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Peculiarities of magnetocaloric effect in manganites connected with magnetic heterogeneous state

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Abstract: Magnetocaloric effect (MCE) or ΔT-effect was studied in $La_{1-x}Sr_xMnO_3$, $Sm_{0.55}Sr_{0.45}MnO_3$ and $PrBaMn_2O_6$ manganites. It has been found that the maximum value of MCE, measured by direct method, is far less than obtainable by computation from the change of the magnetic entropy in Curie temperature T_C. This phenomenon is explained by presence in them of the magnetic two-phase ferromagnetic (F) – antiferromagnetic (AF) state. So in $La_{1-x}Sr_xMnO_3$ the negative contribution from AF portion of sample lowers MCE and displacesmaximum on $\Delta T(T)$-curve to the higher temperature than T_C on 20-40 K. Maximum on $\Delta T(T)$ curve of $Sm_{0.55}Sr_{0.45}MnO_3$ is disposed near T_C=134 K in the cooling in the air single-crystal and ceramic samples. The cooling inoxygen of single-crystal,restored the Mn-O-Mn broken connections, increases the volume of clusters with CE-type of AF order, results to that maximum on $\Delta T(T)$ curve is disposed at Neel temperature T_N of this phase (243 K). Magnetic field, applied to sample during ΔT-measurement, transforms AF clusters into F state and theboth types of clusters decompose at T_N. The $PrBaMn_2O_6$ manganite has two phase transactions: paramagnetic–F at T_C=295 K and F–AF at T_N=231 K. Phase with spontaneous magnetization obtains the understated magnetic moment. Curve $\Delta T(T)$ has the wide maximum near T_C and the sharp minimum near T_N with the small ΔT-values in both extremes: 0,13 K and - 0,2 K respectively. This is connected with presence of AF interactions in F phase and F interactions in AF phase.

Keywords: Magnetocaloric Effect, Nagnetization, Paramagnetic Susceptibility, Magnetic Two-Phase State, Manganite

1. Introduction

The temperature change induced in magnetic material during an adiabatic magnetic field change is the magnetocaloric effect (MCE). MCE provides the physical basis of magnetic refrigeration technology.Application of magnetic cooling will decrease the global consumption of energy and consumer chemistry, which is necessary for weakening the decrease in the ozone layer thickness near the Earth, and can be an alternative to the gas compression in refrigerating engineering in the near future. Therefore, researchers pay particular attention to searching for and studying the materials having a high MCE at near room temperatures. According to classical thermodynamics MCE is estimated from the formula:

$$\Delta T_{th} = \frac{T}{C_H(T)} \Delta S_M(T), \qquad (1)$$

where C_H is specific heat at a constant field and $\Delta S_M(T)$ is the magnetic entropy change of the magnet, when a field is applied adiabatically:

$$\Delta S_M = \int_0^H \left(\frac{dM}{dT} \right)_H dH . \qquad (2)$$

Here M is magnetization. The large change of magnetic entropy in the Curie point was observed in manganites in works [1-17]. In some compounds this change is more, than for Gd, for which the MCE value reaches 5 K in the field 2 T [4,5]. Therefore, manganites should have a large MCE.

But magnetic two-phase ferro-antiferromagnetic (AF) state, caused by strong s - d exchange, exists in manganites [18 - 20]. It should have an impact on the MCE, as MCE for AF's is negative and for ferromagnets (F's) the one is positive properly from relations (1,2). In [21], we showed that a weak exchange coupling between the F and AF parts of a sample exists in this case. Therefore MCE can be presented in the form:

$$\Delta T = \Delta T_F + \Delta T_{AF}, \qquad (3)$$

where ΔT_F and ΔT_{AF} are the MCEs of the F and AF parts of the sample, respectively. As it is seen from Eqs. (1) and (2), ΔT_F is positive and ΔT_{AF} is negative. In this case,

the MCE estimated from the sharp decrease in the magnetization near the Curie temperature (see Eq. (1)) corresponds only to the F part of the sample; hence, it is overestimated because of the fact that negative contribution ΔT_{AF} is not taken into account. Therefore, the magnitude and sign of MCE in manganites can only be determined by direct measurements of this effect.

The purpose of this work is to use a direct method to study MCE. MCE and magnetization were studied in compounds: $La_{1-x}Sr_xMnO_3$, $Sm_{0.55}Sr_{0.45}MnO_3$ and $PrBaMn_2O_6$ belonged to three classes of manganites: $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba), $Sm_{0.5+x}Sr_{0.5-x}MnO_3$ ($0.05 \leq x \leq 0.10$) and $ReBaMn_2O_6$ (Re= Pr, Nd, Sm, Eu, Gd) with the layer crystalline structure. Our results have shown that values of MCE received by direct method (ΔT_{ex}) are well smaller than calculated from the magnetization change in T-region (Δ_{th}).

2. Experimental

MCE was studied on $La_{1-x}Sr_xMnO_3$ ($x = 0.1, 0.125, 0.3$), $Sm_{0.55}Sr_{0.45}MnO_3$ single crystals and $PrBaMn_2O_6$, $Sm_{0.55}Sr_{0.45}MnO_3$ (C-sample) ceramics samples. The ceramic samples were prepared by standard ceramic techniques by A.R. Kaul and single crystals were grown by the floating-zone method by A.M. Balbashov. One single crystal $Sm_{0.55}Sr_{0.45}MnO_3$ was annealed in air (A-sample) and other in oxygen atmosphere (O-sample). Using X-ray diffraction, the all samples were found to be pure single-phase perovskite with the orthorhombic Pnma structure. To achieve a high degree of crystallographic ordering between the Pr and Ba ions in the $PrBaMn_2O_6$ compound, they performed annealing in an oxygen atmosphere. The degree of ordering in the best samples reached 96%,.

MCE was measured by direct method. Magnetic field *H* for quasistatic measurement was ranged from 0 to 14.2 kOe and was created by an electromagnet. The equilibrium temperature *T* of the sample was measured using copper-constantan thermocouple before and after the introduction of a magnetic field. The thermocouple joint was placed inside a sample. The MCE was determined as the difference between these two equilibrium temperatures. Miniminization of the heat losses was reached by high vacuum (not less than 10^{-5} mm Hg), heat screen around the sample and by usage of ultrathin detector wires. The experimental setup was tested with gadolinium sample of 99.99% purity.

The magnetization of the sample was also measured with SQUID and vibrating-sample magnetometers, The paramagnetic susceptibility was measured by weighing with electromagnetic compensation.

## 3. Magnetocaloric Effect in $La_{(1-x)}Sr_xMnO_3$ System

Figure 1 shows the temperature dependences of magnetization *M* in a magnetic field of 8.2 kOe, and Figure 2 shows the temperature dependences of MCE $\Delta T_{exp}(T)$ in the same magnetic field measured by the direct method (*a*) and the $\Delta T_{th}(T)$ calculated by Eq. (1) {*b*} on La_1-

$_xSr_xMnO_3$ ($x = 0.100, 0.125, 0.300$) single-crystal samples. The values of ΔT_{th} was computed from the formula (1) in which ΔS_M was computed with the help (2) from a magnetization, and C_H was taken from [22]. The numerical integration in (1) was realized by Sympson method. It is shown in Figure 2 that on the all curves the maxima are observed, but the temperatures of these maxima for each compound are differed: on experimental curves they on 20-30 K are higher, than on the curves computed from formula (1). It should be noted that curve $\Delta T_{ex}(T)$ has step in those regions temperatures, where is maximum on curve $\Delta T_{th}(T)$. It is possible to explain these facts by the presence of the magnetic two-phase F-AF state in the sample. In this case the difference between curves $\Delta T_{ex}(T)$ and ΔT_{th} (*T*) reflects the contribution of AF part of the sample to the experimentally measured MCE, which is shown in Figure 3. This AF contribution has the shape characteristic of antiferromagnets [23]: it is negative in the temperature range of breaking an AF order, and MCE is positive above this range (which is characteristic of paramagnetic order). It reverses sign at Neel temperature T_N. It follows that the values of T_C and T_N are closely allied in investigated compounds. In this consideration we neglected by an entropy change of F/AF interface. However, in paper [21] we showed that the exchange interaction between F and AF regions is much less than the exchange inside these regions and consequently the transition region between them practically does not exist.

It is known that the F phase occupies almost the entire sample volume in the composition with $x = 0.30$ at low temperatures, although the contribution of the AF part to ΔT_{exp} is high (see Fig. 3). This finding is likely to be related to the fact that the magnetic heterogeneity grows strongly at the T_C-region in this composition. For example, the data of neutron diffraction [24], EPR [25], absorption spectra [26] and other studies reviewed in [19] point to the existence of a mixed F–AF state near T_C in compositions with $x \leq 0.3$.
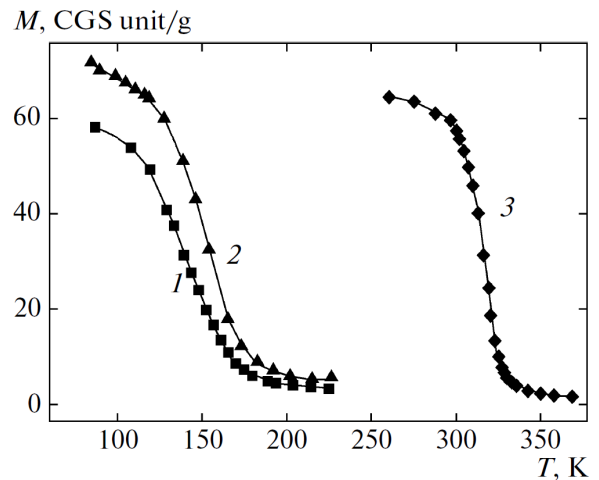
Figure 1. *Temperature dependences of the magnetization of single-crystal $La_{1-x}Sr_xMnO_3$ samples in a magnetic field of 8.2 kOe at x = (1) 0.100, (2) 0.125 and (3) 0.300.*
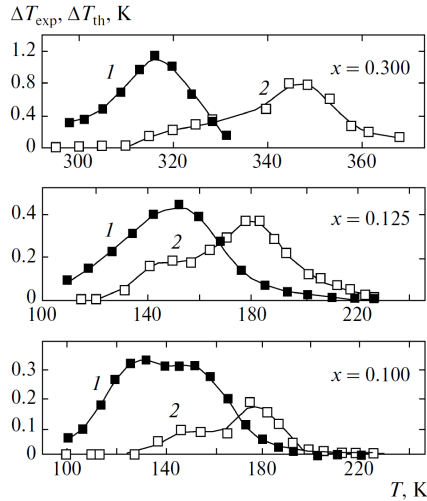
Figure 2. *Temperature dependences of MCE obtained by a direct method ($\Delta Texp(T)$, curves 2) and calculated by Eq. (1) ($\Delta Tth(T)$, curves 1) in a field of 8.2 kOe for single-crystal $La_{1-x}Sr_xMnO_3$ samples.*
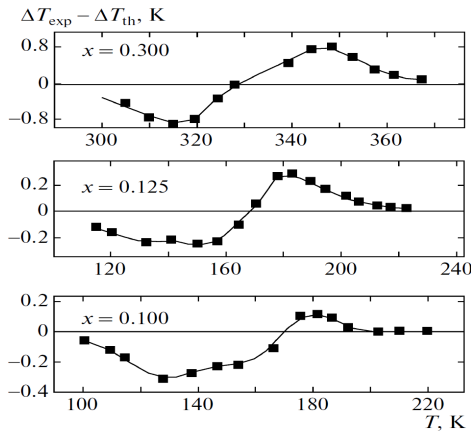
Figure 3. *MCE due to a break in the AFM order in an AFM phase in a field of 8.2 kOe for single-crystal $La_{1-x}Sr_xMnO_3$ samples.*

The Curie temperatures of the compositions under study were determined as the temperatures of the maxima in the $(dM/dT)(T)$ curves measured in a low magnetic field of 100 Oe. They were found to be 140 K, 150 K, and 315 K for the compositions with $x = 0.100$, 0.125, 0.30 respectively. It should benoted that the concept of the Curie and Néel temperatures is rather conventional in magnetically heterogeneous magnets, which also include the compositions under study. Here, these are the temperatures of breaking a magnetic order in the F and AF phases of a sample. As is seen from a comparison of Figures 2 and 3, the negative MCE induced by the AF part of a sample decreases the maximum value of $\Delta Texp(T)$ curve as compared to the value that could be if the sample contained only an F phase and shifts the maximum in the $\Delta Texp(T)$ curve above TC. This maximum in F metals is usually located at the Curie temperature [27].

Thus, with the help of magnetic two-phase F −AF state presence in sample it is possible to explain anomaly behavior of $\Delta T_{ex}(T)$ in these compounds.

4. Magnetocaloric Effect in $Sm_{0.55}Sr_{0.45}MnO_3$

Recent neutron and electron diffraction studies of $Sm_{0.5+x}Sr_{0.5-x}MnO_3$ [28,29] have shown that a magnetic inhomogeneous state consisting of F clusters, A-type AF clusters and CE-type AF clusters is presented .in them, Both F and A-type AF clusters break down in T_C-region and CE-type AF clusters remain at $T > T_C$. The T_C-values of A-, O- and C-samples, determined by us from the AC initial magnetic susceptibility measurements, are 130 K, 134 K and 142 K respectively (See Table I).

Table 1. *Magnetocaloric effect and magnetic characteristics of $Sm_{0.55}Sr_{0.45}MnO_3$ and $PrBaMn_2O_6$.*

| Composition	$T_C (T_N)$, K	θ, K	ΔT_{exp}, K	$T_{max}(T_{min})$ (exp.), K	ΔS_M, J/kg K	ΔT_{th}, K	T_{max} (th.), K
$Sm_{0.55}Sr_{0.45}MnO_3$, sample A	130	225	0.75	133	15.93	6.7	138
$Sm_{0.55}Sr_{0.45}MnO_3$, sample O	134	270	0.40	243	12.62	5.3	144
$Sm_{0.55}Sr_{0.45}MnO_3$, sample C	142	230	0.40	142	8.98	3.8	146
$PrBaMn_2O_6$ polycrystal	(231)	297	-0.20	(236)	-5.06	-5.9[*]	234

* When calculating ΔTth, we borrowed the specific heat from [30].

Figure 4 a,b,c shows the temperature and field dependences of the magnetization M in high magnetic fields (up to 70 kOe) for sample O, and similar curves were recorded for samples A and C. These measurements were carried out on two samples cut from single crystals in the form of the same parallelepipeds. The longest edge was parallel to the c axis or the ab plane of orthorhombic structure and parallel to a magnetic field during the magnetization measurements. The $M(T)$ and $M(H)$ curves of both parallelepipeds are almost the same, which indicates the absence of a magnetic anisotropy in these crystals.. The transition from the spontaneous magnetization to the paramagnetic phase is strongly smeared (see Figure. 4a). As it have been noticed above, this is associated with the presence of three types of magnetic clusters in the sample. The magnetization isotherms first linearly increase above the Curie point (Figure. 4b) due to the magnetization of AF clusters and then increases sharply in the range $Hc_1 \leq H \leq Hc_2$ due to the transition of CE- type AF clusters into the F state. The field dependence of the magnetization becomes linear at T

$\approx$ 240 K (Figure 4 c), which can be considered as the temperature of breaking the CE type AF order (T_{NCE}) and charge ordering in these clusters. When the latter is broken, the crystal lattice changes substantially; i.e., this is an analog of a first order phase transition. The Figure 5 d shows the temperature dependence of inverse paramagnetic susceptibility $1/\chi$ for all studied samples The shown $\{1/\chi\}(T)$ dependence obeys the Curie–Weiss law with paramagnetic Curie temperatures (Θ) of 225, 270, and 230 K for samples A, O, and C respectively.
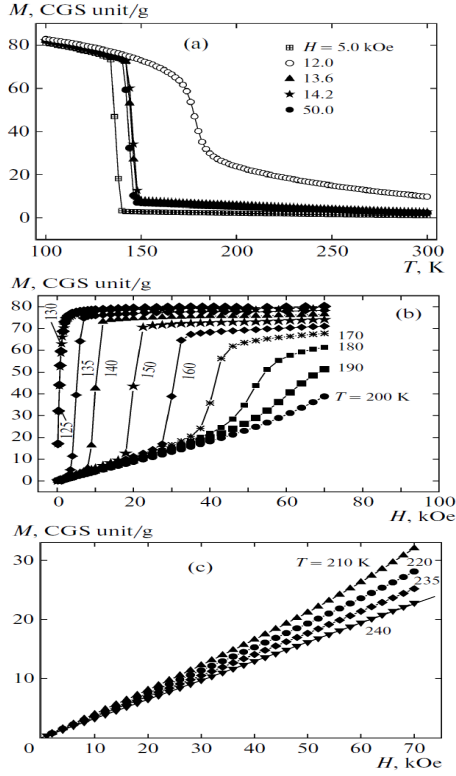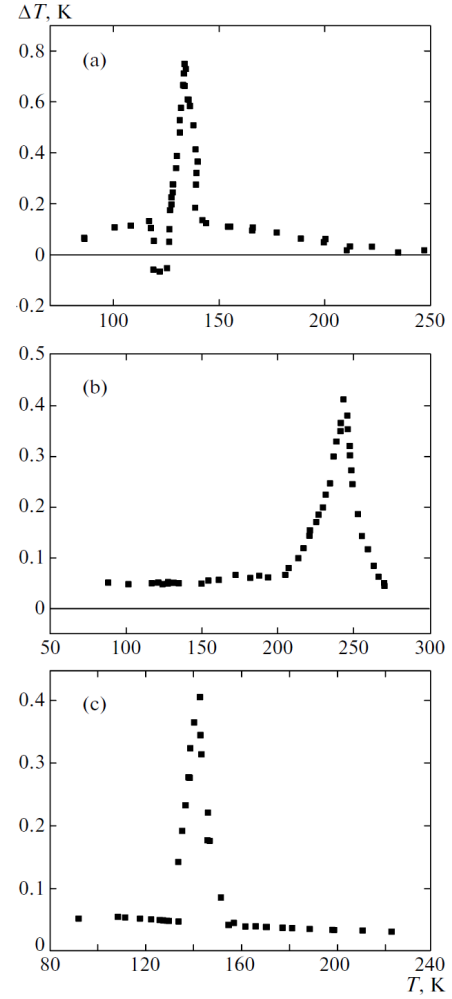

Figure 4. *La$_{1-x}$Sr$_x$MnO$_3$ single-crystal sample O. Magnetization vs. (a) temperature and (b), (c) magnetic field at various temperatures.*
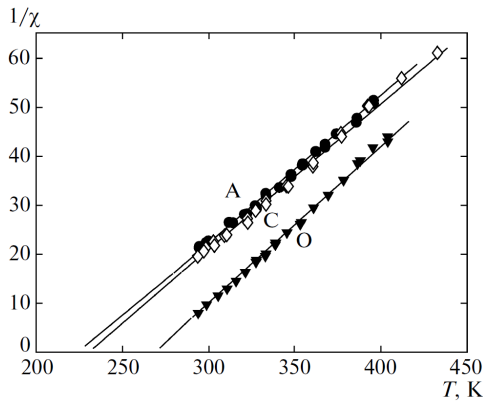
Figure 5. *Temperature dependences of the inverse paramagnetic susceptibility of La$_{1-x}$Sr$_x$MnO$_3$ for single-crystal*

Figure 6 shows the dependence $\Delta T_{ex}(T)$ in magnetic field 14.2 kOe of A-, C- and O-samples. As we can see from Figure 6a the $\Delta T_{ex}(T)$ curve of A-sample has maximum at $T_{max} = 143.3$ K and minimum at $T_{min} = 120$ K with $\Delta T_{ex} = 0.8$ K in maximum and $\Delta T_{ex} = -0.1$ K in minimum. The maximum on the $\Delta T_{ex}(T)$ curve is observed too in the O-sample at $T_{max} = 244$ K (Figure 6 b) and the C-sample

at $T_{max} = 143$ K (Fugure 6c). In these maxima MCE values are 0.41 K and 0.4 K respectively.

Figure 6. *La$_{1-x}$Sr$_x$MnO$_3$ composition. Temperature dependences of MCE in a magnetic field of 14.2 kOe for single-crystal samples (a) A (cooled in air) and (b) O (cooled in an oxygen atmosphere) and (c) for polycrystalline sample C.*

In this time the negative MCE is absent on the $\Delta T_{ex}(T)$ curves of O- and C-samples. Figure 7 shows the $\Delta T_{ex}(H)$ dependence at $T_{max} = 143$ K for sample A, and a similar $\Delta T_{ex}(H)$ dependence at $T = T_{max}$ was observed in samples O and C.

As is seen from Eq. (1), which describes MCE in the paraprocess range, MCE is positive upon a break in the F ordering and is negative upon a break in the AF ordering. Obviously, the maximum on the $\Delta T_{ex}(T)$ curves of samples A and C are related to the sharp decrease in the magnetization of F clusters near their Curie point, and a break in the AF ordering in A-type AF clusters causes the minimum in the $\Delta T_{ex}(T)$ curve of single crystal sample A. It is possible that this break in the AF order also continues at the maximum in the $\Delta T_{ex}(T)$ curve and decreases it; that is, the contribution of the break in the AF order in A-typeAF clusters to the total MCE ofthe, sample decrease its magnitude and slightly shifts the maximum toward high temperatures. It is apparent that the AF contribution decreases the total MCE of C-sample too; This decreasing is smaller in A-sample than in C-samples. As a result, the maximum

onthe $\Delta T_{ex}(T)$ curve is detected slightly above the Curie temperature rather than at this temperature, as in most MCE materials [27].

It clearly demonstrates that technology of preparation of samples may be modified the relation between F and AF portions of sample.
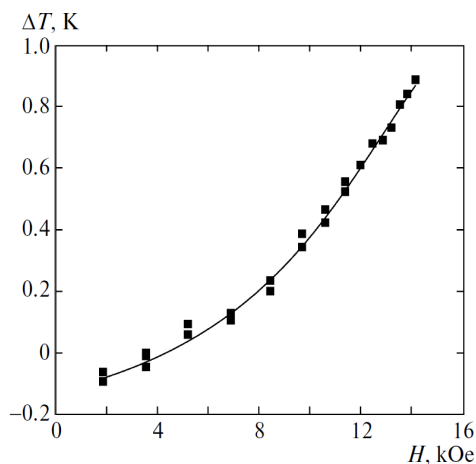
Figure 7. *The dependence of magnetocaloric effect from magnetic field H at T = 143 K of the $Sm_{0.55}Sr_{0.45}MnO_3$ single crystal annealed in air atmosphere (A-sample).*

It is obvious that higher magnitudes of MCE can be achieved in $S_{0.55}Sr_{0.45}MnO_3$ in higher fields. This is indicatedby the fact that the maximum magnitude of MCE increases with H in the magnetic field range up to 14.2 kOe (Figure 7), with the rate of increase at $H > 8$ kOe being higher than at $H < 8$ kOe. As is seen from Figure. 6b, this composition exhibits a jumplike increase in the magnetization in a certain critical field range $Hc_1 < H < Hc_2$, which increases linearly with thetemperature. This jumplike increase is related to thetransition of CE type AF clusters into the F state. It is seen from a comparison of Figures 7 and 4 c, themagnetic field range 8 kOe < H < 14.2 kOe, in which MCE increases faster than at $H < 8$ kOe, is located in the critical field range $Hc_1 < H < Hc_2$ and $Hc_2 > 14.2$ kOe. By this is meant that the $\Delta T_{ex}(H)$ curve is far from saturation and in the stronger magnetic field MCE may be great.

We emphasize that the maximum on $\Delta T_{ex}(T)$ curve of O-sample, cooled in oxygen atmosphere,is disposed at $T_{max} = 243$ K, which is significantly higher than T_C, and isvery close to $T = 240$ K, at which the break of AF of CE-type ordering occur. Apparently the annealing of sample in oxygen closes the broken connection Mn-V-Mn (here V is vacancy of oxygen) and in doing so stabilizes AF phase of CE-type which become a dominating in sample. It should be noted that MCE is positive near 243 K whence it follows that it is connected with the F order break. It is possible that magnetic field, applied to sample at ΔT-measurement, transfers AF phase of CE-type in F state and in T_N both are broken.

With the spontaneous magnetizations of all samples, we calculated MCE by Eqs. (1) and (2) using the specific heat borrowed from [30]. The maxima of calculated values of MCE and those measured by the direct method are given in the table 1, which also contains the Curie

temperatures, the paramagnetic Curie points,andthe temperatures of the MCE maxima (T_{max}) or minima (T_{min}). The calculated values of MCE are seen to be higher than those measured by the direct method by a factor of 9. Therefore, MCE in the $Sm_{0.5+x}Sr_{0.5-x}MnO_3$ ($0.05 \leq x \leq 0.10$) compounds should only be determined by the direct method, and the magnitude of the effect depends strongly on the sample preparation conditions.

5. Magnetocaloric Effect in $PrBaMn_2O_7$

In $PrBaMn_2O_6$ manganite with the layer crystalline structure Pr and Ba ions are crystallographic ordered. Its magnetic properties strongly depend on the degree of this ordering. Recent studies of neutron and electron diffraction and the magnetic susceptibility of $PrBaMn_2O_6$ [11] have shown that the compound with the degree of this crystallographic ordering 96% has two magnetic phase transitions: paramagnetic-F at $T_C = 303$ K and F − AF at $T_N = 252$ K. With the decreasing of the crystallographic ordering degree the quantity of frustrated connections increase and the spin glass state occurs in the fully disordered composition.
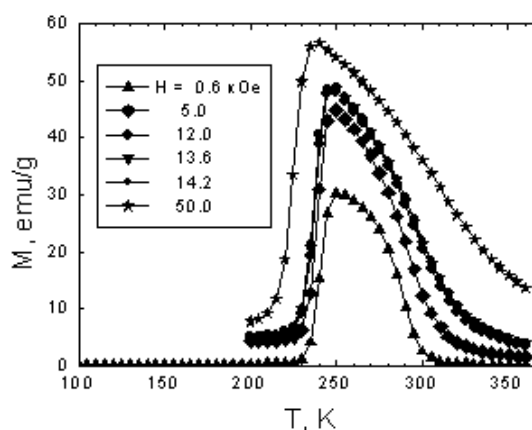
Figure 8. *The temperature dependence of the magnetization of the $PrBaMn_2O_6$ polycrystalline sample in some magnetic fields.*

In our work the sample was studied in which the degree of crystallographic orderingreaches of 96%. Figure 8 shows the temperature dependence of the magnetizationin the several magnetic fields of this sample. T_C, equal to 295 K, was determined as temperature of maximum derivative dM/dT, in the $M(T)$ curve in a magnetic field of 14,2 kOe,It is magnetic field in which MCE was measured. As shows from Figure 8 the sharp drop of magnetization is observed at the Neel temperature $T_N = 231$ K.Small difference of the TC and TNvalues received by we and in [30] is connected with difference of magnetic fields in which they were measured and the technology of samples. The temperature dependence of paramagnetic susceptibility obeys the Curie–Weiss law with a paramagnetic Curie temperature $\Theta = 297.5$ K which is close to the Curie temperature.

Phase with spontaneous magnetization obtains the understated magnetic moment. So magnetic moment calcu-

lated from the maximum magnetization in the M(T)curvesat 14,2 kOe and 50 kOe equal to 4,9 μB. and 4,2 μB per chemicalformula respectively (Figure 8). Chemical formula contain 3 magnetic ions: Mn^{3+} (4 μB), Mn^{4+} (3 μB) and Pr^{3+} (3 μB).Evidently magnetic moment, received from experiment, is smaller than the one at F ordering the all magnetic ions. This is evidenced by the presence of nanoregions with the frustrated connections disposed in phase with spontaneous magnetization.

Figure 9 shows the temperature dependence of MCE.of this composition in a magnetic field of 14,2 kOe. The curve $\Delta T_{ex}(T)$ has two extremes: the broad maximum covered $T_C = 295$ K and the sharp minimum at $T = 234$ K which is close to $T_N = 231$ K. The magnitudes of MCE at both the maximum and minimum are low: it reaches 0.13 K at the maximum and -0.2 K at the minimum. As is seen from the table 1, ΔT_{th} calculated by Eq. (2) upon the transition from the antiferromagnetic to the ferromagnetic state is -5.9 K. Its absolute value is much higher than at the minimum. It is obvious that the low values of MCE at both the maximum and minimum are caused by the fact that ferromagnetic interactions are present in the antiferromagnetic phase and antiferromagnetic interactions exist in the spontaneous magnetization phase.
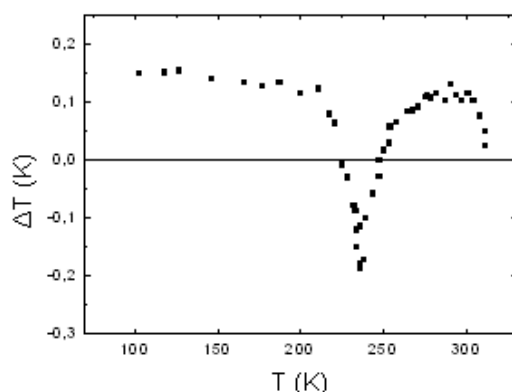

Figure 9. The temperature dependence of the magnetocaloric effect in magnetic field 14,2 kOe ofthe PrBaMn2O6 polycrystalline sample.

6. Conclusions

Using a direct method, we studied the MCE in La1–xSrxMnO3, Sm0.55Sr0.45MnO3, andPrBaMn2O6 compounds, which represent three manganite classes, namely, La1 − xAxMnO3 (A = Ca, Sr, Ba), Sm0.5 + xS0.5 − xMnO3 (0.05 ≤ x ≤ 0.10), and layered ReBaMn2O6 manganite. We measured the magnetization of these compositions and calculated the MCE related to the change in the magnetic part of entropy induced by a break in the spontaneous magnetization at the Curie temperature in the firsttwo compositions and by the transition from an AF into an F state at the Néel temperature of the last composition. The calculated value of MCE was found to be several times higher than the absolute value of MCE measured by a direct method. This difference was shown to be related to the presence of AF regions in the manganites with a predominant F order and the presence of F regions in the manganites with a predominant AF order. On the other hand, the low values of MCE in the manganites indicate the existence of a magnetically heterogeneous F−AF state in them. The presence of a colossal magnetoresistance and a giant volume magnetostriction [16, 20, 32, 33] points to that fact that this magnetically heterogeneous state is caused by a strong s–d exchange and consists of an insulating AF phase and an F phase accumulating charge carriers [18].

It is known [27] that a high value of MCE in metals, e.g., gadolinium, requires a high purity of a metal. Impurities introduced AF bonds decreasing MCE.

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