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Review

Recent progress in magnetocaloric effect: Mechanisms and potential applications

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ABSTRACT

Recent results in understanding of the magnetocaloric effect (MCE) mechanisms in the framework of thermodynamic approach are regarded and discussed. Importance of relation between ΔS_{MT} (magnetic entropy change at constant temperature) and ΔS_{MH} (magnetic entropy change at constant field) and it influence on MCE value is considered. The main contributions to the MCE are discussed. The importance of further development of models of interactions between magnetic and structural subsystems in vicinity of magnetic phase transitions is stressed. It is stated that the present level of MCE parameters (in particular, adiabatic temperature change) can be increased up to 3 times. The necessity of investigation of MCE parameters in dynamic mode and development of new experimental methods and apparatuses for MCE measurements is discussed. The most obvious application for MCE for today is magnetic refrigeration, but MCE also can be used for other applications such as medicine (hyperthermia, drug delivering), etc., which are regarded.

Progrès récents dans l'effet magnétocalorique : mécanismes et applications potentielles

Mots clés : Effet magnétocalorique ; Modèle thermodynamique ; Entropie magnétique

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Nomenclature

T	temperature, K
B	magnetic inductance, T
H	magnetic field strength, A m^{-1}
H_{cr}	critical magnetic field of magnetic phase transition, A m^{-1}
C_H	heat capacity under constant magnetic field, J kg^{-1} K^{-1}
C_{mag}	magnetic part of the heat capacity, J kg^{-1} K^{-1}
M	magnetization, A m^{-1}
ΔS_{MT}	isothermal magnetic entropy change, J kg^{-1} K^{-1}
ΔS_{Mt}	total change of magnetic entropy in adiabatic process, J kg^{-1} K^{-1}
ΔS_{MH}	isofield magnetic entropy change, J kg^{-1} K^{-1}
$\Delta S_{MT}/\Delta H$	specific isothermal magnetic entropy change, J kg^{-1} K^{-1} T^{-1}
S	total entropy, J kg^{-1} K^{-1}
S_M	magnetic entropy, J kg^{-1} K^{-1}
S_l	lattice contribution to the total entropy, J kg^{-1} K^{-1}
S_e	electron contributions to the total entropy, J kg^{-1} K^{-1}
ΔT	adiabatic temperature change, K
$\Delta T/\Delta H$	specific adiabatic temperature change, KT^{-1}
G_{ex}	free energy of the exchange interaction, J
G_{me}	free energy of the magnetoelastic interaction, J
G_a	free anisotropy energy, J
G	Gibbs free energy (thermodynamic potential), J
SAR	specific absorption rate, Wg^{-1}
A	specific energy, absorbed in one cycle of remagnetization, J kg^{-1}, mJ g^{-1}
δQ	release heat, J kg^{-1}

1. Introduction

Research of the magnetocaloric effect (MCE) in magnetic materials is topical both from basic and practical points of view. MCE is strongly related with nature of magnetizm and can give information about magnetic phase transitions and spin structures. Practical interest to MCE is mainly related with its possible application in energy efficient and environmently friendly magnetic refrigerators. Recently it was suggested to use MCE in another application – one of the methods of malignant tumors treatment – hyperthermia (Tishin, 2005, 2006, 2008).

Two main parameters characterize the MCE: the adiabatic temperature change ΔT and the isothermal magnetic entropy change ΔS_{MT} under magnetic field changing. Microscopic consideration of the MCE origin is not developed sufficiently deep for today. Usual approach for understanding of the MCE mechanisms is thermodynamics, which allowed to establish main relation between magnetocaloric and magnetic values and such parameters as pressure, volume, temperature and magnetic field.

One of the main directions in searching of materials with high magnetocaloric characteristics is studying of materials with sharp change of lattice parameters and structure type at the magnetic phase transition points, because such phenomena in magnetic materials are accompanied by sharp change of magnetization and other magnetic characteristics. One of the first studied materials from this set is $Fe_{0.49}Rh_{0.51}$ alloy, in which maximal for today values of ΔT and ΔS_{MT} were discovered by Annaorazov et al. (1992). In this alloy giant MCE was observed at the first order antiferromagnetic – ferromagnetic phase transition, accompanied by abrupt change of crystal lattice parameters. Structural transition associated with order–disorder magnetic phase transition of the first order character and giant MCE was also observed in GdGeSi compounds (Pecharsky and Gschneidner, 1997).

Here we consider some aspects of thermodynamic approach to the MCE, its new possible application in medicine and important items for further investigations.

2. Thermodynamic approach

In adiabatic conditions the temperature change ΔT due to the change of the magnetic field (the magnetocaloric effect or adiabatic temperature change) can be defined by well-known expression:

$$\Delta T = -\int_{H_1}^{H_2} \frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H dH \quad (1)$$

where C_H is the heat capacity under constant magnetic field, M – magnetization, H – magnetic field strength, T – temperature. As one can see from Eq. (1), ΔT is directly proportional to the derivative $(\partial M/\partial T)_H$ and inversely proportional to the heat capacity C_H. Both of them have maxima near order – disorder magnetic phase transition, which cannot coincide on the temperature axis and position of ΔT on temperature maximum is determined by interplay between these two values (Tishin et al., 1999; Pecharsky et al., 2001). Maximum is also observed on isothermal magnetic entropy change on temperature dependence, which is related with ΔT as:

$$\Delta S_{MT} = \frac{C_H}{T}\Delta T \quad (2)$$

For application of a magnetocaloric material in magnetic refrigerators it is necessary that both magnetocaloric parameters ΔT and ΔS_{MT} have large values. At the same time, as one can see from Eqs. (1) and (2) there is a contradiction between the requirement for C_H necessary for high ΔT and ΔS_{MT} – in case of ΔT the heat capacity should be small, and in case of ΔS_{MT} – it should be high. It is necessary to find the ways to affect the heat capacity value and its temperature dependence in order to make the latter wider and its maximal value at the magnetic phase transition lower. One of the steps in this direction is the work of Zverev et al. (2012), where the dependence of magnetic heat capacity on the magnetic field was studied. According to the results obtained for heavy rare earth metals Gd, Tb and Ho the magnetic heat capacity value in high fields tends to constant value and in Gd at the Curie point it is

almost independent on the magnetic field in the whole field range.

In the work of Tishin and Spichkin (2002) the question about the value of magnetic entropy change was considered in another formulation. The total change of magnetic entropy in adiabatic process ΔS_{Mt} was regarded, which was a sum of two contributions – isothermal magnetic entropy change ΔS_{MT} and isofield magnetic entropy change ΔS_{MH}:

$$\Delta S_{Mt}(T,H) = S_{Mt}(T+\Delta T, H+\Delta H) - S(T,H) = \Delta S_{MT}(H,T) + \Delta S_{MH}(H,T) \quad (3)$$

where isothermal magnetic entropy change is determined as:

$$\Delta S_{MT}(H,T) = \int_{H}^{H+\Delta H} \left(\frac{\partial M(H,T)}{\partial T}\right)_{H} dH \quad (3a)$$

and isofield magnetic entropy change is determined as:

$$\Delta S_{MH}(H,T) = \int_{T}^{T+\Delta T} \frac{C_{mag}(H,T)}{T} dT \quad (3b)$$

where C_{mag} – magnetic part of the heat capacity (heat capacity of the magnetic subsystem). The isothermal magnetic entropy change is equal to the change of a total entropy of a magnetic material $\Delta S(T,H)$:

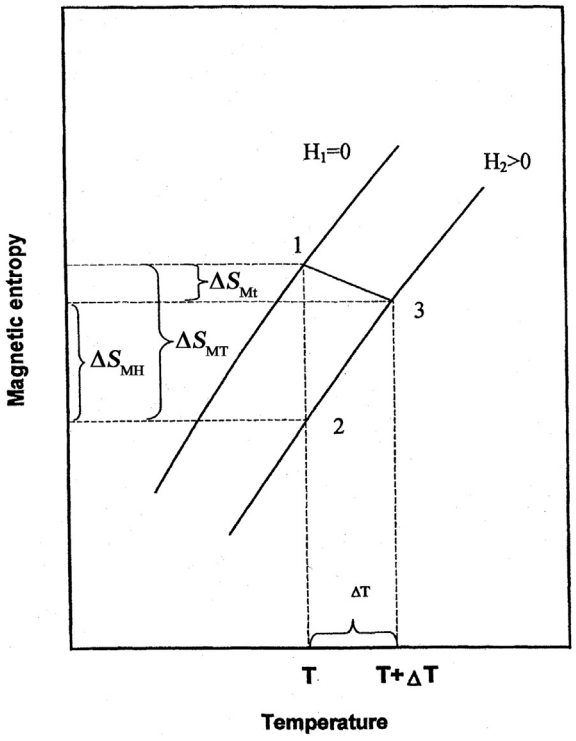

Fig. 1 – Adiabatic magnetization process of a ferromagnet, presented as a sum of two sequential processes: isothermal change of the magnetic field from H_1 to $H_2 = H_1 + \Delta H$ (process 1 → 2) with corresponding isothermal entropy change ΔS_{MT}; and isofield temperature change from T to $T + \Delta T$ (process 2 → 3), where ΔT is the adiabatic temperature change due to MCE. The process is shown in coordinates magnetic entropy S_M – temperature T.

$$\Delta S(T,H) = S(T,H_2) - S(T,H_1) = S_M(T,H_2) - S_M(T,H_1) = \Delta S_{MT}(T,H) \quad (4)$$

where $S(T,H)$ and $S_M(T,H)$ are total and magnetic entropies, correspondingly. The magnetic entropy S_M is one of the main parts of the total entropy S:

$$S(T,H) = S_M(T,H) + S_l(T,H) + S_e(T,H) \quad (5)$$

where S_l and S_e are the lattice and electron contributions to the total entropy, respectively.

Fig. 1 shows the process of adiabatic magnetizations of a ferromagnet and established interrelations between the total change of magnetic entropy in adiabatic process ΔS_{Mt}, isothermal magnetic entropy change ΔS_{MT} and isofield magnetic entropy change ΔS_{MH} (Tishin and Spichkin, 2002). In Fig. 1 the adiabatic temperature change ΔT is presented by the distance between points 2 and 3 on the temperature axis, which is determined by the value of ΔS_{MH} and the displacement of $S_M(T,H)$ curve in the magnetic field. The latter depends on ΔS_{MT}. It can be seen, that increase of the isofield magnetic entropy $\Delta S_{MH}(T,H)$ reduces the value of ΔS_{Mt} and increases of the adiabatic temperature change ΔT.

In the simple case of ferromagnet the change of magnetic entropy should be negative, because the magnetic field orders magnetic moments of atoms, which leads to decrease of the entropy. That is why the maximal value of ΔS_{Mt} can be zero, which corresponds to the situation $|\Delta S_{MH}| = |\Delta S_{MT}|$ (in ferromagnets $\Delta S_{MH} > 0$ and $\Delta S_{MT} < 0$ – see Eqs. (3a) and (3b)), represented by point 3′ in Fig. 1. Positive ΔS_{MH} lead to conclusion that the lowest limit of ΔS_{Mt} can be $|\Delta S_{Mt}| = |\Delta S_{MT}|$, which corresponds to the point 2 in Fig. 1. So, point 3, representing to the final state of a ferromagnet in the magnetic field can move between points 2 and 3′. The position of point 3 on the $\Delta S_M(T, H_2)$ curve is determined by the value of ΔS_{MH} which, in turn, depends on the value of magnetic part of the heat capacity. For the given value of ΔS_{MT} the adiabatic temperature change ΔT is higher for ferromagnets with higher magnetic heat capacity.

So, it is necessary to investigate theoretically and experimentally the behavior of both isothermal and isofield contributions to the magnetic entropy change and possibility to achieve their optimal ratio. Up to present only isothermal magnetic entropy change was studied intensively. The first theoretical step in this direction is made in the work presented on this conference (Zverev et al., 2012).

Thermodynamic consideration of the magnetocaloric effect at the first order magnetic phase transition was considered by Spichkin and Tishin (2005). The Gibbs free energy (thermodynamic potential) of a magnetic material in which one magnetic phase is transformed to another by the field-induced first order magnetic phase transition was written as:

$$G = G_{ex} + G_{me} + G_a - HM \quad (6)$$

where G_{ex} is the free energy of the exchange interaction, G_{me} is the free energy of the magnetoelastic interaction, G_a is the free anisotropy energy, and HM is the magnetic energy. The change of the potential at the transition is (at the transition the potentials of the magnetic phases should be equal, i.e. $G_1 = G_2$):

$$\Delta G_{ex} + \Delta G_{me} + \Delta G_a = H_{cr}\Delta M \quad (7)$$

where symbol Δ denotes the change of the corresponding parameter across the transition ($\Delta M = M_2 - M_1$) and H_{cr} is the critical magnetic field of the transition. The magnetic entropy change at the transition can be calculated on the basis of Eq. (7) and the magnetic Clausius–Clapeyron equation:

$$\frac{dH_{cr}}{dT} = -\frac{\Delta S_M}{\Delta M} \quad (8)$$

and has the form:

$$\Delta S_{MT} = -\left(\frac{\partial \Delta G_{ex}}{\partial T} + \frac{\partial \Delta G_{me}}{\partial T} + \frac{\partial \Delta G_a}{\partial T} - H_{cr}\frac{\partial \Delta M}{\partial T}\right) \quad (9)$$

where $\partial/\partial T$ denotes derivatives of the corresponding values on temperature. Then using Eq. (2), the adiabatic temperature change at the transition was obtained:

$$\Delta T = \frac{T}{C_H}\left(\frac{\partial \Delta G_{ex}}{\partial T} + \frac{\partial \Delta G_{me}}{\partial T} + \frac{\partial \Delta G_a}{\partial T} - H_{cr}\frac{\partial \Delta M}{\partial T}\right) \quad (10)$$

As one can see from Eqs. 9 and 10, there are several contributions to the magnetocaloric effect at the first order transition: the contribution from exchange, magnetoelastic, anisotropy and magnetic energy changes.

Using the experimental data on H_{cr}, ΔM, magnetic anisotropy constants, linear temperature expansion, linear forced magnetostriction and elastic constants, and Eqs. 9 and 10 the temperature dependences of the contributions to ΔS_{MT} and ΔT for the materials with first order order–order (Tb, Dy, $Tb_{0.5}Dy_{0.5}$, $Fe_{0.49}Rh_{0.51}$) and order–disorder ($Gd_5Si_{1.7}Ge_{2.3}$) magnetic phase transitions were obtained (Spichkin and Tishin, 2005). It was shown, that the main contribution to ΔS_{MT} and ΔT at the magnetic phase transitions come from the exchange energy change, which was attributed to the interatomic distance change due to large magnetostriction observed in the regarded materials under the transitions. The interatomic distance change can affect indirect RKKY-type exchange interactions (Ruderman–Kittel–Kasuya–Yosida interaction is a coupling mechanism, which is realized between localized spins in metals through the conduction electrons) in materials with localized magnetic moments and rearrange the conduction electron band structure in the materials with itinerant magnetism. In the investigated materials the magnetic first order transition is accompanied by a structural transition: in Dy and Tb the crystal structure is changed from hcp to orthorhombic and rhombohedral, correspondingly at the transition from helicoidal antiferromagnetic to ferromagnetic phase (Finkel, 1978); in $Gd_5Si_{1.7}Ge_{2.3}$ the crystal structure changes from monoclinic in paramagnetic state to the orthorhombic Gd_5Si_4-type ferromagnetic phase (Choe et al., 2000). In $Fe_{0.49}Rh_{0.51}$ essential increase of the lattice volume (~1%) at the transition from antiferromagnetic to ferromagnetic state was observed (Bergevin and Muldawer, 1961; Kouvel and Hartelius, 1962).

One of the most important questions in MCE studies is what can be the maximal obtainable in practice value of the MCE. Zverev et al. (2010) considered on the basis of thermodynamic approach maximal possible value of the adiabatic temperature change ΔT_{max} in magnetic materials. It was shown that at a magnetic phase transition ΔT_{max} per magnetic field change of 1 T is determined by formula:

$$\Delta T_{max} = \sqrt{T \times \frac{\Delta M}{C_H}} \quad (11)$$

where ΔM is magnetization change at the transition. Eq. (11) was obtained on the basis of Eqs. (1) and (2) in assumption that $(\partial M/\partial T)_H$ is constant near the transition and is equal to zero at other temperatures. For the maximal possible $\Delta M = 10\ \mu_B atom^{-1}$ (calculated effective magnetic moment per atom of Ho is 11.2 μ_B), $C_H = 6k_B\ atom^{-1} = 1.38 \cdot 10^{-23}\ J\ K^{-1}$ (a material with two atoms in a molecular, one of which is nonmagnetic) and T = 300 K it was found that $\Delta T_{max} = 18$ K (per 1 T). Table 1 shows maximal values of specific adiabatic temperature change $\Delta T/\Delta H$ and isothermal magnetic entropy change $\Delta S_{MT}/\Delta H$ for several materials with high magnetocaloric properties, which are promising as working bodies for magnetic refrigerators or already are used in experimental models of magnetic refrigerators. As one can see, $Fe_{0.49}Rh_{0.51}$ has the highest magnetocaloric parameters, although it is still far from the theoretical ΔT_{max} value, estimated by Zverev et al. (2010). Unfortunately, FeRh alloys are too expensive for wide commercial application. So, the further investigations aimed on increasing of $\Delta T/\Delta H$ and $\Delta S_M/\Delta H$ are necessary and reasonable.

3. New applications of MCE

At present time main research activity in the field of MCE and magnetocaloric materials is directed to magnetic refrigeration. However the MCE can find another perspective application – in medicine in treatment of malignant tumors by method of hyperthermia. Hyperthermia is rather well-known method of treatment based on different reaction of atypical

Table 1 – Magnetocaloric and magnetic parameters of some materials with high magnetocaloric properties (T_{tr} – temperature of magnetic phase transition).

Material	T_{tr}, K	$\Delta T/\Delta H$, KT^{-1}	$\Delta S_{MT}/\Delta H$, $J\ kg^{-1}\ K^{-1}\ T^{-1}$	ΔM, $\mu_B atom^{-1}$	Reference
Hypothetical magnetic material	300	18	–	10	Zverev et al. (2010)
$Fe_{0.49}Rh_{0.51}$	308.2	6.62	11.28	~1.5	Annaorazov et al. (1992); Tishin and Spichkin (2002)
$LaFe_{11.57}Si_{1.43}H_{1.3}$	291	3.45	12	~2	Fujieda et al. (2002); Tishin and Spichkin (2002)
$Gd_5Si_2Ge_2$	246	3.7	7	~2.4	Pecharsky and Gschneidner Jr. (1997)
Gd	294	2.9	3.5	7.98	Dan'kov et al. (1998)

(malignant) and healthy cells on increased temperature – the former die at temperatures of about 43 °C, while the latter can stand such conditions.

Initially hyperthermia was fulfilled by heating the patient body in water bath (general hyperthermia), later a local heating was used (local hyperthermia). Local heating was accomplished with the help of radio and microwave electromagnetic radiation. Recently a new method of hyperthermia was proposed, in which local heating was achieved due to remagnetization losses in a system of nanoparticles previously injected into the tumor tissue – this method was called magnetic fluid hyperthermia. It has several advantages in comparison with the previous methods of local hyperthermia, among which are:

- low frequency of using alternating electromagnetic field, which significantly reduces the harm from its effects to the body as compared to high-frequency and microwave radiation;
- minimal invasiveness – the magnetic nanoparticles are introduced in the treated tissue by injection;
- possibility to control the upper temperature limit without introduction of a temperature sensor into the tissue (then the material of nanoparticles is heated above its magnetic ordering temperature, it loses its magnetic properties and heating stops automatically) and to establish the limit on necessary temperature by selection of the material composition, which essentially simplifies the treatment protocol;
- possibility to perform simultaneously with the hyperthermia procedure of drug delivering to the tissue under treatment using drug-containing coating of the particles capable to release the drug under heating (temperature sensitive polymers, etc.);
- possibility to deliver and hold magnetic nanoparticles in the tissue with the help of magnetic fields (in this case even injection can be excluded from the treatment procedure because the particles can be delivered to the necessary place through the bloodstream).

The parameter characterizing effectiveness of transformation of the energy of alternating electromagnetic field into heat is specific absorption rate (SAR), which is determined as:

$$\mathrm{SAR} = f \cdot A, \tag{12a}$$

where f is the frequency of the electromagnetic field, and A is specific energy, absorbed in one cycle of remagnetization (it is equal to the hysteretic loop square):

$$A = \oint H dB \tag{12b}$$

where B is magnetic induction. This energy is released in environment as a heat.

The efficiency of the nanoparticles, which are applied in the local magnetic hyperthermia is determined by parameter A. Currently in clinical practice nanoparticles of iron oxide with $A \approx 2.9$ mJ g^{-1} and magnetic field strength of $\sim 8 \cdot 10^3$ A m^{-1} at frequencies $\sim$100 kHz are used in local magnetic fluid hyperthermia (Johannsen et al., 2005). Material of such particles is in magnetically ordered state and the temperatures of the particles application are far from the Curie temperatures of iron oxide. That is why MCE value in such nanoparticles is negligible and cannot give contribution to A. At the same time in materials with magnetic ordering temperatures close to temperature of a human body this contribution can be essential. Using of MCE in local hyperthermia procedure was proposed in patents (Tishin, 2005, 2006, 2008). Because the mechanism of heating in this case is different from the local magnetic fluid hyperthermia, it is possible to call such hyperthermia local magnetocaloric hyperthermia. For thermodynamic Carnot cycle the energy absorbed in one cycle in a magnetocaloric material (i.e. parameter A) is determined as (Zatsepina et al., 2009):

$$A = \Delta T \cdot \Delta S_{\mathrm{MT}}. \tag{13}$$

For the alloy $Fe_{0.49}Rh_{0.51}$, which has magnetic ordering temperature close to the temperature of a human body, this value for 0.1 T is $\sim$7.5 mJ g^{-1} ($\Delta T/\Delta H = 6.62$ KT^{-1}, $\Delta S_{\mathrm{MT}}/\Delta H = 11.28$ J kg^{-1} K^{-1} T^{-1} (Annaorazov et al., 1992). Then to achieve currently using in magnetic fluid hyperthermia value of SAR = 300 Wg^{-1} (Johannsen et al., 2005) it is necessary to use frequency of 40 kHz. It should be noted that ΔT and ΔS_{MT} and, consequently, parameter A value increase with magnetic field amplitude increasing, contrary to case of remagnetization losses, which don't increase in high magnetic fields because their value is determined by hysteretic loop square. So, magnetocaloric contribution to heating in magnetic fluid hyperthermia can be high for a material with high MCE parameters using near the temperature of a magnetic phase transition. It is also possible to anticipate increase of MCE properties in a system of nanoparticles due to the effect of superparamagnetic enhancement (Tishin and Spichkin, 2002). As was mentioned above, according to estimations of Zverev et al. (2010), the upper theoretical limit of the adiabatic temperature change for bulk materials can be 18 KT^{-1}.

Another way to use MCE in medicine is medicine (drug) delivery and release. Delivery of medicine to target organs in a human organism is one of the basic problems in treatment of various diseases, especially oncological, and in diagnostics. It is also often necessary to carry out controlled release of one or several medicine into an organism. Traditional taking of medicine – oral intake or injection – cannot provide long time controlled release, but just instant release with subsequent rather fast decrease of medicine concentration in blood. At the same time the effectiveness of treatment can be essentially increased when concentration of medicine is maintained on necessary fixed level for a long time or if medicine is released at predetermined moment. Often there is a strong need to subject to treatment particular tissue or organ by highly toxic drug, as it takes place in oncology (chemotherapy). Injection to tissue or organ in many cases is complicated or even not possible and injection into bloodstream or oral intake will cause damage to all organism. Target drug delivery reduces general toxicity of a medicine and its long release provides longer action reducing necessary doses.

One of the possible solutions of the drug delivery problem is the use of magnetic drug carriers in form of nanoparticles, which can be transported by blood flow in the bloodstream and localized in the necessary place by means of magnetic field. The magnetic nanoparticles displaying magnetic and

magnetocaloric properties can be covered by a film of temperature-sensitive polymer containing medicine (or other bioactive compound), which is released by polymer under change of temperature. Such heat-sensitive polymers as N-isopropyl acrylamide (NIPAAm) and N-tert-butyl acrylamide (tBuAM) copolymers under cooling undergo phase transition from water insoluble (solid substrate) to soluble state, at the temperature called the lower critical solution temperature (LCST) (Tishin et al., 2006a–d, 2008, 2009). In soluble state the medicine is released into environment. Cooling of the polymer film can be accomplished with the help of MCE arising in magnetic material of a nanoparticle under demagnetization (in ferromagnets), or magnetization (in materials with antiferromagnetic spin structure). The material suitable for such purposes is $Fe_{0.49}Rh_{0.51}$ alloy regarded above. Its magnetic phase transition temperature from antiferromagnetic to ferromagnetic state is 308.2 K, which is close to the temperature of human body and it has negative MCE (i.e. it cools under magnetization).

In single magnetization (or demagnetization) of the particles with high MCE the heat δQ will be released (or absorbed) according to equation:

$$\delta Q = T \cdot \Delta S_{MT}. \quad (14)$$

For the alloy $Fe_{0.49}Rh_{0.51}$ δQ value in the field of 2 T is ~ 7 mJ g^{-1} ($T = 310$ K), which is rather high value to cool down the film of the polymer.

Among other temperature-sensitive polymers copolymers of methacrylamide (for example, propyl methacrylamide), polymers containing ethylene oxide groups, cellulose derivatives (ethyl hydroxyethyl cellulose, cellulose acetate) can be mentioned (Tishin et al., 2006a–d, 2008, 2009). Temperature-sensitive polymers has LCST lying in physiological range: for NIPAAm it is 32.4 °C, for poly-NIPAAm ~34 °C, for copolymers of NIPAAm and tBuAM LCST varies from 25.2 °C (15% of tBuAM) to 9.6 °C (50% of tBuAM). Under heating up by the blood the polymers return to insoluble state and the drug release stops. This allows to control the drug release during the treatment procedure. It is also possible to use nanoparticles covering with the polymers with different LCST (or layer covering of nanoparticles) and obtain by this way the temperature or magnetic field controlled drug release. Formation of the temperature sensitive polymer films on magnetocaloric nanoparticles can be made, for example, using alcohol solutions of the corresponding polymers.

4. Future perspectives

As was noted above there are two main fields of practical MCE applications – magnetic refrigeration and medicine (hyperthermia, drug delivering). Both of them require materials with high magnetocaloric performances. In recent decade a set of new magnetocaloric materials appears, but their characteristics are still rather far from desired for commercial realization of magnetic refrigeration and from theoretical limit of adiabatic temperature change established by Zverev et al. (2010).

In searching of effective materials for magnetic refrigeration not only theoretical investigations, but also experimental studies play an important role. In particular, it was shown that magnetic field sweep rate can affect the character of $\Delta T(H)$ curves for materials with the first order magnetic phase transitions (Tishin et al., 2007). For Dy in the temperature interval of helicoidal antiferromagnetic (HAFM) spin structure existence there were pronounced dependence of the critical field of the HAFM structure destruction observed on $\Delta T(H)$ curves on magnetic field change rate. Also on $\Delta T(H)$ curves measured in the temperature interval from the Curie temperature to the tricritical temperature the field hysteresis (for increasing and decreasing magnetic field) was observed. These dynamic effects, especially changing of $\Delta T(H)$ curves character with changing of the magnetic field sweep rates, can have considerable influence on the heat exchange processes in magnetic refrigerators, and thus affect the technical characteristics of the devices. At the same time the dynamic effects are hidden in the most experimental data obtained for today by indirect methods of ΔS_{MT} and ΔT determination (with the help of Maxwell relation on the basis of magnetization data or from the heat capacity temperature dependences data measured in zero and nonzero magnetic fields), and even by direct method of ΔT measurements made in usual manner, i.e. by measuring only initial (in zero field) and final (in presence of magnetic field) temperatures. For indirect methods it is related with the fact that measurements are accomplished in static or quasi-static conditions (in magnetic refrigerators the magnetic working body operates in dynamic conditions). For usual direct ΔT measurements the data on $\Delta T(H)$ dependence is just omitted due to the scheme of experiment. So, the measurements in dynamic mode are very important for development of real magnetic working bodies for magnetic refrigerators.

The MCE dynamic measurements are also important for medical applications of MCE. Another important from medical and also fundamental points of view direction of the MCE experimental investigations is studies of adiabatic temperature change in dynamic mode in rather weak magnetic fields (up to 10^5 A m^{-1}). Up to now the main attention in MCE experimental studies was paid to measurements in strong magnetic fields – up to 2 T or higher and almost nobody made measurements in low magnetic fields. This is related with the fact that the main investigation activity was concentrated on creation of the working materials for magnetic refrigerators, it was necessary to obtain ΔS_{MT} and ΔT values as high as possible and these parameters increase with increasing magnetic field.

At the same time for application of the MCE in hyperthermia it is particularly necessary to get high MCE in relatively low magnetic fields (up to $\sim 8 \cdot 10^4$ A m^{-1}). This is related first of all with design of hyperthermia apparatuses for magnetic field creation – they can be essentially simplified for lower fields. Secondly, magnetic and magnetocaloric properties of nanoparticles are in essential part determined by magnetic anisotropy of different nature that can achieve essential values (Gubin et al., 2002). The anisotropy contribution to MCE mainly display itself in the region of magnetization rotation on magnetization curve, which belongs to relatively low fields. Investigations of MCE in low fields can also give additional information about contribution of magnetocrystalline anisotropy and domain structure (the low field region corresponding to domain walls displacement) to MCE necessary to understanding of

fundamental mechanisms of magnetic ordering in bulk materials. It should be noted that dynamic mode of MCE measurement can get in low field region especially important information because hysteretic effects here can be pronounced.

For experimental investigations of the MCE at low fields it is necessary to increase sensitivity of direct methods of ΔT measurements. This task can be solved by the use of methods of lock-in detection of periodically changing signals. The alternating magnetic field in this case can be created by a solenoid for the field range up to $2 \cdot 10^4$ A m^{-1} or by the Halbach-type field source with variable magnetic field for higher fields. The thermal response of a sample under investigation arising due to MCE can be detected by a lock-in amplifier. So, in such method the dynamic mode and high sensitivity are combined together.

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