

Evidence for broken ergodicity in strain glass

Yu Wang,^{1,2} Xiaobing Ren,^{1,2,*} Kazuhiro Otsuka,^{1,2} and Avadh Saxena³

¹*Multi-disciplinary Materials Research Center and Department of Physics, Xi'an Jiaotong University, Xi'an 710049, China*

²*National Institute for Material Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*

³*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

(Received 19 June 2007; revised manuscript received 12 July 2007; published 12 October 2007)

A recent study has indicated that there exists a different class of glass, the strain glass, in the nontransforming composition regime of Ti-Ni alloys. However, the critical proof for a glass, the evidence for the nonergodicity in the glassy state, has been missing in this system. By a zero-field-cooling/field-cooling measurement of static strain, we show experimentally that the ergodicity of the frozen strain glass is indeed broken. The creep measurement clearly shows the slowing down of kinetics upon strain glass transition. These features are physically parallel to other well-known glasses such as cluster-spin glasses and ferroelectric relaxors; thus, we introduce the notion of a ferroic glass and suggest a common underlying physics.

DOI: [10.1103/PhysRevB.76.132201](https://doi.org/10.1103/PhysRevB.76.132201)

PACS number(s): 64.70.Pf, 61.43.Fs, 62.20.Dc, 64.70.Kb

Glass is a ubiquitous phenomenon in nature and has been observed in a wide range of complex systems. Glass is a frozen metastable disordered state when the corresponding high temperature, dynamically disordered state fails to reach a thermodynamically favored ground state, limited by kinetics. Previous studies¹⁻³ showed that the formation of glass is governed by a kinetic rather than a thermodynamic origin, that is, the glass transition relies on the slowing down of kinetics. When a glass transition occurs, the relaxation time required for the system to go from one state to another increases dramatically from a short time scale to an experimentally inaccessible time scale.^{2,4} This results in the freezing of the system into a certain metastable state. There is a substantial interest in this slowing-down process because it challenges the basic assumption of statistical physics: its fundamental “hypothesis of ergodicity,” i.e., a system can visit all its possible states on the experimental time scale,^{5,6} becomes invalid in a frozen glass state. Due to the fundamental importance of the loss of ergodicity in glass, the glass phenomenon has attracted much interest in condensed matter physics for decades. The nonergodicity calls for a new paradigm that must go beyond equilibrium statistical mechanics.⁷

Glass has been found in ferromagnet-derived systems such as cluster-spin glasses^{4,8} and spin glasses,^{4,9,10} which are formed by diluting a ferromagnetic system with nonmagnetic atoms, and ferroelectric-derived systems such as relaxor ferroelectrics,^{11,12} which are usually formed by doping point defects (dopants) into a normal ferroelectric system. However, for decades the glass in the physically parallel ferroelastic/martensitic system was not considered to exist. Very recently, we found that there exists frequency dispersion of anomalies in the AC elastic modulus and the corresponding mechanical loss in the “nontransforming” composition regime of a Ni-rich intermetallic compound $\text{Ti}_{50-x}\text{Ni}_{50+x}$ (for $x > 1$).¹³ This is an important glass feature for this ferroelastic/martensite-derived system. Nevertheless, the critical proof for a glass, i.e., evidence for nonergodicity, has been missing. In the present work, we employ zero-field-cooling/field-cooling measurement of static strain to provide this critical evidence. We demonstrate experimentally that this Ni-rich Ti-Ni system does show broken ergodicity and slowing down of kinetics, which are similar to that of a wide

range of glasses.^{8,10,12,14-16} Therefore, we demonstrate that there indeed exists a ferroelastic/martensitic glass and it may be the beginning of a large class of ferroelastic glasses.

This different class of glass in a ferroelastic/martensitic system is formed through doping point defects (excess solute atoms or alloying elements) into a normal martensitic alloy. Due to the competing interactions between randomly distributed stresses produced by the random point defects, the long-range strain ordering (lattice distortion) toward a martensite phase is prohibited and instead the system is frozen into a “strain glass” state, in which only local strain order exists.^{13,17} In the following, we shall show the experimental evidence for broken ergodicity and associated slowing down of kinetics of strain glass. We shall demonstrate clearly that the system undergoes a kinetics-governed freezing transition of locally ordered strains, in which dynamically disordered local strains (unfrozen strain glass) transform into frozen locally ordered strains (frozen strain glass) below its freezing temperature T_g .^{13,17}

The nonergodicity of frozen glass can be proved experimentally by measuring its unique characteristics, that is, the frozen glass state depends on its temperature-field history. This contrasts an ergodic system, which is history independent. A well-known experimental method for detecting the nonergodicity of glass is the so-called zero-field-cooling (ZFC)/field-cooling (FC) measurement,¹⁰ first established to prove the broken ergodicity of spin glass. Following the established ZFC/FC measurement of spin glass, the corresponding experimental process performed for the strain glass (the field herein is the tensile stress) is shown in Fig. 1. The $\text{Ti}_{48.5}\text{Ni}_{51.5}$ strain glass sample with a size of $15 \times 0.17 \times 0.15 \text{ mm}^3$ was firstly cooled to well below T_g under zero stress (ZFC, process 1). Then, it was loaded (stress = 40 MPa) and heated to far above T_g under this stress (field heating or FH, process 2). Thereafter, the sample was cooled with the stress (FC, process 3) and then heated again at the same stress (FH, process 4). The static strain curves for process 2 and process 4 are called ZFC curve and FC curve, respectively, and a deviation between the two curves is a signature for the “history dependence,” or nonergodicity, of a strain system. The strain response of the system was moni-

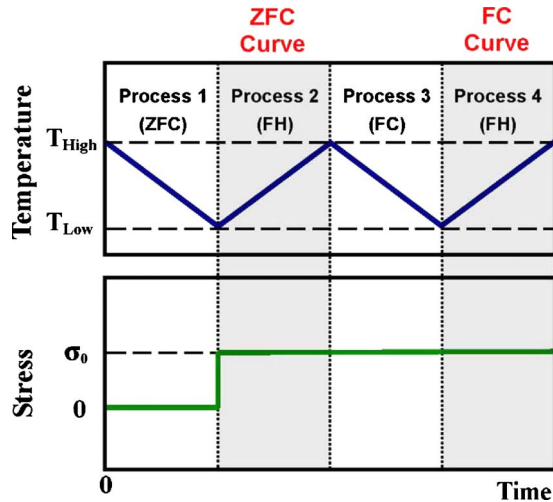


FIG. 1. (Color online) Procedure of the zero-field-cooling (ZFC)/field-cooling (FC) measurement for strain glass, which can reveal the nonergodicity of a glass system. The strain glass sample was first cooled to a temperature (T_{low}) well below the glass transition temperature T_g under zero stress (ZFC, process 1). Then, an external tensile stress was applied and the sample was heated to a temperature (T_{high}) far above T_g under this stress (field heating or FH, process 2). Thereafter, the sample was cooled to T_{low} again with the stress (FC, process 3) and then heated to T_{high} again at the same stress (FH, process 4). The static strain curves that measured in process 2 and process 4 are called the ZFC curve and the FC curve, respectively, and their deviation is a signature for nonergodicity.

tored during the whole process by a thermal mechanical analyzer with a very high strain resolution ($\sim 10^{-6}$); thus, the difference between ZFC and FC curves can be identified.

Figure 2(a) shows the ZFC/FC curves of $\text{Ti}_{48.5}\text{Ni}_{51.5}$ strain glass. The ZFC curve for $\text{Ti}_{48.5}\text{Ni}_{51.5}$ shows a peak at 168 K upon heating. By contrast, the FC curve decreases monotonically upon heating. The ZFC and FC curves of strain glass coincide at temperatures far above the peak temperature of the ZFC curve; however, they begin to deviate around the peak temperature and the deviation becomes significantly larger well below the peak temperature. The large deviation between the ZFC and FC curves below the peak temperature demonstrates that the strain state of our sample is history dependent below this temperature. This is a direct evidence for the broken ergodicity in a frozen strain glass state. The peak temperature of the ZFC curve corresponds to the freezing temperature T_g (168 K) for the strain glass. More interestingly, the ZFC/FC curves of the strain glass depicted in Fig. 2(a) exhibit striking similarity with the ZFC/FC curves for a ferroelectric relaxor and a cluster-spin glass shown in Fig. 2(b) (Ref. 12) and Fig. 2(c) (Ref. 8), respectively. As shown in Fig. 2, the ZFC peaks are quite broad and the FC curves deviate from the ZFC ones from above T_g in the three glass systems. It demonstrates that the loss of ergodicity begins from above T_g and gradually evolves during cooling through T_g . Such effect is due to existence of a distribution in the size of nanodomains; larger nanodomains lose ergodicity at higher temperature but smaller ones become nonergodic at lower temperature.¹² It is noted that spin glasses¹⁰ and dipolar glasses¹⁶ do not show such an effect; this is because they

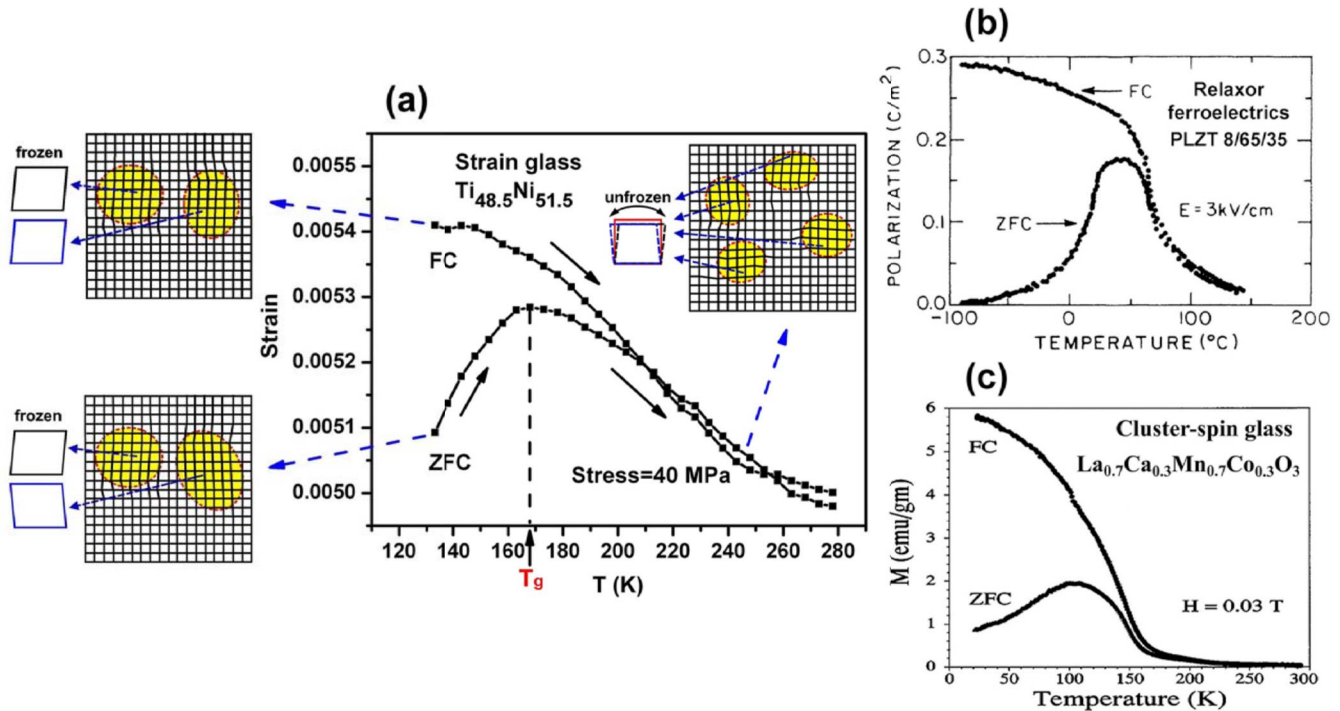


FIG. 2. (Color online) The ZFC/FC curves of strain glass in comparison to that of a ferroelectric relaxor and cluster-spin glass, which demonstrate the broken ergodicity of these glasses. (a) ZFC/FC curves of $\text{Ti}_{48.5}\text{Ni}_{51.5}$ strain glass show a large deviation below T_g (168 K), which is very similar to (b) the ZFC/FC curves of a ferroelectric relaxor [PLZT 8/65/35 (reproduced from Ref. 12)] and (c) the ZFC/FC curves of a cluster-spin glass [$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ (reproduced from Ref. 8)]. The inset depicts the unfrozen strain state above T_g , whereas the two panels on the left exhibit two different frozen strain states below T_g .

are a dilute solution of defect magnetic moments and defect electric dipoles, respectively, where no nanodomains exist. The remarkable similarity among ferroelastic/martensitic glass (strain glass), ferroelectric glass (relaxor ferroelectric), and ferromagnetic glass (cluster-spin glass) can be understood within the framework of a more general *ferroic glass*, which appears to be governed by a common feature of frozen short-range order, although the physical nature of the order (viz., strain, dipole, and magnetic moment) and the microscopic origin of these glasses are quite different.

The broken ergodicity of strain glass, i.e., the deviation of the ZFC and FC curves of static strain, can be understood by the slowing down of strain kinetics in strain glass. When the strain glass is cooled down with different histories (ZFC or FC), different configurations of the local orientational variants of strain are frozen. In the ZFC process (process 1), local variants are frozen in random orientations at the temperature below T_g , which results in an averaged zero strain. However, in the FC process (process 3), the local variants tend to align along the direction of dc stress and thus are frozen in a more orderly fashion below T_g , so a nonzero average strain will result. In the FH process (process 2) after the ZFC process, the disordered configuration of local variants frozen in ZFC is essentially unchanged when the specimen was loaded at a temperature well below T_g because it takes a very long time (much longer than the experimental time) to relax to a more ordered configuration. Thus, the static strain at the lowest temperature (143 K) of the ZFC curve is much smaller than that of the FC curve. With increasing temperature, the difference between ZFC and FC becomes smaller because the relaxation time for traversing from a disordered local-variant configuration to a more ordered one becomes shorter. At a temperature far above T_g , the relaxation time becomes sufficiently short and the strain glass is in its ergodic state, which is independent of system history, so the ZFC curve and the FC curve of the strain glass essentially overlap.

Next, we provide direct evidence for the slowing down of kinetics during the strain glass transition of our sample. Figure 3(a) shows the creep (strain relaxation at constant stress) curves for $\text{Ti}_{48.5}\text{Ni}_{51.5}$ strain glass at different temperatures spanning its T_g (=168 K). Above T_g , the creep strain saturated very fast with time, which is a signature of a fast kinetics with short relaxation time. As the temperature approaches T_g , the relaxation of the creep strain becomes slower. When the temperature is well below T_g , the creep strain increases monotonically and exhibits no saturation within the test time; this clearly demonstrates a slow kinetics with very long relaxation time.

The relaxation behavior of the strain glass can be quantitatively fitted with the Kohlrausch-Williams-Watts relation, $\varepsilon(t)/\varepsilon(0) = a + b \exp[-(t/\tau)^\beta]$, which has been used to describe the kinetics of orientational glasses.¹⁵ Here, τ is an approximate average relaxation time of the relaxation spectrum of the glass system and β is an exponent in the stretched exponential.¹⁸ $\beta=1$ corresponds to an ideal Debye relaxation and $\beta=0$ corresponds to a relaxation with infinite relaxation time. Figure 3(b) shows the temperature dependence of relaxation time τ and the exponent β . With decreasing temperature from above T_g to below T_g , the relaxation

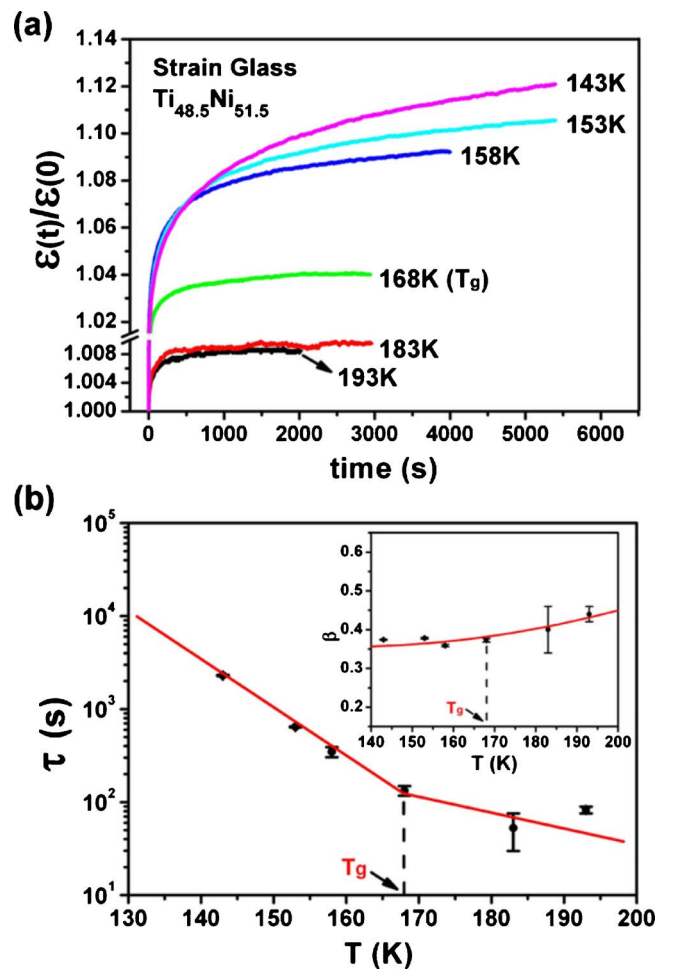


FIG. 3. (Color online) The slowing down of kinetics of $\text{Ti}_{48.5}\text{Ni}_{51.5}$ strain glass. (a) The kinetics of strain relaxation in strain glass measured at different test temperatures, where $\varepsilon(t)/\varepsilon(0)$ is a normalized strain. (b) Average relaxation time τ and the exponent β (inset) as a function of temperature, which were obtained by fitting curves in (a) with the Kohlrausch-Williams-Watts relation, $\varepsilon(t)/\varepsilon(0) = a + b \exp[-(t/\tau)^\beta]$. The lines are guides for the eye. The experiment was performed with a dynamic mechanical analyzer in a three-point bending mode. The $\text{Ti}_{48.5}\text{Ni}_{51.5}$ strain glass sample with a size of $60 \times 7 \times 0.75 \text{ mm}^3$ was cooled to different test temperatures spanning T_g at zero field (stress) first; then, it was suddenly loaded with a constant stress (20 MPa), and subsequently a time dependent relaxation of strain, i.e., the creep curve of strain, was recorded.

time τ shown in Fig. 3(b) increases by 2 orders of magnitude, which clearly demonstrates the slowing down of kinetics in the strain glass. The $\log \tau$ - T curve shows a change in slope in the vicinity of T_g . The slope of the $\log \tau$ - T line below T_g is larger than that above T_g . This feature is apparently different from that of a structural glass. In addition, the inset of Fig. 3(b) shows that the exponent β also decreases with decreasing temperature. The exponent β is quite different from 1 in the whole temperature regime studied; this indicates that the glass system possesses a complex relaxation process with a distribution of relaxation time^{2,4} rather than a simple Debye relaxation with a single relaxation time.

The origin of strain glass transition and the associated broken ergodicity can be explained as follows. Strain glass is a system that is formed by doping point defects into a normal martensitic system. These random point defects distort the surrounding crystal lattice and thus generate random local stresses. The random distribution of local stresses brings about significant effects. Firstly, the long-range strain ordering is prohibited and instead a frozen local strain ordering is formed. This is because the random local stresses dictate a random local strain order, so a long-range strain ordering becomes inaccessible. As a result, during cooling, the system has no choice but to freeze into a frozen disordered state, i.e., the strain glass. This is the origin of strain glass. Secondly, such a strain glass system is ergodic at $T > T_g$ and gradually becomes nonergodic at $T < T_g$. At high temperature ($T > T_g$), thermal activation energy $k_B T$ (k_B is Boltzmann's constant) is sufficiently high to overcome the energy barrier (created by local stresses) for the nanodomains (local strain order) to switch from one strain orientation to another; thus, the domains switch freely from one state to other possible states, i.e., the unfrozen glass is ergodic. However, when the system is cooled to $T < T_g$, the thermal activation energy $k_B T$ becomes lower than the local energy barrier. Then, the nanodomains gradually become immobile or frozen. This results in a frozen strain glass state with frozen disordered local strains. Since the nanodomains can no longer switch to other

possible orientations in the frozen strain glass, the ergodicity of the system is broken.

In conclusion, we proved experimentally the broken ergodicity and the associated slowing down of kinetics for strain glass. These two attributes of strain glass provide an essential proof for the existence of frozen strain glass state and strain glass transition in a ferroelastic/martensitic system. Notably, the ZFC/FC curves of the strain glass bear a striking similarity with the ZFC/FC curves of a cluster-spin glass and a ferroelectric relaxor, despite the large differences in their physical nature. We thus introduced the notion of a ferroic glass. Clearly, multiferroic glasses could also exist with two or more ferroic properties being simultaneously glassy. A recent study¹⁹ seems to indicate the existence of a simultaneous freezing of the charge, spin, and strain degrees of freedom. Our work suggests that the formation of all these seemingly different glasses is governed by a common physical principle: the destruction of long-range order due to strong quenched-in (or frozen) disorder.

The present work was supported by Grant-in-Aid for Scientific Research (B) of JSPS, National Science Foundation of China, National Basic Research Program of China under Grant No. 2004CB619303, as well as the 111 Project of China. We thank T. Suzuki, S. Sarkar, G. L. Fan, Y. M. Zhou, and J. Zhang for technical support and helpful discussions.

*Author to whom correspondence should be addressed; ren.xiaobing@nims.go.jp

¹B. Jérôme and J. Commandeur, *Nature (London)* **386**, 589 (1997).

²K. Binder and A. P. Young, *Rev. Mod. Phys.* **58**, 801 (1986).

³L. Santen and W. Krauth, *Nature (London)* **405**, 550 (2000).

⁴J. A. Mydosh, *Spin Glasses* (Taylor & Francis, Philadelphia, 1993).

⁵R. G. Palmer, *Adv. Phys.* **31**, 669 (1982).

⁶M. Buchanan, *Nature (London)* **435**, 281 (2005).

⁷D. L. Stein, in *Decoherence and Entropy in Complex Systems*, edited by H.-T. Elze (Springer, Berlin, 2003).

⁸N. Gayathri, A. K. Raychaudhuri, S. K. Tiwary, R. Gundakaram, A. Arulraj, and C. N. R. Rao, *Phys. Rev. B* **56**, 1345 (1997).

⁹D. Hüser, L. E. Wenger, A. J. van Duynveldt, and J. A. Mydosh, *Phys. Rev. B* **27**, 3100 (1983).

¹⁰S. Nagata, P. H. Keesom, and H. R. Harrison, *Phys. Rev. B* **19**,

1633 (1979).

¹¹G. A. Samara, *J. Phys.: Condens. Matter* **15**, R367 (2003).

¹²D. Viehland, J. F. Li, S. J. Jang, L. E. Cross, and M. Wuttig, *Phys. Rev. B* **46**, 8013 (1992).

¹³S. Sarkar, X. Ren, and K. Otsuka, *Phys. Rev. Lett.* **95**, 205702 (2005).

¹⁴J. Hessinger and K. Knorr, *Phys. Rev. Lett.* **65**, 2674 (1990).

¹⁵J. Hessinger and K. Knorr, *Phys. Rev. B* **47**, 14813 (1993).

¹⁶U. T. Höchli, P. Kofel, and M. Maglione, *Phys. Rev. B* **32**, 4546 (1985).

¹⁷Y. Wang, X. Ren, and K. Otsuka, *Phys. Rev. Lett.* **97**, 225703 (2006).

¹⁸S. H. Chung and J. R. Stevens, *Am. J. Phys.* **59**, 1024 (1991); G. F. Signorini, J. L. Barrat, and M. L. Klein, *J. Chem. Phys.* **92**, 1294 (1990).

¹⁹P. A. Sharma, S. B. Kim, T. Y. Koo, S. Guha, and S-W. Cheong, *Phys. Rev. B* **71**, 224416 (2005).