Low-temperature relaxation of magnetization in manganite $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$

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Low-temperature relaxation of magnetization in $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ ceramics was measured after cooling in a magnetic field and aging at temperatures from 5 K to 38 K near the transition temperature to the magnetically ordered state. It was found that the relaxation process has a thermoactivation character at the first stage and is described in terms of the Arrhenius equation. Its activation energy $Q \approx 1.1$ meV is comparable with the antiferromagnetic interaction energy in this compound. The temperature–time dependence of the relaxation rate at the second stage is described by a power law. The relaxation slows down as the temperature approaches the critical value, which may be associated with the formation of a cluster structure in the studied compound under these conditions. *Published by AIP Publishing.* https://doi.org/10.1063/1.5052685

1. Introduction

The unique properties of manganites result from interdependent phase transitions in the crystal, spin, and charge subsystems of these complex compounds.[1] Dynamic properties of such substances are described by a set of relaxation times. Their manifestation in the measurements of magnetization and dynamic susceptibility is associated with magnetic frustrations caused by anisotropy of interactions between manganese ions of various valence. An informative method for studying the dynamics of processes occurring in a solid state at low temperatures is the thermoactivation analysis method, which was successfully developed for the study of dislocation mobility,[2,3] as well as magnetic relaxation in the mixed state of superconductors,[4–6] which has a number of features common with magnetic state of magnets in the vicinity of the phase transition induced by a magnetic field.[7] The description of the magnetic relaxation in manganites with large negative magnetoresistance, in terms of thermoactivation analysis, is of interest. It is known that the ground state of solid solutions of manganites with the perovskite structure $RMnO_3$ can be fundamentally changed by replacing the rare-earth ion R^{3+} with alkaline-earth metal ions A^{2+}. Moreover, as shown by numerous experiments, the concentration x of substituted atoms, which corresponds to the amount of manganese ions Mn^{4+}, plays a decisive role in the formation of the magnetic and charge states of the $R_{1−x}A_xMnO_3$ compounds. The exchange interaction between the aliovalent manganese ions, which competes with the antiferromagnetic superexchange, leads to a change in the magnetotransport properties and the manifestation of the extremely large value of negative magnetoresistance in the vicinity of the metal–dielectric transition.[8] The deformation component associated with the difference between the ionic radii of initial substance and dopants,[9,10] which contributes to the formation of an inhomogeneous state, plays an essential role in this process. The optimally doped compounds of praseodymium manganites and their substitutional compounds are currently the most promising among them.

The composition and physical properties of $Pr_{0.7}Ca_{0.3}MnO_3$ attract special attention,[11,12] including the doping effect.[13–16] $R_{1−x}Ca_xMnO_3$ manganites are dielectrics in the zero field at any calcium concentration.[17–26] Further, a small difference in the energies of the dielectric and metallic states can be expected for concentrations in the vicinity of $x \simeq 0.3$.[27] Owing to numerous studies of neutrons, spectroscopic, magnetic, and other analyses, it was established that the magnetic state of such compounds is inhomogeneous in relatively weak fields up to 500 Oe, and can be changed both in external fields and by the replacement of ions. However, its nature remains unclear — ferromagnetic clusters, the spin-glass component in the canted antiferromagnetic phase, nonmetallic ferromagnetic inclusions in the charge-ordered antiferromagnetic phase, as well as interpenetrating antiferromagnetic and ferromagnetic regions are discussed in the literature. Magnetocaloric measurements revealed manifestations of the behavior typical for spin glasses.[13] Relaxation studies also contribute to clarification of the nature of the ground state of such compounds.[28]

The base manganite $Pr_{0.7}Ca_{0.3}MnO_3$ was doped in the present work with bismuth Bi^{3+} (ionic radius $r_{Bi} = 0.96$ nm).[29] The magnetic relaxation of the ceramics of the obtained compound $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ was studied in the low-temperature ordering region.

2. Experimental procedure

Ceramic samples were prepared by solid-phase diffusion. X-ray and chemical analyses results confirmed the chemical and structural single-phase nature of the obtained samples. Measurements of the time dependencies of magnetization were carried out in a SQUID magnetometer of the original design, using the technique described earlier in Ref. 15, at temperatures in the range of 5–40 K after cooling in a magnetic field of 100 Oe. The waiting time prior to the measurement of magnetization relaxation was 200 s.
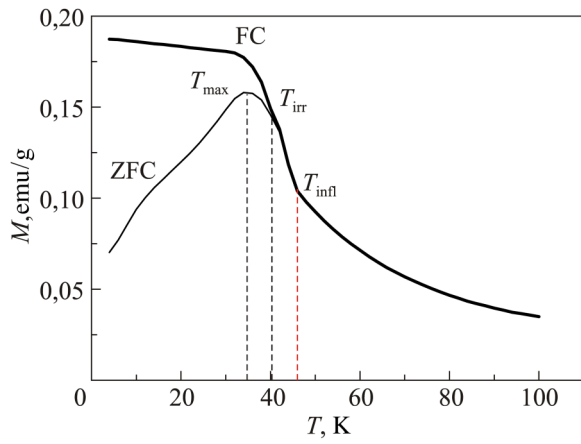
Fig. 1. Dependencies of the magnetization on the temperature of the compound $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$, measured in a 100 Oe magnetic field after zero field cooling (ZFC) and 100 Oe field cooling (FC). Ordering temperature T_{infl}, irreversibility temperature T_{irr}, and ZFC magnetization maximum temperature T_{max} are shown.

3. Measurement results and discussion

The behavior of the studied compound $Pr_{0.4}Bi_{0.3}Ca_{0.3}$ MnO_3 in the vicinity of the temperature of transition to a low-temperature ordered phase in a relatively weak magnetic field (100 Oe) is typical of the behavior of anisotropic magnetic systems. In particular, a temperature magnetization hysteresis below the ordering temperature is observed. As seen in Fig. 1, the temperature dependencies of the magnetization diverge in the field cooling (FC) mode and in the zero field cooling (ZFC) mode, which indicates the formation of an inhomogeneous cluster[30–33] or spin-glass[34–36] magnetic states.

The ordering temperature, which was determined by the standard method at the inflection point on the common part of the temperature dependence of the ZFC and FC magnetization, was $T_{infl} = 46$ K. The irreversibility temperature $T_{irr} = 40.5$ K differs insignificantly from the maximum magnetization temperature T_{max}, which, according to Refs. 35, 37, confirms a predominantly uniform distribution of magnetic inhomogeneities.

Dependencies of the change in magnetization with time $\frac{M(t)}{M_0}$, which were measured at various temperatures below the temperature of transition to the ordered phase, and the corresponding relaxation dependencies $R(t) = \frac{M(t)-M_0}{M_0}$ [Fig. 2(b)],
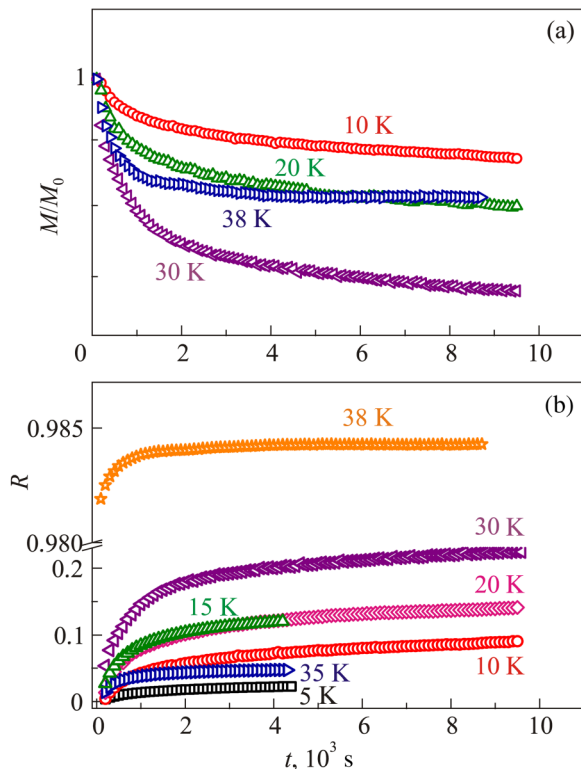

Fig. 2. Characteristic time dependencies of the reduced magnetization $\frac{M(t)}{M_0}$ (a) and its relaxation $R(t) = \frac{M(t)-M_0}{M_0}$ (b) for temperatures T, K: 5 (□), 10 (○), 15 (△), 20 (◇), 30 (◁), 35 (▷), 38 (☆), obtained after 100 Oe magnetic field cooling.
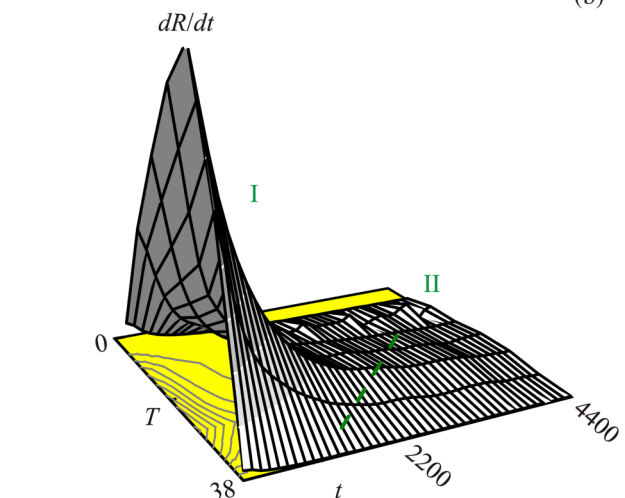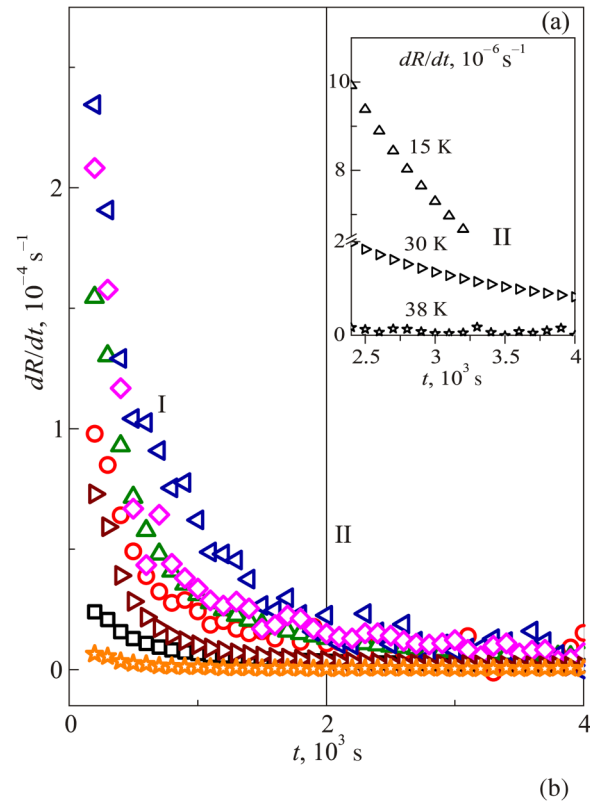

Fig. 3. Dependence of the magnetization relaxation rate on time at temperatures T, K: 5 (□), 10 (○), 15 (△), 20 (◇), 30 (◁), 35 (▷), 38 (☆), The inset illustrates a decrease in the relaxation rate with an increase in temperature at stage II (a); change in the relaxation rate with time and temperature (b).
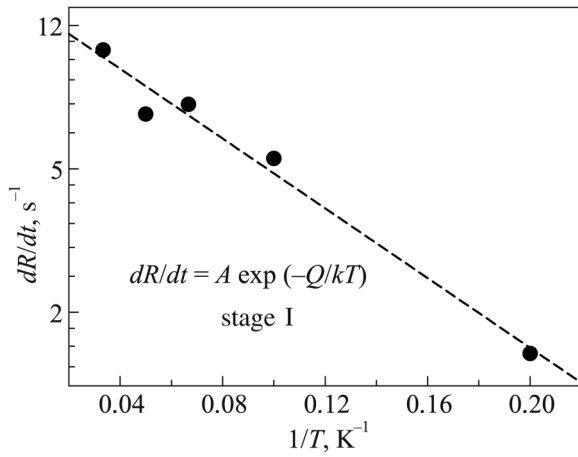
Fig. 4. Dependence of the magnetization relaxation rate on the reciprocal temperature in semilogarithmic coordinates; the slope corresponds to the activation energy value $Q \simeq 1.1$ meV.

where M_0 is the magnetization value at the beginning of measurement, are presented in Fig. 2(a). All measurements were carried out after 100 Oe field cooling.

Dependencies of the relaxation rate on time $\frac{\partial R}{\partial t} = f(t)$ for various temperatures obtained according to the data presented in Fig. 2(b) are demonstrated in Fig. 3. Regions of rapid relaxation (stage I) and slow relaxation (stage II) are visible in this Figure. The inset of Fig. 3 demonstrates, on an enlarged scale, that the relaxation rate decreases with an increase in temperature at stage II, in contrast with that at the rapid relaxation stage.

At the first stage, the temperature dependence of the magnetization relaxation rate $\frac{\partial R}{\partial t}$ for a fixed time is well described (Fig. 4) by the Arrhenius equation:

$$\frac{\partial R(t)}{\partial t}(T) = A\exp\left[-\frac{Q}{kT}\right], \qquad (1)$$

where Q is the process activation energy, and the factor A depends on the frequency $\omega = \frac{1}{t}$ and, possibly, on the temperature. This indicates the thermoactivation nature of the relaxation process at this stage. A general idea of the
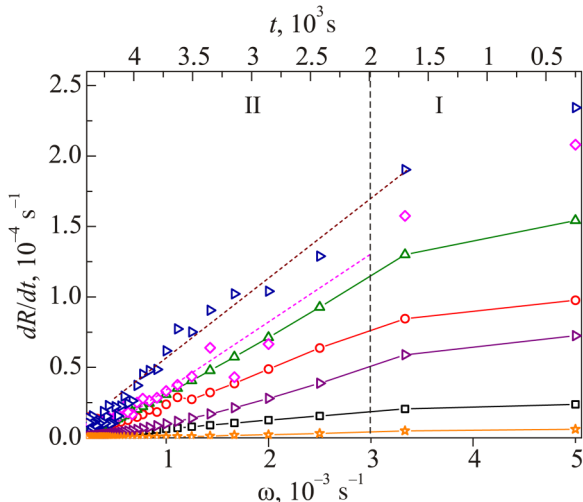
temperature–time dependence of the relaxation rate is given by the 3D diagram shown in Fig. 3(b).

The activation energy for magnetization relaxation was determined by the slope of the line in Fig. 4, and given by $Q \approx 1.1$ meV. This value is an order of magnitude smaller than the activation energy of atomic displacements, and is close to the value of the energy of antiferromagnetic interaction between manganese ions Mn^{3+} ($J \approx 1$–1.5 meV) in such compounds.[11]

Taking into account the possible temperature dependence of the factor A in (1), we obtained experimental data on the change in the relaxation rate at stage I with time, for various temperatures (Fig. 5). These data allow us to estimate the contribution of A to the total activation energy. As shown in the Figure, this contribution is considerably lower than the exponential contribution, and may be neglected in our case.

The temperature dependence of the relaxation rate apparently considerably changes at the transition from the first stage to the second stage; this is well described by a power law dependence

$$\frac{\partial R(t, T)}{\partial t} = A't^{-n}, \qquad (2)$$

where A' is a temperature-dependent factor.[28] According to our experimental data, the exponent n also depends on temperature — $n(T)$ increases linearly as the transition temperature is approached (Fig. 6).

Processing of the present experimental data and that from the literature[38] showed that the temperature dependence A' in the range of 5–38 K is well described as $A' \simeq \exp(-2.7 + 0.009T)$, and n — as $\exp(7.46 - 0.002T)$; T is the dimensionless temperature relative to one degree, which retains its numerical value.

For a fixed time $t = t^*$, we obtain:

$$\ln\left[\frac{\partial R}{\partial t}\right] \simeq -2.7 + 0.09T - (0.9 + 0.002T) \times \ln t^*. \qquad (3)$$

Then, at $t^* = 4000$ s — the time at which the relaxation process is almost completely stabilized (inset in Fig. 7):

$$\ln\left[\frac{\partial R}{\partial t}\right] \simeq -10.16 - 0.0076T. \qquad (4)$$

Fig. 5. Dependence of the magnetization relaxation rate on frequency at temperatures T, K: 5 (□), 10 (○), 15 (△), 20 (◇), 30 (◁), 35 (▷), 38 (☆) at the stage II.
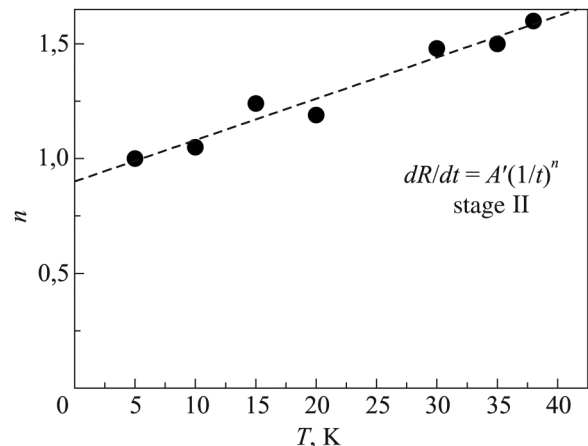

Fig. 6. The experimentally determined temperature dependence of the exponent n in (2).
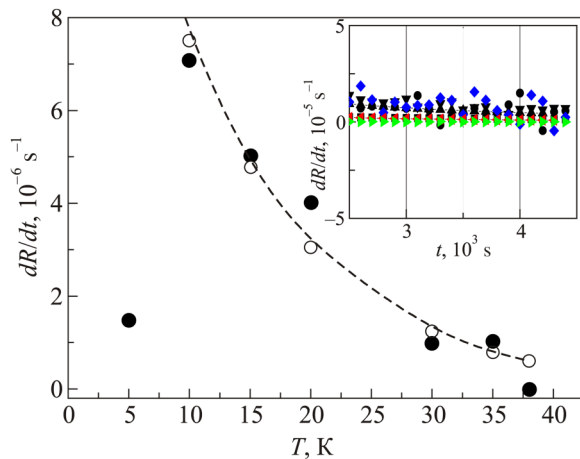
Fig. 7. The temperature dependence of the magnetization relaxation rate at stage II (●), which was determined from the experimental data, in comparison with the dependence (○) following from the theory.[38] The inset shows the enlarged section of Fig. 3(a) at $t > t^*$.

The dependence (4) obtained from the experimental data agrees well with the theory from[38] (Fig. 7).

Thus, the obtained results indicate a thermoactivation mechanism of the dynamic process in the magnetic subsystem at an early relaxation stage. The power law dependence of the relaxation rate on time observed during the steady-state relaxation phase of the $Pr_{0.4}Bi_{0.3}Ca_{0.3}MnO_3$ compound is associated with the formation of an inhomogeneous magnetic state with spin-glass dynamics observed in manganites in the low-temperature ordering region.[39] It should be noted that staging of this type is generally typical for relaxation processes in glass systems.[40]

The present work was initiated by Viktor Valentinovich Yeremenko.

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[1] A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1999).
[2] V. D. Natsik, Fiz. Nizk. Temp. **5**, 400 (1979) [Sov. J. Low Temp. Phys. 5, 191 (1979)].
[3] V. Natsik and H. Kaufmann, Phys. Status Solidi A **65**, 571 (1981).
[4] Y. Yeshurun, A. Malozemoff, and A. Shaulov, Rev. Mod. Phys. **68**, 911 (1996).
[5] V. A. Sirenko, Fiz. Nizk. Temp. **10**, 207 (1984) [Sov. J. Low Temp. Phys. **10**, 108 (1979)].
[6] V. Yu. Monarkha, V. P. Timofeev, A. A. Shablo, Fiz. Nizk. Temp. **38**, 39 (2012) [Low Temp. Phys. **38**, 31 (2012)].
[7] V. V. Yeremenko and V. A. Sirenko, *Magnetic and Magnetoelastic Properties of Antiferromagnets and Superconductors* (Cambridge Scientific Publishers, 2007).
[8] I. Troyanchuk, D. Karpinsky, M. Bushinsky, V. Sirenko, V. Sikolenko, and A. Franz, Fiz. Nizk. Temp. **43**, 1219 (2017) [Low Temp. Phys. **43**, 982 (2017)].
[9] I. O. Troyanchuk, N. V. Samsonenko, T. K. Solovykh, V. A. Sirenko, G. Shimchak, and A. Nabyalek, Fiz. Nizk. Temp. **23**, 1074 (1997) [Low Temp. Phys. **23**, 807 (1997)].
[10] E. Fertman, A. Beznosov, V. Desnenko, L. Pal-Val, P. Pal-Val, and D. Khalyavin, J. Magn. Magn. Mater. **308**, 278 (2007).
[11] R. Ewings, T. Perring, O. Sikora, D. Abernathy, Y. Tomioka, and Y. Tokura, Phys. Rev. B **94**, 014405 (2016).
[12] H. Gencer, T. Izgi, N. Bayri, M. Pektas, V. S. Kolat, and S. Atalay, J. Supercond. Novel Magn. **29**, 2443 (2018).
[13] M. Roy, J. Mitchell, A. Ramirez, and P. Schiffer, Phys. Rev. B **62**, 13876 (2000).
[14] M. Roy, J. Mitchell, A. Ramirez, and P. Schiffer, Philos. Mag. B **81**, 417 (2001).
[15] V. A. Desnenko, A. I. Rykova, V. A. Sirenko, A. V. Fedorchenko, A. S. Chernyi, E. N. Khatsko, and A. V. Yeremenko, Fiz. Nizk. Temp. **38**, 261 (2012) [Low Temp. Phys. **38**, 206 (2012)].
[16] R.-W. Li, A. A. Belik, Z.-H. Wang, and B.-G. Shen, J. Phys. Condens. Matter **21**, 076002 (2009).
[17] E. Pollert, S. Krupicka, and E. Kuzmicova, J. Phys. Chem. Solids **43**, 1137 (1982).
[18] Z. Jirak, S. Krupicka, V. Nekvasil, E. Pollert, G. Villeneuve, and F. Zounova, J. Magn. Magn. Mater. **15–18**, 519 (1980).
[19] Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha, and S. Vratislav, J. Magn. Magn. Mater. **53**, 153 (1985).
[20] Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, R 1689 (1996).
[21] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, J. Phys. Soc. Jpn. **65**, 1043 (1996).
[22] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **52**, R 13145 (1995).
[23] Y. Moritomo, H. Kuwahara, Y. Tomioka, and Y. Tokura, Phys. Rev. B **55**, 7549 (1997).
[24] D. Cox, P. Radaelli, M. Marezio, and S.-W. Cheong, Phys. Rev. B **57**, 4257 (1997).
[25] K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Phys. Rev. **78**, 4257 (1997).
[26] V. Smolyaninova, A. Biswas, X. Zhang, K. Kim, B. G. Kim, S. W. Cheong, and R. Greene, Phys. Rev. B **62**, 6093 (2000).
[27] T. Hotta and E. Dagotto, Phys. Rev. B **61**, 11879 (2000).
[28] F. Rivadulla, M. López-Quintela, and J. Rivas, Phys. Rev. Lett. **93**, 167206 (2004).
[29] R. Shannon and C. Prewitt, Acta Crystallogr. A **32**, 785 (1976).
[30] G. Williams, in *Magnetic Susceptibility of Superconductors and Other Spin Systems* (Plenum, New York, London, 1991).
[31] J. Dormann, R. Chrkaoui, L. Spinu, M. Noguès, F. Lucari, F. D'Orazio, D. Fiorani, A. García, E. Tronc, and J. P. Jolivet, J. Magn. Magn. Mater. **187**, L139 (1985).
[32] H. Mamiya, I. Nakatani, and T. Furubayashi, Phys. Rev. Lett. **80**, 177 (1998).
[33] J. A. D. Toro, M. A. L. de la Torre, J. M. Riveiro, R. S. Puche, A. Gomez-Herrero, and J. C. Otero-Diaz, Phys. Rev. B **60**, 12918 (1999).
[34] J. A. Midosh, *Spin Glasses: An Experimental Introduction* (Taylor Francis, London, 1993).
[35] S. Chikuzami, *Physics of Ferromagnetism*, Clarendon, Oxford (1997).
[36] G. Williams, in *Magnetic Susceptibility of Superconductors and Other Spin Systems* (Plenum Press, New York, London, 1991).
[37] L. Nagamine, B. Mevel, B. Dienty, B. Rodmacq, J. R. Regnard, C. Revenant-Brizard, and I. Manzini, J. Magn. Magn. Mater. **195**, 437 (1999).
[38] M. Ulrich, J. García-Otero, J. Rivas, and A. Bunde, Phys. Rev. B **67**, 24416 (2003).
[39] V. Yeremenko, V. Sirenko, A. Baran, E. Čižmár, and A. Feher, J. Phys. Condens. Matter **30**, 205801 (2018).
[40] V. D. Natsik, E. N. Vatazhuk, P. P. Pal-Val, L. N. Pal-Val, and V. A. Moskalenko, Fiz. Nizk. Temp. **39**, 1381 (2013) [Low Temp. Phys. **39**, 1078 (2013)].

Translated by CWG