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THE MAGNETOCALORIC EFFECT OF SUPERFINE MAGNETS

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The magnetocaloric effect (MCE) of aqua suspensions based on superfine magnetite (Fe_3O_4), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), samarium ferrite ($SmFe_2O_4$) and gadolinium ferrite ($GdFe_2O_4$) as well as of magnetite-based ferrofluids was calorimetrically determined in the range of the temperatures from 283 to 253 K. MCE has a positive magnitude for all investigated systems except a hematite-based system. For the suspensions on the basis of MCE temperature dependence it was determined that superfine magnetite transformed into α-Fe_2O_3 at the temperature above 328 K in contrast to monocrystal magnetite. For aqua suspensions of samarium ferrite and gadolinium ferrite and magnetite-based ferrofluids MCE temperature dependence has an extreme behavior which is connected with a second-order phase transition. For the first time it is established that the magnetocaloric effect (MCE) is greatly increased when the magnet is a nanosized material.

Keywords: *ferrites, hematite, maghemite, magnetite, magnetocaloric effect, microcalorimeter, second-order phase transition*

Introduction

For some magnets a strong interaction between electron and spin subsystems and crystal lattice takes place resulting in the anomalies of their magnetic, electric, optic, magnetothermal and elastic properties. Therefore the most interesting properties in respect to the practical application and the theoretical value are the giant magnetocaloric effect (MCE) and the magnetostriction as well as the colossal magnetoresistance which are observed for some magnets close to Curie temperature (T_c). Rare-earth manganite MCE (in particular MCE for nanosized manganite) was not practically studied. Moreover this effect can be compared with gadolinium MCE. These magnetocaloric materials are perspective for magnetic refrigeration, for hyperthermia, etc. On the other hand at present it was experimentally determined that T_c for nanosized materials was sharply decreased. Thus, the search of nanosized materials having large magnitudes of the indicated effects in the range of the room temperatures under weak applied magnetic fields is an extremely actual task.

Experimental

Superfine magnetite was synthesized according to the procedure described [1] by means of the precipitation of Fe^{2+} and Fe^{3+} in ammonia excess. The magnetite suspension obtained was repeatedly washed by distilled water up to pH=7. Specific conductance of rinsing water was 1.77 mS cm^{-1} after the removal of sulphate-ions and chloride-ions. Ethanol-based suspension was obtained by means of repeated alcohol ablution and decantation of an aqua suspension. Washing from water was controlled by IR-spectroscopic method. γ-Fe_2O_3 and α-Fe_2O_3 were obtained by means of burning superfine magnetite under 553 and 593 K respectively during 1 h [2]. Ferrofluids were synthesized according to the procedure described [3]. Oleic acid and polyethylsiloxane (PES-5) were used as surfactant and disperse medium respectively.

An average size of magnetite nanoparticles was determined by a radiographic method [4]. The size was about 10 nm for ferrofluids. For aqua suspensions the particles (size was about 6–10 nm and specific surface was about 130 m^2 g^{-1}) formed aggregates. An aggregate size of the largest fraction determined microscopically was 1 micron [4]. The size and the polydispersity of magnetite particles for alcohol suspension were smaller in comparison with an aqua suspension. Particle size of α-Fe_2O_3 and γ-Fe_2O_3 was about 0.5–5 micron.

MCE measuring was carried out by means of a microcalorimeter [5]. The microcalorimetric cell with a thermostatic system was located between the poles of electromagnet. It allowed to measure the magnitude of the magnetocaloric effect and the heat capacity under magnetic fields applied from 0 to 0.7 T and in the range of the temperatures from 283 to 253 K.

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Results and discussion

Before the consideration of the results it is necessary to give a description of the crystal and magnetic structure of the magnets studied.

Magnetite is a typical specimen of spinel oxides. It has a molecular formula $FeO{\cdot}Fe_2O_3$. Low-level cell of magnetite contains 56 ions (32 O^{2-}, 8 Fe^{2+}, 16 Fe^{3+}). O^{2-} ions form a face-centered cubic lattice. The ions of Fe^{3+} occupy tetrahedral positions made by 4 O^{2-} ions whereas the ions of Fe^{2+} and remaining Fe^{3+} ions occupy octahedral positions made by 6 O^{2-} ions. Owing to this structure magnetite displays ferrimagnetism [6].

Ferric oxide γ-Fe_2O_3 called maghemite has a reversed spinel crystal structure containing vacant centers. The distribution of ions can be represented as $(Fe^{2+})O{\cdot}(Fe^{3+}_{5/3}V_{1/3})O_3$, where V is a vacant centre. This ferrite possesses ferrimagnetic properties.

α-Fe_2O_3 is hematite which belongs to corundum-type oxides. These crystals form a hexagonal structure. 2/3 octahedral positions between oxygen ions forming hexagonal close-packed lattice are occupied by metallic ions. At the temperature below 250 K called Morin's point hematite displays antiferromagnetism. Above 250 K hematite possesses weak ferromagnetic properties that is the so-called parasitic ferromagnetism takes place [6].

Gadolinium and samarium ferrites ($MeFe_2O_3$) have a spinel crystal lattice and possess ferrimagnetic properties.

The temperature change of a magnet at the finite field change and adiabatic conditions is described by means of a well-known thermodynamic relationship [1]:

$$\Delta T = -\frac{T}{C_H}\left(\frac{dM}{dT}\right)_H \Delta H \tag{1}$$

where ΔT is a magnetocaloric effect (MCE), T is a temperature, C_H is a heat capacity under constant magnetic field, $(dM/dT)_H$ is a derivative of magnetization with respect to temperature, ΔH is a magnetic field change.

Many studies which are connected with the research of the magnetocaloric effect for monocrystal magnets [7–11] exist. Hence for nanosystems (ferrofluids, suspensions, superfine powders) the MCE data practically lack. On the basis of our research it is obvious that the magnetothermal phenomena for nanosystems have some peculiarities and differ from magnetothermal properties of bulk and monocrystal systems.

Figures 1–8 show field and temperature MCE dependences of the systems. It should de noted that for all systems except hematite the MCE magnitudes are positive, i.e. the temperature increases when the magnetic field is tuned on and the temperature decreases at tuning off the magnetic field. Below we shall consider MCE changes which take place only at tuning on the magnetic field.

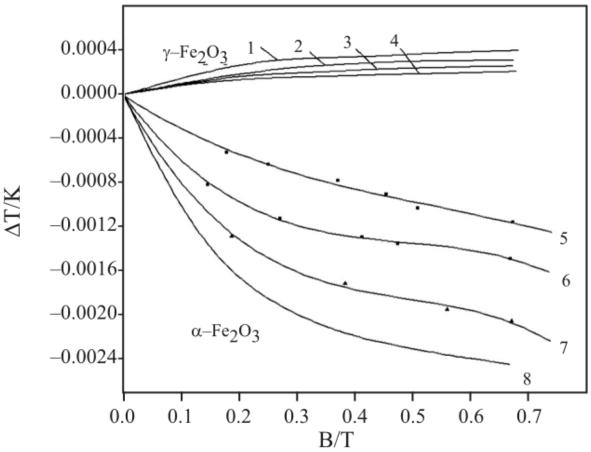

Fig. 1 MCE of α-Fe_2O_3 and γ-Fe_2O_3 being in aqua suspensions as a function of applied magnetic field at various temperatures: 1 – 298, 2 – 313, 3 – 328, 4 – 343, 5 – 298, 6 – 313, 7 – 328, 8 – 343 K

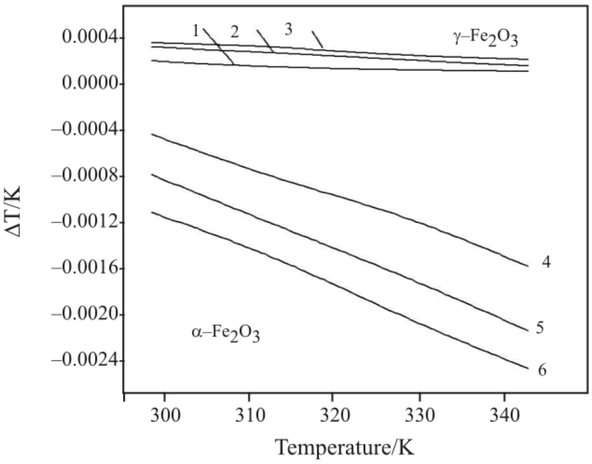

Fig. 2 MCE of α-Fe_2O_3 and γ-Fe_2O_3 being in aqua suspensions as a function of temperature in various applied magnetic fields: 1 – 0.15, 2 – 0.35, 3 – 0.65, 4 – 0.15, 5 – 0.35, 6 – 0.65 T

Figures 1 and 2 show field and temperature MCE dependences of aqua suspensions of α-Fe_2O_3 and γ-Fe_2O_3. Regardless of the identical elemental composition these oxides possess various crystal and magnetic structures and various magnetism. The MCE behavior also has essential distinctions. For γ-Fe_2O_3 MCE has a positive magnitude whereas for α-Fe_2O_3 MCE has a negative magnitude. With rising the magnetic field the absolute MCE values for both oxides increase at all temperatures (Fig. 1). With rising the temperature for γ-Fe_2O_3 the MCE values decrease and for α-Fe_2O_3 the MCE values are negative and increase modulo (Fig. 2).

Figures 3 and 4 show field and temperature MCE dependences of aqua magnetite suspensions. It should de noted that the nature of MCE dependences for ethanol suspensions are similar MCE dependences for aqua suspensions. The MCE values increase up to 328 K with rising the magnetic field (Fig. 3). Above 328 K the MCE values become negative and the nature of the MCE change is similar to that of α-Fe_2O_3. Such MCE sign change corresponds to a phase transition of $Fe_3O_4 \rightarrow \alpha$-$Fe_2O_3$. Such transition is observed for ethanol suspension, but it takes place at the higher temperature. Phase transition under all magnetic fields is observed on temperature MCE dependence of magnetite (Fig. 4). Field dependences for nanoparticles of magnetite (diameter is about 10 nm) are similar dependences plotted in Fig. 3. Temperature MCE dependence for magnetite is characterized by the presence of a narrow high maximum increasing with rising the magnetic field (inset, Fig. 6).

Figures 5 and 6 show field and temperature MCE dependences for all the systems studied. It should be noted that the MCE values for all magnets are taken for about one concentration (ω=65%). For all ferrimagnetics the MCE values are positive and increase with rising the magnetic field (Fig. 5). For magnetite (curves 1, 2, 5) with decreasing the size of particles the increase of the MCE value takes place. For nanosized particles of magnetite the MCE values under the largest fields are increased more than ten times (curve 5). Since in ferrofluids the magnetite particles are covered by a monomolecular layer of a surfactant the temperature phase transition cannot be

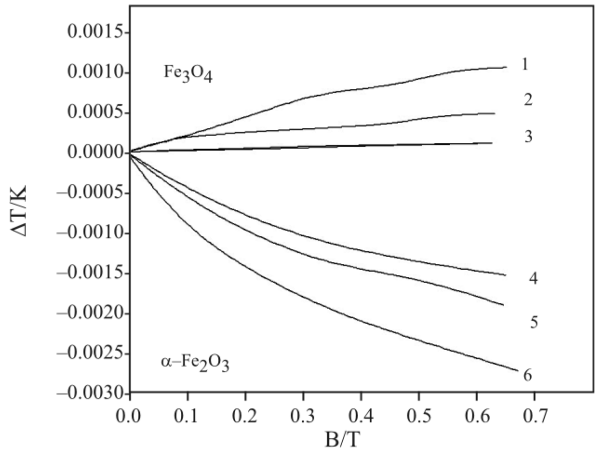

Fig. 3 MCE of Fe_3O_4 and α-Fe_2O_3 being in aqua suspensions as a function of applied magnetic field at various temperatures: 1 – 298, 2 – 313, 3 – 328, 4 – 333, 5 – 343, 6 – 353 K

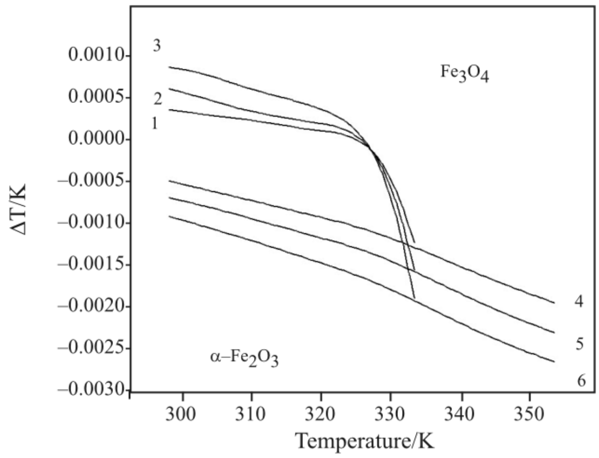

Fig. 4 MCE of Fe_3O_4 and α-Fe_2O_3 being in aqua suspensions as a function of temperature in various applied magnetic fields: 1 – 0.15, 2 – 0.375, 3 – 0.6, 4 – 0.15, 5 – 0.375, 6 – 0.6 T

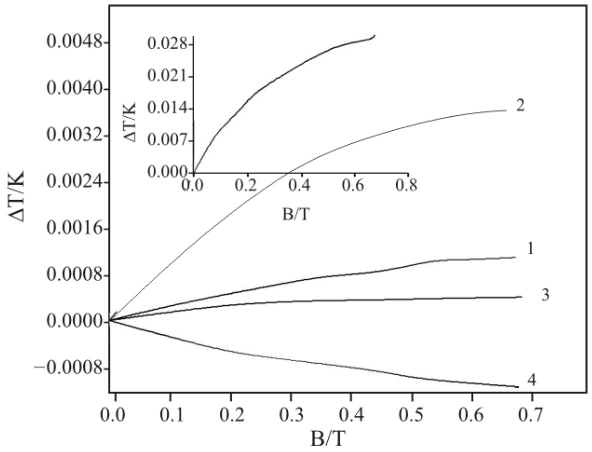

Fig. 5 MCE as a function of applied magnetic field at 298 K for: 1 – aqua suspension of Fe_3O_4, 2 – ethanol suspension of Fe_3O_4, 3 – aqua suspension of γ-Fe_2O_3, 4 – aqua suspension of α-Fe_2O_3, 5 – PES-5-based magnetite colloid

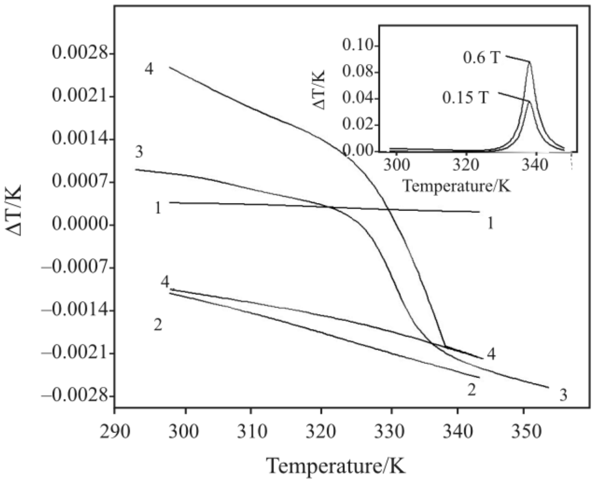

Fig. 6 MCE as a function of temperature in applied magnetic field 0.6 T for: 1 – γ-Fe_2O_3, 2 – α-Fe_2O_3, 3 – Fe_3O_4 in aqua suspension, 4 – Fe_3O_4 in ethanol suspension, PES-5-based magnetite colloid (inset)

observed (Fig. 6, inset). It is shown that temperature dependence for nanosized magnetite has an extreme behavior. The maximum at 338 K increases with rising the magnetic field. A maximum in the given range of the temperatures for the systems with nanoparticles of magnetite is found for the first time and can be evidently connected with a magnetic transition of the «order-order»-type in a magnetite magnetic structure [12]. With rising the temperature for γ-Fe_2O_3 the MCE values are positive and decrease and for α-Fe_2O_3 the MCE values are negative and increase modulo (Fig. 6, curves 1, 2). For magnetite in ethanol suspension (curve 4) MCE values decrease and above 332 K become negative. With decreasing the temperature during experiment the curve 4 does not repeat and MCE values remain negative. It is connected with the temperature phase transition i. e. the magnetite transforms to α-Fe_2O_3. For magnetite in aqua suspension the dependence is similar.

Figures 7 and 8 show field and temperature MCE dependences of gadolinium and samarium ferrites. On field dependences (Fig. 7) the MCE values increase nonlinearly with rising the magnetic field at all temperatures and under magnetic fields from 0 to 0.7 T. Temperature MCE dependences under various magnetic fields are presented in Fig. 8. For aqua suspension of gadolinium ferrite a great increase of MCE values is observed in the temperature range from 296 to 300 K. MCE values achieve maximum at the same temperature (298 K) and under all magnetic fields, peak of maximum increasing with rising the magnetic field. For samarium ferrite at 313 K the maximum takes place as well, but the value of the maximum is much smaller. Maximum in the given temperature range for system containing nanoparticles of gadolinium ferrite is connected with a magnetic second-order phase transition. Such transition was found for polycrystalline gadolinium [4] at 292 K. Maximums of the magnetocaloric effect for gadolinium and samarium ferrites and polycrystalline gadolinium indicate that the temperature in the point of maximum is Curie point in which a magnetic second-order phase transition takes place.

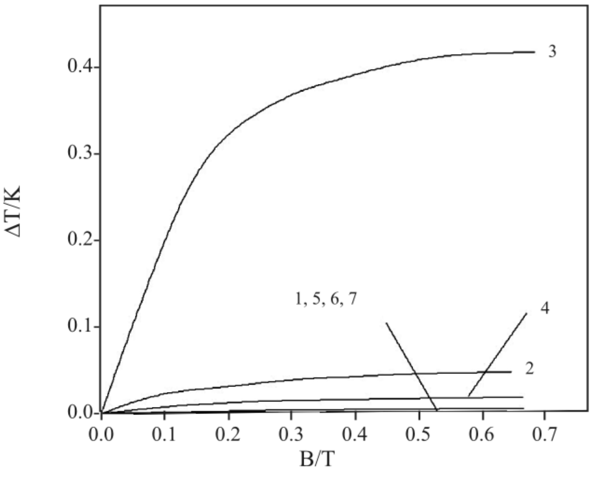

Fig. 7 MCE of gadolinium ferrite in aqua suspension as a function of applied magnetic field at various temperatures: 1 – 293, 2 – 296, 3 – 298, 4 – 300, 5 – 303, 6 – 307, 7 – 312 K

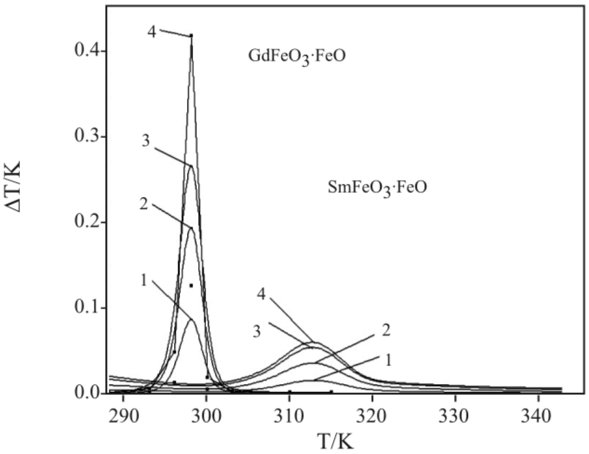

Fig. 8 MCE of gadolinium ferrite in aqua suspension as a function of temperature in applied magnetic fields: 1 – 0.05, 2 – 0.15, 3 – 0.375, 4 – 0.65 T

It should be noted that MCE values for both ferrites and for oxides of iron are taken to the same concentration of magnet. Hence MCE for ferrites is greater and MCE for gadolinium ferrite in the point of maximum is about 0.5°C at 298 K.

Acknowledgements

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