Magnetic phase segregation and glass nature of $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ manganite

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The results of detailed investigations of magnetic properties of $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ manganites at low temperatures are presented. The performed investigations of temperature, field and frequency dependences of magnetization and susceptibility as well as the magnetization relaxation processes indicate that below $T_C = 44$ K the manganite $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ is in the magnetic phase-segregated state with ferromagnetic inclusions forming a cluster glass. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3693578]

INTRODUCTION

For many years, a magnetic state of substituted $(R_{1-x}A_x)MnO_3$ (R — rare earth, A — alkaline earth) manganites in the region of the ferromagnetic Curie temperature T_C has attracted attention of researchers due to formation of particular magnetic structures responsible for appearing the effect of negative colossal magnetoresistance (CMR).[1] It has been shown that a role of substitutions in the CMR formation is related to creating special conditions of competition between double ferromagnetic exchange among Mn^{3+}–Mn^{4+} ions, forming hole-rich ferromagnetic clusters, and antiferromagnetic superexchange Mn^{3+}–Mn^{3+}. Conditions optimal for appearance of CMR correspond to $x = 0.3$. A compound $PrMnO_3$, in contrast to antiferromagnetic compounds of this series, is a paramagnet, and an ionic radius of Pr^{3+} has the smallest among rare earths value, 0.129 nm. The substitution of it by Ca^{2+} ions is, as opposed to others R^{3+}, a substitution by an ion of larger radius. In spite of it the compound $Pr_{0.7}Ca_{0.3}MnO_3$ reveals magnetic features, typical to other manganites with optimal doping level, such as a close relationship between structural, magnetic and transport properties, phase separation (magnetic as well as electronic), presence of magnetic phase transitions.[2–4] In this work, low-temperature magnetic investigations of effect of replacing praseodymium by Bi^{3+} ions on magnetic properties of this compound were performed. The literature data on the subject are quite controversial. Available works indicate both the weakening of ferromagnetic interactions when doped with bismuth[5] and their enhancement.[6] A low-temperature magnetic state of the compound $(Pr_{0.4}Bi_{0.3})_{0.7}Ca_{0.3}MnO_3$ was investigated and it was shown that at the temperature $T < T_C = 44$ K it is a weakly magnetic paramagnetic or antiferromagnetic matrix, including ferromagnetic nanoparticles self-organizing into cluster glass.

EXPERIMENTAL PROCEDURE

The polycrystalline samples were obtained by the method of solid-state reaction in the mixture of powders Pr_2O_3, $CaCO_3$ and Mn_2O_3 taken in the required ratio. A chemical and structural homogeneity of the samples was confirmed by an X-ray analysis.

Temperature dependences of static magnetization $M(T)$ and magnetization variations in time were measured by a non-commercial SQUID-magnetometer in the temperature range 4.2–300 K in fields with the intensity 1 mT–5 T on heating in the regime of cooling a sample (before measurements) in the field (FC — field cooling) and without the field (ZFC — zero field cooling). An experimental measurement error of temperature does not exceed 1 K over the whole range.

A dynamical susceptibility $\chi'(\omega)$, $\chi''(\omega)$ was measured by a vibration magnetometer in an alternating field with the amplitude of 1 mT in the frequency range from 100 to 10 000 Hz.

RESULTS AND THEIR DISCUSSION

Temperature dependences of static magnetization

Fig. 1 demonstrates temperature dependences of an inverse susceptibility $\chi^{-1}(T)$ of the polycrystalline sample $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ in weak stationary magnetic fields 10, 30, 100 Oe (i.e., 1, 3 and 10 mT). A typical turn on the curves below 50 K can indicate appearance of a ferromagnetic component at low temperatures. In order to define the Curie temperature T_C more exactly (see Fig. 2, the bottom inset) derivatives of magnetization with respect to temperature dM/dT in the field of 1 mT (100 Oe) both at cooling in the field (FC) and without the field (ZFC) are shown which give the Curie temperature $T_C = 44$ K. Fig. 2 shows for comparison temperature dependences of magnetization measured in a weak ($H = 10$ Oe; 1 mT) and in a strong ($H = 5 \cdot 10^5$ Oe; 0.5 T) constant field after cooling the sample in the field (FC) and without it (ZFC), which indicate a significant effect of magnetic field on a value of the magnetization and its behavior. In this connection, it is interesting to perform measurements of $M(T)$ in intermediate fields (30 Oe, 100 Oe, 300 Oe, 800 Oe, 2000 Oe; 3 mT, 10 mT, 30 mT, 80 mT, 0.2 T). It appeared that temperature dependences of magnetization $M(T)$ measured in FC and ZFC-regimes are "split" at some temperature T^* lower than the Curie temperature T_C and depending on a field strength. The dependence $T^*(H)$ is shown in the upper inset of Fig. 2.

The "splitting" of ZFC and FC magnetization curves in many works devoted to manganites is interpreted as manifestation of magnetic phase separation: the magnetic state is a paramagnetic (or antiferromagnetic) matrix in which

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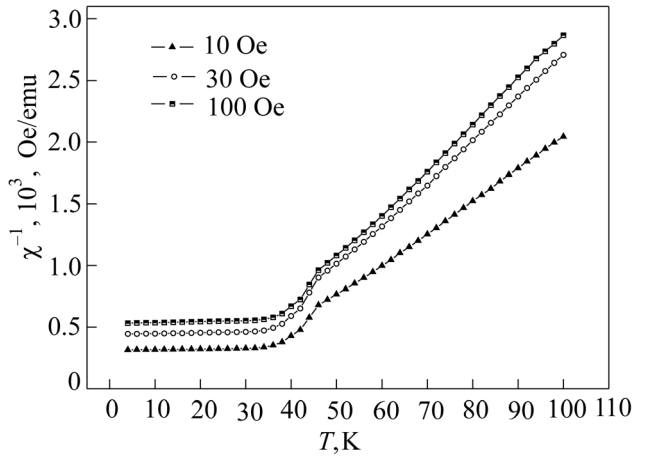

FIG. 1. Temperature dependences of inverse magnetic susceptibility in $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ for different magnetic fields.

ferromagnetic inclusions self-organize. A presence of such ferromagnetic nanoparticles in the matrix can form a superparamagnetic state (with and without a significant magneto-dipole interaction) or a spin glass (classical or cluster). Thus, the "splitting" (bifurcation) indicates the phase separation in this compound.

Furthermore, a maximum is observed in the temperature dependences of magnetization measured at ZFC. Its temperature, $T_{max}(H)$ also depends on strength of magnetic field. The dependence $T_{max}(H)$ is shown in the upper inset in Fig. 2.

A field dependence of the temperature $T^*(H)$ (splitting of FC and ZFC curves $M(T)$) is well described by the formula suggested in theoretical works[3,4] (Fig. 2, the upper inset),

$$T^*(H) = a - bH^p. \quad (1)$$

In our case, $a = 44$ K, $b = 1.05$ (if H is measured in oersteds) and $p = 0.29$. The theory[7,8] for a classical spin glass gives $p = 2/3$, and in the case of $p < 2/3$ a cluster spin glass is assumed. At the same time it is implied that a cluster spin glass is assumed if regions with a nonzero total moment are distinguished in a system with zero total moment.[9]

A behavior of the temperature T_{max} on ZFC curves of the temperature dependence of magnetization upon changing magnetic field is well described by both the formula (1), solid curve in the upper inset of Fig. 2, and the formula (2), proposed in the theoretical works[10–13] (dotted line in the upper inset in Fig. 2),

$$T_{max}(H) = T_{max}(0)/(1 + cH). \quad (2)$$

In the first case, $T_{max}(H)$ is well described for the values of adjustable parameters $a = 44$ K, $b = 1.6$, $p = 0.35$; in the second, for the parameters $T_{max}(0) = 44$ K and $c = 6.1 \cdot 10^{-3}$ Oe^{-1}.

It is necessary to bear in mind the temperature T_{max} on ZFC curve of temperature dependence of magnetization is determined by an average size of a magnetic cluster (if a cluster glass is concerned and at T_{max}), whereas the temperature T^* of divergence of FC and ZFC curves is determined by its maximal dimensions.[10] The values of the parameter p in the both cases differ slightly ($p = 0.29$ for T^*, $p = 0.35$ for T_{max}).

Dynamical susceptibility

A behavior of $T_{max}(H)$ is described by both the formula (1) for a spin glass and the formula (2), proposed in Refs. 10–13 for superparamagnetic materials with a strong magneto-dipole interaction between particles.

In order to clarify which one of the possibilities is realized in $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$, a dynamical magnetic susceptibility was investigated at different frequencies of an alternating field.

The dynamical magnetic susceptibility was investigated in the alternating magnetic field with the amplitude of 1 mT at the frequencies from 100 Hz to 10 kHz. Fig. 3 shows temperature dependences of a real part of dynamical magnetic susceptibility χ' on frequency, the inset demonstrates the frequency dependence of temperature of the maximum χ' in a semi-log scale. It is seen that the dependence is linear. Usually the considered shift of the temperature is characterized by the quantity,

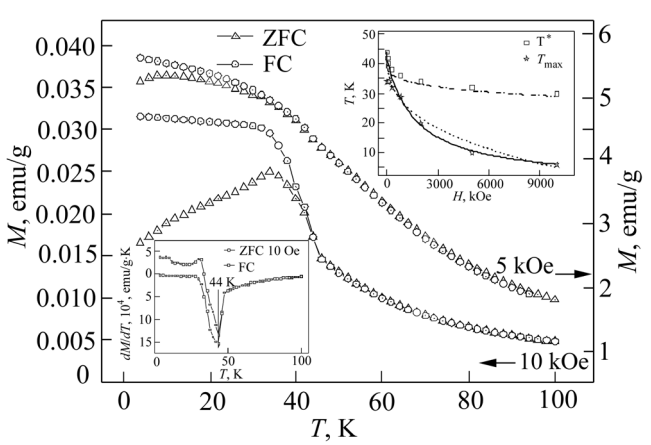

FIG. 2. Typical temperature dependences of magnetization for different cooling regimes: with (FC) and without (ZFC) the field. The upper inset: experimental field dependences of the "splitting" temperature T^* of curves $M(T)$ in the FC and ZFC regimes (light squares) and temperatures of a maximum on the magnetization curves T_{max} in the ZFC regime (stars). Solid and dotted lines are approximations in different models (see the text). The bottom inset: dependence of dM/dT on temperature in the field 1 mT.

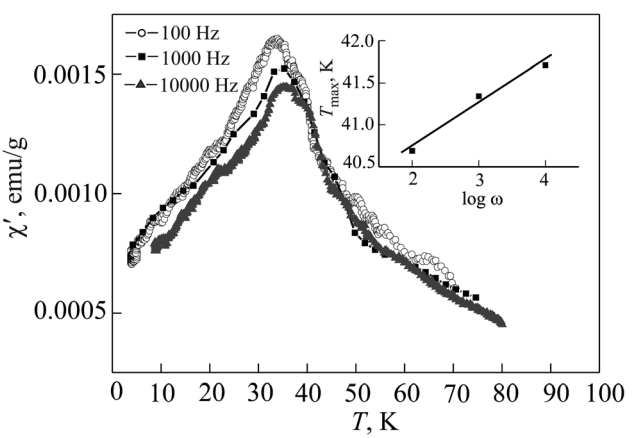

FIG. 3. Temperature dependence of a real part of dynamical magnetic susceptibility χ'; the inset shows a dependence of temperature of a maximum of χ' on frequency.

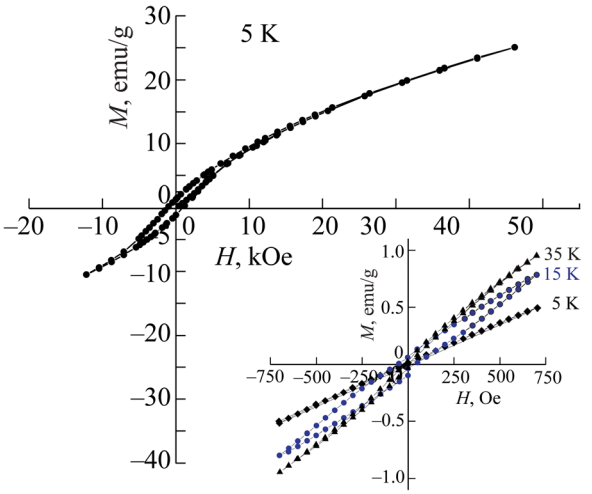

FIG. 4. Magnetization curves at $T = 5$ K. In the inset: magnetization curves at the temperatures 5, 15 and 35 K in small magnetic fields.

$$\delta T_{\max} = \frac{\partial \ln T_{\max}}{\partial \ln \omega}. \qquad (3)$$

In our case, $\delta T_{\max} = 0.015$.

Our result for $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ corresponds to a criterion for a glass, $\delta T_\omega < 0.02$, that does not contradict estimations made for glass systems.[16]

Magnetization curves

The dependences of magnetization $M(H)$ on the strength of external magnetic field H up to 5 T demonstrates an absence of saturation of the curve $M = f(H)$ at 5 K (Fig. 4). In general, it is typical to both a superparamagnet and spin glass. A presence of magnetic hysteresis and noticeable coercive force allow to conclude that it is rather a glass. All curves in Fig. 4, the main as well as in the inset (small field), were obtained upon cooling without a magnetic field (ZFC).

Relaxation of magnetization

Some information on nature of a phase-segregated magnetic system can be obtained from an investigation of the magnetization relaxation after turning off the magnetizing field. In Fig. 5, an initial part of the fast magnetization relaxation in $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ is presented. The experiment was performed in the following way. The sample was cooled down to 4.2 K at ZFC. Then the magnetic field ($H = 0.3$ T) was applied, and after keeping in the field during 20–30 min the field was removed. In so doing, the fast relaxation was observed: during 3–5 s the magnetization decreased by almost 50%, and then it decreased very slowly. This experiment was performed by a vibration magnetometer the sensitivity of which was not enough to investigate a region of slow relaxation. However, because in this setup a magnetic field was created in a solenoid of a copper wire, a delay of magnetic flux withdrawal typical to superconducting solenoids was excluded.

The slow relaxation was studied on a setup with high sensitivity, SQUID magnetometer. In the inset in Fig. 5 the slow relaxation of magnetization after removing a magnetic field ($T = 4.2$ K) is demonstrated. Using the curves of the magnetic relaxation, in Fig. 6 time dependences of the characteristic quantity W are plotted in a log scale. This quantity according to Ref. 17 was determined as

$$\log W = \frac{\partial}{\partial t}\left(-\log\frac{M(t)}{M(0)}\right); \quad W = t^{-n}. \qquad (4)$$

Here, t is the time, $M(0)$ and $M(t)$ are the magnetization at initial time and the magnetization at given time, respectively. In determining the parameter n we took into account only linear regions in the range of long times characterizing a steady state of magnetization relaxation. Fig. 6 shows time dependences $\lg W(t)$ as a function of $\lg(t)$ in the temperature range from 5 to 60 K. Using them the exponent n was found for various temperatures (bottom inset in Fig. 6).

An increase of the exponent n on approaching T_C from low temperatures indicates clusterness of the spin glass under study and is related to increasing interaction between clusters (see for instance Ref. 13). The vertical dotted line in the lower inset in Fig. 6 corresponds to the temperature $T_C = 44$ K, i.e., this temperature separates the phase-

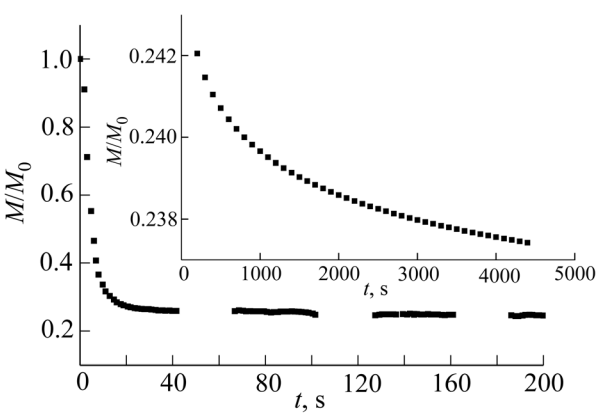

FIG. 5. An initial region of the fast relaxation of ZFC magnetization after removing the magnetic field $H = 3$ kOe, $T = 4.2$ K. In the inset: an example of slow magnetization relaxation at 5 K after removing a magnetic field.

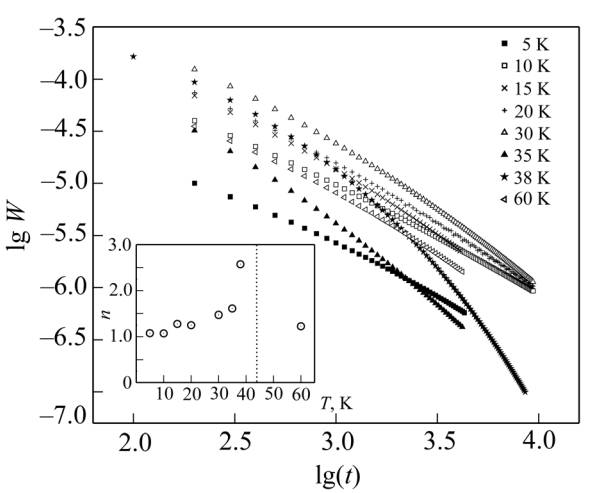

FIG. 6. Dependences of magnetization relaxation rate W on time t for different temperatures in a log-log scale. In the inset: temperature dependence of the exponent n in the equation $W \sim t^{-n}$ determining the rate of steady-state relaxation of magnetization.

segregated state with a ferromagnetic component and paramagnetic one.

CONCLUSION

The results of all investigations performed, the temperature dependence of magnetization at field cooling and zero-field cooling in the wide magnetic field range, the temperature dependence of dynamical magnetization at various frequencies of alternating field, the dependence of magnetization on external magnetic field at low temperatures, the magnetization relaxation after removing the magnetizing field indicate that below $T_C = 44\,\mathrm{K}$ a manganite $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ is in a magnetic phase-segregated state with ferromagnetic inclusions forming a cluster spin glass.

The presence of bifurcation of the curves $M(T)$ gives evidence of the phase segregation of a magnetic subsystem in $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$.

The field dependences of temperatures of the maximum $T_{\max}$ and "splitting" T^* are well described by expressions for a cluster glass.

The dependence of the shift of $T_{\max}$ on frequency indicates the existence of a spin glass in $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$.

Doping compounds $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ by bismuth leads to suppression of ferromagnetism and to a shift of the Curie temperature towards lower temperatures.

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[1]A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1977).
[2]I. G. Deac, J. F. Mitchell, and P. Shriffer, Phys. Rev. B **63**, 172408 (2001).
[3]L. M. Fisher, A. V. Kalinov, I. F. Voloshin, N. A. Babushkina, K. I. Kugel, and D. I. Khomskii, Phys. Rev. B **68**, 174403 (2003).
[4]S. Mercone, V. Hardy, C. Martin, C. Simon, D. Saurel, and A. Brulet, Phys. Rev. B **68**, 094422 (2003).
[5]I. Kammoun, W. Cheikhrouhou-Koubaa, W. Boujelben, and A. Cheikhrouhou, J. Alloys Compd. **452**, 195 (2008); I. Kammoun, W. Cheikhrouhou-Koubaa, W. Boujelben, and A. Cheikhrouhou, J. Mater. Sci. **43**, 960 (2008).
[6]N. Kumar, J. Alloys Compd. **504**(2), L39 (2010).
[7]J. R. L. de Almaida and D. J. Thoules, J. Phys. A: Math. Gen. **11**, 983 (1978).
[8]D. S. Fisher and D. A. Huss, Phys. Rev. B **38**, 373 (1988).
[9]B. Sherrington and S. Kirckpatrick, Phys. Rev. Lett. **35**, 1792 (1975).
[10]P. Allia, F. Celegato, M. Coisson, A. Da Re, F. Ronconi, F. Spizzo, P. Tiberto, and F. Vinai, J. Magn. Magn. Mater. **290–291**, 580 (2005).
[11]O. Margeat, M. Tran, M. Spasova, and M. Farle, Phys. Rev. B **75**, 134410 (2007).
[12]P. Alia, M. Coisson, P. Tiberto, F. Vinai, M. Knobel, M. A. Novak, and W. C. Nunes, Phys. Rev. B **64**, 144420 (2001).
[13]J. Du, B. Zhang, R. K. Zheng, and X. X. Zhang, Phys. Rev. B **75**, 014415 (2007).
[14]C. P. Bean and J. D. Livingtone, J. Appl. Phys. **10**, S120 (1959).
[15]K. Binder and A. P. Joung, Rev. Mod. Phys. **58**, 801 (1986).
[16]S. Sullow, G. J. Nienwenhuys, A. A. Menovsky, J. A. Mydosh, S. A. Mentink, T. E. Mason, and W. J. L. Buyers, Phys. Rev. Lett. **78**, 354 (1997).
[17]F. Rivadulla, M. Lopez-Quintela, and J. Rivas, Phys. Rev. Lett. **93**, 167206 (2004).

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