration and cooling technologies, provided all theoretical and practical aspects of continuous magnetic refrigeration are adequately matured.

MCE manifests itself in emitting or absorption of a heat by a magnetic material under change of its magnetic state (for example, magnetization or demagnetization by the external magnetic field \( H \)).

In essence, the MCE in solids is the result of the entropy variation due to the coupling of a magnetic spin system with the magnetic field. It is well known that the total entropy \( S \) of a magnetic solid, where the magnetism is due to localized magnetic moments is the sum of the electronic, lattice, and magnetic entropies (\( S_E, S_L \) and \( S_M \) respectively). At constant pressure, all three functions are functions of temperature \( T \) (Tishin and Spichkin, 2002),

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\[ S(H,T)_p = [S_E(H,T) + S_L(H,T) + S_m(H,T)]_p \] (1)

Among the three, the magnetic entropy strongly depends on the magnetic field \( H \), while usually the electronic and the lattice entropies are practically magnetic-field independent. The electronic contribution to the MCE in this case can be calculated from the experimental electronic heat capacity data if they are available.

Consider a total entropy \( S \) of magnetic material at isobaric conditions as a function of temperature, \( T \), and magnetic field \( H \): \( S = S(T,H) \). The total differential of the \( S \) has a form

\[
dS(H,T) = \left( \frac{\partial S(H,T)}{\partial T} \right)_H dT + \left( \frac{\partial S(H,T)}{\partial H} \right)_T dH. \] (2)

Using Maxwell equation

\[
\left( \frac{\partial S(H,T)}{\partial H} \right)_T dH = \left( \frac{\partial M(H,T)}{\partial T} \right)_H dT.
\] (3)

and the general formula for heat capacity at constant pressure and field

\[
C_H(H,T) = T \left( \frac{\partial S(H,T)}{\partial T} \right)_H
\] (4)

one can obtain the following equation:

\[
dS(H,T) = \frac{C_l(H,T)}{T} dT + \frac{C_e(H,T)}{T} dT + \frac{C_{magn}(H,T)}{T} dT + \left( \frac{\partial S_{magn}(H,T)}{\partial H} \right)_T dH,
\] (5)

Where \( C_l(T) \) is a lattice contribution to heat capacity, \( C_e(T) \) is an electronic contribution and \( C_{magn}(T,H) \) is a heat capacity of magnetic subsystem. So one can see that heat capacity of magnetic material is a sum of the electronic, lattice, and magnetic heat capacities.

The largest MCE in moderate magnetic fields changing from 0 to 1–10 T is observed in the vicinity of a magnetic phase transformation. Usually it is assumed that the maximum MCE in simple ferromagnetic materials occurs at the Curie temperature \( T_c \). It is well known that the Curie temperature is a distinct point on a temperature scale at which magnetic ordering occurs or vanishes spontaneously as the material’s temperature decreases or increases, respectively. This definition applies to the change of magnetic order with temperature at ambient pressure and zero magnetic field. It is assumed that when \( T > T_c \) then the magnetic order parameter \( \eta \) is equal to zero. Magnetic phase transitions in most common magnetic materials, however, are smeared out over a range of temperature. This broadening is usually associated with chemical impurities, imperfections of the crystal lattice, short-range magnetic order and, perhaps, a more complicated behavior of the thermodynamic potential. Various physical properties manifest different behaviors near the \( T_c \). Heat capacity, magnetic susceptibility, and MCE anomalies may occur above or below the true \( T_c \).

As rule the value of the MCE can be characterized by adiabatic temperature change (\( \Delta T \)) or isothermal magnetic entropy change (\( \Delta S_M \)). There are several methods of measuring of \( \Delta T \) and \( \Delta S_M \) temperature and field dependences, necessary for scientific and application purposes. These methods can be divided into two main groups – indirect and direct methods.

In the indirect group of methods \( \Delta T \) and \( \Delta S_M \) are calculated by means of some theoretical equations from temperature and field dependences of such physical parameters as magnetization, heat capacity, etc. So, on the basis of the magnetization isotherms (\( M(H) \)) it is possible to calculate the field and temperature dependences of the magnetic entropy change with the help of Maxwell equation (Tishin and Spichkin 2003):

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\begin{equation}
\Delta S_a(T, H) = \int_{H_1}^{H_2} \left( \frac{\partial M(H, T)}{\partial T} \right)_{H} dH.
\end{equation}

The adiabatic temperature change is also given as

\begin{equation}
\Delta T_{ad}(T)_{Mr,p} = T_f - T_0 = -\int_{H_1}^{H_2} \frac{T(H)}{C(T, H)} \left( \frac{\partial M(H, T)}{\partial T} \right)_{H, p} dH,
\end{equation}

where \( \Delta T_{ad}(T) \) is the MCE, \( H_1 \) is the initial magnetic-field strength at which the initial temperature of a magnetic material is \( T_0 \), and \( H_2 \) is the final magnetic-field strength at which the final temperature is \( T_f \). Thus, a temperature where MCE reaches its maximum for magnetic-field change \( \Delta H = H_f - H_0 \), is dependent on both the behavior of the \( \left( \frac{T(H)}{C(T, H)} \right) \) and the behavior of the magnetization derivation with respect to temperature at constant field, \( \left( \frac{\partial M(H, T)}{\partial T} \right)_{H, p} \). Obviously, the MCE is large when \( \left( \frac{\partial M(H, T)}{\partial T} \right)_{H, p} \) is large and \( C(H, T) \) is small at the same initial temperature \( T \). In case of zeroth magnetic field, the position of magnetic phase transition point (Curie temperature \( T_C \)) can be defined by an approximate Belov-Goryaga method (Arrot plots). At the same time the exact method of definition of magnetic phase transformation point even in low magnetic field is absent and this point can be roughly selected as a point on the \((T, H)\) phase diagram where \( \left( \frac{\partial M(H, T)}{\partial T} \right)_{H, p} \) reaches its peak values (or at least is approached to this temperature at certain value of magnetic field). So, from first point of view the peak of the MCE in low magnetic field should follow (or at least should be close) the temperature of the transformation of magnetic structure of a simple ferromagnet from ferromagnetic (FM) to paramagnetic (PM) state. However, the heat capacity also is quite large in the vicinity of the magnetic ordering temperature and quickly changes its value in narrow temperature range of the vicinity of point of the transformation. It appears from Eq. (7) that the maximum \( |\Delta T_{ad}(T)\) for a given field change can be in principle reached when \( \left( \frac{\partial M(H, T)}{\partial T} \right)_{H, p} \) and \( C(H, T) \) peaks do not coincide. It is worth mentioning the equations (6) and (7) are easily derived from general thermodynamics, but both fail to describe the MCE during a truly discontinuous ideal first-order phase transition when \( \left( \frac{\partial M(H, T)}{\partial T} \right)_{H, p} \) does not exist. As it has been theoretically shown and experimentally checked in the appropriate works (Tishin et al., 1999, Pecharsky et al., 2001) the exact position of maximum MCE in a simple ferromagnet should occur above the zero magnetic-field heat-capacity peak according to the approximate formula

\begin{equation}
\Delta T_{ad}(H, T_0)_{Peak} = -T_0 \Delta C(H, T),
\end{equation}

where \( T_f \) is a final temperature of the material. It was experimentally approved for different materials in the fields up to 10 T. For low magnetic fields and/or for relatively high temperatures, (e.g. when \( T_0 \) is close to room temperature) \( \frac{\Delta T(H, T_0)}{T_0} \), is small and can be neglected. Thus Eq. (8) at temperature \( T_{Max}(H) \), where the peak (maximum or minimum) MCE occurs can be written as

\begin{equation}
C(0, T_{Max}) \cong C(H, T_f),
\end{equation}

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During recent decade the exact understanding of nature of this point and an answer to the question why the MCE maximum is located close to this point is not still found and need to be investigated. As well as the investigation of the question why at certain temperature the impact of magnetic field on heat capacity is changing its character from the decreasing to increasing of magnetic part of the heat capacity and is absent at all in this point. Please, note that it has been shown in the previous work that magnetic materials can have a few of this kind of points connected with corresponding transformations of magnetic structure (Tishin et al, 1999, Pecharsky et al, 2001).

Thus the influence of the magnetic field on MCE maximum (minimum) in case of strong fields is known from literature. At the same time the behavior of MCE maximum, magnetization and heat capacity anomalies in case of low magnetic fields is not yet well described. For example, Dan’kov et al (1998) remarked that the heat capacity peak shifts towards higher temperatures in stronger fields but made no comment on the fact that the 20 kOe dependence in their Fig. 7 peaks at a distinctly lower temperature than the $H=0$ curve does. Checking the literature on other ferromagnets, one can find surprisingly little information on whether the maximum of the specific heat shifts under a magnetic field. Authors found little experimental information describing the shift of peak values of these properties in the magnetic fields and especially in low ones. That’s why the authors see the aim of the present work in elaborating the adequate theoretical model which will allow describing mentioned above phenomena.

2. THEORETICAL MODEL.

Consider the simplest case of ferromagnetic-paramagnetic transition for the ideal ferromagnet. As it was shown by Tishin et al. (1999), for a simple ferromagnet and for given magnetic-field change it is possible to define a certain temperature $\Theta(H)$ in the vicinity of which the maximum magnetocaloric effect should occur. This temperature is higher than the temperature of the zero magnetic field heat-capacity peak. When magnetic field decreases in the adiabatic process, then the maximum MCE approaches the characteristic temperature $\Theta(H)$, where the heat capacity of the material is not affected by the magnetic field. In a general case, when magnetic order is different from that of simple ferromagnetism and antiferromagnetism (Nikitin and Tishin 1987), or for the cases when there is more than one magnetic phase transition, the behavior of the MCE as a function of temperature becomes more complicated, featuring maxima and/or minima, depending on how many and where the characteristics points $\Theta(H)$ exist.

According to Eq. (7) the following expression exactly defines the infinitesimal change of the magnetic material’s $dT$ in an adiabatic-isobaric process:

$$dT_{ad}(T)_{M,T} = -\frac{T(H)}{C(H,T)} \left[ \frac{\partial M(H,T)}{\partial T} \right]_{H} dH$$

(11)

Recalling that $\left( \frac{\partial (dT_{ad})}{\partial T} \right)_{H,P} = 0$ at the temperature where the MCE reaches its maximum or minimum it may seem that one can find the perfect way of MCE maximum point definition by solving the appropriate differential equation. But according to mathematics it’s not correct to obtain the equation for magnetization as an unknown function from the condition $\left( \frac{\partial (dT_{ad})}{\partial T} \right)_{H,P} = 0$ because such a condition supposes that one is going to search the MCE maximum point i.e. to receive an equation at a concrete value of temperature. Moreover even through we formally get the differential equation and solve it taking into account infinitesimal change of magnetic field and connected with it infinitesimal MCE it can lead to the very inaccurate definition of MCE maximum point.

In this case we can offer the alternative method of finding this point namely one can consider Eq. (7) as a functional with regard to the derivative of magnetization and then solve a variational maximum problem by means of calculus of variations. Roughly speaking we offer to solve simplest problem of calculus of variations because we consider the case of the finite magnetic field change from $H_1$ to $H_2$.

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Knowing of experimental dependencies of magnetization derivatives and taking into consideration the fact that \( \left[ \frac{\partial M(H,T)}{\partial T} \right]_H \) is the largest at \( T \to T_c \) when \( H \to 0 \), and since \( \left( \frac{T(H)}{C(T,H)} \right) \) is weakly dependent on temperature (since \( T \) at room temperatures is close to 300 K with changes of 1-2\% and \( C(H,T) \) is defined by Dulong-Petit law then \( \left( \frac{T(H)}{C(T,H)} \right) \) is considered to be a constant with great accuracy), then the maximum magnetocaloric effect in weak magnetic fields approaches the Curie temperature. Thus, our consideration shows that at certain assumptions we can predict that as magnetic field decreases, \( \Theta(H) \) also approaches \( T_c \).

As it was shown by Pecharsky et al. (2001) the maximum MCE shifts towards higher temperatures in strong magnetic fields. We tried to define the behavior of the MCE maximum point in low magnetic fields. As regards the relative border between low and strong magnetic fields we follow Kuz’min (2008) who investigated the behavior of heat capacity maximum shift and showed that in the fields up to 24 kOe the heat capacity maximum shifts towards lower temperatures and vice versa it shifts towards higher ones in the fields above 24 kOe. So we consider this value as the border between low and strong fields.

The theoretical supposition of the possible shift direction can be given in the frames of our model. Since the MCE maximum point is defined by heat capacity dependences intersection point and it’s known that this point shifts towards higher temperatures while field increases one can suppose that the MCE maximum point also shifts towards higher temperatures even in low magnetic fields.

We carried a set of experiments where we managed to watch the shift of MCE maximum point towards higher temperatures in low magnetic fields. The results for Gd polycrystalline can be seen in Fig.1.

Fig. 1. MCE in Gd polycrystalline of 99.98 wt. % versus temperature in different low magnetic fields. The upper curve (yellow online) is 18 kOe and the lower one (pink online) is 2 kOe. The step of field change is 2 kOe. The measurements in the fields lower than 2 kOe are connected with great technical problems because of noise existence. The dependences were approximated by normal distribution.
It can be seen from the picture that in comparison with MCE maximum point for Gd polycrystalline which is about 293.5 K the point shifts towards higher temperatures with the approximate velocity of 1.5 T/K (short dot line). So it’s shown that the behavior of MCE maximum point in the same in both low and strong magnetic fields. As we suppose generally the same character of the MCE maximum point behavior can be seen from some of literature experimental data of different intermetallic compounds but the question is needed to be more carefully investigated especially using single crystal materials.

Since it was shown by Pecharsky et al. (2001) and in the present paper that the temperature at which MCE reaches its maximum is not constant and depends on magnetic field introduce a function \( T_{\text{MAX}} = T_{\text{MAX}}(H) \) which describes the behavior of MCE maximum point in dependence on magnetic field.

After differentiation of Eq. (11) by \( T \) and recalling that \( \left( \frac{\partial (dT_{\text{ad}})}{\partial T} \right)_{H,P} = 0 \) at the temperature where the MCE reaches its maximum or minimum one can obtain

\[
\frac{1}{C(H,T)} \left[ \frac{\partial M(H,T)}{\partial T} \right]_{H} \ dH = -T_{\text{MAX}}(H) \left[ \frac{\partial^2 M(H,T)}{\partial T^2} \right]_{H} \ dH
\]  

or

\[
\left[ \frac{\partial M(H,T)}{\partial T} \right]_{H} = -T_{\text{MAX}}(H) \left[ \frac{\partial^2 M(H,T)}{\partial T^2} \right]_{H}
\]

Eq. (14) is received for the case when \( \left( \frac{\partial (dT)}{\partial T} \right) = 0 \) and \( \left( \frac{T(H)}{C(T,H)} \right) \) can be considered as a constant.

After solution of Eq. (13) one can obtain the following temperature dependence of magnetization at constant magnetic field in the MCE maximum point,

\[
M_{H} = C_{1} \ln T_{\text{MAX}}(H) + C_{0},
\]

where \( C_{1}, C_{0} \) are defined from initial conditions in each case. The obvious condition is the necessary positiveness of magnetization. The temperature dependence is said in the meaning that the temperature at which MCE reaches its maximum depends itself on magnetic field and that’s why Eq. (14) can be understood as a complex temperature-field dependence of magnetization in the MCE maximum point. Eq. (14) in each case (at concrete magnetic field value) connects only concrete values of magnetization and MCE maximum point but when one collects all possible values of the field one can get the general behavior of magnetization dependence on \( T_{\text{MAX}}(H) \).

Also there is one more potentially successful method of investigation of the connection between peak values of magnetization and heat capacity and therefore the MCE.

It is based on the formula, offered by Kuz’min (2008) for specific heat in a nonzero magnetic field

\[
C_{\text{magn}}(T,H) = -\frac{\tau}{T_{C}} \left[ \Phi_{0}(\tau) + \frac{M_{0}}{2} \sigma^{-2} - \frac{M_{0}[a(\tau)]^{2} \sigma^{2}}{a(\tau) + 3a_{0}k\sigma^{2} + 5a_{0}(1-k)\sigma^{4}} \right],
\]

where \( \tau = \frac{T}{T_{C}}, \sigma = \frac{M}{M_{0}} \) (\( T_{C} \) is the Curie temperature, \( M_{0} \) is the saturation magnetization), \( \Phi_{0}(\tau) \) is zeroth-order Landau’s coefficient, \( a(\tau) = a_{0} \left( \frac{\tau^{3} - 1}{1 + p \tau^{3/2}} \right) \) (\( a_{0}, p \) - parameters), \( k = \frac{b}{a_{0}} \) (\( b \) is taken from the equation for thermodynamic potential written as an expansion in even powers of magnetization \( M \)

\[
\Phi(M,H,T) = \Phi_{0} + \frac{1}{2} AM^{2} + \frac{1}{4} BM^{4} + \frac{1}{6} CM^{6} + \ldots - MH.
\]

Furthermore, in the absence of magnetic field, the specific heat of a ferromagnet is described by a conjunction of two explicit expressions (Kuz’min 2008),

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\[
C_{\text{magn}}(T, H) = -\frac{\tau}{T_c} \left[ \Phi_0^\prime(\tau) + \frac{M_0}{2} a^\prime(\tau)\sigma^2 - \frac{M_0[a(\tau)]^2}{2a_0[\kappa + 2(1 - \kappa)\sigma^2(\tau)]} \right], \quad \tau < 1 , \tag{17}
\]

\[
C_{\text{magn}}(T, H) = -\frac{\tau}{T_c} \Phi_0^\prime(\tau), \quad \tau > 1
\]

According to Eq. (10) and taking into account the fact that MCE maximum point shifts towards higher temperatures one can compare Eq. (15) and the second part of Eq. (17) i.e. the case of \( T > T_c \).

As a result one can obtain the following equation which connects magnetization, \( T_{\text{MAX}} \) which is a temperature at which MCE reaches its maximum and the final temperature of the material \( T_F \) (roughly speaking it’s the temperature at which MCE is practically null at the concrete value of magnetic field e.g. for Gd \( T_c \) equals approximately 310 K):

\[
T_{\text{MAX}} \left[ \Phi_0^\prime(\tau) + \frac{M_0}{2} a^\prime(\tau)\sigma^2 - \frac{M_0[a(\tau)]^2}{a(\tau) + 3a_0\kappa\sigma^2 + 5a_0(1 - \kappa)\sigma^4} \right] = T_F \Phi_0^\prime(\tau), \tag{18}
\]

Since Eq. (10) was obtained from known equation (Nikitin and Tishin 1987),

\[
C_{p,H}(T_F) = C_{p,H}(T_{\text{MAX}}) \frac{T_F}{T_F - \Delta T} \left( 1 - \frac{d\Delta T(T, H)}{dT} \right) \tag{19}
\]

using the conditions that in low magnetic field we can assume that \( \Delta T \ll T_F \) and also recalling that \( \left( \frac{\partial(dT_{m})}{dT} \right)_{T,F} = 0 \) at the temperature where the MCE reaches its maximum or minimum, the dependence on \( \tau \) in Eq. (18) means dependence on \( T_{\text{MAX}} = T_{\text{MAX}}(H) \).

Thus from Eq. (18) one can obtain the temperature-field dependence of reduced magnetization in the MCE maximum point very much like in the Eq. (14). The problem for experimental solving is to find the explicit function \( T_{\text{MAX}} = T_{\text{MAX}}(H) \). This function must in some meaning unify Eq. (14) and the equation for reduced magnetization which can be get from the Eq. (18). The only problem with that one last equation is the complexity of mathematical transformations and parametric kind of dependence. \( a, a_0, \kappa \) - are parameters.

\section*{3.CONCLUSIONS.}

The new method of finding the precise value of temperature at which MCE reaches its maximum is proposed. It’s based on the solving of variational maximum problem as regards integral Eq. (7) for MCE. Also it was experimentally shown that the MCE maximum point shifts towards higher temperatures in low magnetic fields. So the general character of MCE maximum point behavior is determined i.e. while the magnetic field increases the MCE maximum point shifts towards higher temperatures from the approximate point in \( T_c \) in the case of zeroth-magnetic field. According to this we offer to consider the MCE maximum point not as a constant but as function of magnetic field. Two complex temperature-field dependences of magnetization based on such an approach are received. The question of the explicit character of this function stays open and should be solved experimentally.

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REFERENCES