Time-Dependent Phenomena in a Short-Range Ising Spin-Glass, $Fe_{0.5}Mn_{0.5}TiO_3$

A. Ito, H. Aruga, and E. Torikai
Department of Physics, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan

and

M. Kikuchi, Y. Syono, and H. Takei
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan
(Received 25 April 1986)

Magnetization measurements have been made on an insulating random mixture, $Fe_{0.5}Mn_{0.5}TiO_3$. An Ising spin-glass behavior has been observed below $T_g = 21.1$ K. It is shown that the time-dependent phenomena are well characterized by an algebraic function with the exponent described by an exponential function of temperature. The results are compared with the computer-simulation results obtained by Ogielski. In addition, we suggest the existence of a thermodynamic equilibrium state in magnetic fields.

PACS numbers: 75.40.Dy, 75.25.+z, 75.50.Ee

Recent progress of theoretical and experimental studies on spin-glasses is noticeable, and much understanding about them has been obtained. However, some fundamental problems are still controversial: A phase transition and thermodymamic equilibrium in spin-glass systems are questioned.

In order to understand better the nature of spin-glasses, distinguishing features of spin-glasses such as the irreversible magnetization and the time-dependent phenomena should be investigated in more detail. The temperature-dependent behavior has been studied in many spin-glass systems. Some investigators have reported a logarithmic time dependence,[1] and others an algebraic dependence.[2,3] Recently, on the other hand, Chamberlin, Mozurkewich, and Orbach fitted the time decay of the thermoremanent magnetization M_{TRM} measured for 2.6% Ag:Mn + 0.46% Sb with a stretched exponential.[4] Ferré *et al.* have also shown that the data of $Eu_{0.4}Sr_{0.6}S$ taken by Ferré, Rajchenbach, and Maletta[2] can be fitted better with a stretched exponential[5] than with a power law used by Ferré, Rajchenbach, and Maletta,[2] after reanalyzing their data in more detail. Chamberlin, Mozurkewich, and Orbach have emphasized that a stretched exponential characterizes the time decay of M_{TRM}. However, an algebraic dependence suggested on the basis of the Sherrington-Kirkpatrick mean-field model seems to be still attractive.[6] Recently, moreover, Ogielski investigated the dynamic behavior of short-range Ising spin-glasses by using a specially designed fast computer, and he suggested an algebraic decay for correlation functions in the spin-glass phase.[7] Therefore, the behavior of Ising systems should be closely checked. Here, we report experimental results on a newly found short-range Ising spin-glass, $Fe_{0.5}Mn_{0.5}TiO_3$.

Both $FeTiO_3$ ($T_N = 58.0$ K) and $MnTiO_3$ ($T_N = 63.6$ K) are antiferromagnets having easy-axis anisotropy along the hexagonal *c* axis. Nevertheless, we expected that a spin-glass state appears at certain concentrations of a random mixture $Fe_xMn_{1-x}TiO_3$, which is based on the fact that spins within a *c* layer are coupled ferromagnetically in $FeTiO_3$, but antiferromagnetically in $MnTiO_3$. The interlayer antiferromagnetic coupling J' is much weaker than the intralayer coupling J: $J'/J \sim -0.2$ in $FeTiO_3$[8] and $J'/J \sim 0.04$ in $MnTiO_3$.[9] Therefore, the competition between the ferromagnetic and antiferromagnetic interaction within a *c* layer is considered to be predominant. We grew a single crystal of $Fe_{0.5}Mn_{0.5}TiO_3$ by the floating-zone method in a controlled oxygen partial pressure.

The magnetization M was measured with magnetic fields H between 2 Oe and 12.8 kOe by use of a SQUID magnetometer. The zero-field-cooled (ZFC) magnetization M^{ZFC} was measured by heating after zero-field cooling to 4.5 K. On the other hand, the field-cooled (FC) magnetization M^{FC} was measured by applying a measuring field H at high temperatures and then cooling. Figure 1 shows ZFC and FC susceptibility ($\chi \equiv M/H$) measured with various values of H parallel to the hexagonal *c* axis. The ZFC susceptibility $\chi_{\parallel}^{ZFC}$ measured with $H = 2$ Oe has a sharp cusp at 21.1 K, and the corresponding FC susceptibility $\chi_{\parallel}^{FC}$ is nearly temperature independent below 21.1 K. $\chi_{\parallel}$ is irreversible below 21.5 K, slightly above the cusp temperature. The *c*-plane susceptibility was also measured. Details will be published elsewhere, but we point out here that $Fe_{0.5}Mn_{0.5}TiO_3$ is strongly anisotropic and behaves as an Ising spin-glass with $T_g = 21.1$ K, like YEr.[10] Since $\chi_{\parallel}$ exhibits a typical spin-glass character, we direct our attention to the behavior of $M_{\parallel}$ or $\chi_{\parallel}$ in the present work. For simplicity, we omit the subscript $\parallel$ henceforth. The cusp of χ^{ZFC} is drastically broadened with increasing H, which is similar to other spin-glass systems.[11] The tempera-

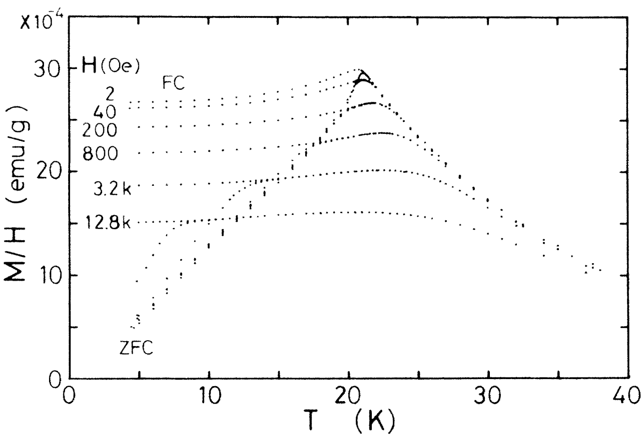

FIG. 1. Temperature dependence of field-cooled (FC) and zero-field–cooled (ZFC) magnetizations divided by measuring fields (M/H) for $Fe_{0.5}Mn_{0.5}TiO_3$. Magnetic fields are applied parallel to the c axis.

ture below which the irreversibility appears shifts toward lower temperatures with H; we define this temperature as $T_g(H)$.

We examined the time-dependent phenomena existing below $T_g(H)$ by observing the decay of M_{TRM} and the growth of M^{ZFC}. The former was measured as follows: (1) A magnetic field H of 80 Oe or 3200 Oe was applied to the sample at ~ 40 K well above T_g, (2) the sample was field cooled to a temperature below $T_g(H)$, (3) H was removed and M_{TRM} was recorded as a function of time t. The waiting time at $T < T_g$ before H was removed was not carefully controlled but it scattered by ± 30 s around 200 s. On the other hand, the growth of M^{ZFC}, i.e., the growth of the isothermal remanent magnetization M_{IRM}, was measured as follows: (1) The sample was zero-field cooled from ~ 40 K to a temperature below $T_g(H)$, (2) H of 80 Oe or 3200 Oe was applied to the sample and M^{ZFC} was recorded as a function of t. We put $t=0$ when H was removed (M_{TRM}) or when H reached the measuring field (M_{IRM}). However, the measurements were started at $t=300$ s, because a certain time (< 300 s) was needed in order to bring our superconducting magnet to the persistent mode. Below, we show the results obtained by use of $H=3200$ Oe, but similar features are also derived from the results for $H=80$ Oe.

In Fig. 2(a), log-log plots of M_{TRM} vs t are shown at four temperatures. The data points at each temperature lie on a straight line. This indicates that the decay of M_{TRM} proceeds with a power law

$$M_{TRM} = At^{-\alpha}. \quad (1)$$

In order to check critically whether our data can be fitted by a stretched exponential $M_{TRM} = M' \times \exp[-C(\omega t)^{1-n}/(1-n)]$ or not, we show in Fig.

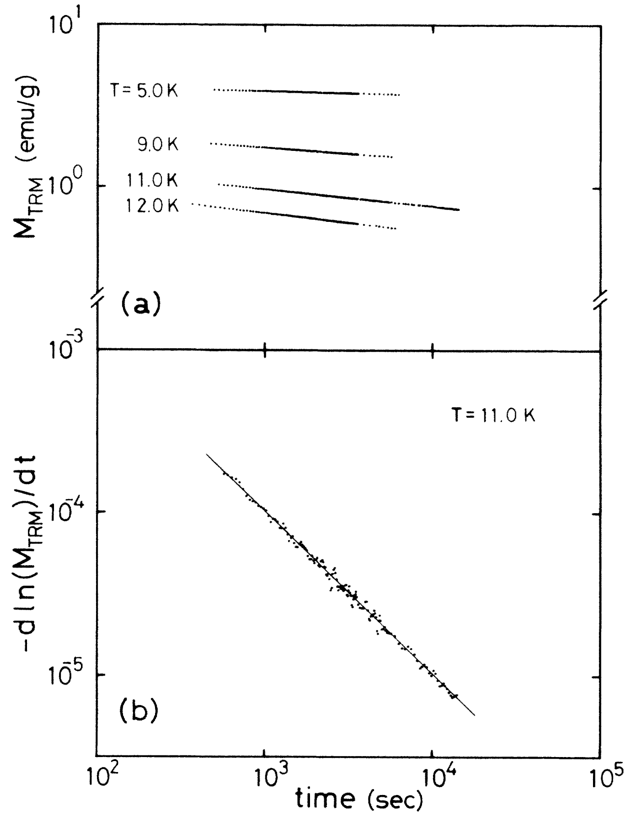

FIG. 2. (a) Log-log plot of the thermoremanent magnetization M_{TRM} of $Fe_{0.5}Mn_{0.5}TiO_3$ when cooled in $H=3200$ Oe as a function of time at various temperatures. (b) Log-log plot of $-d\ln(M_{TRM})/dt$. The solid line is the best fit to the data. The slope of this line gives $n=1.00$ when M_{TRM} is expressed in a form of the stretched exponential as $M_{TRM} = M' \exp[-C(\omega t)^{1-n}/(1-n)]$.

2(b) a log-log plot of $-d\ln(M_{TRM})/dt$ vs t for the data at 11 K. As is clearly seen from Fig. 2(b), the slope gives $n=1.00$. Similar results are obtained for the data at three other temperatures ($n=1.00$–1.02). This fact just supports an algebraic decay instead of a stretched exponential one. We have also checked that the decay of M_{TRM} is not a logarithmic function of time.

In Fig. 3, we give a similar plot for the growth of M^{ZFC}. The ordinate in Fig. 3 is not M^{ZFC} itself but $M_0 - M^{ZFC}$, where M_0, which depends on fields too, is a fitting parameter. The value of M_0 is determined so as to make the log-log plot of $M_0 - M^{ZFC}$ vs t a straight line. The value of M_0 thus determined is listed in Table I. This result means that the growth of M^{ZFC} is well described by

$$M^{ZFC} = M_0 - At^{-\alpha}. \quad (2)$$

It has been also checked that the slope of a log-log plot of $-d\ln(M_0 - M^{ZFC})/dt$ vs t gives $n=0.95$–1.02, and that the growth of M^{ZFC} cannot be fitted with a loga-

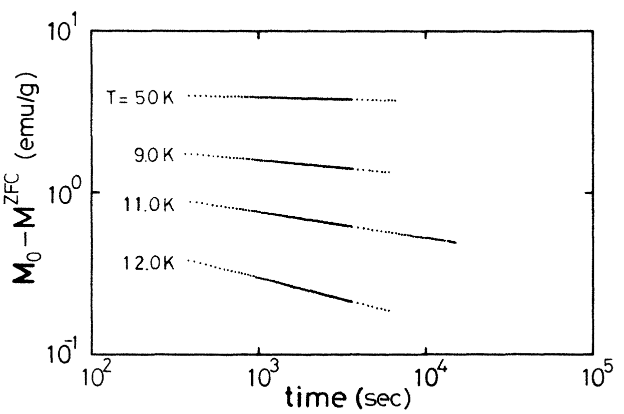

FIG. 3. Log-log plot of $M_0 - M^{ZFC}$ in $Fe_{0.5}Mn_{0.5}TiO_3$ as a function of time, where M^{ZFC} is the zero-field–cooled magnetization, and M_0 is a fitting parameter. The value of M_0 is determined so as to make a log-log plot of $M_0 - M^{ZFC}$ vs t a straight line (see Table I). The measuring field is 3200 Oe.

rithmic function. As is clear from Eq. (2), M_0 is the saturation value which the zero-field–cooled magnetization reaches at an infinite time. In other words, M_0 is the thermodynamic equilibrium value of the magnetization in a magnetic field H. Thus, our finding strongly suggests that there exists a thermodynamic equilibrium state for spin-glasses exposed to magnetic fields. This is also supported by the fact that the saturation value M_0 is very close to M^{FC} (see Table I). It is well known that the value of M^{FC} depends on the cooling rate at which a temperature below T_g is reached[12] and that the decay rate of M_{TRM} is remarkably affected by the waiting time before H is removed.[13] From these experimental facts, it is thought that the field-cooled state reached at least within a finite time is not in thermodynamic equilibrium. On the other hand, however, it is also known that the cooling rate dependence of M^{FC} is very small and the value of M^{FC} does not change appreciably with time when a temperature is kept constant.[14] Accordingly, it is believed that M^{FC} observed in the field-cooled state is very close to thermodynamic equilibrium value. Therefore, if Eq. (2) describes reasonably the time dependence of the growth of M^{ZFC} and if the system can attain a thermodynamic equilibrium state at long times, M_0 should be close to but a little larger than M^{FC}.[14] Our observation shows that M_0 is equal to or a little larger than M^{FC} (see Table I). Thus, by investigating the growth of M^{ZFC}, we suggest the existence of a thermodynamic equilibrium state for an Ising spin-glass in magnetic fields.

The temperature dependences of the exponent α and the prefactor A determined from Figs. 2(a) and 3 are shown in Fig. 4. The α_{IRM} for the growth of M_{IRM} is larger than the α_{TRM} for the decay of M_{TRM}, indicating that the system is forced to relax faster by the applied field. The exponent α_{IRM} increases rapidly with increasing temperature. We have a semilog plot of α_{IRM} vs $\tau[\equiv 1 - T/T_g(H)]$ and we have found that α_{IRM} increases exponentially with temperature as $\alpha_{IRM} = 1.6\exp(-\tau/0.17)$. On the other hand, the prefactor A_{IRM} decreases linearly with increasing temperature and the extrapolated value becomes zero at a temperature a little below but close to $T_g(H)$. [Notice that A_{IRM} corresponds to the isothermal remanent magnet-

TABLE I. The values of M_0 in Eq. (2) at various temperatures determined so as to make the log-log plot of $M_0 - M^{ZFC}$ vs t a straight line (see Fig. 3). The measuring field is 3200 Oe. The corresponding M^{FC} is also shown.

T (K)	M_0 (emu/g)	M^{FC} (emu/g)
5.0	6.0(0.1)	6.04(0.00$_5$)
9.0	6.1(0.05)	6.04(0.00$_5$)
11.0	6.24(0.03)	6.12(0.00$_5$)
12.0	6.17(0.02)	6.15(0.00$_5$)

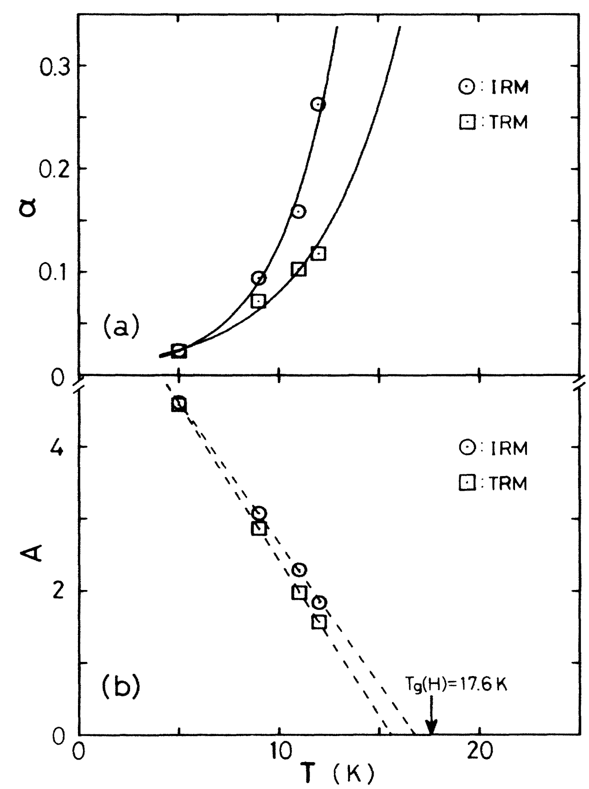

FIG. 4. (a) Temperature dependence of the exponent α for the algebraic decay or growth of M_{TRM} or M^{ZFC}. The solid lines are the best fits by $\alpha = a\exp(-\tau/b)$:$\alpha_{TRM} = 0.48\exp(-\tau/0.24)$ and $\alpha_{IRM} = 1.6\exp(-\tau/0.17)$, respectively. (b) Temperature dependence of the prefactor A of the algebraic decay or growth of M_{TRM} or M^{ZFC}. The dashed lines are guides for the eye. The cooling field or the measuring field is 3200 Oe.

ization at $t=1$ s. Therefore, it is natural that $A_{\rm IRM}$ becomes zero at a temperature a little below $T_g(H)$.] These temperature dependences of $\alpha_{\rm IRM}$ and $A_{\rm IRM}$ indicate that the irreversibility disappears at $T_g(H)$ in a manner that the relaxation becomes very fast and at the same time the irreversible part of the magnetization itself approaches zero. This fact strongly suggests that $T_g(H)$ is the temperature determining a phase boundary. The temperature dependence of the exponent $\alpha_{\rm TRM}$ for the decay of $M_{\rm TRM}$ is also well fitted with an exponential function, $\alpha_{\rm TRM}=0.48\exp(-\tau/0.24)$. The prefactor $A_{\rm TRM}$ changes also linearly with temperature. A temperature where $A_{\rm TRM}$ is extrapolated to zero is a little lower than that for $A_{\rm IRM}$; we believe that the difference between them is not essential.

Theoretically, a power-law dependence below T_g has been predicted by calculations based on the mean-field model[6] and by computer simulations.[7,15] Ogielski investigated the dynamic behavior of a model of short-range Ising spin-glasses[7] which can be said to be a representative of our system $Fe_{0.5}Mn_{0.5}TiO_3$. He has stated in his paper that in the spin-glass phase the decay of the order parameter

$$q(t)=\langle\overline{Sx(0)Sx(t)}\rangle$$

is fitted by a power law of time, $q(t)\propto t^{-X(\tau)}$, where $\tau\equiv 1-T/T_g$. He has also described that variation of the exponent $X(\tau)$ with temperature above T_g seems to be linear but different temperature dependence is observed below T_g. Since he did not give a functional form of $X(\tau)$ below T_g, we read the values of $X(\tau)$ on Fig. 17 in Ref. 7 and made a semilog plot of $X(\tau)$ as a function of τ. As a result, we have found that $X(\tau)$ below T_g is well described by an exponential function of $\tau: X(\tau)\approx 0.07\exp(-\tau/0.28)$, in which we put $T_g=1.175$ according to his choice.

Thus, the computer simulation done by Ogielski reproduces very nicely the time-dependent behavior of $Fe_{0.5}Mn_{0.5}TiO_3$, which is a short-range Ising spin-glass, including the functional form of temperature variation of the exponent for the algebraic decay. It should be noted that the temperature dependences of the exponents $\alpha_{\rm TRM}(\tau)$ and $X(\tau)$ are very similar to each other except for the values of prefactor of the exponential function. Ogielski has investigated the dynamics of equilibrium fluctuations. On the other hand, we have observed the nonequilibrium relaxation of the system. Nevertheless, the similarity between our experimental results and his computer simulation is remarkable. This may intimate that the decay of $M_{\rm TRM}$ and the growth of $M^{\rm ZFC}$ can be treated as a relaxation of fluctuated deviations from equilibrium obeying the fluctuation-dissipation theorem.[16]

In conclusion, we have suggested the existence of a thermodynamic equilibrium state in magnetic fields by observing the growth of $M^{\rm ZFC}$. We have also shown that the time-dependent phenomena in an Ising spin-glass are well described by an algebraic function. The prefactors $A_{\rm IRM}$ and $A_{\rm TRM}$ decrease linearly with increasing temperature and become zero at temperatures a little below $T_g(H)$. The exponents $\alpha_{\rm IRM}$ and $\alpha_{\rm TRM}$ are also temperature dependent and they increase exponentially with temperature. We point out that a recent computer simulation for short-range Ising spin-glasses done by Ogielski gives a correlation function with a similar algebraic decay including the functional form of the temperature variation of the exponent.

We are grateful to H. Ikeda for allowing us to use the SQUID magnetometer and for his valuable discussions. We are also deeply indebted to N. Hashitsume and H. Takayama for their stimulating discussions. This work was supported in part by the Mitsubishi Foundation.

[1]C. N. Guy, J. Phys. F **8**, 1309 (1978); S. Oseroff, M. Mesa, M. Tovar, and R. Arce, J. Appl. Phys. **53**, 2208 (1982); Y. Yeshurun, L. J. P. Ketelsen, and M. B. Salamon, Phys. Rev. B **26**, 1491 (1982).

[2]J. Ferré, J. Rajchenbach, and H. Maletta, J. Appl. Phys. **52**, 1697 (1981).

[3]K. Katsumata, T. Nire, and M. Tanimoto, Solid State Commun. **43**, 711 (1982).

[4]R. V. Chamberlin, G. Mozurkewich, and R. Orbach, Phys. Rev. Lett. **52**, 867 (1984).

[5]J. Ferré, M. Ayadi, R. V. Chamberlin, R. Orbach, and N. Bontemps, J. Magn. Magn. Mater **54–57**, 211 (1986).

[6]H. Sompolinsky and A. Zippelius, Phys. Rev. Lett. **47**, 359 (1981).

[7]A. T. Ogielski, Phys. Rev. B **32**, 7384 (1985).

[8]H. Kato, M. Yamada, H. Yamauchi, H. Hiroyoshi, H. Takei, and H. Watanabe, J. Phys. Soc. Jpn. **51**, 1769 (1982).

[9]Y. Todate, Y. Ishikawa, K. Tajima, S. Tomiyoshi, and H. Takei, presented at the Meeting of the Physical Society of Japan, Okayama, 1983 (unpublished).

[10]A. Fert, P. Pureur, F. Hippert, K. Baberschke, and F. Bruss, Phys. Rev. B **26**, 5300 (1982).

[11]R. V. Chamberlin, M. Hardiman, L. A. Turkevich, and R. Orbach, Phys. Rev. B **25**, 6720 (1982).

[12]L. E. Wenger and J. A. Mydosh, J. Appl. Phys. **55**, 1717 (1984).

[13]R. V. Chamberlin, Phys. Rev. B **30**, 5393 (1984).

[14]L. Lundgren, P. Svedlindh, and O. Beckman, Phys. Rev. B **26**, 3990 (1982).

[15]S. Kirkpatrick and D. Sherrington, Phys. Rev. B **17**, 4384 (1978).

[16]M. Ocio, H. Bouchiat, and P. Monod, J. Magn. Magn. Mater. **54–57**, 11 (1986).