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2007 J. Phys.: Condens. Matter 19 145238

(http://iopscience.iop.org/0953-8984/19/14/145238)

J. Phys.: Condens. Matter **19** (2007) 145238 (5pp) doi:10.1088/0953-8984/19/14/145238

Magnetic ordering of $CoCl_2$-GIC, a spin ceramic: hierarchical successive transitions and the intermediate glassy phase

Masatsugu Suzuki[1], **Itsuko S Suzuki**[1] **and Motohiro Matsuura**[2]

[1] Department of Physics, State University of New York at Binghamton, Binghamton, NY 13902-6000, USA
[2] Department of Management and Information Science, Fukui University of Technology, Fukui, Fukui 910-8505, Japan

E-mail: suzuki@binghamton.edu and matsuura@ccmails.fukui-ut.ac.jp

Received 7 September 2006
Published 23 March 2007
Online at stacks.iop.org/JPhysCM/19/145238

Abstract
Stage-2 $CoCl_2$-graphite intercalation compound (GIC) is a spin ceramic which shows hierarchical successive transitions at T_{cu} (=8.9 K) and T_{cl} (=7.0 K) from the paramagnetic phase into an intra-cluster (two-dimensional ferromagnetic) order with inter-cluster disorder and then to an inter-cluster (three-dimensional antiferromagnetic like) order over the whole system. The nature of the inter-cluster disorder was suggested to be of spin glass by nonlinear magnetic response analyses around T_{cu} and by studies on dynamical aspects of ordering between T_{cu} and T_{cl}. Here, we present a further extensive examination of a series of time dependence of zero-field cooled magnetization M_{ZFC} after the ageing protocol below T_{cu}. The time dependence of the relaxation rates $S_{ZFC}(t) = (1/H)\,\mathrm{d}M_{ZFC}(t)/\mathrm{d}\ln t$ dramatically changes from the curves of simple spin glass ageing effect below T_{cl} to those of two peaks above T_{cl}. The characteristic relaxation behaviour apparently indicates that there coexist two different kinds of glassy correlated region below T_{cu}.

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

1. Introduction

From the viewpoint of cooperative dynamics, a spin ceramic is an interesting system. It is composed of mesoscopic spin clusters on the regular lattice, coupled mutually through random interface boundaries. It is heterogeneous morphologically. The ordering characteristic should be different qualitatively from those both in regular spin systems and in spin glasses. An attractive system is a stage-2 $CoCl_2$ graphite intercalation compound (GIC), in which each intercalate $CoCl_2$ layer is not extended infinitely, forming island-like ferromagnetic (F) clusters

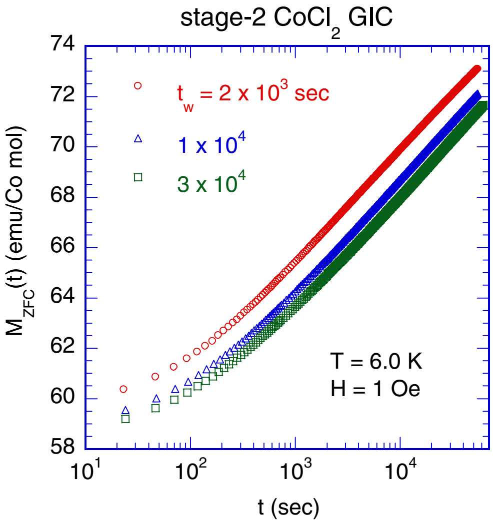

Figure 1. t dependence of $M_{ZFC}(t)$ at $T = 6.0$ K for stage-2 $CoCl_2$ GIC. The system was cooled from 50 K at T and isothermally aged at a wait time t_w ($= 2.0 \times 10^3$, 1.0×10^4, 3.0×10^4 s). Immediately after the magnetic field was switched on to H (=1 Oe), the ZFC magnetization was measured as a function of t.

of mesoscopic scale. It shows successive magnetic transitions of a hierarchical nature at temperatures T_{cu} (=8.9 K) and T_{cl} (=7.0 K) and was identified to be from the paramagnetic into the three-dimensional (3D) antiferromagnetic (AF) order over the whole system through 2D ferromagnetic (F) order between T_{cu} and T_{cl} [1–3].

Such a picture, however, was not so appropriate because a number of peculiar phenomena observed so far suggested rather that the intermediate state was a disordered state among the clusters and also that the nature was of a spin glass [1–3]. In particular, nonlinear magnetic response analysis in the vicinity of T_{cu} and recent study of the dynamical aspect of ordering processes established that the transition at T_{cu} is certainly of a spin-glass type [2, 3]. Surprisingly, in the latter, the time dependence of the relaxation rates $S_{ZFC}(t)$, defined in section 2, was found to have two distinguishable peaks in the temperature range between T_{cu} and T_{cl}, forming a contrast to the simple spin-glass feature observed below T_{cl} [2]. Such relaxation phenomena apparently indicate that two correlated regions coexist in the intermediate temperature range, reflecting a complex situation of the intermediate glassy phase so far speculated. Under such a circumstance, we have carried out, in this work, a further extensive and detailed study of the ageing effect on the relaxation processes of $M_{ZFC}(t)$ in a wider temperature region below T_{cu}.

2. Experimental procedure

We have measured the time dependence of $M_{ZFC}(t)$ of stage-2 $CoCl_2$-GIC. Before $M_{ZFC}(t)$ measurement, the following zero-field cooled (ZFC) ageing protocol was undertaken. First the system was annealed at 50 K, a temperature far above T_{cu} for 1.2×10^3 s. Then the system was quenched from 50 K to the measured temperature T ($<T_{cu}$) in the absence of magnetic field and isothermally aged at the temperature for a wait time t_w ($= 2.0 \times 10^3$, 1.0×10^4, 3.0×10^4 s in the present case). Immediately after the magnetic field H (=1 Oe) was turned on, at $t = 0$, $M_{ZFC}(t)$ was measured as a function of time t. Figure 1 shows an example of the relaxation

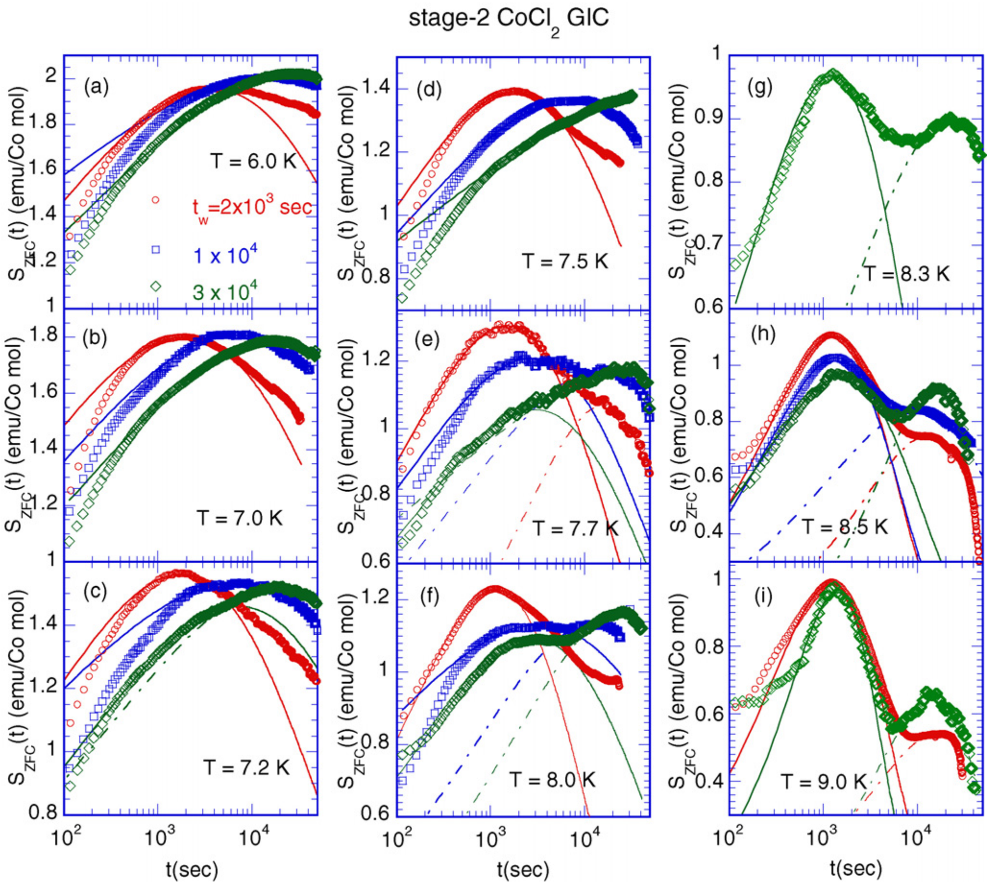

Figure 2. t dependence of the relaxation rate $S_{ZFC}(t)$. $t_w = 2.0 \times 10^3$, 1.0×10^4, and 3.0×10^4 s. The solid lines are curves fitted to the SER form. (a) $T = 5.5$ K. (b) 6.0 K, (c) 7.0 K, (d) 7.2 K, (e) 7.5 K, (f) 7.7 K, (g) 8.0 K, (h) 8.5 K, and (i) 9.0 K.

process of M_{ZFC} plotted against t for different t_w at 6.0 K, a temperature well below T_{cl}. It clearly indicates an ageing time dependence of $M_{ZFC}(t)$. The ageing characteristic, however, could be demonstrated more distinguishably in the relaxation rate $S_{ZFC}(t)$, which is derived from $M_{ZFC}(t)$ as

$$S_{ZFC}(t) = (1/H)\,\mathrm{d}M_{ZFC}(t)/\mathrm{d}\ln t. \tag{1}$$

3. Experimental results and discussion

Figures 2(a)–(i) show the $S_{ZFC}(t)$ versus t curves at various t_w for $T = 6.0$–9.0 K. Figure 2(a) shows the $S_{ZFC}(t)$ versus t curves for various t_w at 6.0 K. Each curve exhibits a single broad maximum around t_w, and shifts to the longer-t side with increasing t_w. Such an ageing time dependence of the relaxation rate is well known as a characteristic feature of spin-glass dynamics and has actually been found in typical spin-glass systems [4]. Figure 2(h) shows the $S_{ZFC}(t)$ versus t curves at 8.5 K, a temperature well above T_{cl} and below T_{cu}. The $S_{ZFC}(t)$ versus t curves show two separated peaks, forming a remarkable contrast to those at 6.0 K. Such

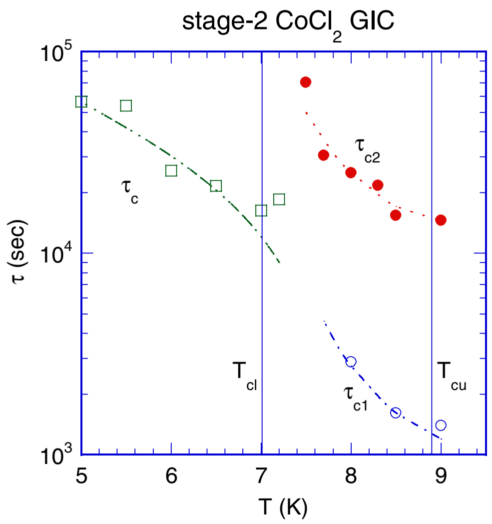

Figure 3. T-dependence of the SER relaxation time τ, which is derived from the least squares fit of $S_{ZFC}(t)$ versus t ($H = 1$ Oe, $t_w = 3.0 \times 10^4$ s) to the SER form. The SER relaxation time τ is almost equal to the peak time t_{cr} of $S_{ZFC}(t)$ versus t for $T < T_{cl}$ and 8.0 K $< T < T_{cu}$. Two SER peaks are observed at $t < 3.0 \times 10^3$ s (○) and at $t > 1.0 \times 10^4$ s (●) above 8.0 K, while a single peak below T_{cl} (□). The solid lines are guides to the eyes.

a qualitative difference apparently indicates two different relaxation processes and therefore the coexistence of two different correlated regions in the present system [4]. The peaks appear at about 2.0×10^4 and 1.0×10^3 s, respectively, and the location of the peaks seems to be almost independent of t_w. In such a way, the relaxation behaviours for $T < T_{cl}$ and for $T > T_{cl}$ are qualitatively different. So, in order to examine how the characteristic relaxation behaviour for $T > T_{cu}$ changes to that for $T < T_{cl}$ with decreasing T and to identify the glassy state in the temperature range between T_{cu} and T_{cl}, we observed the time dependence of $S_{ZFC}(t)$ systematically at various successive temperatures below T_{cu}.

As shown in figures 2(a)–(i), $S_{ZFC}(t)$ versus t curves for $T < T_{cl}$ exhibit a single broad peak around a characteristic time τ_c, which shifts to the longer-t side with increasing t_w. It reflects that the relaxation process and the ageing effect are qualitatively the same as those at 6.0 K. Therefore we conclude that the state below T_{cl} is of a typical spin glass. We also find that the $S_{ZFC}(t)$ versus t curves for well above T_{cl} (8.0 K $< T < T_{cl}$) exhibit two peaks at τ_{c1} and τ_{c2} ($> \tau_{c1}$), suggesting that the state in the region is essentially the same as that at 8.5 K. The values of τ_{c1} and τ_{c2} seem to be almost independent of t_w (see figures 2(h) and (i)). The $S_{ZFC}(t)$ versus t curves above and near T_{cl} ($T_{cl} < T <$ 8.0 K), however, are complicated and more or less intermediate. The identification of the state in this temperature region is thus difficult. So we tried to analyse all the data as a superposition of stretched exponential relaxation (SER) curves [5]. The obtained temperature dependence of the SER relaxation time τ is summarized in figure 3, where τ is equal to τ_c for $T < T_{cl}$, and separated into τ_{c1} and τ_{c2} for 8.0 K $< T < T_{cu}$. From the relaxation behaviour and the characteristic ageing effect in figures 2 and 3, the system below T_{cl} is apparently in the spin-glass ordered state, while the system above T_{cl} is roughly divided into two correlated domains or subsystems. One is characterized by an SER process of longer relaxation time τ_{c2} and the other by another SER process of shorter relaxation time τ_{c1}. As shown in figure 3, the value of τ_{c2} is very long ($\approx 2 \times 10^4$ s) and increases with decreasing temperature. Below about 7.5 K, the relaxation process is not observable, probably due to the longer relaxation time. The value of τ_{c1} increases also as T decreases. The relaxation process of this τ_{c1} seems to change the character across T_{cl} and to turn finally into the spin-glass state below T_{cl}. The relaxation process and its ageing time dependence below T_{cl} are in a reasonable agreement with the spin-glass-like memory phenomena of M_{TRM} (thermoremanent magnetization) and M_{ZFC} so far observed in a series of heating and cooling processes below T_{cl} of the system [2, 6].

4. Concluding remarks

From the present experimental result we conclude that the nature of the intermediate state between T_{cu} and T_{cl} is qualitatively different from that below T_{cl}, where ageing dynamics of a typical spin glass was found. In the intermediate state, the system is divided into two subsystems. One goes into a spin-glass-like ordered state at T_{cu}. The other goes into a similar glassy state below T_{cu}, but of much shorter relaxation time.

The latter subsystem is probably composed of the ferromagnetic moments already ordered below T_{cu} within each intercalated cluster, referring to the previous experimental results. Then, the former may be speculated to consist of the spins located in the boundary region of each intercalated cluster and to have an effect on the latter as a random field because of the much longer relaxation time. Such a picture of the present system in the intermediate temperature range between T_{cu} and T_{cl} is expected to bring a reasonable explanation of the remaining questions including the anomalous memory phenomena of M_{TRM} and M_{ZFC} across T_{cl} [2, 6].

Acknowledgments

We are grateful to Professor H Suematsu for providing us with single crystals of kish graphites. This work is supported in part by FUT Research Promotion Fund.

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