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Ageing dynamics of ferromagnetic and re-entrant spin glass phases in a stage-2 $Cu_{0.80}Co_{0.20}Cl_2$ graphite intercalation compound

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Abstract

Ageing dynamics of a re-entrant ferromagnet stage-2 $Cu_{0.8}Co_{0.2}Cl_2$ graphite intercalation compound has been studied using DC magnetization measurements. This compound undergoes successive transitions at the transition temperatures T_c ($\approx$8.7 K) and T_{RSG} ($\approx$3.3 K). The relaxation rate $S_{ZFC}(t)$ exhibits a characteristic peak at t_{cr} below T_c. The peak time t_{cr} at constant t_w shows a local maximum around 5.5 K, indicating a slow dynamics arising from a frustrated nature of the ferromagnetic phase. It drastically increases with decreasing temperature below T_{RSG}. The spin configuration imprinted at the stop and wait process at a stop temperature T_s ($<T_c$) during the field-cooled ageing protocol becomes frozen on further cooling. On reheating, the memory of the ageing at T_s is retrieved as an anomaly of the thermoremnant magnetization at T_s. These results indicate the occurrence of the ageing phenomena in the ferromagnetic phase ($T_{RSG} < T < T_c$) as well as in the re-entrant spin glass phase ($T < T_{RSG}$).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, the slow dynamics of re-entrant ferromagnets has been extensively studied from the time evolution of the magnetization $M(t)$ and the absorption of AC magnetic susceptibility $\chi''(t)$ after the appropriate ageing protocol [1–9]. The re-entrant ferromagnet undergoes two phase transitions at the critical temperatures T_{RSG} and T_c ($T_c > T_{RSG}$): the re-entrant spin glass (RSG) phase below T_{RSG} and the ferromagnetic (FM) phase between T_{RSG} and T_c. The ageing behaviour in the RSG phase has been reported in many re-entrant ferromagnets, including $(Fe_{0.20}Ni_{0.80})_{75}P_{16}B_6Al_3$ [1–4], $CdCr_{2x}In_{2(1-x)}S_4$ (x = 0.90, 0.95, and 1.00) [5–7], and the $Cu_{0.2}Co_{0.8}Cl_2$–$FeCl_3$ graphite bi-intercalation compound (GBIC) [8, 9]. The ageing behaviour of the RSG phase is similar to that of the spin glass (SG) phase of spin glass systems. In contrast, there have been few reports on the observation of the ageing behaviour in the FM phase. The measurement of the relaxation rate $S(t)$ $(=(1/H)\mathrm{d}M(t)/\mathrm{d}\ln t)$ for $(Fe_{0.20}Ni_{0.80})_{75}P_{16}B_6Al_3$ [1–4] and $Cu_{0.2}Co_{0.8}Cl_2$–$FeCl_3$ GBIC [8, 9] has revealed that not only the RSG phase but also the FM phase exhibit ageing phenomena. For $CdCr_{2x}In_{2(1-x)}S_4$ with $x = 0.90, 0.95$, and 1.0 [5–7], the ageing behaviour of the absorption $\chi''(\omega, t)$ is observed both in the FM and RSG phases.

In this paper we report our experimental results on the nonequilibrium ageing dynamics of the FM phase and the RSG phase in the re-entrant ferromagnet, stage-2 $Cu_{0.8}Co_{0.2}Cl_2$ graphite intercalation compound (GIC) using DC magnetization measurements. This system undergoes magnetic phase transitions at $T_{\mathrm{RSG}} \approx 3.30$ K and $T_{\mathrm{c}} \approx 8.70$ K [10, 11]. We examine the ageing behaviour of this system using the zero-field-cooled (ZFC) magnetization measurements. The relaxation rate $S_{\mathrm{ZFC}}(t)$ exhibits a peak at a characteristic time t_{cr} below T_{c}, indicating the occurrence of the ageing phenomena both in the RSG phase and the FM phase. We will also show that the t dependence of $S_{\mathrm{ZFC}}(t)$ around $t \gtrsim t_{\mathrm{w}}$ is well described by a stretched exponential relaxation (SER), $S_{\mathrm{ZFC}}(t) \approx (t/\tau)^{1-n} \exp[-(t/\tau)^{1-n}]$, where t_{w} is a wait time, n is an SER exponent and τ is an SER relaxation time which is of the same order as t_{cr} (experimentally). The temperature dependence of t_{cr} and τ shows a very characteristic behaviour, which is very similar to that observed in $Cu_{0.2}Co_{0.8}Cl_2$–$FeCl_3$ GBIC [9]. We will also report two kinds of the memory phenomena in the measurement of thermoremnant magnetization (TRM) and the field-cooled (FC) magnetization. When the system is cooled down, a memory of the cooling process is imprinted in the spin structure. This memory is recalled in a continuous heating measurement. The TRM and FC magnetization curves are recovered on heating the system after the specific cooling protocols. The comparison of these curves yields information on the ageing and memory effects.

2. Experimental procedure

We used the same sample of stage-2 $Cu_{0.8}Co_{0.2}Cl_2$ GIC as was used in the previous papers [10, 11]. The details of the sample characterization and synthesis were presented there. The stoichiometry of this compound is described by $C_xCu_{0.80}Co_{0.20}Cl_2$ with $x = 11.04 \pm 0.02$. The c-axis repeat distance is given by $d_c = 12.83 \pm 0.05$ Å. The DC magnetization and AC magnetic susceptibility were measured using a SQUID magnetometer (Quantum Design, MPMS XL-5) with an ultra-low field capability option. The remnant magnetic field was reduced to zero (specifically, less than 3 mOe) at 298 K. The experimental procedure for each measurement is presented in the text and figure captions. The DC magnetic susceptibility for $150 \leqslant T \leqslant 298$ K obeys a Curie–Weiss law with the Curie–Weiss temperature $\Theta = 2.52 \pm 0.22$ K and the average effective magnetic moment $P_{\mathrm{eff}} = 2.98 \pm 0.02\mu_{\mathrm{B}}$. For the AC susceptibility, the amplitude of the AC magnetic field h was 50 mOe and the AC frequency f ranged between 0.01 and 1000 Hz.

After the ZFC ageing protocol (see section 3.2 for details), $M_{\mathrm{ZFC}}(t)$ was measured as a function of t. The relaxation rate defined by $S_{\mathrm{ZFC}}(t)$ $(=(1/H)\mathrm{d}M_{\mathrm{ZFC}}(t)/\mathrm{d}\ln t)$ exhibits a peak at a characteristic time t_{cr} [12]. Theoretically [13, 14] and experimentally [15–21] it has been noticed that the time variation of the ZFC susceptibility $\chi_{\mathrm{ZFC}}(t)$ $(=M_{\mathrm{ZFC}}(t)/H)$ may be described by an SER form

$$\chi_{\mathrm{ZFC}}(t) = \chi_0 - A(t/\tau)^{-m} \exp[-(t/\tau)^{1-n}], \tag{1}$$

where χ_0 and A are constants, m may be a positive exponent and is very close to zero, n is an SER exponent, and τ is an SER relaxation time. In the present work, we consider only the case of $m = 0$, which may be suitable for the description of the long-time ageing behaviour for

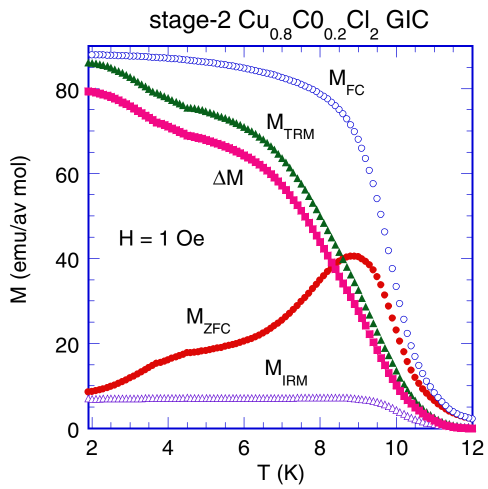

Figure 1. T dependence of M_{FC}, M_{ZFC}, M_{TRM}, M_{IRM}, and ΔM (=$M_{\mathrm{FC}} - M_{\mathrm{ZFC}}$). H (or H_c) = 1 Oe, which is applied along the c plane (perpendicular to the c axis). H_c is the magnetic field during the FC ageing protocol. The details of the cooling protocol for each magnetization are described in the text. The remnant field effect is corrected for each curve of M versus T.

$t \gtrsim t_{\mathrm{cr}}$. Then the relaxation rate $S_{\mathrm{ZFC}}(t)$ can be described by

$$S_{\mathrm{ZFC}}(t) = S^0_{\max} F(n, t/\tau), \tag{2}$$

using a scaling function $F(n, \xi)$ (=$e\xi^{1-n}\exp(-\xi^{1-n})$), where $S^0_{\max} = A(1-n)/e$ and e (=2.7182) is the basis of the natural logarithm. This relaxation rate $S_{\mathrm{ZFC}}(t)$ has a peak (=$S^0_{\max}$) at a characteristic time $t = \tau$.

3. Result

3.1. Magnetic phase transitions at T_{RSG} and T_c

We have measured the T dependence of the ZFC magnetization M_{ZFC}, the FC magnetization M_{FC}, the TRM magnetization M_{TRM}, and the isothermal remnant magnetization M_{IRM}. We used two types of cooling protocol: (i) the ZFC ageing protocol consisting of annealing at 50 K for 1.2×10^3 s and cooling from 50 to 1.9 K in the absence of H, and (ii) the FC ageing protocol consisting of annealing at 50 K for 1.2×10^3 s and cooling from 50 to 1.9 K in the presence of the magnetic field H_c. The magnetization M_{ZFC} was measured with increasing T in the presence of H (=1 Oe) after the ZFC ageing protocol. The magnetization M_{TRM} was measured with increasing T in the absence of H after the FC ageing protocol. The magnetization M_{FC} was measured with decreasing T during the FC ageing protocol. The magnetization M_{IRM} was measured with increasing T immediately after the ZFC ageing protocol was completed at $T = 1.9$ K and then the magnetic field H (=1 Oe) was applied at $T = 1.9$ K for $t = 1.0 \times 10^2$ s and was turned off. Figure 1 shows the T dependence of M_{ZFC}, M_{FC}, M_{TRM}, M_{IRM}, and ΔM (=$M_{\mathrm{FC}} - M_{\mathrm{ZFC}}$) at H (or H_c) = 1 Oe. Note that the effect of the remnant magnetic field was corrected by the subtraction of the magnetization M_{corr}, which was measured with decreasing T under the remnant magnetic field (3 mOe). The magnetization M_{ZFC} has a shoulder around $T = 3.5$ K and a peak at $T = 9.0$ K. The deviation of M_{ZFC} from M_{FC} appears below $T_f = 12.5$ K, implying that the irreversible effect of magnetization occurs below this temperature. The magnetization M_{FC} drastically increases with decreasing T below 10 K.

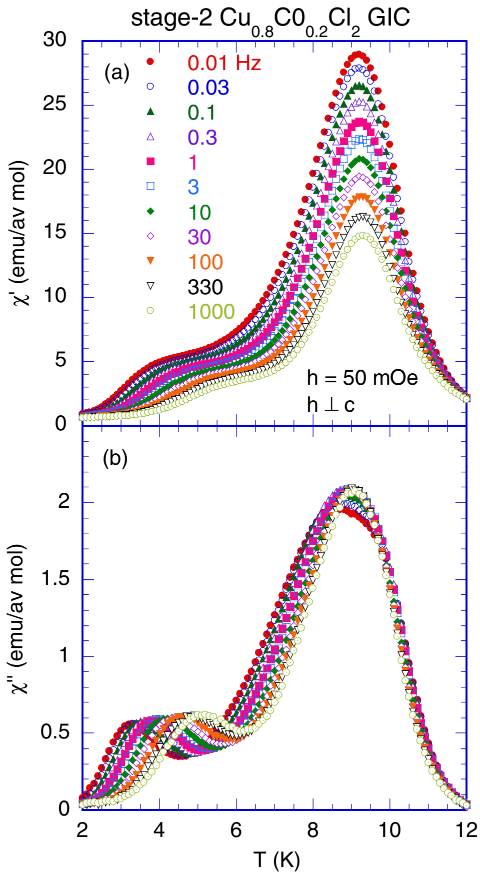

Figure 2. T dependence of the AC magnetic susceptibility at various frequencies f: $\omega = 2\pi f$. (a) The dispersion $\chi'(\omega, T)$ and (b) the absorption $\chi''(\omega, T)$. $h = 50$ mOe. $H = 0$. $h \perp c$.

Figure 2 shows the T dependence of χ' and χ''. The absorption χ'' has two peaks at T_{RSG} and T_c. The peak at T_{RSG} shifts to the high-T side with increasing f: 3.20 K at $f = 0.007$ Hz and 5.12 K at 1 kHz. The peak at T_c slightly shifts to the high-T side with increasing f: 8.7 K at $f = 0.01$ Hz and 9.1 K at 1 kHz. The dispersion χ' has a single peak and a shoulder. The peak shifts slightly from 9.20 to 9.30 K with increasing f from 0.01 Hz to 1.0 kHz, while the shoulder shifts greatly from 3 to 6 K. The peak height is strongly dependent on f. The details of the analysis on the T and f dependence of χ' and χ'' were described by our previous paper [10]. From these results it may be concluded that our system undergoes phase transitions at T_c ($\approx$8.7 K) and T_{RSG} ($\approx$3.3 K). The low temperature phase below T_{RSG} is an RSG phase and the intermediate phase between T_{RSG} and T_c is an FM phase.

3.2. Ageing behaviour of $S_{ZFC}(t)$

In order to confirm the existence of the ageing behaviour, we have measured the t dependence of the ZFC magnetization $M_{ZFC}(t)$ at various T. Our system was cooled from 50 K to T (1.9 K $\leqslant T \leqslant$ 9 K) in the absence of an external magnetic field. This ZFC ageing process is completed at $t_a = 0$, where t_a is defined as an age (the total time after the ZFC ageing protocol process). The system is isothermally aged at T until $t_a = t_w$, where t_w

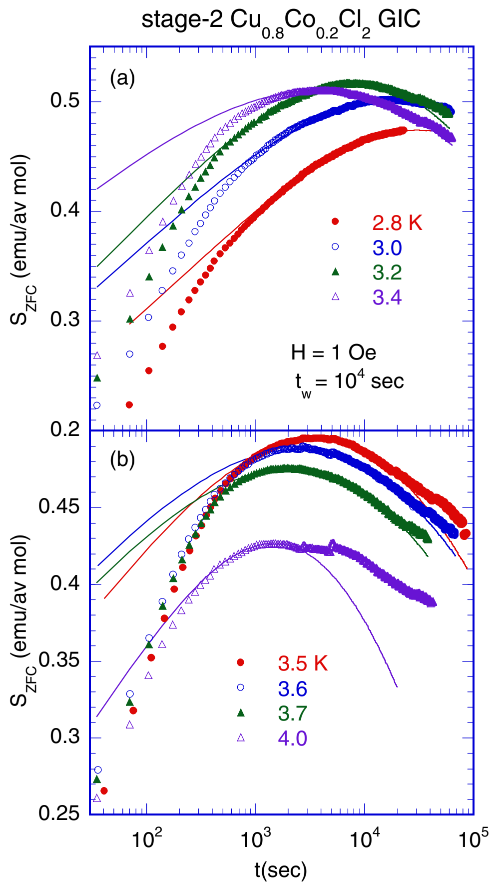

Figure 3. t dependence of the relaxation rate S_{ZFC} $(=(1/H)\,dM_{ZFC}(t)/d\ln t)$ at various T. (a) $T = 2.8$–3.4 K. (b) $T = 3.5$–4.0 K. Each measurement was carried out after the ZFC ageing protocol: annealing of the system at 50 K for 1.2×10^3 s at $H = 0$, quenching from 50 K to T, and then isothermal ageing at T and $H = 0$ for a wait time t_w $(=1.0 \times 10^4$ s). The M_{ZFC} measurement was started at $t = 0$ when the field H (=1 Oe) was turned on. The solid lines denote the least-squares fitting curves to (2). The parameters τ, n, and S^0_{max} are given in figure 5.

$(2.0 \times 10^3 \leqslant t_w \leqslant 3.0 \times 10^4$ s) is a wait time. The magnetic field H (=1 Oe) is turned on at $t_a = t_w$ or the observation time $t = 0$. The ZFC magnetization $M_{ZFC}(t)$ was measured as a function of time t.

Figures 3 and 4 show the t dependence of the relaxation rate $S_{ZFC}(t)$ at various T $(2.8 \leqslant T \leqslant 11.0$ K), where $t_w = 1.0 \times 10^4$ s and $H = 1$ Oe. The relaxation rate $S_{ZFC}(t)$ exhibits a broad peak at a characteristic time t_{cr} in the FM phase as well as in the RSG phase. We find that $S_{ZFC}(t)$ is well described by an SER form given by (2) for $t \gtrsim t_{cr}$. Note that the curves of $S_{ZFC}(t)$ versus t greatly deviate from the curves denoted by (2) for $t \ll t_{cr}$. The least-squares fit of these data to (2) yields the parameters τ, n, and S^0_{max}. The solid lines present the least-squares fitting curves to (2). The T dependence of t_{cr}, τ, S_{max}, S^0_{max}, and n is shown in figures 5(a)–(c). In figure 5(a) we show the T dependence of t_{cr} and τ for $t_w = 1.0 \times 10^4$ s and $H = 1$ Oe. The T dependence of t_{cr} is very similar to that of τ for 2.0 K $\leqslant T \leqslant 9.0$ K. The relaxation time τ $(\approx t_{cr})$ starts to increase around $T = T_c$ with decreasing T. It shows a broad peak centred around 5.5 K between T_{RSG} and T_c, and a local minimum around T_{RSG}. It

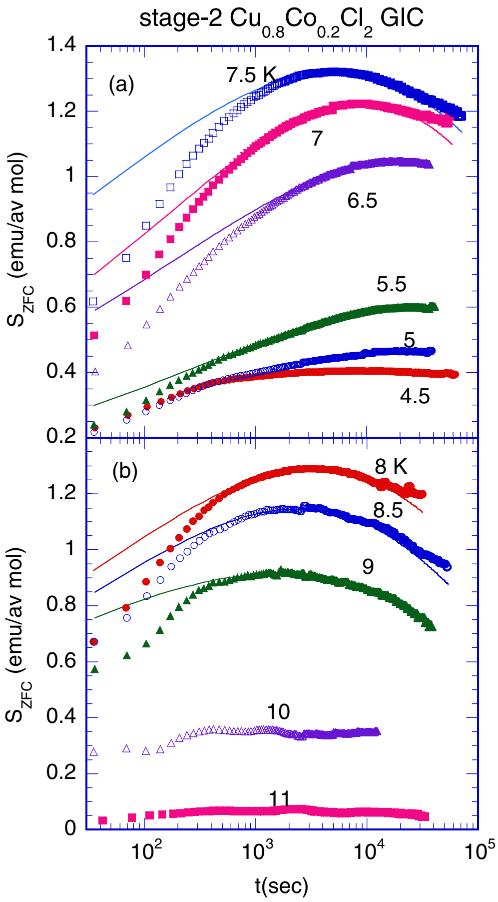

Figure 4. t dependence of $S_{ZFC}(t)$ at various T. $H = 1$ Oe. $t_w = 1.0 \times 10^4$ s. (a) $T = 4.5$–7.5 K. (b) $T = 8.0$–11.0 K. The solid lines are curves fitted to (2).

drastically increases with further decreasing T below T_{RSG}. Note that very similar behaviour of t_{cr} versus T (τ versus T) is also observed in the re-entrant ferromagnet $Cu_{0.2}Co_{0.8}Cl_2$–$FeCl_3$ GBIC [9]. The existence of the broad peak around 5.5 K suggests the chaotic nature of the FM phase in our system (see section 4). The drastic increase of t_{cr} (or τ) below T_{RSG} with decreasing T is a feature common to the SG phases of typical SG systems. Figure 5(b) shows the T dependence of S_{max} (the peak height of $S_{ZFC}(t)$ at $t = t_{cr}$) and S^0_{max} for $H = 1$ Oe and $t_w = 1.0 \times 10^4$ s. We find that the T dependence of S^0_{max} agrees well with that of S_{max}. The peak height S_{max} at $H = 1$ Oe exhibits two peaks around $T = 3.2$ K and at 7.5 K just below T_c.

In figure 5(c) we show the plot of the SER exponent n as a function of T, where $t_w = 1.0 \times 10^4$ s and $H = 1$ Oe. The exponent n increases with increasing T and exhibits a peak at $T \approx T_{RSG}$. The exponent n decreases with further increasing T. It shows a local minimum around 5.0 K and a local maximum at $T \approx T_c$. Similar behaviour of n versus T has been reported by Hoogerbeets *et al* [17] for dilute metallic spin glasses: n increases as T approaches the spin freezing temperature T_{SG} from below. In summary, we find two relations: $t_{cr}(T) \approx \tau(T)$ and $S_{max}(T) = S^0_{max}(T)$. These relations indicate that the SER form holds well in our system at least for $t \gtrsim t_{cr}$.

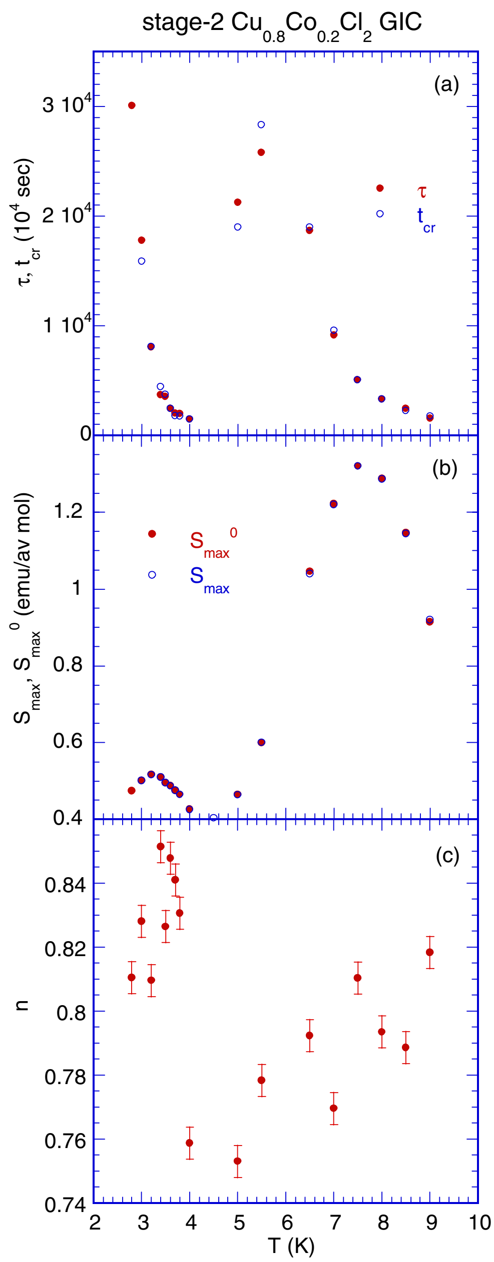

Figure 5. T dependence of (a) the peak time t_{cr} (○) and the SER relaxation time τ (●), (b) the maximum value S_{max} (○) and the amplitude S_{max}^0 (●), and (c) the SER exponent n. The relaxation rate $S_{ZFC}(t)$ takes a maximum (S_{max}) at the peak time t_{cr}, where $t_w = 1.0 \times 10^4$ s and $H = 1$ Oe. The parameters τ, S_{max}^0, and n are derived from the least-squares fits of the data of $S_{ZFC}(t)$ versus t for $t \gtrsim t_{cr}$ to (2).

We have measured the t dependence of $M_{ZFC}(t)$ at $T = 8.0$ and 5.5 K, as the wait time t_w is varied as a parameter ($2.0 \times 10^3 \leqslant t_w \leqslant 3.0 \times 10^4$ s). Figures 6(a) and (b) show the t dependence of $S_{ZFC}(t)$ at $T = 8.0$ and 5.5 K, respectively. As shown in figure 6(a), $S_{ZFC}(t)$

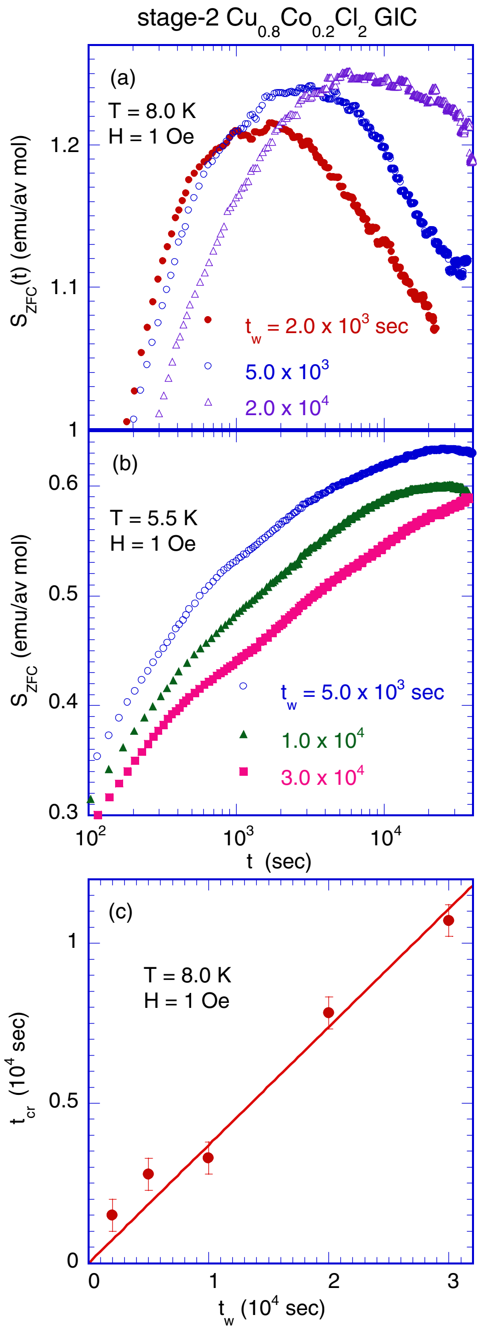

Figure 6. t dependence of $S_{ZFC}(t)$ at various wait times t_w. $H = 1$ Oe. (a) $T = 8.0$ and (b) 5.5 K. (c) The peak temperature t_{cr} versus t_w at $T = 8.0$ K, obtained in part from (a).

at $T = 8.0$ K exhibits a peak at $t = t_{cr}$ for each t_w. This peak shifts to the long-t side with increasing t_w, showing the ageing behaviour. In figure 6(c) we show the relation between t_{cr} and t_w at $T = 8.0$ K. The time t_{cr} is proportional to t_w: $t_{cr} = (0.37 \pm 0.02)t_w$. In figure 6(b), in contrast, $S_{ZFC}(t)$ at 5.5 K seems to show a peak at $t = t_{cr} \approx 2.8 \times 10^4$ s for $t_w = 1.0 \times 10^4$ s. It is noted that no peak is observed in $S_{ZFC}(t)$ for $t < 5.0 \times 10^4$ s for $t_w = 3.0 \times 10^4$ s.

3.3. Genuine TRM measurement

In order to examine the ageing and memory effects, we have carried out the genuine TRM measurement. The sample was first rapidly cooled in the presence of H_c (=1.0 Oe) from 50 K. The FC ageing protocol was interrupted by stop and wait at an intermittent stop temperature T_s ($3.5 \leqslant T_s \leqslant 8.5$ K). After the isothermal ageing for a wait time t_s ($=3.0 \times 10^4$ s) at T_s, the cooling of the system was resumed from T_s down to 2.0 K. At 2.0 K the magnetic field was switched off. Subsequently, the TRM magnetization was measured with increasing T from 2.0 to 14.0 K at $H = 0$ ($M_{TRM}(T; T_s, t_s)$ as the single-stop curve). The result is compared with the TRM magnetization without any intermittent stop during the FC ageing protocol ($M_{TRM}^{ref}(T)$ as the reference curve). Figures 7 and 8 present the difference curves $\Delta M_{TRM}(T; T_s, t_s)$ with $t_s = 3.0 \times 10^4$ s, obtained by subtracting the reference curve from the single-stop curves for different stop temperatures T_s, where $\Delta M_{TRM}(T; T_s, t_s)$ is defined as

$$\Delta M_{TRM}(T; T_s, t_s) = M_{TRM}(T; T_s, t_s) - M_{TRM}^{ref}(T). \qquad (3)$$

The differences $\Delta M_{TRM}(T; T_s, t_s)$ at $T_s = 3.5$, 4.0, 8.0, and 8.5 K exhibit a positive sharp peak at a temperature close to T_s. Similar memory effects are observed in the genuine ZFC magnetization measurement for the 3D Ising spin glass $Fe_{0.55}Mn_{0.45}TiO_3$ [22].

In contrast, the differences $\Delta M_{TRM}(T; T_s, t_s)$ at $T_s = 5.0$, 6.5, and 7.0 K are rather different from those at $T_s = 3.5$, 4.0, 8.0, and 8.5 K. They exhibit a relatively broad peak near $T = T_s$ as well as a negative local minimum around $T = 8$ K. The broad peak at $T = T_s$ for $T_s = 5.0$, 6.5, and 7.0 K may be closely related to the divergence of t_{cr} and τ around $T = 5.5$–6.0 K. Such a slow dynamics between T_{RSG} and T_c may be related to a possible FM ordered cluster coupled with random dipole–dipole interaction. This FM state smoothly changes into a conventional SG state below T_{RSG}. The cause of the local minimum around 8.0 K in $\Delta M_{TRM}(T; T_s, t_s)$ is not certain in the present stage.

The ordered domains generated at $T = T_s$ are frozen in and survive the spin reconfiguration occurring at lower temperature on shorter length scales. The rejuvenation of the system occurs as the temperature is decreased away from T_s. The spin configuration imprinted at T_s is recovered on reheating. In this sense, the system sustains a memory of an equilibrium state reached after a stop–wait process at T_s. The influence of the spin configuration imprinted at a stop–wait protocol is limited to a restricted temperature range around T_s on reheating. The width of this region may be assigned to the existence of an overlap between the spin configuration attained at T_s and the corresponding state at a very close temperature ($T_s + \Delta T$). The overlap length $L_{\Delta T}$ is inversely proportional to $|\Delta T|$ [12]. In our system, the spin configuration imprinted during the stop–wait protocol at $T = T_s$ for a wait time t_s is unaffected by a small temperature shift such that the overlap length $L_{\Delta T}$ is larger than the average domain sizes. There is a sufficient overlap between the equilibrium spin configurations at the two temperatures T_s and $T_s + \Delta T$. The situation is different when the temperature shift becomes large. The overlap length becomes shorter than the original domain sizes. A smaller overlap between spin configurations promotes the formation of broken domains. When the temperature shift is sufficiently large, the overlap length is much shorter than the original domain sizes, leading to the rejuvenation of the system [23].

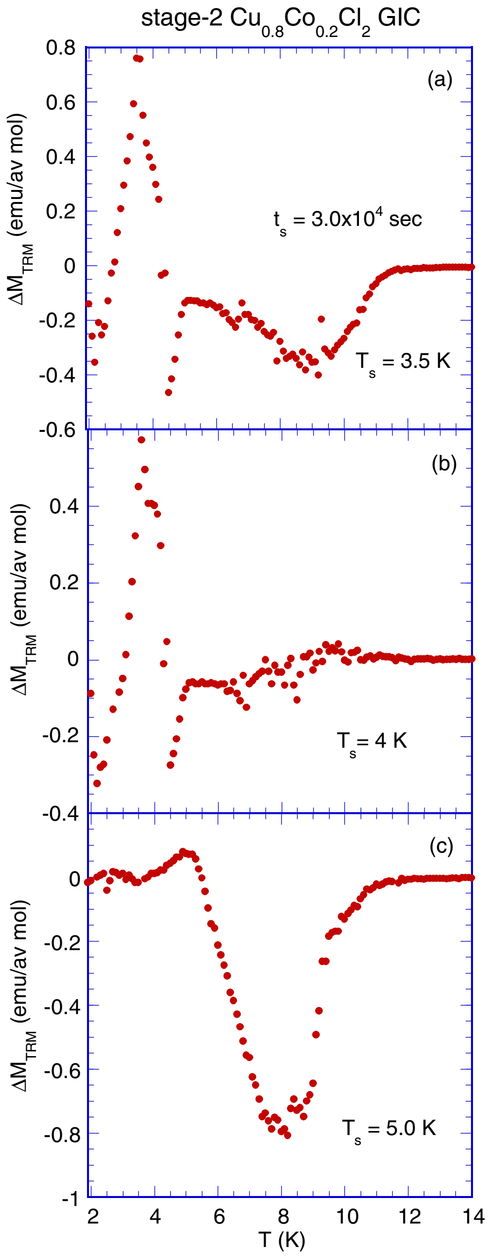

Figure 7. T dependence of the difference $\Delta M_{\mathrm{TRM}}(T; T_s, t_s)$ ($=M_{\mathrm{TRM}}(T; T_s, t_s) - M_{\mathrm{TRM}}^{\mathrm{ref}}(T)$). $t_s = 3.0 \times 10^4$ s. $H_c = 1$ Oe. (a) $T_s = 3.5$ K, (b) $T_s = 4.0$ K, and (c) $T_s = 5.0$ K. $M_{\mathrm{TRM}}(T; T_s, t_s)$ is measured with increasing T at $H = 0$ from 2.0 K, after the FC cooling protocol at $H_c = 1$ Oe with a stop–wait at the stop temperature T_s for a wait time $t_s = 3.0 \times 10^4$ s. $M_{\mathrm{TRM}}^{\mathrm{ref}}(T)$ is measured with increasing T at $H = 0$ from 2.0 K, after the FC ageing protocol at $H_c = 1$ Oe without such a stop–wait procedure.

3.4. Memory effect of FC magnetization

We have also examined the memory effect of the FC magnetization under the FC ageing protocol with a stop and wait process. Our result is shown in figure 9. Our system was cooled

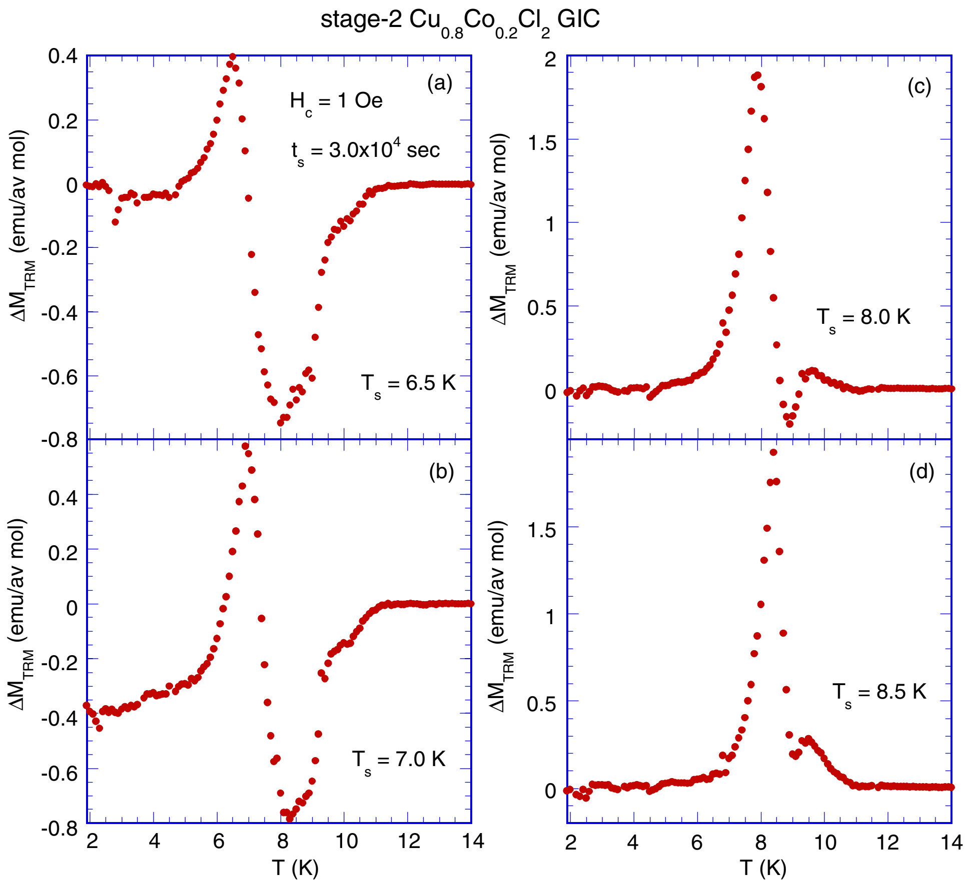

Figure 8. T dependence of the difference $\Delta M_{\mathrm{TRM}}(T; T_s, t_s)$ $(=M_{\mathrm{TRM}}(T; T_s, t_s) - M_{\mathrm{TRM}}^{\mathrm{ref}}(T))$. $t_s = 3.0 \times 10^4$ s. $H_c = 1$ Oe. (a) $T_s = 6.5$ K, (b) $T_s = 7.0$ K, (c) $T_s = 8.0$ K, and (d) $T_s = 8.5$ K. The definition of $M_{\mathrm{TRM}}(T; T_s, t_s)$ and $M_{\mathrm{TRM}}^{\mathrm{ref}}(T)$ is the same as for figure 7.

through the FC ageing protocol from 50 K in the presence of $H = 5$ Oe. When the system was cooled down to intermittent stop temperatures T_s (=8.5, 7.0, and 5.5 K), the field was cut off ($H = 0$) and kept at T for t_w ($=3.0 \times 10^4$ s). In this case, the magnetization $M_{\mathrm{FC}}^{\mathrm{IS}}(T\downarrow)$ decreases with time due to the relaxation. After the wait time t_w at each stop temperature, the field ($H = 5$ Oe) was applied again and the FC ageing process was resumed. Such an FC ageing process leads to a step-like behaviour of the $M_{\mathrm{FC}}^{\mathrm{IS}}(T\downarrow)$ curve. The value of $M_{\mathrm{FC}}^{\mathrm{IS}}(T\downarrow)$ after resuming below $T = 5.5$ K behaves almost in parallel to that of the FC magnetization without the intermittent stops (M_{FC} curve as the reference, see figure 9(a)). After reaching 1.9 K, the magnetization $M_{\mathrm{FC}}^{\mathrm{IS}}(T\uparrow)$ was measured in the presence of H (=5 Oe) as T is increased at the constant rate (0.05 K min^{-1}). The magnetization $M_{\mathrm{FC}}^{\mathrm{IS}}(T\uparrow)$ thus measured exhibits a peak at a characteristic temperature $T_a = 6.2$ K between the stop temperatures $T_s = 5.5$ and 7.0 K, a peak at $T_a = 7.6$ K between $T_s = 7.0$ and 8.5 K, and a kink at $T_a = 8.8$ K above $T_s = 8.5$ K. It is assumed that the anomaly of $M_{\mathrm{FC}}^{\mathrm{IS}}(T\uparrow)$ at $T = T_a$ is related to the spin configuration imprinted at $T = T_s$ ($<T_a$) and $H = 0$ for a wait time t_w during the FC ageing protocol. If a temperature difference ΔT is defined as $\Delta T = T_a - T_s$, we have $\Delta T = 0.7$ K for the peak at $T_a = 6.2$ K ($T_s = 5.5$ K), $\Delta T = 0.6$ K for the peak at $T_a = 7.6$ K ($T_s = 7.0$ K), and

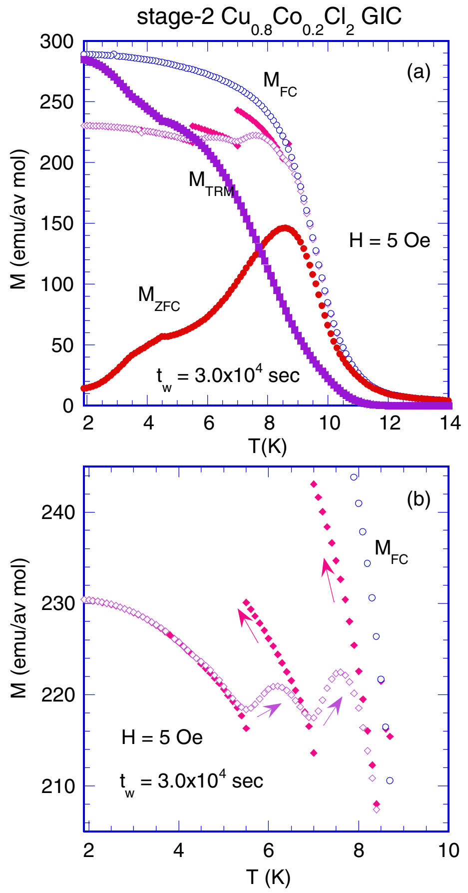

Figure 9. (a) and (b) T dependence of $M_{FC}^{IS}(T\downarrow)$ (♦) and $M_{FC}^{IS}(T\uparrow)$ (◇) observed in the following FC ageing protocol. The system was quenched from 50 to 15 K in the presence of H (=5 Oe). $M_{FC}^{IS}(T\downarrow)$ was measured with decreasing T from 15 to 1.9 K but with intermittent stops at $T_s = 7.0$ and 5.5 K for a stop time $t_w = 3.0 \times 10^4$ s. The field is cut off during each stop. $M_{FC}^{IS}(T\uparrow)$ was measured at $H = 5$ Oe with increasing T after the above FC ageing protocol. For comparison, the T dependences of M_{FC}, M_{TRM} and M_{ZFC} at H (or H_c) = 5 Oe are also shown as reference curves. These reference curves are measured after either the usual FC protocol or the usual ZFC protocol without the intermittent stop.

$\Delta T = 0.3$ K a cusp at $T_a = 8.8$ K ($T_s = 8.5$ K). The difference ΔT tends to decrease with increasing T_s.

In summary, the spin configuration imprinted at the intermittent stop at T_s for a wait time t_w at $H = 0$ during the cooling process strongly affects the T dependence of $M_{FC}(T\uparrow)$ when T is increased, exhibiting a peculiar memory effect. Our result is qualitatively in agreement with the results reported by Sun *et al* [24] for superparamagnetic ($Ni_{81}Fe_{19}$) nanoparticles. Sasaki *et al* [25] have proposed a model that the ageing and memory effects of such systems may originate solely from a broad distribution of relaxation times in ferromagnetic domains.

4. Discussion

First our results on the ageing behaviour of $S_{ZFC}(t)$ versus t are compared with those observed in two typical re-entrant ferromagnets. The first case is the result of the $Cu_{0.2}Co_{0.8}Cl_2$–$FeCl_3$ GBIC ($T_{RSG} = 3.5$ K and $T_c = 9.7$ K) [9]. The ageing behaviour of $S_{ZFC}(t)$ is observed in both the RSG phase and the FM phase. The peak time t_{cr} for $t_w = 3.0 \times 10^4$ s shows a broad peak centred around 4–5 K between T_{RSG} and T_c, and a local minimum around T_{RSG}. It increases with further decreasing T below T_{RSG}. The broad peak in t_{cr} around 4–5 K suggests the chaotic nature of the FM phase. The peak height S_{max} at $H = 1$ Oe exhibits two peaks around $T = T_{RSG}$ and at 7.0 K just below T_c, independent of t_w (=1.5 × 10^4 s or 3.0 × 10^4 s). The second case is the result of $(Fe_{0.20}Ni_{0.80})_{75}P_{16}B_6Al_3$ ($T_{RSG} = 14.7$ K and $T_c = 92$ K) [1–4]. The ageing behaviour of $S_{ZFC}(t)$ versus t is also observed in both the RSG phase and the FM phase. The peak time t_{cr} shows a local minimum around 23 K, and increases with further increasing T between 25 and 30 K. Although no data have been reported for $S_{ZFC}(t)$ versus t above 30 K, it is assumed that t_{cr} shows a local maximum between 30 K and T_c, since t_{cr} should reduce to zero well above T_c. The peak height S_{max} ($H = 0.5$ Oe and $t_w = 1.0 \times 10^3$ s) exhibits a peak at 13 K just below T_{RSG}, having a local minimum at 25 K, and tends to increase with further increasing T. It is assumed that S_{max} shows a local maximum between 30 K and T_c, since S_{max} should reduce to zero above T_c. These two peaks of S_{max} versus T are similar to two local maxima around T_{RSG} and between T_{RSG} and T_c in our system.

The features of the ageing behaviour common to the above two re-entrant ferromagnets as well as our system are as follows. The peak time t_{cr} drastically increases with decreasing T below T_{RSG}. In this sense, the RSG phase below T_{RSG} is a normal SG phase. The dynamic nature of the FM phase is rather different from that of an ordinary ferromagnet. The peak time t_{cr} as a function of T exhibits a local maximum between T_{RSG} and T_c. The FM phase just above T_{RSG} shows a dynamic behaviour characterized by an ageing effect and chaotic nature similar to that of RSG phase.

According to a model proposed by Aeppli *et al* [26], the RSG phase is caused by the random field effect. The FM order is broken down by a random molecular field due to the freezing of spins in the PM clusters which do not contribute to the FM spin order. In the high temperature FM phase the fluctuations of the spins in the PM clusters are so rapid that the FM network is less influenced by them and their effect is only to reduce the net FM moment. On approaching T_{RSG} the thermal fluctuations of the spins in the PM clusters become slower and the coupling between these spins and the FM network becomes significant. Then the molecular field from the slow PM spins acts as a random magnetic field, causing a break-up of the FM network into finite domains.

5. Conclusion

The stage-2 $Cu_{0.2}Co_{0.8}Cl_2$ GIC undergoes successive transitions at the transition temperatures T_c (≈ 8.7 K) and T_{RSG} (≈3.3 K). The relaxation rate $S_{ZFC}(t)$ exhibits a characteristic peak at t_{cr} below T_c, indicating the occurrence of ageing phenomena in both the RSG and the FM phases. The relaxation rate $S_{ZFC}(t)$ is well described by a stretched exponential relaxation only for $t \gtrsim t_{cr}$. The peak time t_{cr} at constant t_w exhibits a local maximum around 5.5 K, indicating the existence of the slow dynamics in the FM phase. This result is also supported by the T dependence of the genuine TRM magnetization. It exhibits a sharp peak at $T = T_s$ when the stop temperature T_s is close to T_c and T_{RSG}. This peak becomes very broad at T centred around T_s (≈5.5 K). The ordered domains generated at $T = T_s$ ($T_{RSG} < T_s < T_c$) are frozen in and survive the spin reconfiguration occurring at lower temperature on shorter length scales. The rejuvenation of the system occurs as the temperature is decreased away from T_s. The spin configuration imprinted at T_s is recovered on reheating, indicating the memory effect.

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