MAGNETISM
AND FERROELECTRICITY

Adiabatic Calorimetric Study of the Intense Magnetocaloric Effect and the Heat Capacity of $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$

A. V. Kartashev[a], I. N. Flerov[a, b], N. V. Volkov[a, b], and K. A. Sablina[a]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,*
Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: akartashev@iph.krasn.ru
[b] *Siberian Federal University, Svobodnyi pr. 79, Krasnoyarsk, 660079 Russia*
Received March 11, 2008

Abstract—The temperature dependences of the intense magnetocaloric effect $\Delta T_{AD}(T, H)$ and the heat capacity $C_p(T)$ of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite are directly measured using adiabatic calorimetry. The experimental dependences $\Delta T_{AD}(T)$ are in satisfactory agreement with those calculated from the data on the behavior of the magnetization. The factors responsible for the absence of an anomaly in the experimental temperature dependence of the heat capacity $C_p(T)$ in the range of the magnetic phase transition are discussed.

1. INTRODUCTION

Over the last decade, considerable interest has been expressed by researchers in materials based on the $LaMnO_3$ manganite, which have a perovskite-like structure and undergo magnetic phase transitions. This circumstance is associated in particular with the challenging prospects of the use of inherent anomalous properties of these materials, such as colossal magnetoresistance, giant bulk magnetostriction, metal—insulator transitions, and considerable magnetocaloric effect. The last property opens up possibilities for using manganites in the design of cooling devices based on solid coolants [1]. Compared to gas coolants, these materials offer a number of advantages, including the small specific volume, a higher ecological safety, and a considerable energy effectiveness [1, 2]. By ranking somewhat below other solid materials, for example, gadolinium [2] and $Gd_5(Si_xGe_{1-x})_4$ alloys [3] in a maximum caloric efficiency, solid solutions based on manganites, first, allow one to vary the phase transition temperature over a wide range of temperatures and thus provide a wider range of operating temperatures [1, 4–7] and, second, are more energetically favorable.

As a rule, solid solutions of manganites with a mixed valence of cations have been produced through the replacement of La^{3+} cations in the $LaMnO_3$ compound by Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} cations. An increase in the concentration of divalent cations leads to an increase in the temperature of the transition between the paramagnetic and ferromagnetic phases [1]. This phenomenon is especially pronounced in the $La_{1-x}Pb_xMnO_3$ system ($T_C \approx 170$ and 350 K at $x = 0.1$

and 0.3, respectively) and accompanied by an increase in the magnitude of the magnetocaloric effect [6].

The isovalent substitution of rare-earth cations for lanthanum results in a rapid decrease in the phase transition temperature, which, for example, for the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ solid solution reaches $T_C \approx 119$ K [8]. This manganite exhibits a number of specific features. First, unlike the parent rhombohedral compound $La_{0.7}Pb_{0.3}MnO_3$, this solid solution is characterized by tetragonal symmetry $P4/m$. Second, the solid solution has an inhomogeneous structure over a wide range of temperatures $T^*-T_C \approx 100$ K. Above the temperature T^*, the manganite is a homogeneous paramagnet with a polaron conductivity. In the temperature range T^*-T_C, there arise ferromagnetic clusters with a higher conductivity; in this case, the size and number of clusters increase with a decrease in the temperature. At the temperature T_C, the paramagnetic matrix transforms into the ferromagnetic state, and, subsequently, two different ferromagnetic phases coexist in the sample. It should be noted that the interaction between these phases at the interface is antiferromagnetic in character.

The influence of the two-phase state due to the coexistence of regions with the ferromagnetic and antiferromagnetic ordering in samples on the magnetocaloric effect was investigated for the $La_{1-x}Sr_xMnO_3$ solid solution system [9]. It was revealed that the directly measured temperature dependences of the change in the temperature upon application of the magnetic field under adiabatic conditions differ radically from those calculated from the magnetization.

In order to elucidate the influence of specific features of the magnetic state on the magnetothermal prop-
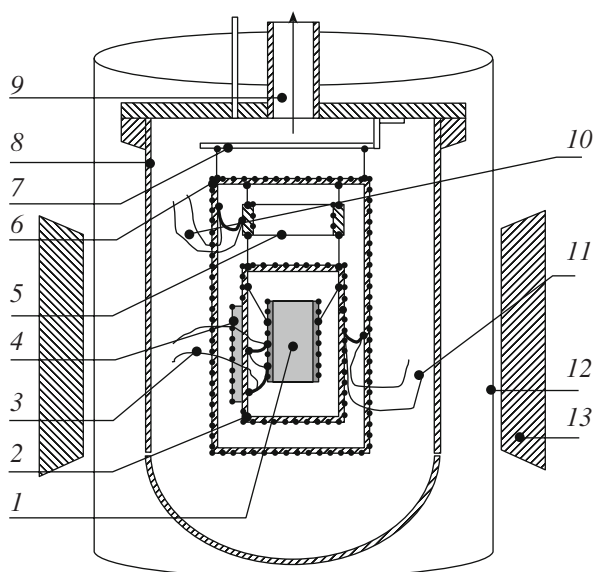
Fig. 1. Schematic drawing of the cryostat of the adiabatic calorimeter for investigation of the magnetocaloric effect.

erties of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite, in this work, the heat capacity and the magnitude of the magnetocaloric effect were investigated using adiabatic calorimetry in the temperature range 80–220 K.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

There are two types of the magnetocaloric effects, i.e., the intensive and extensive magnetocaloric effects [1]. The former effect is a change ΔT_{AD} in the temperature of a magnetic material upon application of a magnetic field under adiabatic conditions. The latter effect is associated with the change in the entropy ΔS_{MCE} in an isothermal process. Only the magnitude of the intense magnetocaloric effect ΔT_{AD} can be directly measured in experiments, whereas the change in the entropy is calculated from the temperature dependences of the heat capacity in magnetic fields. Information on both effects can also be indirectly obtained, namely, from the data on the dependence of the magnetization on the temperature and the magnetic field with the use of the known Maxwell equations [1]. In the vast majority of cases, information on the effects has been obtained with the former approach. However, the analysis of numerous experimental data has demonstrated that the results thus obtained on the quantities ΔT_{AD} and ΔS_{MCE} are not necessarily reliable. First, these data are characterized by a considerable error, which was analyzed in [1]. Second, they are unreliable in the case where the sample undergoes two phase transitions (especially with different natures, for example, magnetic and antiferromagnetic transitions) with close temperatures or contains a set of two and more magnetic phases [9]. Only in specific cases, the quantity ΔT_{AD} has been directly determined,

as, for example, in [10], by continuously recording the temperature of the sample in the course of periodic application and removal of the magnetic field but at a rather high rate of change in the temperature (≈0.5 K/min), which, undeniably, does not allow one to treat experimental conditions as equilibrium and close to adiabatic.

In our opinion, an adiabatic calorimeter is the most convenient tool for parallel investigation of the magnetocaloric effect and the heat capacity in samples. In our work, we used the design proposed earlier for the study of the electrocaloric effect in ferroelectric materials (Fig. 1) [11, 12].

Single crystals of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite were grown through spontaneous crystallization from a solution in the melt. A mixture of the PbO and PbF_2 compounds served as a solution. The crystals chosen for investigations had the form of a cube $1 \times 1 \times 1$ mm in size with lustrous faces. The $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ sample 1.35 g in weight was placed in furniture in the form of a polished aluminum foil with a cemented constantan wire as a heater. In order to provide a secure thermal contact between the sample and furniture, we used a vacuum grease.

"Sample + furniture + grease" system *1* was suspended by thin fibers with a low thermal conductivity inside first adiabatic screen *2* (Fig. 1). The inner surface of the screen was coated by silver and polished in order to minimize the heat exchange between the screen and the sample. The temperature difference between these elements was controlled using a battery of copper–constant thermocouples *3*. The thermocouple signal was amplified by a factor of 5×10^3, which made it possible to maintain the temperature drift of the sample in required limits $dT/dt \approx \pm(10^{-3}–10^{-4})$ K/min by regulating the temperature of the first screen. The temperature of the sample was measured with platinum resistance thermometer *4* located at the first adiabatic screen (Fig. 1). Check measurements showed that a variation in the quantity dT/dt in the above range was accompanied by a small error in the determination of the temperature of the sample (smaller than 0.01 K).

Second screen *5* was used to eliminate the temperature gradient across thin wires ($d \le 10^{-2}$ cm) connecting the first screen and the sample to external electronic devices located at room temperature. Finally, third screen *6* played the role of the "environment" (with a uniform temperature field) for the first and second screens situated inside it. The system of three screens was suspended from "cold" screen *7*. This screen had a secure thermal contact with chamber *8*, which was evacuated to a residual pressure of ~$10^{-5}–10^{-4}$ mmHg, and prevented direct transmission of thermal radiation through vacuum line *9* to thermally regulated elements of the calorimetric system. The temperature difference between screens *5–6* and *2–6* was controlled using copper–constantan thermocouples *10* and *11*.
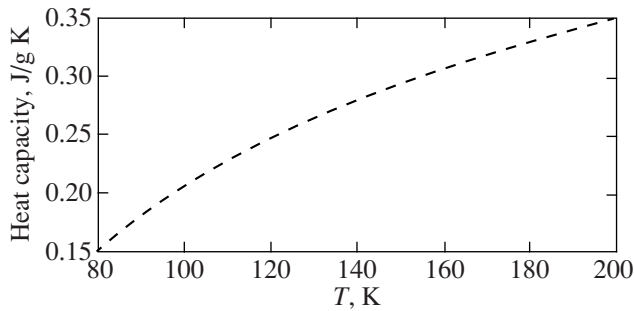
Fig. 2. Temperature dependence of the heat capacity of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ crystal.

Fig. 3. Time dependence of the temperature of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ sample in magnetic fields with strengths of (1) 0, (2) 1.1, (3) 2.1, (4) 3.2, (5) 4.1, (6) 4.8, (7) 5.4, and (8) 6.1 kOe.
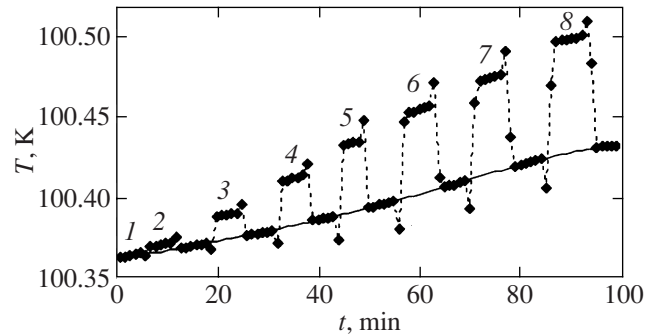
Chamber 8 with the system of thermal screens ensuring the conditions close to adiabatic was placed in Dewar vessel 12 with liquid nitrogen, which was located between poles of conventional dissipative electromagnet 13. The maximum magnetic field strength in the region of the sample was as high as 6.1 kOe.

The magnetocaloric effect was studied upon application and removal of the magnetic field according to the following procedure. At a specific temperature, the adiabatic calorimeter was adjusted so that the temperature drift was within the permissible limits for one hour and close to linear. This temperature behavior means that the conditions close to adiabatic conditions to a maximum extent are provided in the cryostat: the system is stabilized and occurs in stable dynamic equilibrium. In this state, the maximum sensitivity to a change in the temperature of the sample is at the level of the temperature drift and, in the best case, it is possible to ensure a drift $dT/dt \leq 10^{-4}$ K/min. It is this value that, to a first approximation, determines the error in the measurement. In the majority of our experiments, the error in the measurement could be no higher than 10^{-3} K and even 5×10^{-3} K. This enabled us to accelerate significantly the performance of experiments by decreasing the requirements for the temperature drift.

The heat capacity was measured in the course of discrete and continuous heating. In the former case, the calorimetric step was varied from 1.5 to 3.0 K. In the latter case, the "sample + furniture + grease" system was heated at rates $dT/dt \approx 0.15$–0.30 K/min. In order to determine the heat capacity of the sample, we experimentally measured the heat capacity of the furniture $C_{furn}(T)$. The heat capacity of the vacuum grease $C_r(T)$ was investigated in [13].

3. EXPERIMENTAL RESULTS

The measured temperature dependence of the heat capacity of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ crystal over a wide range of temperatures in the absence of the external magnetic field is plotted in Fig. 2. The dependence $C_p(T)$ represents a smooth curve without noticeable

anomalies in the temperature range of the phase transition to the ferromagnetic state. The factors responsible for this somewhat unexpected circumstance will be discussed below.

The magnetocaloric effect in the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite was studied at temperatures above and below the point T_C in magnetic fields with the strengths $H = 1.10$, 2.10, 3.15, 4.10, 4.80, 5.40, and 6.10 kOe. The results for one of the series of experiments performed in the vicinity of a temperature of 100 K, i.e., in the range of the existence of the two-phase ferromagnetic state of the sample, are presented in Fig. 3. The average rate of change in the temperature of the sample in the course of the experiment under consideration (100 min) was $dT/dt \approx 7 \times 10^{-4}$ K/min. It can be seen from Fig. 3 that a substantial magnetocaloric effect is inherent in the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite: the application (removal) of the magnetic field is attended by the reliably established increase (decrease) in the temperature. It is also evident that the effect is characterized by a high degree of reversibility: after removal of the magnetic field, the temperature of the sample returns to the expected temperature obtained by extrapolating the temperature behavior of the quantity dT/dt from the temperature range preceding the application of the field.

The dependence $T(t)$ exhibits stepwise changes ("spikes") in the temperature at the instants of application of the magnetic field due to the noise of the emf induction in the high-sensitivity amplifier of the thermocouple signal. The constancy of the quantity dT/dt under measurement conditions with and without magnetic field suggests that this spurious effect does not affect the control of the adiabatic conditions. In order to check that the true change in the temperature ΔT_{exp} does not depend on the imaginary change in the temperature due to the noise, we carried out similar experiments with the opposite direction of the magnetic field. Since the magnetocaloric effect is independent of the field direction, the result should remain the same, but the
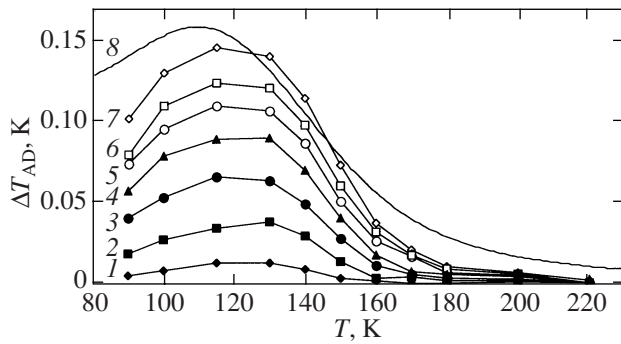
Fig. 4. Temperature dependences of the quantity ΔT_{AD} in magnetic fields with strengths of (*1*) 1.1, (*2*) 2.1, (*3*) 3.2, (*4*) 4.1, (*5*) 4.8, (*6*) 5.4, and (*7*) 6.1 kOe. Solid line *8* indicates the dependence $\Delta T_{AD}(T)$ calculated from the data on $M(T)$ at $H = 10$ kOe [8].

temperature spikes should change their polarity. The validity of this assumption was experimentally confirmed, and the magnitude of the reversible change in the temperature of the sample remained the same to within the limits of experimental error.

However, the spurious effect was responsible for the noninstantaneous (1–10 ms) application (removal) of the magnetic field, because, in this case, the temperature spike was so large that the controlling devices of the calorimeter began to operate unstably. A slow (for ~10 min) increase (decrease) in the field strength to a maximum (6.1 kOe) resulted in a deterioration of the adiabatic conditions of the experiment. The empirically chosen optimum rate of field application (removal) was $dH/dt \approx 60$ Oe/s.

The measurements of the intense magnetocaloric effect at other temperatures, including the temperatures of the paramagnetic phase, were performed in a similar manner.

4. DISCUSSION OF THE RESULTS

In Section 2, when describing the sample preparation and the technique for measuring the heat capacity and the magnetocaloric effect for the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite, we called attention to the necessity to use the furniture with the heater and the contact grease. In this respect, the heat released (absorbed) upon application (removal) of the magnetic field is spent for changing the temperature not only of the sample but also of the entire system as a whole: sample + furniture + grease. As a consequence, the quantity ΔT_{exp} smaller than the true quantity ΔT_{AD} is experimentally measured by varying the magnetic field. The above quantities are related by the expression

$$\Delta T_{AD} = \Delta T_{exp}\left(1 + \frac{C_{furn} + C_r}{C_{sample}}\right), \tag{1}$$

where C_{furn}, C_r, and C_{sample} are the heat capacities of the furniture, the grease, and the sample, respectively.

Therefore, in order to minimize the difference $\Delta T_{AD} - \Delta T_{exp}$, it is necessary to decrease the contribution of the quantity $(C_{furn} + C_r)$ to the total heat capacity measured in the experiment. The calorimetric measurements demonstrated that the heat capacity of the furniture and the grease, on the one hand, and the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ sample, on the other hand, appeared to be almost equal to each other in the temperature range 80–220 K.

Figure 4 shows the temperature dependences of the intense magnetocaloric effect ΔT_{AD} calculated with due regard for the aforementioned losses in different magnetic fields. The temperature range of maximum intense magnetocaloric effects is very smeared, in particular, due to the second-order nature of the phase transition. In the paramagnetic phase, the magnitude of the magnetocaloric effect ΔT_{AD} rapidly decreases and becomes equal to zero to within the limits of error in the determination at ≈ 220 K even in the field $H = 6.1$ kOe. In the range of this temperature, the temperature dependence of the reciprocal of the magnetic susceptibility deviates from the Curie–Weiss law and ferromagnetic clusters are formed in the paramagnetic matrix [8].

By using the data on the behavior of the magnetization of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite in magnetic fields [8] and the heat capacity measured in our work, we calculated the temperature dependence of the magnetocaloric effect ΔT_{AD} from the following relationship:

$$\Delta T_{AD} = -\frac{T}{C_p(T, H)}\int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \tag{2}$$

The calculated results presented in Fig. 4 indicate that, in the field $H = 10$ kOe, the maximum magnetocaloric effect is as high as $\Delta T_{AD} \approx 0.17$ K. It should be noted that, on the whole, the results of calculations are in qualitative agreement with the experimental data for $H = 6.1$ kOe over the entire range of temperatures under investigation. Correspondingly, the calculated magnitude of the intense magnetocaloric effect at a field strength of 30 kOe is $\Delta T_{AD} \approx 0.4$ K.

For the $La_{0.7}Pb_{0.3}MnO_3$ manganite, the application of the field $H = 20$ kOe leads to a considerably larger adiabatic change in the temperature $\Delta T_{AD} \approx 1$ K [6]. However, it should be noted that the temperature dependence $\Delta T_{AD}(T)$ in [6] appears to be very strange: the intense magnetocaloric effect remains significant (≈ 0.4 K) at temperatures considerably higher and lower than the transition temperature, i.e., far from the range of the anomalous behavior of the quantity ΔT_{AD}, which according to relationship (2) is associated with the large derivatives $(\partial M/\partial T)_H$.

As was noted above, the dependence $C_p(T)$ does not exhibit a noticeably anomaly in the form of the excess heat capacity ΔC_p governed by the phase transition to the ferromagnetic phase. The possible factors responsible for this circumstance are as follows: (1) a wide temperature range of the "smearing" of the phase transition due to the combined (heterovalent and isovalent) replacement of lanthanum cations in the complex solid solution $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ and (2) an insignificant value of the excess heat capacity ΔC_p that cannot be recorded by adiabatic calorimetry. The validity of the former assumption is confirmed, for example, by the results of investigations of the $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ solid solution system, for which it was revealed that the excess heat capacity ΔC_p decreases by a factor of five with an increase in x from 0 to 0.11 [10].

The possible value of the excess heat capacity at the point of the transition of the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite to the ferromagnetic state can be calculated using the data on the temperature and field dependences of the magnetization [8].

Since the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite at the temperature T_C undergoes the second-order phase transition, the related anomalous contribution to the Gibbs energy in the presence of the magnetic field H has the form [14]

$$\Delta\Phi = \alpha_T(T - T_C)M^2 + \beta M^4 + \ldots - MH. \qquad (3)$$

Here, M is the specific magnetization, which is the sum of the spontaneous magnetization M_s and the magnetization M_i induced by the magnetic field.

The excess heat capacity ΔC_p in the vicinity of the temperature T_C at $H = 0$ can be evaluated from the expression

$$\Delta C_p = T\left(\frac{\partial^2 \Delta\Phi}{\partial T^2}\right) = -T\alpha_T(\partial M^2/\partial T). \qquad (4)$$

The equilibrium condition $\partial\Delta\Phi/\partial M = 0$ leads to the equation of state that describes the real magnetization in the vicinity of the Curie temperature; that is,

$$2\alpha_T(T - T_C)M + 4\beta M^3 = H \qquad (5)$$

which permits one to determine the temperature dependences of the parameters $\alpha_T(T - T_C)$ and β.

Since data on the temperature dependence of the spontaneous magnetization $M_s(T)$ for the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite were not available, we calculated the quantities α_T and ΔC_p from expressions (4) and (5) with the use of the data on the magnetization $M(T)$ in a field of 50 Oe [8]. The maximum value of the excess heat capacity associated with the changes in the magnetic subsystem of the solid solution amounted to only $\approx 0.05\%$ of the specific heat capacity; i.e., it turned out to be too small to be recorded experimentally. This circumstance is not unique and was repeatedly observed, for example, in the study of the $Cr_3^{2+}[Cr^{3+}(CN)_6]_2 \cdot 12(H_2O)$ compound [15].

5. CONCLUSIONS

Thus, the influence of the replacement of lanthanum in the $La_{0.7}Pb_{0.3}MnO_3$ compound by europium (which in oxides can occur in divalent and trivalent states) on the heat capacity and the intense magnetocaloric effect was investigated by adiabatic calorimetry using the $(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO_3$ manganite as an example.

The performed investigations of the complex solid solution made it possible to draw the following conclusions.

(1) The anomaly of the heat capacity in the range of the transition to the two-phase ferromagnetic state is so small that cannot be recorded by the very sensitive calorimetric method used in the measurements.

(2) The magnitude of the intense magnetocaloric effect is substantially suppressed as compared to that in the parent compound $La_{0.7}Pb_{0.3}MnO_3$. This suggests that, most likely, europium is incorporated into the crystal lattice in the trivalent state that is nonmagnetic.

(3) The calculated and experimental values of the quantity ΔT_{AD} are in satisfactory agreement. This allows us to argue that the antiferromagnetic interaction at the interface between two ferromagnetic phases does not make a considerable contribution to the magnitude of the magnetocaloric effect.

A further elucidation of the factors responsible for the decrease in the intense magnetocaloric effect in $(La_{1-x}Eu_x)_{0.7}Pb_{0.3}MnO_3$ solid solutions will be favored by planned magnetothermal investigations of compositions with a lower europium content.

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Translated by O. Borovik-Romanova