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Spin dynamics in Fe$_2$O$_3$-TeO$_2$ glass: Experimental evidence for an amorphous oxide spin glass

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We have examined spin dynamics including magnetic aging and memory effects as well as critical slowing down for 20Fe$_2$O$_3$·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$_2$O$_3$·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, 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. 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.

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$_2$O$_3$-SiO$_2$ system manifest spin glass-like transitions. Assuming the presence of magnetic clusters, they applied a simple super-paramagnetic 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. 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 superparamagnetic 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$_2$MnFeF$_9$ glasses, and observed a cusp-like maximum of susceptibility at 11.77 and 5.26 K, respectively. 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$_2$O$_3$-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. A similar dependence of spin-freezing temperature on frequency of ac field and $^{57}$Fe nuclear precession time was demonstrated for Li$_2$O-B$_2$O$_3$-Fe$_2$O$_3$ glasses. Recently, Shaw et al. reported that Fe$_2$O$_3$-P$_2$O$_5$ glasses show a spin glass transition due to an antiferromagnetic superexchange interaction among iron ions.

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$_2$O$_3$-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$_2$O$_3$·80TeO$_2$ (mol %) was prepared by using a conventional melt-quenching method. Reagent grade Fe$_2$O$_3$ 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 Kα 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. It was ascertained by
energy-dispersive x-ray spectroscopy that the actual composition of the glass was 22Fe2O3·78TeO2 because of vaporization of TeO2 during the glass melting. For the sake of simplification, however, the sample is hereafter referred to as 20Fe2O3·80TeO2 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 20Fe2O3·80TeO2 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 \( \tau \) is equal to \( 1/\nu(f) \) 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, \( T_c \), 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 \( f \); \( \tau \) 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\(^3\)

\[
\tau = \tau_0 \left( \frac{T_f(f) - T_c}{T_c} \right)^{-\nu}, \tag{1}
\]

where \( \nu \) is the dynamic exponent and \( \tau_0 \) is a microscopic relaxation time. In the present case, the best fitting of Eq. (1) to the experimental data yields \( \nu = 10 \), \( T_c = 8.8 \) K, and \( \tau_0 = 10^{-13} \) s, as shown in the inset of Fig. 1. The values of \( \nu = 10 \) 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 \( \tau_0 \) denotes a spin flip time of individual magnetic moments belonging to atoms or ions. In contrast, it has been observed that \( \tau_0 \approx 10^{-6} \) s for interacting magnetic nanoparticles systems or super spin glasses, for which \( \tau_0 \) 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 Fe2O3-TeO2 system.

In order to discuss magnetic aging effects in the magnetically ordered phase of 20Fe2O3·80TeO2 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 \( T_s = 8.8 \) 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 $\chi_{\text{ref}}(T)$. The difference between $\chi(T)$ and $\chi_{\text{ref}}(T)$ 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 $\Delta T$ 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. 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. The observation of this memory effect is generally an indication of collective nature in spin dynamics, so the present result strongly suggests that the very low temperature magnetic phase of the 20Fe$_2$O$_3$·80TeO$_2$ glass is a spin glass.

An aging effect in a magnetic field was also explored for the present 20Fe$_2$O$_3$·80TeO$_2$ glass. The experiments were performed in the following way. The glass was cooled from a temperature well above $T_s$ = 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 $T_c$, 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 $\chi(T)$ 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, $\chi_{\text{ref}}(T)$ 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 $\chi_{\text{ref}}(T)$ 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 $\chi_{\text{ref}}(T)$ curve at a temperature well above $T_s$. A similar behavior was reported for the ferromagnetic phase of the reentrant spin glass Cu$_{0.2}$Fe$_{0.8}$Cl$_2$-FeCl$_3$ graphite bi-intercalation compound. 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 Fe$_{0.5}$Mn$_{0.5}$TiO$_3$ and the reentrant spin phase glass of Cu$_{0.2}$Co$_{0.8}$Cl$_2$-FeCl$_3$ graphite bi-intercalation compound, 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 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:

$$R_T(t_w) = \left( \frac{t_w}{\tau_0} \right)^{b_T/T_c},$$

and

$$L_T(t) = \left( \frac{t}{\tau_0} \right)^{b_T/T_c},$$

where the exponent $b = 0.17$. For 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 20Fe$_2$O$_3$·80TeO$_2$ glass. This indicates that the 20Fe$_2$O$_3$·80TeO$_2$ 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 20Fe$_2$O$_3$·80TeO$_2$ glass exhibits critical slowing down and
The strength of superexchange interactions among Fe$^{3+}$ ions, which are connected by the antiferromagnetic interaction, can be caused by a spatially random distribution of Fe$^{3+}$ ions, in the glass structure. Magnetic frustration in 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.

In conclusion, we have revealed that the 20Fe$_2$O$_3$-80TeO$_2$ 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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