Observation of an unusual field dependent slow magnetic relaxation and two distinct transitions in a family of new complexes

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Abstract

An unusual field dependent slow magnetic relaxation and two distinct transitions were observed in a family of new rare earth-transition metal complexes, 

\[\text{[Ln}(\text{bipy})(\text{H}_2\text{O})_4\text{M(CN)}_6] \cdot 1.5\text{bipy} \cdot 4\text{H}_2\text{O} \text{ (bipy = 2,2’-bipyridine; Ln = Gd}^{3+}, \text{Y}^{3+}; \text{M = Fe}^{3+}, \text{Co}^{3+}) \text{. The novel magnetic relaxation, which is quite different from those in normal spin glasses and superparamagnets but very resembles qualitatively those in single-molecule magnet Mn}_{12}\text{-Ac even if they possess different structures, might be attributed to the presence of frustration that is incrementally unveiled by the external magnetic field. The two distinct transitions in [GdFe] were presumed from DC and AC susceptibility as well as heat capacity measurements.}

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Recently there has been growing interest in studying frustrated systems, and a variety of magnetic systems with geometrically frustrated structures, such as the three-dimensional (3D) cubic pyrochlore lattice [1-3], the two-dimensional (2D) kagome lattice [4, 5], and some disordered molecular systems [6-10], etc., have been extensively investigated. A number of new phenomena, like noncollinear Neél long-range order, quantum disorder, order by disorder, order with disorder, etc., have been predicted or observed at low temperatures[1-10]. Those systems are not genuine spin glasses, but they exhibit spin glass-like behaviors, showing the salient role of frustration which is normally generated by the competition between different kinds of interactions or by special lattice structures. Here we report novel, unusual but universal properties in a class of new complexes which are geometrically frustrated rare earth-transition metal cyanides.

The compounds \([Ln\ (\text{bipy})\ (H_2O)_4\ M(CN)_6\cdot1.5\ \text{bipy})\cdot4H_2O\ (Ln = \text{Gd}^{3+},\text{Y}^{3+};\ M = \text{Fe}^{3+},\text{Co}^{3+})\) (abbreviated as \([\text{GdFe}],\ [\text{YFe}]\) and \([\text{GdCo}],\) respectively) were prepared by mixing aqueous solution of \(K_3[M(CN)_6]\) (1mmol) and alcohol solution of 2,2’-bipyridine in a 1/3 molar ratio, then by dropping \(\text{Ln(NO}_3)_3\) (1mmol) aqueous solution slowly without stirring. Single crystals were obtained by slow evaporation of the solution at room temperature. Single crystal X-ray analysis revealed that they are isomorphous, and only the structure of \([\text{GdFe}]\) was exemplified here. The transition metal ion \(\text{Fe}^{3+}\) and lanthanide ion \(\text{Gd}^{3+}\) are bridged by cyano group CN, forming a chain as shown in Fig.1(a). Within the chain, \(\text{Gd-Fe, Fe-Fe (or Gd-Gd)}\) separations are 5.5 and 10.89Å, respectively. In \(ab\) plane, the chains are connected through hydrogen bonds with nearest inter-chain \(\text{Gd-Fe, Fe-Fe (or Gd-Gd)}\) separations 7.7, 9.75 (= \(a\)) and 10.66 (= \(b\))Å. Within the layer, the connection of \(\text{Fe}^{3+}\) ions (solid line) or \(\text{Gd}^{3+}\) ions (dash line) gives rise to a slightly deformed triangular lattice, respectively. The nearest separation of \(\text{Fe or Gd ions}\) between the two neighbor layers are 9.906, 10.81Å for A-B, and 11.44 Å for B-A, as shown in Fig. 1(b). Since the separation between the \(\text{Fe}^{3+}\) (or \(\text{Gd}^{3+}\)) ions in the chain (10.89Å) is comparable with the nearest inter-chain and inter-layer separations (9.75 – 11.44Å), \([\text{GdFe}]\) cannot be regarded as a good one-dimensional compound. Furthermore, the inter-layer interactions should be
weaker than those in ab plane due to the weaker π-π stack of pyridine rings between layers. As a result, [GdFe] is actually an anisotropic 3D magnetic system in which the interactions along the c-axis are smaller than that within ab plane. It is this weak residue interactions along the c-axis to make the system exhibit magnetic long-range order. The physical properties of these systems are predominantly determined by magnetic ions within the plane. Apparently, if the coupling between Fe$^{3+}$ (or Gd$^{3+}$) ions in ab plane are antiferromagnetic (AFM), the frustration will occur. If really so, [LnM] can be in principle viewed as geometricaly frustrated systems. Although spin glass-like behaviors are expected for such systems, rather weak interactions between Fe$^{3+}$ (or Gd$^{3+}$) ions (due to long separations) and the intervention of the rare earth ions will complicate the situation.

χ$_M$T (or equivalently, the effective magnetic moment μ$_{eff}$ = (8χ$_M$T)$^{1/2}$) of [GdFe] was measured in 100Oe to 5kOe DC fields with a SQUID magnetometer (Quantum Design MPMS5) with crystalline sample confined in parafilm. The results show an unusual inverse field-dependence of χ$_M$T below 4K, namely, with increasing temperature it first increases to reach a maximum, and then decreases, after undergoing a plateau, to approach a constant value (atomic limit), as shown in Fig. 2(a). The drops of χ$_M$T below 2.5K, signal the existence of AFM interactions among the metal ions. When the magnetic field is stronger than 5kOe, the peak disappears and the AFM behavior is dominant. We note that the seemingly similar behaviors of χ$_M$T were also reported in the highly frustrated triangles-in-triangles crystalline system [4,5]. Apart from the strong peak around 2.5K, there is a shoulder occurring around 3K especially in low fields, suggesting that there must be a phase transition at a field-independent temperature, because the shoulders appear at the same position in different fields. The field-dependence of magnetization for [GdFe] was measured at 1.5K, and a small but clear hysteresis loop was observed as shown in the inset of Fig. 2(a). This is an intrinsic behavior, not induced by impurity, because a single-crystal sample, which was examined by X-ray analysis to be in a single phase, was used in measurements. Combining these facts we could identify that the system might be magnetic ordering with Curie temperature $T_c$ estimated to be around 3K. This will be further verified by the specific
heat measurement. For a comparison, the temperature dependence of $\chi_M T$ for [YFe] and [GdCo] were also measured at 1kOe and 5kOe, respectively, as shown in Fig. 2(b). Since Y$^{3+}$ and Co$^{3+}$ [11] are diamagnetic ions, the results for [YFe] reveal the contribution from Fe-Fe interactions, while those for [GdCo] reveal the contribution from Gd-Gd interactions. From the observed results one may judge that the interactions between Fe$^{3+}$ (or Gd$^{3+}$) ions are AFM in character, whereas, the increase of $\chi_M T$ below 4K for [GdFe] when the field is less and equal to 1kOe, suggests a weak ferromagnetic (F) interaction between Gd and Fe ions. The magnitudes of the couplings between metal ions are overall small, being orders of several wave numbers [12-14], which can be estimated to be $|J_{Gd-Fe}| \sim |J_{Fe-Fe}| \gtrsim |J_{Gd-Gd}|$, if the localization property of f electrons is considered. Since Gd$^{3+}$ ions have large moments, the dipolar interactions between Gd-Gd, though still small, should not be ignored apart from superexchange interactions. However, the dipolar interactions between Fe-Fe and Gd-Fe can be ignored, as Fe$^{3+}$ ions are in low spin states ($S = 1/2$), and the separations between metal ions are not so small. The combination of these interactions leads eventually to the magnetic ordering observed.

The AC susceptibility of [GdFe] was first measured in zero DC bias field down to the lowest temperature limit 1.5K for our measurement system (Oxford MagLab 2000), as shown in the upper panel of Fig. 3(a). No frequency dependent cusp was observed for either the in-phase component $\chi'_M$ or the out-of-phase component $\chi''_M$. As is seen, $\chi''_M$ is negligibly small, while $\chi'_M$ decreases with increasing temperature, and is independent of frequency. Since no remarkable structural disorder was found in [LnM], the experimental measurements rule out the possibility that the system under interest is a spin glass. However, a shoulder was observed in $\chi'_M$ versus $T$ around 3K which is frequency independent, being almost the same temperature at which a shoulder appears in DC measurements in $\chi_M T$ versus $T$ presented in Fig.2(a), which shows that this singularity is unique and intrinsic. This particular temperature is nothing but the Curie temperature $T_c$. Then, can the nonzero applied DC magnetic fields influence the dynamic behaviors of the magnetic compound, especially when the field is stronger than 5kOe? The answer is replied in the lower panel of
Fig. 3(a). When the intermediate DC bias field (> 5kOe) was applied, a very interesting phenomenon occurs: $\chi'_M$ first decreases to a minimum roughly at temperature $T_c$, and then increases to a maximum at a finite temperature, denoted by $T_p$, and then decreases with increasing temperature, while $\chi''_M$ first increases, reaching a maximum, and then decreases to vanishing with increasing temperature. When the frequency is increased from 133 to 9333Hz, the basic shapes of $\chi'_M$ versus $T$ remain unaltered, but the magnitudes become about 40% smaller and the positions of peaks move to higher temperatures in the range of 5 – 11K. Apart from that the positions of peaks, similar to $\chi'_M$, also move to higher temperatures, the magnitude of $\chi''_M$ exhibits different frequency dependent behaviors, i.e., it becomes larger with increasing frequency. From Fig. 3(a) it can be presumed that there might exist two distinct transitions, one occurring at $T_c$ which is field and frequency independent, and another occurring at $T_p$ which depends strongly on field and frequency. The former may indicate an occurrence of magnetic long-range orderings at $T_c$, while the latter may indicate the presence of an unknown transition which is closely tied to the observed unusual magnetic relaxation.

The frequency dependence of AC susceptibilities $\chi'_M$ and $\chi''_M$ for [YFe] were also measured for a comparison in zero and 1kOe field respectively, as shown in Fig. 3(b). Zero-field AC susceptibility for [YFe] is very similar to that for [GdFe], i.e., $\chi''_M$ was detected to be almost zero, and no frequency dependence of $\chi'_M$ and $\chi''_M$ was observed. As regards the AC susceptibility in a DC bias field for [YFe], the measured $\chi'_M$ and $\chi''_M$ are shown in the lower panel of Fig.3(b). It can be seen that both $\chi'_M$ and $\chi''_M$ increase from vanishingly small value to a maximum and then decrease with increasing temperature. However, only one peak was observed for $\chi'_M$ versus $T$ in [YFe], but in [GdFe] there are first a minimum and then a peak observed. Moreover, $\chi'_M$ approaches to the same value when $T < 3K$ for different frequencies, implying that the AC susceptibility for [GdFe] has no frequency-dependence at $T \leq 3K$. Similar measurements were carried out for [GdCo] under zero and 5kOe DC fields, respectively, as shown in Fig. 3(c). Apparently, [GdCo] shows even stronger field and frequency dependences. This seems to suggest that the weak interactions between
long-distanced metal ions (Gd-Gd/Fe-Fe: 9.75 – 10.89Å) may play a crucial role in such an unusual magnetic relaxation in [GdCo] and [YFe], respectively.

To confirm the phase transition really existing in [GdFe], the heat capacity of pressed microcrystalline sample was measured in different DC fields using a MagLabHC microcalorimeter (Oxford Instruments, UK). Fig. 4 presents the temperature dependence of the total heat capacity ($C$) including the contribution from the lattice. From the inset it can be seen that in zero field, an anomaly was clearly observed at ca. 2.6K. The position of this anomaly is surprisingly consistent with the positions of shoulders observed in DC and AC susceptibility measurements respectively, probably indicating an onset of spontaneous magnetic long-range ordering at $T_c$ which is independent of frequency and field. When further cooling below 2K, $C$ increases very fast, and no maximum is reached down to 0.5K which is the working limit for our calorimeter. This singularity was not seen in DC and AC susceptibility measurements down to 1.5K. However, on the basis of analyses in physics, there should be a maximum appearing in $C$ vs. $T$ curve in zero field below 0.5K, also in order to consist with the results of $C$ obtained in nonzero applied fields. This maximum should occur at $T_p$, marking the onset of the unknown transition caused by contributions of frustration of metal ions. When a DC field is increased, the peaks of the specific heat appear, and move to higher temperatures from 1K (10kOe) to 1.5K (20kOe), then ca. 2K (40kOe), and finally disappear in a high field (80kOe), indicating that the high magnetic fields smear the peaks out. By combining the heat capacity and DC, AC data, we may say that this transition is strongly field and frequency dependent, and can be probably coined as “magnetic relaxation phase” because it is unusual compared with spin glass (SG) and superparamagnet (SP).

In addition, the novel magnetic relaxation may be understood from other aspects. In zero bias field, the frequency dependent peaks of $\chi_{ac}$ exist in SG as well as in SP, but are absent in [LnM]. In a word, $T_p$ in [LnM] occurs only after a magnetic field was applied, which is obviously different from the behaviors in SG and SP. Although the peaks of $\chi_{ac}$ for SG and SP also show frequency dependence, but the frequency dependence of $\chi_M$ in our
[LnM] compounds is rather strong and slow. If we calculate the value of relative variation of peak temperature ($T_p$) per decade of frequency, $\phi = \Delta T_p/(T_p \Delta (\log f))$, $\phi$ is 0.53, 0.43, 1.22 for [GdFe], [YFe] and [GdCo] in DC fields 5kOe, 1kOe and 5kOe, respectively, while the typical value for SG is normally less than 0.1. If we invoke Neél’s model which is normally assumed for isolated SP particles to estimate the magnetic relaxation time $\tau_0$, we find $\tau_0 = 2.1 \times 10^{-7}$s for [GdFe] in 5kOe field; $9.2 \times 10^{-7}$s for [YFe] in 1kOe field; $2.7 \times 10^{-5}$s for [GdCo] in 5kOe field. The value of $\tau_0$ is ca. 4 – 6 orders larger than that obtained for normal SP particles [15], showing rather slow magnetic relaxation. These facts imply that the magnetic relaxation in these complexes is really unusual, neither SG nor SP behaviors.

Another fact must be mentioned that the fitting results for the peaks of $\chi''_M$ also give an “energy barrier” $E/k_B$, namely, they are 36K for [GeFe] in 5kOe field, 27K for [YFe] in 1kOe field, and 24K for [GeCo] in 5kOe field. It is very interesting that $\phi$, $\tau_0$ and $E/k_B$ for these [LnM] compounds are comparable with those in single-molecule magnet, such as Mn$_{12}$-Ac whose $\phi$, $\tau_0$ and $E/k_B$ are 0.23, $2.1 \times 10^{-7}$s, and 64K, respectively [16]. However, the present magnetic systems have extended structures than an isolated molecule.

Here, we would like to point out that this field-dependent unusual magnetic relaxation seems to be a rather general phenomenon in many magnetic molecular systems with extended structures, not only limited to the systems presently studied. We have investigated several other systems, including the quasi-dimer [GdMnDTPA], 1D [LnMnDTPA] [17], 2D [Ln$_2$M$_3$EDTA] [18], [LnCu] [19], [NdCo] [20], and 3D [Nd$_2$Co(EGTA)] [20], etc. They all show behaviors similar to those reported above. Why do they reveal so similar behaviors? From the structural point of view, the connection of metal ions in these compounds shares a common character, namely, geometrically triangular arrangements for metal ions in a layer, forming frustrated structures. By considering this, we can infer that the physical source for this unusual magnetic relaxation observed in the new complexes may result from frustration which suppresses the long-range ordering generating correlated spin clusters with slow fluctuations. However, the key questions remain: why do the systems not exhibit any magnetic relaxation in absence of an applied field? How does the intermediate field induce
the magnetic relaxation? We could offer a brief yet tentative argument for the two questions. When the applied magnetic field is zero or small, the magnetic interactions between the metal ions are overall rather weak due to the weak Ln-M, M-M and Ln-Ln interactions (owing to the localization of f orbitals and large M-M separation), concealing the frustration unobserved. When the magnetic field is increasing, the AFM short-range correlations between metal ions are increasing and dominant, as experimentally revealed, which gives rise to frustrations unconcealed due to the coupled triangular arrangements between AFM transition metal or lanthanide ions. In other words, this kind of frustration is somehow unveiled by the magnetic field, as partial degeneracies of the system can be lifted by an intermediate field, and the phenomenon of the observed unusual slow magnetic relaxation disappears when the applied field is strong enough. On account of this, the frustration may be an important ingredient responsible for the observed unusual magnetic relaxation in the compounds. The frustrated system possesses highly degenerate ground states which are separated by energy barriers with order of a few kelvin, and external magnetic fields can destroy the ground state, causing the spin glass-like behavior observed. Our findings might be a universal phenomenon existing in the weak-interacting magnetic systems so long as frustration is geometrically present. Furthermore, the two distinct transitions are presumed from the DC, AC susceptibility measurements and the heat capacity data in [GdFe]. One transition is the usual order-disorder phase transition at Curie temperature $T_c$, which is field and frequency independent, and could be attributed to the contributions of Gd-Fe interactions since no long-range ordering was observed in [YFe] and [GdCo]; while another transition occurring at temperature $T_p$ which depends strongly on field and frequency, is unknown at the moment, but we could speculate that it might be closely related to the unusual magnetic relaxation. Seemingly, these two transitions have distinct mechanisms and no relation. Since the results uncovered in these compounds are quite complicated, a simple theoretical model is not feasible now. But we hope that a proper theory could be sooner established to explain these unusual behaviors.
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FIGURE CAPTIONS

Fig.1. (a) Illustration of Fe-CN-Gd chains and connections of Fe$^{3+}$ ions (solid line) and Gd$^{3+}$ ions (dash line) in ab layer for [GdFe]. (b) The connection of Fe (or Gd) ions in and between layers.

Fig.2. (a) $\chi_M T$ versus temperature ($T$) for [GdFe] in different fields. Inset: hysteresis loop for [GdFe] at 1.5K. (b) $\chi_M T$ versus temperature ($T$) for [GdCo] and [YFe] in different fields.

Fig.3. Temperature dependencies of the in-phase AC magnetic susceptibility, $\chi'_M$, and the out-of-phase AC susceptibility, $\chi''_M$, in absence (upper) and presence (lower) of a bias DC field for different frequencies. (a): [GdFe]; (b): [YFe]; (c): [GdCo].

Fig.4. Temperature dependence of the heat capacity for [GdFe] in different fields. Left inset: Enlarged plot in temperature range of 0 – 6K; Right inset: Enlarged plot in temperature range of 2 – 3.0K.
Fig. 1 Gao et al
Fig.1, S. Gao et al.
Fig. 2(a), S. Gao et al.

$\chi_M T$ (cm$^3$ mol$^{-1}$K)

$T$ (K)

$H$ (kOe)

$M$ (N$\beta$mol$^{-1}$)

$T = 1.5$ K

[GdFe]

- $\square$ 100 Oe
- $\triangledown$ 1k Oe
- $\bigcirc$ 200 Oe
- $\diamondsuit$ 5k Oe
- $\triangle$ 500 Oe
Fig. 2(b), S. Gao et al.

\[ \chi_M T (\text{cm}^3 \text{mol}^{-1} \text{K}) \]

- [GdCo], 5 kOe
- [YFe], 1 kOe
$\chi_M''$ and $\chi_M'$ (cm$^3$ mol$^{-1}$)

Fig. 3a, S. Gao et al.

Fig. 3b, S. Gao et al.

Fig. 3c, S. Gao et al.
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