A magnetic glass state over the first-order ferromagnetic-to-antiferromagnetic transition in FeRh film

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ABSTRACT

The intermetallic FeRh system has displayed tremendous fascination to investigators due to its remarkable physical properties and potential applications. Here we synthesized near-equiatomic FeRh films on MgO (001) substrate by magnetron co-sputtering of Fe and Rh, and our results revealed a magnetic glass (MG) state existing after field cooling to low temperature. The MG state is nonequilibrium with a configuration of metastable supercooled ferromagnetic (FM) and equilibrium antiferromagnetic (AFM) phases, and arises from a kinetic arrest of the first-order FM–AFM phase transition. Our finding is beneficial to a better understanding of the underlying mechanism of the FeRh phase transition.

IMPACT STATEMENT

The presence of magnetic glass state over ferromagnetic–antiferromagnetic transition in co-sputtered FeRh film is certified, and may benefit the understanding of the origin of FeRh phase transition and the communities of multiferroic.

A binary alloy FeRh has recently attracted ever-increasing amount of interests for both experimental and theoretical studies, primarily due to its nontrivial fundamental properties [1–3]. The ordered FeRh near-equiatomic composition adopts CsCl structure and undergoes a paramagnetic to ferromagnetic (FM) transition at around 670 K and a ferromagnetic to antiferromagnetic (FM–AFM) transition at around 370 K [4,5]. Unlike the general magnetic phase transition, the latter FM–AFM transition of FeRh is a first-order transition, accompanied by an abrupt volume contraction in unit cell of about 1% and a large isothermal magnetic entropy change [6,7]. Besides, experiments have evidenced strong changes in the electronic structures during the magnetic phase transition, accompanied by a giant magnetoresistance effect with a relative change of about 50% [8–10].

The similar first-order transition is not new, but has been observed in some other systems, such as Gd$_3$Ge$_4$ and Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$ [11,12]. However, FeRh is more attractive mainly because its phase transition occurs just above room temperature, and the transition temperature ($T_t$) is sensitive to the chemical substitution [13] and various external fields, including strain [14–17], pressure [18], spin-polarized current [19] and magnetic field [20]. For instance, it is reported that Pt or Ir doping can increase $T_t$ of FeRh, while Ni, Pd or Au doping decrease it [6]. Plenty of experiments have also shown that external magnetic field is beneficial to stabilize the FM phase and decrease $T_t$ at a rate of $\sim 8$ K/T. Besides, the compressive in-plane strain on FeRh will drive the system into more AFM dominate state. Using this concept, Lee et al. and Cherifi et al. involved FeRh in the multiferroic systems and reported the FM–AFM transition and the related magnetization or magnetic resistance could be manipulated by piezoelectric strain in FeRh/ferroelectric heterostructures [14,15,17]. The aforementioned features...
make FeRh a potential candidate for applications of sensors, energy conversion and heat-assisted magnetic recording devices [21,22].

In spite of these advantages and applications of FeRh, the underlying mechanism of this characteristic transition is still under debate. Scientists have made great efforts to clarify it, trying to study the driving force and the domain evolution of the metamagnetic transitions [23–26]. A FM/AFM phase separation, that is, coexistence of FM and AFM phases, was previously observed during the FM–AFM transition. For example, Phillips et al. [14] observed a FM/AFM phase separation on a ~1-μm length scale across the transition by using photoelectron emission microscopy with X-ray excitation (XPEEM); Lee et al. [15] certified the separation and found that the proportion of FM phases reduced and AFM phases increased with lowering the temperature by using magnetic force microscopy (MFM). In this study, we prepared near-equatomic FeRh films and carefully examined the magnetic properties of the FeRh film over the FM–AFM transition. The phenomena are coincided with typical features of magnetic glass (MG) state, which implies a nonequilibrium magnetic state with a configuration of AFM phase and metastable supercooled FM phase clusters frozen randomly in experimental time scale.

In experiment, we used magnetron co-sputtering from separate Fe and Rh targets, and adjusted the parameters to grow near-equatomic FeRh films on MgO (001) substrates with a total growth rate of about 0.1 nm/s and a film thickness of about 150 nm. The base pressure was set to be 3 × 10−7 Torr, the argon pressure during growth was 2 mTorr and the substrate temperature was 673 K. After deposition, the films were annealed at 973 K for 1 h with the base pressure to promote the chemical ordering. The crystal structure and epitaxy of the films were characterized by X-ray diffractometer (XRD, Rigaku D, Japan). The thickness and stoichiometry were measured via field emission scanning electron microscope (SEM, Hitachi S-4800) and equipped energy dispersive spectrometer (EDS). Magnetic properties were measured using superconducting quantum interference device (SQUID), by which zero-field cooled warming (ZFCW), field cooled cooling (FCC) and field cooled warming (FCW) procedures were performed to examine the temperature and magnetic field dependence of the magnetization. In the ZFCW mode, the sample was cooled down to 50 K from 400 K without magnetic field, and then the measurement was performed while warming up the sample with the measuring magnetic field. In the FCC and FCW mode, the measuring field was applied at 400 K and then the measurement was made while cooling down to 50 K and warming up to 400 K. The time dependence of magnetization was also measured by SQUID.

The X-ray diffraction spectra are shown in Figure 1(a). Clear (001) and (002) reflection peaks of the chemically ordered FeRh (α' phase) structure are observed in the θ-2θ scan, indicating the ordered FeRh film with CsCl structure was obtained. The φ scan of the [110] peaks of the FeRh (inset of Figure 1(a)) exhibits a four-fold symmetry characteristic, indicating an epitaxial growth of the FeRh film on MgO (001) substrate. Following the procedure described by Warren [27], the chemical order parameter of the film is determined to be $S = 0.823$, where the quantity $S$ is the fraction of Fe(Rh) sites occupied by Fe(Rh) atoms. $S = 0$ when the atoms are randomly distributed and $S = 1$ for the perfect order. The imperfect chemical order of the film is also indicated by the appearance of a tiny peak near 48° in θ-2θ pattern, which corresponds to the γ phase, that is, Rh-rich FeRh. Given the co-deposition growth, it is likely that there exists a composition fluctuation of Fe and Rh. As shown in the EDS mapping (Figure 1(b)), the distribution of Fe is somewhat heterogeneous, while the distribution of Rh is approximately homogeneous. Besides, EDS elemental data of four spots were collected and the Fe/Rh atomic ratios were 0.528:0.472, 0.605:0.395, 0.596:0.404 and 0.523:0.478, respectively. The composition fluctuation is considered to be the origin of the following magnetic properties.

The temperature-dependent magnetization ($M$–$T$ curves) of the FeRh film was first measured with the in-plane magnetic field of 10 kOe (Figure 2(b)). During warming (ZFCW and FCW procedures), the sharp AFM–FM transition above room temperature is normal and similar to the previous reports. From the differential of magnetization, the AFM–FM transition temperature $T_\text{c}$ is determined to be 360 K (Figure 2(d)). In FCC procedure, magnetic responses with temperature were divided into two stages during the FM–AFM transition. First magnetization decreases rapidly from 340 K (the starting temperature of transition $T_\text{d}$) to a turning point around 310 K with a thermal hysteresis of about 35 K, corresponding to a fast dynamic of FM–AFM transition. This stage is in accordance with the nature of the first-order magnetic phase transition. Then the magnetization turns to decrease more gradually along with lowering temperature from 310 to 50 K. Besides the turning point, a small bifurcation (∼10 emu/cm³) is observed between ZFCW and FCW curves at low temperature range (insets of Figure 2(b)). This bifurcation is typically a kind of thermomagnetic irreversibility (TMI). In order to further examine it, similar $M$–$T$ measurements were performed with different magnetic fields of...
Figure 1. (a) $\theta$-2$\theta$ XRD pattern of FeRh film on MgO (001) substrate. The insert shows the $\phi$-scan XRD pattern of the (110) FeRh peaks and (b) SEM image and the EDS mappings of Fe and Rh elements in the same area of the FeRh film.

Figure 2. Magnetization ($M$) vs. temperature ($T$) plots for FeRh film obtained in ZFCW, FCC and FCW procedures in different measuring fields (a) $H_m = 5$ kOe, (b) $H_m = 10$ kOe and (c) $H_m = 20$ kOe. The insets show the magnified versions of the data at low temperature. (d) $dM/dT$ vs. $T$ plots of FCC and FCW procedures in (b).
5 and 15 kOe, as shown in Figure 2(a) and 2(c). With the increase in magnetic field, the TMI of magnetization becomes more prominent. This is in striking contrast to the spin-glass state, in which TMI phenomenon is obvious at low magnetic field and gets unapparent at high field [28,29], as observed in nanocrystalline fcc phase FeRh [30]. From literature [29,31], such magnetic field dependent magnetization bifurcation between ZFCW and FCW curves is regarded to be a product of kinetic arrest of the first-order FM–AFM transition, which gives rise to a MG state. ‘Kinetic arrest’ here represents the viscous retardation of nucleation and growth of the low temperature AFM phase out of a metastable supercooled FM phase. Such MG state has been reported in several magnetic systems such as Ce(Fe0.96Ru0.04)2 and La2/3Pr0.41Ca3/8MnO3 and doped FeRh with relatively low $T_{St}$. And the AFM and FM phases in the MG state have long-range magnetic orders, indicating the MG is independent of the underlying microscopic nature of magnetic interactions [32–36]. On this view, the FeRh film in our experiment could be regarded to be a completely FM phase above $T_{St}$, while a MG state with equilibrium AFM and supercooled FM phases frozen randomly and some stable FM phases at low temperature, as schematically shown in Figure 3. The stable FM phase may come from the slightly Fe-rich FeRh and disordered equiatomic FeRh, contributing to the magnetization of over 200 emu/cc at low temperature in ZFCW procedure [37,38].

In order to verify the MG state, we further performed the magnetization relaxation measurements at certain temperatures. In MG state, the supercooled FM phase is metastable and there is a free energy barrier separating it from the equilibrium AFM phase. From the energy perspective, a slow transformation from the supercooled FM to equilibrium AFM phase would occur due to the thermal activation, and the transition is influenced by a competition between the thermal energy of the supercooled FM phase and the energy barrier between the FM and AFM phases. Therefore, the magnetization of the MG state shows relaxation behaviors at certain temperature in the FCC procedure, as shown in Figure 4.

On the contrary, the spin-glass state is an equilibrium state in the FCC procedure and no relaxation of magnetization can be observed [29]. In Figure 4, cooling the film from 400 K to the measured temperature with magnetic field of 10 kOe, $M_0$ was obtained after stabilizing at the certain temperature. At the temperature above $T_g$ (the forming temperature of glass state, i.e. the turning point of about 310 K in our case), for example, 335 K, as the transition experiences a dynamic process and the $M/M_0$ data can be well fitted with the power law equation: $M(t)/M_0 = -1 + 2t^{\gamma}$, probably resulting from the coexisting FM and AFM clusters created by the heterogeneous nucleation of AF domains. The value of $\gamma$ indicates the extent of relaxation and is negative here [32]. FM phase converts to the equilibrium AFM phase at a great speed, that is also reflected by the rapid drop of $M$ from 340 to 310 K in Figure 2. On decreasing the temperature below $T_g$, the FM phase starts to transform into a metastable supercooled FM phase. The barrier between metastable FM phase and equilibrium AFM phase competes with thermal energy, resulting in different magnetization relaxations. Specifically, at 250 K, $M$ decreases slowly owing to the comparatively higher barrier, which hinders the transition from metastable FM phase to equilibrium AFM phase. And at 175 K, $M$ drops relatively fast, due to the comparatively larger kinetic energy. But below $T^*$ (the limit temperature of supercooling [31], that is, about 60 K in 1 T, where dM/dT of the FCC curve merges with that of FCW curve, as shown in Figure 2(d)), for example, 50 K, $M$ only presents a weeny change as a consequence of tiny thermal energy though the barrier vanishes. So the metastable supercooled FM phase...
phase emerges at $T < T_g$ and the kinetics of the transformation to AFM phase gets arrested, resulting in the gradual decrease of $M$ and the TMI phenomenon. As shown in Figure 4, the relaxation data fit well with the Kohlrausch–Williams–Watt (KWW) stretched exponential function $M(t)/M_0 \propto \exp\left[\left(-t/\tau\right)^\beta\right]$, where $\tau$ is the characteristic relaxation time and $\beta$ is a shape parameter [34,39]. The values of $\beta$ here are 0.85, 0.8 and 0.75 for curves at 50, 175 and 250 K, respectively. The stretched exponential function is a typical hallmark of glassy dynamics and has been well studied to interpret the time relaxation of the MG state in recent studies [31,33]. Besides, the magnetization relaxation measurements in ZFCW procedure at 50, 175 and 250 K were also performed. As they all look identical, the representative data obtained at 250 K were added in Figure 4 for simplicity. Compared with the MG state in the FCC procedure, the change in $M/M_0$ with time in the ZFCW state is negligible and the ZFCW state can be regarded as an equilibrium state, consistent with the typical features of systems with MG [29].

Another feature of MG state is the lack of end-point memory after field cycling in FCC procedure because the metastable supercooled FM in MG state can be erased by field cycling. The isothermal magnetic hysteresis cycles of this FeRh film were performed after field cooling (10 kOe) from 400 K, and exhibited the typical feature as shown in Figure 5. By continuously cycling the magnetic field in the range of 10–0 Oe, it is clearly manifested that the magnetizations measured at a certain end-point magnetic field (10 kOe here) are different in every cycle, that is, lack of end-point memory. While a spin-glass state in the FCC procedure is known to be equilibrium and the magnetization hysteresis loops show end-point memory [35]. The MG state in FeRh films has not been reported in previous studies from stoichiometric FeRh alloy target. According to previous research [35,36,40], the formation of the MG state presumably originates from the composition fluctuations or disorders. As discussed above the film grown by magnetron co-sputtering in this case are partially chemical composition heterogeneous, it is likely to form the MG state.

In summary, the existence of an MG state over the first-order FM–AFM transition was certified by three typical features in the co-sputtered FeRh film, including a more prominent TMI phenomenon at higher magnetic fields, the magnetization relaxation and a lack of end-point memory after field cycling in FCC procedure. During field cooling, the kinetic of the transformation from supercooled FM phase to AFM phase gets arrested when $T < T_g$, and the supercooled FM phase can persist at a low temperature. That is, the FeRh thin film exhibits a complete FM phase above the transition temperature, and a MG state with the coexistence of equilibrium AFM and metastable FM phases at a low temperature. Studying the magnetic response during phase transition is benefit to further explore the origin of the first-order transition of FeRh and promote advance applications in spintronics.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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