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Spin dynamics in Fe_2O_3-TeO_2 glass: Experimental evidence for an amorphous oxide spin glass

Hirofumi Akamatsu, Katsuhisa Tanaka,* Koji Fujita, and Shunsuke Murai
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

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We have examined spin dynamics including magnetic aging and memory effects as well as critical slowing down for $20Fe_2O_3 \cdot 80TeO_2$ (mol %) glass. Scaling analysis on critical slowing down reveals that the present glass exhibits a critical behavior as observed in a prototype of spin glasses. Aging and memory effects peculiar to spin glasses have been observed in the magnetically ordered phase of the present glass. These experimental results strongly confirm that the $20Fe_2O_3 \cdot 80TeO_2$ glass is converted into a spin glass phase at a very low temperature. It is thought that a disordered structure of the oxide glass gives rise to randomness and frustration in the magnetic structure, leading to the spin glass phase transition.

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Spin glass has attracted considerable attention since its experimental discovery,[1] as many vigorous investigations have been carried out to clarify its curious magnetic structure and phase transition. The spin glass system is also a matter of interest from the viewpoint of its analogy to many complex systems, such as associative memory in the brain.[2] One of the most interesting phenomena observed in spin glasses involves spin dynamics. Magnetic moments are frozen in such a way that the direction of each of the magnetic moments is randomly oriented in a spin glass below its transition temperature, and it takes an infinite time to reach a thermodynamic equilibrium state. Experimental, theoretical, and numerical approaches have been performed for clarification of the spin dynamics peculiar to spin glass phase, such as critical slowing down and aging phenomena involving rejuvenation and memory effects.[3–18]

Amorphous solids derived from ionic compounds, such as oxide and fluoride glasses, bearing a large amount of magnetic ions can be categorized into a lattice in which a disordered distribution of magnetic moments is dominant. There are some reports as to magnetic properties of the oxide and fluoride glasses. Temperature dependence of field-cooled and zero-field-cooled susceptibilities indicates that these glasses exhibit magnetic transitions like those of spin glasses or superparamagnets. For instance, in 1975, just three years after the discovery of a canonical spin glass of Au-Fe alloys, Verhelst *et al.* found that oxide glasses in a CoO-Al_2O_3-SiO_2 system manifest spin glass-like transitions.[19] Assuming the presence of magnetic clusters, they applied a simple superparamagnetic model to the magnetic transition observed in temperature variation of zero-field-cooled susceptibility. For this glass system, the relaxation process of remanent magnetization below the transition temperature was explored by Rechenberg *et al.*[20] They measured the time dependence of remanent magnetization after the external field was turned off for a field-cooled sample and analyzed the experimental results in terms of the superparamagneic model in which a distribution of anisotropy energy for the superparamagnetic clusters was assumed. Renard *et al.* examined temperature dependence of ac susceptibility for $PbMnFeF_7$ and Pb_2MnFeF_9 glasses, and observed a cusp-like maximum of susceptibility at 11.77 and 5.26 K, respectively.[21] They also revealed that the cusp-like maximum was rounded by application of an external dc field of 200 Oe for the $PbMnFeF_7$ glass. This fact suggests that nonlinear susceptibility manifests some change at the transition temperature of the $PbMnFeF_7$ glass, although dependence of nonlinear susceptibility on temperature at around the transition temperature was not directly clarified. Sanchez *et al.* studied temperature dependence of ac susceptibility and ^{57}Fe Mössbauer spectrum for FeO-Al_2O_3-SiO_2 glasses and clarified that the variation of magnetic transition temperature with frequency of ac field along with precession time of ^{57}Fe nuclear spin was described well in terms of empirical Vogel-Fulcher relation.[22] A similar dependence of spin-freezing temperature on frequency of ac field and ^{57}Fe nuclear precession time was demonstrated for Li_2O-B_2O_3-Fe_2O_3 glasses.[23] Recently, Shaw *et al.* reported that Fe_2O_3-P_2O_5 glasses show a spin glass transition due to an antiferromagnetic superexchange interaction among iron ions.[24]

Although there exist some reports on magnetic properties of oxide and fluoride glasses as mentioned above, decisive evidence has not been provided to ascertain that those oxide and fluoride glasses truly exhibit a spin glass phase transition. Further experiments, in particular, those relevant to spin dynamics, are necessary to comprehend the mechanism of magnetic transition as well as magnetic structure of the glasses derived from ionic compounds. In the present investigation, we have carried out experiments concerning the spin dynamics for magnetically ordered phase of a glass in Fe_2O_3-TeO_2 system. We have found that the glass manifests memory effect below its magnetic transition temperature, and that the critical slowing down is observed at around the transition temperature as well. We demonstrate that the magnetically ordered phase of the present glass has many features very similar to those observed for a prototype of spin glasses.

The glass with nominal composition of $20Fe_2O_3 \cdot 80TeO_2$ (mol %) was prepared by using a conventional melt-quenching method. Reagent grade Fe_2O_3 and TeO_2 powders were used as starting materials. After they were melted in a platinum crucible at 1000 °C for 1–2 h, the melt was poured onto a stainless steel plate and cooled in air. X-ray diffraction analysis with Cu $K\alpha$ radiation was carried out to confirm that the sample was amorphous. ^{57}Fe Mössbauer spectroscopy revealed that most of the Fe ions were present as Fe^{3+} and occupied octahedral sites in the glass.[25] It was ascertained by

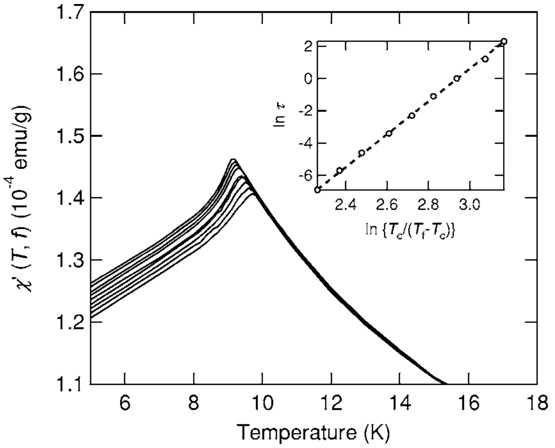

FIG. 1. Temperature dependence of the real part of ac susceptibility for the $20Fe_2O_3 \cdot 80TeO_2$ glass. The frequency f is 0.1, 0.3, 1, 3, 10, 30, 100, 300, and 1000 Hz (from top to bottom). The inset illustrates the relationship between maximum relaxation time τ and spin-freezing temperature $T_f(f)$ in critical slowing down analysis.

energy-dispersive x-ray spectroscopy that the actual composition of the glass was $22Fe_2O_3 \cdot 78TeO_2$ because of vaporization of TeO_2 during the glass melting. For the sake of simplification, however, the sample is hereafter referred to as $20Fe_2O_3 \cdot 80TeO_2$ glass. The glass sample was subjected to measurements of magnetic properties such as dc and ac susceptibilities by using a superconducting quantum interference device (SQUID) magnetometer to clarify magnetic aging effects and critical slowing down. The experimental protocols employed for clarification of spin dynamics are described in detail in the following.

Figure 1 illustrates the temperature dependence of the real part of ac susceptibility obtained by zero-field cooling for the $20Fe_2O_3 \cdot 80TeO_2$ glass. The amplitude of the ac magnetic field was kept at 3 Oe and the ac frequency was varied from 0.1 to 1000 Hz. The spin-freezing temperature $T_f(f)$, dependent on frequency f, can be defined as a temperature at which the real part of ac susceptibility $\chi'(T,f)$ manifests a maximum. In other words, the maximum relaxation time of the system τ is equal to $1/f$ at $T_f(f)$. Although $T_f(f)$ is often taken as a temperature at which $\chi'(T,f)$ is 0.98 times the equilibrium susceptibility,[3] it is reasonable to define $T_f(f)$ as a temperature of maximum susceptibility in the $\chi'(T,f)$ curve for dynamical scaling analysis, as demonstrated previously.[3,4] It is found in Fig. 1 that $T_f(f)$ increases with an increase in f; τ becomes longer as the temperature is lowered. According to the dynamic scaling hypothesis, provided that this system exhibits a conventional critical slowing down toward the transition temperature T_c, the variation of maximum relaxation time with transition temperature is described by[5]

$$\tau = \tau_0 \left(\frac{T_f(f) - T_c}{T_c} \right)^{-z\nu}, \qquad (1)$$

where $z\nu$ is the dynamic exponent and τ_0 is a microscopic relaxation time. In the present case, the best fitting of Eq. (1) to the experimental data yields $z\nu = 10$, $T_c = 8.8$ K, and $\tau_0 = 10^{-13}$ s, as shown in the inset of Fig. 1. The values of $z\nu = 10$ and $\tau_0 = 10^{-13}$ s are in good agreement with those reported for a prototype of spin glasses.[4,26] In particular, the value of $\tau_0 = 10^{-13}$ s is identical in magnitude with those for atomic spin glasses, for which τ_0 denotes a spin flip time of individual magnetic moments belonging to atoms or ions. In contrast, it has been observed that $\tau_0 \sim 10^{-6}$ s for interacting magnetic nanoparticles systems or super spin glasses, for which τ_0 corresponds to a time of reversal of superparamagnetic magnetizations.[3] The results of this analysis imply that a transition takes place from paramagnetic phase to atomic spin glass phase in the present oxide glass of the Fe_2O_3-TeO_2 system.

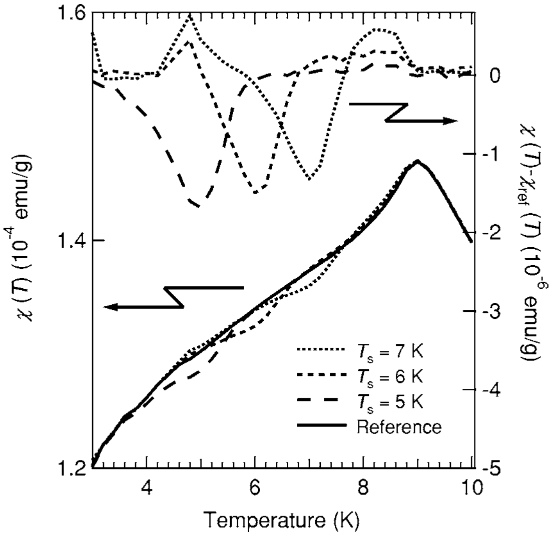

FIG. 2. Temperature dependence of dc susceptibility measured on heating after zero-field cooling with and without an intermittent stop at T_s. The difference between $\chi(T)$ and $\chi_{ref}(T)$ is illustrated as well.

In order to discuss magnetic aging effects in the magnetically ordered phase of $20Fe_2O_3 \cdot 80TeO_2$ glass, the temperature dependence of dc susceptibility $\chi(T)$ was inspected by utilizing a protocol of zero-field cooling memory experimentation proposed by Mathieu *et al.*[6] In this protocol, $\chi(T)$ is measured on heating after zero-field cooling with an intermittent stop at a temperature below the transition temperature. In the present case, the glass was cooled from a temperature well above $T_c = 8.8$ K to a stopping temperature T_s, which was lower than T_c, at a rate of 0.2 K/min, and was kept at T_s for 3 h. Here, T_s was selected to be 7, 6, and 5 K. After a stop for 3 h, the glass was cooled to 3 K at a rate of 0.2 K/min. Subsequently, a magnetic field of 50 Oe was applied and $\chi(T)$ was measured on heating at a rate of 0.2 K/min. As a reference, $\chi_{ref}(T)$ was determined by measuring temperature dependence of zero-field-cooled susceptibility without any intermittent stops. The results thus obtained are shown in Fig. 2. The $\chi(T)$ curves involving a stop coincide with the $\chi_{ref}(T)$ curve in a temperature range well below T_s. In contrast, the $\chi(T)$ curves deviate downward from the $\chi_{ref}(T)$ curve as the temperature approaches T_s. As the temperature increases in a range above T_s, the $\chi(T)$ curves gradually merge with the $\chi_{ref}(T)$ curve and eventually coincide with the $\chi_{\mathrm{ref}}(T)$. The difference between $\chi(T)$ and $\chi_{\mathrm{ref}}(T)$ as a function of temperature is also illustrated in Fig. 2. The effect of aging at T_s is reflected by a dip at around T_s. For comparison, we performed the same experiments by making T_s 10 K, i.e., a temperature above T_c, and found that aging at 10 K had no influence on the $\chi(T)$ curve (not shown). The appearance of memory dips indicates that spin configurations attained during a stop at T_s are preserved after cooling and subsequent heating. A finite temperature range of the memory dips reflects a temperature chaos in equilibrium spin configurations. Since an equilibrium spin configuration at a particular temperature T is completely different from another spin configuration at a different temperature $T+\Delta T$ if ΔT is sufficiently large, an aging effect at T does not affect a spin structure at $T+\Delta T$ at all. This memory effect has been confirmed for spin glasses and strongly interacting nanoparticles systems.[6–10] On the other hand, it has been experimentally and theoretically demonstrated that the memory effect according to this protocol is not observed in simple superparamagnets due to the absence of magnetic interactions among magnetic particles.[9] The observation of this memory effect is generally an indication of collective nature in spin dynamics,[9,10] so the present result strongly suggests that the very low temperature magnetic phase of the $20\mathrm{Fe_2O_3}\cdot 80\mathrm{TeO_2}$ glass is a spin glass.

An aging effect in a magnetic field[11] was also explored for the present $20\mathrm{Fe_2O_3}\cdot 80\mathrm{TeO_2}$ glass. The experiments were performed in the following way. The glass was cooled from a temperature well above $T_c=8.8$ K to 3 K at a rate of 0.2 K/min. Subsequently, a magnetic field of 50 Oe was applied and $\chi(T)$ was measured upon heating to a stopping temperature T_s, which was 4 or 5 K, at a rate of 0.2 K/min. Then the temperature was fixed to be T_s for 5.5 h, and $\chi(T_s)$ as a function of time was measured. After the stop at T_s, $\chi(T)$ was determined upon heating further at a rate of 0.2 K/min. As a reference, $\chi_{\mathrm{ref}}(T)$ was measured in zero-field and field-cooling processes without any long-term stops (5.5 h in the present case) at fixed temperatures. The $\chi(T)$ and $\chi_{\mathrm{ref}}(T)$ thus obtained are depicted in Fig. 3. As found in the inset of Fig. 3, $\chi(T)$ increases logarithmically with time at T_s. After a stop for 5.5 h at T_s, $\chi(T)$ at first decreases with an increase in temperature and merges with the $\chi_{\mathrm{ref}}(T)$ curve at a temperature well above T_s. A similar behavior was reported for the ferromagnetic phase of the reentrant spin glass $\mathrm{Cu_{0.2}Co_{0.8}Cl_2}$-$\mathrm{FeCl_3}$ graphite bi-intercalation compound.[12] The decrease of $\chi(T)$ just above T_s observed in Fig. 3 is thought to be a rejuvenation effect attributed to a chaotic nature of spin configurations which depend on temperature. The present behavior is somewhat different than that observed for three-dimensional (3D) Ising spin glass $\mathrm{Fe_{0.5}Mn_{0.5}TiO_3}$[11]and the reentrant spin glass phase of $\mathrm{Cu_{0.2}Co_{0.8}Cl_2}$-$\mathrm{FeCl_3}$ graphite bi-intercalation compound;[12] for these two systems, $\chi(T)$ monotonically increases as the temperature is raised from T_s after a stop and then merges with a reference curve at a temperature well above T_s. It was concluded for the $\mathrm{Fe_{0.5}Mn_{0.5}TiO_3}$ that $\chi(T)$ is explained well in terms of a scaling description derived from droplet theory for spin glasses, where the susceptibility depends on two length scales $R_T(t_w)$ and $L_T(t)$ as follows:[11]

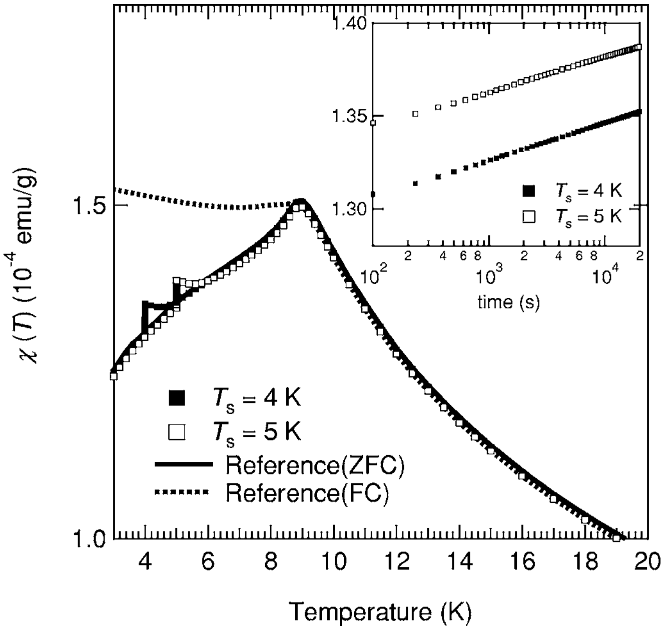

FIG. 3. Temperature dependence of dc susceptibility measured on heating with and without an intermittent stop at T_s under an external magnetic field of 50 Oe after zero-field cooling. Temperature dependence of field-cooled dc susceptibility is also shown. The inset depicts time dependence of susceptibility at T_s.

$$\chi(T,t) = F[R_T(t_w), L_T(t)]. \tag{2}$$

Here $R_T(t_w)$ is the mean size of spin glass domains grown during a waiting time t_w (or a stopping time in zero field), and $L_T(t)$ is the maximum size of domains excited within a probing time t. Several kinds of theoretical equations have been suggested to express the growth laws of $R_T(t_w)$ and $L_T(t)$.[27–29] One of the theories proposes a power law as follows:

$$R_T(t_w) \approx \left(\frac{t_w}{\tau_0}\right)^{bT/T_c} \tag{3}$$

and

$$L_T(t) \approx \left(\frac{t}{\tau_0}\right)^{bT/T_c}, \tag{4}$$

where the exponent $b \approx 0.17$.[28] For $\mathrm{Fe_{0.5}Mn_{0.5}TiO_3}$, by assuming that $L_T(t)$ grows continuously even if the temperature is changed discontinuously, $\chi(T)$ can be scaled by a scaling function F which increases continuously with $L_T(t)$. The validity of this scaling law warrants an accumulative nature of aging dynamics involving the continuous growth of $L_T(t)$ within a laboratory time scale. In the present experiments, $\chi(T)$ does not increase monotonically with time as reflected in the decrease of $\chi(T)$ just above T_s. Hence, it is clear that this scaling law cannot be applied to the $20\mathrm{Fe_2O_3}\cdot 80\mathrm{TeO_2}$ glass. This indicates that the $20\mathrm{Fe_2O_3}\cdot 80\mathrm{TeO_2}$ glass manifests a nonaccumulative aging effect, presumably due to a chaotic nature within the laboratory time scale.

As mentioned above, it is demonstrated that the $20\mathrm{Fe_2O_3}\cdot 80\mathrm{TeO_2}$ glass exhibits critical slowing down and aging effects similar to those observed for spin glasses. However, the $20Fe_2O_3 \cdot 80TeO_2$ glass has a microscopic feature different from a prototype of spin glasses. In spin glasses, ferromagnetic and antiferromagnetic interactions are randomly distributed, while the antiferromagnetic superexchange interaction via oxide ions is dominant among Fe^{3+} ions in the $20Fe_2O_3 \cdot 80TeO_2$ glass, as speculated from the negative value of paramagnetic Curie temperature θ (-142 K)[25] defined by the following Curie-Weiss equation:

$$\frac{1}{\chi} = \frac{3k_B(T-\theta)}{NM_B^2\mu_B^2}. \tag{5}$$

It is naturally anticipated that magnetic structure of the present oxide glass depends on the arrangement of Fe^{3+} ions in the glass structure. Magnetic frustration in the oxide glass can be caused by a spatially random distribution of Fe^{3+} ions, which are connected by the antiferromagnetic interaction. The strength of superexchange interactions among Fe^{3+} ions has a distribution due to the site-dependent variations in Fe-O-Fe bond angles and Fe-O bond lengths. Thus, not only randomness but also frustration is present in the magnetic structure of the $20Fe_2O_3 \cdot 80TeO_2$ glass, leading to a transition into spin glass phase at very low temperatures, even in the absence of random distributions of magnetic interactions with opposite signs.

In conclusion, we have revealed that the $20Fe_2O_3 \cdot 80TeO_2$ glass displays aging and memory effects and critical slowing down, indicating that the present oxide glass exhibits spin glass phase transition. A disordered structure of the oxide glass is thought to be responsible for the frustration in spin configuration. The mechanism of magnetic transition presumably depends on the glass system, the concentration of magnetic ions, the preparation process of the glass, and so forth. Therefore, further extensive studies will be required to understand the magnetic properties of various oxide glasses. Investigations of magnetic properties for other oxide glasses are in progress.

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*Corresponding author. Electronic address: tanaka@dipole7.kuic.kyoto-u.ac.jp

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