Observation of re-entrant spin glass behavior in (Ce$_{1-x}$Er$_x$)Fe$_2$ compounds

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2010 EPL 91 67006

(http://iopscience.iop.org/0295-5075/91/6/67006)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 59.162.23.19
The article was downloaded on 27/10/2010 at 05:45

Please note that terms and conditions apply.
Observation of re-entrant spin glass behavior in \((\text{Ce}_{1-x}\text{Er}_x)\text{Fe}_2\) compounds

A. Haldar\(^1\), K. G. Suresh\(^1(a)\) and A. K. Nigam\(^2\)

\(^1\)Magnetic Materials Laboratory, Department of Physics, Indian Institute of Technology Bombay
Mumbai-400076, India
\(^2\)Tata Institute of Fundamental Research - Homi Bhabha Road, Mumbai-400005, India

received 23 July 2010; accepted in final form 6 September 2010
published online 6 October 2010

PACS 75.50.Lk – Spin glasses and other random magnets
PACS 75.30.Kz – Magnetic phase boundaries (including classical and quantum magnetic transitions, metamagnetism, etc.)
PACS 75.60.Nt – Magnetic annealing and temperature-hysteresis effects

Abstract – Experimental evidence of re-entrant spin glass (RSG) state has been revealed in Er-doped CeFe\(_2\) compounds. The zero-field–cooled-field-cooled bifurcation in dc magnetization, frequency dependence of freezing temperature, relaxation in zero-field–cooled magnetization and presence of large remanence have been discussed in detail. Frequency dependence is found to follow the critical slowing-down mechanism of the type: \(\tau = \tau_0 (T_f/T_{SG} - 1)^{-zv}\). The RSG state is found to be associated with the randomly magnetized clusters instead of atomic level randomness.

Copyright © EPLA, 2010

Introduction. – Among the RFe\(_2\) (R = rare-earth element) series of compounds, CeFe\(_2\) has attracted a lot of attention from various researchers in view of its anomalous magnetic properties such as low Curie temperature \((T_C = 230 \text{ K})\), low saturation magnetic moment \((M_S = 2.4 \mu_B/\text{f.u.})\) as compared to that of LuFe\(_2\) \((T_C = 610 \text{ K}, M_S = 2.9 \mu_B/\text{f.u.})\) \([1,2]\). These anomalies are explained in terms of the 4\(f\) band magnetism scenario \([1]\). The fact that the light rare-earth Ce couples antiferromagnetically with the 3\(d\) moment is well understood in this scenario. CeFe\(_2\) is known to be a ferromagnet (FM) with a fluctuating antiferromagnetic (AFM) ground state. This AFM state gets stabilized by certain substitutions such as Ru, Re, Ir, Al, Ga, Si etc. at the Fe site, thereby giving rise to a FM-AFM transition on cooling \([3-6]\). It is established that doped CeFe\(_2\) compounds can be a model system to understand the physics of metamagnetic transitions, metastability and phase co-existence. This is important to understand the properties of certain functional materials which have drawn a lot of interest recently \([6-8]\). However, much less attention has been devoted to the substitution at the Ce site by other rare-earth elements \([9-13]\). Enhancement of Curie temperature has been found with R substitution, which enhances the trivalent behavior of Ce in them \([9,12,13]\). While investigating the effect of various R (heavy) doping, we have found that Er substitution shows remarkable differences with regard to the magnetic properties, as compared to the other rare-earth dopants such as Gd or Ho. These include large magnetic hysteresis at low temperatures and the bifurcation of the zero-field–cooled (ZFC) and field-cooled (FC) magnetization data. In order to highlight these special features of Er in CeFe\(_2\), we focus on \((\text{Ce}_{1-x}\text{Er}_x)\text{Fe}_2\) compounds with \(x = 0.08, 0.12, 0.15, 0.25\). We find that Er doping induces the re-entrant spin glass (RSG) state in this series for \(x \leq 0.25\).

The physics of spin glasses is still to be resolved and there are a few well-known spin glass systems available in reality \([14-16]\). On the other hand, the re-entrant spin glass behavior is realized in a variety of systems such as AuFe, (Eu, Sr)S, FeCr, NiMn, AlFe, (Pd, Fe)\(_{1-x}\)Mn\(_x\), (Eu, Sr)Te, (Eu, Sr)As, amorphous (a-) FeNi, a-FeMn, a-FeCr and a-ZrFe, a-(Fe\(_{1-x}\)Mn\(_x\))\(_{75}\)P\(_{16}\)B\(_6\)Al, a-(Fe\(_{1-x}\)Ni\(_x\))\(_{75}\)P\(_{16}\)BAl\(_3\) \([17-26]\). Recently RSG has been seen in some oxides \([27-32]\), shape memory alloys \([33,34]\) and rare-earth–transition metal intermetallics \([35]\) as well. RSG behavior occurs when the material shows spin glass behavior at temperatures lower than the ferromagnetic/antiferromagnetic ordering temperature. The observation of RSG behavior is sometimes controversial and ambiguous as similar experimental features appear due to the deviation from perfect ferromagnetic
or antiferromagnetic state and/or competition between ferromagnetic and antiferromagnetic phases. So it is necessary to confirm the RSG with proper experimental tools. It is indeed possible to confirm RSG behavior as there are some unique experimental outcomes in the case of RSG \cite{14,15}.

In the present case of Er-doped CeFe\textsubscript{2} compounds, we discuss the observation of RSG behavior as revealed by dc and ac susceptibility measurements. The distinct features of spin glass behavior below the Curie temperature is established by examining the frequency dependence of susceptibility, relaxation in dc magnetization and remanence present in these compounds. To the best of our knowledge, RSG state has not been observed in any of the doped CeFe\textsubscript{2} compounds. Though certain substitutions at the Fe site are known to give rise to a magnetic glass due to the first-order transition, the observation of spin glass state is quite unexpected in the CeFe\textsubscript{2} compounds.

**Experimental details.** Polycrystalline compounds, (Ce\textsubscript{1−x}Er\textsubscript{x})Fe\textsubscript{2} (x = 0.08, 0.12, 0.15, 0.25) were prepared by the arc melting method in a water-cooled copper hearth under argon atmosphere. The constituent elements, of at least 99.9\% purity, were melted by taking their stoichiometric proportion. The alloys buttons were remelted several times to ensure homogeneity. The arc melted samples were annealed for 10 days in the following way: 600 °C for 2 days, 700 °C for 5 days, 800 °C for 2 days and 850 °C for 1 day \cite{5}. The structural analysis was performed by the Rietveld refinement of room temperature X-ray diffraction (XRD) patterns. The ac magnetic susceptibility data has been carried out in PPMS (quantum design) in the frequency range 33–9997 Hz. The ac measurements have also been performed in various ac amplitudes and various dc bias fields. All the ac measurements have been taken during heating after cooling the sample in zero field. The dc magnetization and heat capacity measurements were also performed in the PPMS. DC magnetization has been measured during heating after zero-field cooling (ZFC) and field cooling (FC) the sample.

**Results.** All the compounds have formed in single phase which is confirmed by analyzing room temperature X-ray diffraction patterns. At room temperature, these compounds possess the MgCu\textsubscript{2} type cubic structure with the space group \textit{Fd\textbar{3}m}. The lattice parameter is found to increase from 7.3029(2) Å for x = 0.08 to 7.3047(2) Å for x = 0.25. This variation is in good agreement with the report by Tang et al. \cite{9}.

Figure 1 shows the temperature variation of dc magnetization, M(T), for all the compounds at H = 100 Oe. It can be noticed that all the compounds undergo paramagnetic (PM) to ferromagnetic transition and that the T\textsubscript{C} monotonically increases with Er content. Therefore, it is clear that there is a net enhancement of the ferromagnetic ordering with Er. It can be seen that the FC curves reflect the ferromagnetic behavior in all the cases, except in x = 0.25 (see fig. 1(d)). This latter compound does not follow the FM behavior, possibly due to the fact that the T\textsubscript{C} in this case is more than 330 K and that the field cooling is not started from the paramagnetic state. Figure 1 also shows that at temperatures below T\textsubscript{C}, the ZFC and FC data follow different paths, resulting in a large bifurcation between them. This behavior roughly indicates the magnetic frustration and glassy behavior at low temperatures (T < T\textsubscript{C}). It is of interest to note that undoped CeFe\textsubscript{2} does not exhibit this bifurcation as can be seen from the inset of fig. 1(c). In the presence of a higher field (1 kOe), the ZFC-FC difference decreases and at H = 4 kOe, the ZFC data shows almost a normal ferromagnetic behavior (see inset of fig. 1(b)), in the case of x = 0.12. Therefore the M-T data is indicative of a possible spin glass phase below the Curie temperature in these compounds. As is clear from the inset of fig. 1(a), the heat capacity does not show any anomaly close to the region where the ZFC magnetization decreases considerably.

Notably, a spin glass state shows characteristic frequency dependence in the ac susceptibility. Figure 2 shows the temperature variation of the in-phase (\chi\textsubscript{ac}′) and the out-of-phase (\chi\textsubscript{ac}′′) components of ac magnetic susceptibility for the x = 0.15 compound as a typical example, at different frequencies over a wide temperature range from 5 K to the Curie temperature, at fixed H\textsubscript{dc} = 5 Oe and H\textsubscript{ac} = 0. It is to be noted here that when the temperature is reduced below T\textsubscript{C}, the in-phase component decreases giving a high value at T\textsubscript{C} (fig. 2(a)). On the other hand,
Observation of re-entrant spin glass behavior in (Ce$_{1-x}$Er$_x$)Fe$_2$ compounds

Fig. 2: (Colour on-line) (a) Temperature variation of in-phase (upper panel) and out-of-phase (lower panel) of ac susceptibility at $H_{ac} = 5$ Oe for (Ce$_{0.82}$Er$_{0.18}$)Fe$_2$ at different frequencies. Inset of upper panel shows the expanded square region. Inset of lower panel shows the ac amplitude dependence of out-of-phase ac susceptibility. (b) Frequency dependence of the freezing temperature in $x = 0.12$ and 0.15 along with the fit to the critical slowing-down formula, $\tau = \tau_0(T_f/T_{SG} - 1)^{-zv}$. The $x = 0.12$ data shows a weak peak at $T_C$, but a pronounced peak is observed close to the temperature at which the ZFC dc magnetization changes considerably. The decrease of $\chi''_{ac}$ usually indicates the reduction in the ability of the material to respond to the low ac magnetic field. The behavior of $\chi''_{ac}(T)$ is determined by the change of domain wall motion and domain magnetization reorientation in the alternating magnetic field [36]. The peak in $\chi''_{ac}$ plot indicates energy absorption associated with the domain wall motion and domain rotation, which implies that such losses are quite large at temperatures below $T_C$ in the present case.

To further probe the ac response of these compounds, the frequency dependence of the ac magnetic susceptibility was measured, as shown in fig. 2(a). It is evident from the inset of fig. 2(a) that the $\chi''_{ac}$ data shows strong frequency dependence, with an upward shift of the curve, at around 90–130 K. Similarly, the peak in the $\chi''_{ac}$ data (in the same region) also shows a significant upward shift (lower panel of fig. 2(a)). These observations underline the frustrated magnetic state associated with the spin glasses. This kind of large frequency dependence in $\chi''_{ac}$ is also observed in shape memory alloys [33]. Furthermore, the crossing of the $\chi''_{ac}$ curves as seen here was also reported in spin glass systems [37]. On the other hand, the frequency dependence of the peak at $T_C$ is found to be quite negligible, for both the in-phase and the out-of-phase components. The low-frequency (33 Hz) ac susceptibility anomaly coincides with the temperature at which the dc (low-field) magnetization falls rapidly. We define this temperature as $T_f$, the freezing temperature from the position of the maximum of $\chi''_{ac}(T)$ and sudden drop at ZFC dc $M(T)$ data. The frequency shift $Q = \Delta T_f/[T_f \log_{10}(f)]$ [15], is calculated to be 0.09 and 0.07 for $x = 0.12$ and 0.15 compounds, respectively. It is of interest to note that the present values compare well with the values of 0.06 seen in certain shape memory alloys showing RSG state [33], 0.037 seen in metallic glasses [38] and 0.095 reported in LaCo$_{0.5}$Ni$_{0.5}$O$_3$ [39]. The $T_f$ is found to obey the critical slowing-down dynamics (see fig. 2(b)) governed by the relation $\tau = \tau_0(T_f/T_{SG} - 1)^{-zv}$, where $\tau$ is relaxation time and $zv$ is known as dynamic exponent [29]. The maximum frequency used here is 10 kHz, which is good enough to investigate the critical behavior. We found the best fit with $T_{SG} = 82$ K, $\tau_0 = 2.7 \times 10^{-7}$ s, $zv = 5.55$ for the $x = 0.12$ and $T_{SG} = 95$ K, $\tau_0 = 1.4 \times 10^{-6}$ s, $zv = 6.67$ for $x = 0.15$. For a conventional spin glass, $\tau_0$ is $\sim 10^{-10} - 10^{-13}$ s and $zv$ lies in the range of 4–13 [38]. It is important to note here that the order of $\tau_0$ value remains in the range $10^{-6} - 10^{-8}$ s while varying the $T_f$ value by $\pm5$ K. The fact that the present $\tau_0$ values are higher implies that the relaxation is slower and that the RSG phase is constituted by randomly magnetized clusters, instead of atomic level randomness. Such higher $\tau_0$ values have also been found in other RSG systems such as Heusler alloys, LaCo$_{0.5}$Ni$_{0.5}$O$_3$, pyrochlore molybdates etc. [33,39,40]. It should be mentioned that though we tried log$_{10}(f)$ vs. $1/T_f$ fitting, the fit was not as good as the critical slowing-down fitting shown in fig. 2(b). It is also found that the magnitude of the peak in $\chi''_{ac}$ increases with increase in frequency. This is again a signature of conventional spin glasses, though some known RSG systems show the opposite trend [33]. It is of importance to mention here that the strong frequency dependence that we have seen in $x = 0.08$, 0.12 and 0.15 is absent in the case of $x = 0.25$.

By applying a dc bias field ($H_{dc}$), the response of the ac susceptibility is found to show significant modification in its behavior. The magnitude of $\chi''_{ac}$ is strongly suppressed by the dc bias field. Furthermore, it shows a well-defined double-lump behavior for $H_{dc} \geq 500$ Oe. The variation of $\chi''_{ac}$ is also more or less similar to that of $\chi'_ac$. 
It is noteworthy that the $\chi''_{ac}$ peak broadens with dc bias field. At $H_{dc}=4\,\text{kOe}$, both $\chi'_{ac}$ and $\chi''_{ac}$ become almost zero. This shows that the material is unable to respond at low $H_{dc}$ value ($\approx 5\,\text{Oe}$) when the dc bias field is as large as 4$k$Oe. Similar findings have been reported in the case of re-entrant spin glass compound La$_{0.96-x}$Nd$_x$K$_{0.04}$MnO$_3$ [30].

Varying the amplitude of the ac field also causes a huge enhancement and modification of both the in-phase and the out-of-phase susceptibility near the freezing temperature (see inset of fig. 2(a)). With increase in the ac field both the in-phase and the out-of-phase peaks shift towards lower temperatures. This observation is consistent with the fact that a higher ac magnetic amplitude weakens the occurrence of spin glass state which in turn shifts the $T_f$ towards lower temperature.

The metastability of the low-temperature glassy phase has been investigated by magnetization relaxation measurement. Comparison of the time dependent ZFC and FC magnetization data is shown in fig. 3. This is one of the measurement protocols used to investigate the glassy dynamics [29,41]. For this measurement, the sample was cooled in presence (FC) or absence (ZFC) of a field to the measurement temperature. Subsequently the measuring field was applied in the ZFC case, while the cooling field was retained in the FC case. The time variation of the growth of magnetization was recorded. The ZFC magnetization measured in this way shows a huge relaxation at $T=25\,\text{K}$ (for $x=0.08$) and $40\,\text{K}$ (for $x=0.12$), which indicates the metastability of the low-temperature magnetic state. However, there is no considerable relaxation observed in the FC magnetization. This is in sharp contradiction with a magnetic glass where FC magnetization relaxes and ZFC shows no relaxation [41]. This difference, shown in fig. 3, clearly shows that the Er-doped compounds are not magnetic glasses like Ce(Fe$_{0.96}$Ru$_{0.04}$)$_2$, but re-entrant spin glasses. In this respect we would also mention here that we have performed measurement of $M(T)$ after cooling and heating the sample in unequal fields which was proposed recently by the authors of ref. [38]. Interestingly this system shows similar behavior as shown by a typical re-entrant spin glass material Au$_{82.1}$Fe$_{18}$ [41]. In the present compounds, the ZFC magnetization at a constant field and temperature grows as a function of time and the growth can be fitted well to a stretched exponential of the type: $M_t = M_0(H) + [M_{\infty}(H) - M_0(H)]\left[1 - \exp(-(t/\tau)\theta)\right]$, where $\tau$ is the characteristic relaxation time and $\alpha$ is called stretching parameter that ranges between 0 and 1. Best fit curve gives $\alpha = 0.58$ and 0.53 for the $x = 0.08$ and 0.12 compounds, respectively.

Another important characteristic of the RSG state is the presence of considerable remanence and coercivity [29]. To probe this, the $M-H$ plots have been recorded in all the compounds both under ZFC and FC modes. It is found that there is no difference in the data between these two modes. Magnetization isotherms (ZFC only), which are presented in fig. 4, show clear hysteresis at $T=3\,\text{K}$ and $30\,\text{K}$ which was not observed in undoped CeFe$_2$ (see inset in the upper corner of fig. 4(a)). We would like to highlight here that no such hysteresis was observed with other rare earths such Gd or Ho even at the lowest temperature. Tang et al. have shown that even with Er, the hysteresis is visible only when the Er concentration is below a critical value ($x = 0.7$) [9]. Though Gd substitution does not alter the magnetocrystalline anisotropy considerably, replacing Ce with Ho should have increased the net rare-earth sublattice anisotropy. The absence of hysteresis in both Gd and Ho compounds positively indicates that the
hysteresis seen in the present (Er doping) case is not
due to the increase in the magnetocrystalline anisotropy
usually expected with Er addition. We would like to
emphasize that even in the field-cooled mode, the $M-H$
loops are all symmetric with respect to both the $M$ and
$H$ axes, thereby indicating the absence of any exchange
bias/exchange anisotropy.

The magnetization is found to be saturated in all the
compounds at around 15 kOe and the saturation value is almost unchanged between 3 and 30 K, except
in $x = 0.25$. In this compound ($x = 0.25$), the saturation magnetization is found to be more at 30 K as compared
to that at 3 K, indicating the predominant ferrimagnetic
coupling in this compound. It may be noted that the
$M-T$ curve in the FC mode (fig. 1) also indicated this
behavior, though it is true that the field cooling did
not start from the paramagnetic phase. But since the
$M-H$ plots in the other Er concentrations showed no
difference between the FC and ZFC modes, we can take
the anomalous $M-H$ behavior of $x = 0.25$ as real. At this
point, it may be recalled that the frequency dependence of
ac susceptibility was almost negligible in this compound.
With increase in temperature, the hysteresis in $M(H)$
isotherms is found to decrease as can be seen from the
decrease in the coercive field ($H_C$) shown in the insets
in the lower right corners of fig. 4. The demagnetization
correction was ignored as only a qualitative analysis of
the hysteresis curves is of importance in this context. The
value of $H_C$ is found to increase with $x$. The remanent
magnetization ($M_r$) initially increases and then decrease
at $x = 0.25$ (see the inset in the upper left corner of
fig. 4(b)). We have also observed that at $x = 0.5$, the $M-H$
curve at 3 K shows a metamagnetic transition (not shown),
similar to that seen in other reports [9]. It has also been reported that $(\text{Ce}_{1-x}\text{Tb}_x)\text{Fe}_2$ as well as $(\text{Ce}_{1-x}\text{Dy}_x)\text{Fe}_2$
show metamagnetic transition around $x = 0.5$ [12,13].
We would also like to mention here that there was no frequency dependence in $(\text{Ce}_{1-x}M_x)_2$ ($M=\text{Ga, Si, Al}$)
compounds, which are known to be magnetic glasses [41].

Discussion. - Occurrence of RSG state in
$(\text{Ce}_{1-x}\text{Er}_x)\text{Fe}_2$ is rather unexpected. The RSG state
is found to be a result of randomly magnetized clusters,
instead of random atomic moments. The fact that it is
not achieved with rare earths such as Ho or Gd makes it
even more interesting to probe its origin. An experimental
observation that has been seen with various rare-earth
dopings in CeFe$_2$ is that the $T_C$ increases with the
rare-earth content. This implies that there is an increase
in the net ferromagnetic coupling with the addition
of R, even when the low-temperature state shows spin
glass signatures. It should also be noted that the moment
on Ce in undoped CeFe$_2$ is quite small, due to the de-
localized character of the 4f shell. In fact this is the
main reason for the low $T_C$ of CeFe$_2$. Substitution of rare
earths at the Ce site is found to change the valence state of Ce [9,12,13]. It has been reported that the Ce valency
in CeFe$_2$ is close to 3.29, which decreases to almost 3
on R substitution, resulting in an increase in the Ce
moment. Because of the reduction in the delocalization of Ce, the Fe sublattice moment would also increase,
resulting in the increase in $T_C$ because of the increase
in the 3d-3d exchange. Since Er occupies random (Ce)
positions in the unit cell, it is quite likely that the Ce
moment is non-uniform in the Er-doped compounds. It is
also known that the coupling of both Ce and heavy rare
earths, with Fe is anti parallel. All these point towards
the fact that the magnetic structure in doped compounds,
especially with smaller $x$ values, is non-collinear. One
can attribute the magnetic glassiness and the frustration
to this non-collinearity. But the interesting point is that
though Er doping resulted in the RSG state, the Ho
doping did not show any evidence of it, though the
$T_C$ and the lattice parameter variations are identical
to those of Er. In this context, it is to be noted that ErFe$_2$ is the only member in the RFe$_2$ series which shows
magnetic compensation (at 468 K) in the $M-T$ data.
The $(\text{Ce}_{1-x}\text{Er}_x)\text{Fe}_2$ shows compensation below 300 K [9].
However, there are no reports of such compensation in Gd
or Ho doping. The absence of ZFC-FC bifurcation and
magnetic hysteresis completely rule out the existence
of RSG state in Gd- and Ho-doped CeFe$_2$ compounds [42].
Therefore, it seems that the formation of spin glass
state depends on whether the Fe and (R + Ce) sublattice
moments are comparable or not. If they are comparable,
it is reasonable to assume that the direct FM coupling
of the Fe sublattice competes with the indirect AFM
coupling between Fe and (R + Ce) moments. The fact
that above a certain concentration of Er, the compound
behaves more or less like a normal ferrimagnet supports
this proposition. Another noteworthy point is the absence
of any exchange bias in the FC magnetization isotherms.
This probably indicates that in the RSG state, there is no
FM component, unlike in some materials in which the spin
glass state is assumed to coexist with the FM state [33].
It should be mentioned here that, like Er substitution,
a certain concentration of Tb and Dy doped in CeFe$_2$
(namely Ce$_{0.6}$Tb$_{0.4}$Fe$_2$ and Ce$_{0.6}$Dy$_{0.4}$Fe$_2$, respectively)
is reported to show a compensation point, with the former
showing the compensation below 300 K [13].

Conclusions. – In this report we have shown that
$(\text{Ce}_{1-x}\text{Er}_x)\text{Fe}_2$ ($x = 0.08, 0.12, 0.15, 0.25$) compounds
show re-entrant spin glass behavior. Frequency depend-
ce of ac susceptibility, relaxation in ZFC dc magneti-
zation below the freezing temperature and intrinsic
remanence are shown to establish the re-entrant spin
glass state. We show here that the freezing temperature
follows the critical slowing-down mechanism and that the
parameters obtained are comparable to those of typical
spin glasses and other known RSG systems. The RSG
state is attributed to the random distribution of Er and
the modification of the Ce and Fe moments due to the
band structural changes brought about by the lattice
expansion. We further conclude that the occurrence and the strength of the RSG state in this system are dependent on the Er concentration. With increase in Er concentration, the system is found to gradually change to a non-collinear ferrimagnet and finally to a normal ferrimagnet at $x = 1$. The fact that all rare earths do not give rise to these features makes this study interesting.

***

KGS and AKN thank Board of Research on Nuclear Sciences (Department of Atomic Energy, Government of India) for providing the financial support for carrying out this work.

REFERENCES