Static magnetic response of clusters in $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_{1.95}\text{Ho}_{0.05}\text{O}_4$ spinel oxide

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Abstract

Earlier investigations of $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ spinel oxide has shown the existence of "super-ferromagnetic" clusters containing $\text{Fe}^{3+}$ and $\text{Ho}^{3+}$ ions along with small size clusters of $\text{Fe}^{3+}$ ions (Bhowmik et al., J. Magn. Magn. Mater. 247, 83 (2002)). Here, we report the static magnetic response of these clusters. The experimental data suggest some interesting magnetic features, such as, enhancement of magnetization; re-entrant magnetic transitions with paramagnetic to ferromagnetic state below $T_C \approx 225$ K and ferromagnetic to spin glass like state below $T_m \approx 120$ K; appearance of field induced ferromagnetic state. We also observe an unusual maximum in the thermoremanent magnetization (TRM) vs temperature data. Our measurements suggest that this unusuality in TRM is related to the blocking of "super-ferromagnetic" clusters, out of the ferromagnetic state, along their local anisotropy axis.

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I. INTRODUCTION

In present scenario of condensed matter physics rare earth ions are playing an active role in magnetic oxides and this is intensively studied in case of perovskites and pyrochlores [1,2]. The spinel oxides with formula unit AB$_2$O$_4$ [3] represent another most important and interesting class of magnetic materials. The magnetic disorder and exchange frustration in spinel structure, introduced by size mismatch of cations and competition between superexchange interactions amongst A and B site moments, gives rise to various kinds of magnetic order [4]. Inspite of the enormous substitution works in spinel oxide [3,5], less attention has been paid for the substitution of rare earth (RE) ions in spinel oxide. However, the theoretical and experimental investigation of RE substitution are also equally important, as given for transition ion substitution in spinel, for the understand of coupling effect between 3d-4f spins in spinel oxide. For example, the vector mean-field model (Heisenberg) [6] predicts the appearance of a re-entrant phase in a disorder magnet [4,7] where the ferromagnetic order of longitudinal spin components coexists with the spin glass order of transverse spin components. On the otherhand, strong crystalline electric field effect of rare earth (RE) ions rotate the spins along its local anisotropy axis and therefore, gives an Ising character to the spins. Consequently, the critical phenomena like magnetic transitions with AT and GT lines in rare earth containing disorder magnetic systems are expected to be different in comparison with the isotropic (Heisenberg) spin glass behaviour of transition metal ions [8]. Therefore, a systematic and detailed investigations of rare earth substitution are very essential over a wide range of spinel oxides, with different magnetic structure such as long range ferro/ferrimagnet, antiferromagnet, spin glass/cluster spin glass etc.

In most of the earlier known cases, rare earth (RE) ions were substituted in a long range ferrimagnetic spinel oxides like Ni-Zn ferrite, Co-ferrites [9,10]. The lack of sufficient experimental reports dealing with rare earth substitution in a frustrated and magnetically diluted spinel oxide motivated us to study the effects of rare earth ions in Co$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ spinel oxide. This system with cations distribution (Zn$^{2+}_{0.8}$Fe$^{3+}_{0.2}$)$_A$[Co$^{2+}_{0.2}$Fe$^{3+}_{1.8}$]$_B$O$_4$ (A: tetrahedral
site, B: octahedral site] is highly A site magnetically diluted, whereas the B site moments form finite clusters and the spins inside the clusters form canted structure [11]. If RE$^{3+}$ ions are introduced in this system, the B site Fe$^{3+}$ ions will be replaced due to strong B site occupancy of RE$^{3+}$ ions and we assume that some of the clusters will contain the RE$^{3+}$ ions. Aside from the large values of free ion magnetic moment ($\sim 10 \mu_B$ for Ho$^{3+}$, Dy$^{3+}$ etc.), the competition between the single ion anisotropy of RE$^{3+}$ ions and random field anisotropy of the spin canting states may strongly modify the cluster glass properties of Co$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ [11].

With the above expectation, we prepared polycrystalline samples of Co$_{0.2}$Zn$_{0.8}$Fe$_{2-x}$RE$_x$O$_4$ ($x \sim 0.05$; RE = Dy, Ho and Er) using conventional solid state method and compared their magnetic properties [12]. It was observed that the magnetic properties of these samples are almost similar irrespective of Dy, Ho and Er ions substitution in place of Fe$^{3+}$ ions. A detailed AC susceptibility measurements [13] on Co$_{0.2}$Zn$_{0.8}$Fe$_{1.95}$Ho$_{0.05}$O$_4$ spinel oxide have indicated the following interesting magnetic behaviours [13]: (i) A re-entrant like magnetic behaviour with paramagnetic$\leftrightarrow$ ferromagnetic$\leftrightarrow$ cluster spin glass order, (ii) Existence of two types of clusters, viz, "super-ferromagnetic cluster" and small clusters associated with two potential barriers as $E_{\pm} = \frac{E_B}{H} [H \mp 2K/Ms]^2$ [13], and (iii) Unusual TRM maximum at $\approx 170$ K comparing the conventional magnetic materials. In this communication we present the static magnetic response of the clusters, i.e., small clusters and "super-ferromagnetic" clusters in Co$_{0.2}$Zn$_{0.8}$Fe$_{1.95}$Ho$_{0.05}$O$_4$ spinel oxide, by performing systematic dc magnetization measurements as a function of temperature, magnetic field and time.

II. EXPERIMENTAL

We have carried out the low field ($< 100$ Oe) dc magnetization measurements using home made magnetometer [14] and high field ($\geq 100$ Oe) magnetic measurements using SQUID (Quantum Design MPMS) magnetometer and vibrating sample magnetometer (Oxford Inc.). The dc magnetization was measured from 10 K to 300 K under zero field cooled (ZFC) and
field cooled (FC) modes. In ZFC (FC) mode the sample was cooled in absence (presence) of magnetic field from 300 K to the measurement temperature (e.g. 10 K), then constant dc field (say, 30 Oe) was applied and magnetization data were recorded while increasing temperature. In FC mode the cooling field and measurement fields are same in magnitude. The field dependence of magnetization was studied under ZFC mode. The experimental procedure of the time dependence of magnetization (relaxation experiment in ZFC and FC mode) and the temperature dependence of thermoremanent magnetization (TRM) are described in discussion section.

III. RESULTS AND DISCUSSION

A. Temperature dependence of magnetization

Fig. 1 shows the comparative ZFC magnetization data at 30 Oe for Co$_{0.2}$Zn$_{0.8}$Fe$_{2-x}$Ho$_x$O$_4$ ($x = 0, 0.05, 1.0$) system. The immediate striking feature is that introduction of 0.05 concentration ($x$) of Ho enhances the magnetization by a factor of about 7 compared to that of undoped sample. We believe that this enhancement primarily arises due to large moment of Ho$^{3+}$ (free ion moment $\approx 10 \mu_B$) which is replacing the moment of Fe$^{3+}$ (free ion moment $\approx 5 \mu_B$). Larger substitution of Ho, instead of further enhancement of magnetization, results in a reduction of magnetization, though it is still higher than that for $x = 0$ sample. This observations are consistent with our argument [12] that at higher concentration ($x$), all the Ho ions are not incorporated in the lattice but results in an impurity phase with low magnetic moment. We do see that substitution of even 0.05 concentration of Ho, suppresses the short range ferrimagnetic transition at $T_{m2} \approx 260$ K occuring in the undoped sample.

The low field dc susceptibility ($M/H$) in Fig. 2 not only shows irreversibility below 220 K between ZFC (Fig. 2a) and FC (Fig. 2b) magnetizations, the temperature dependences are distinctly different (shown together in Fig. 2a inset for 0.2 Oe). While the temperature dependence of ZFC magnetization shows a peak (Fig. 2a), the FC magnetization shows a
distinct plateau region (Fig. 2b) which is typical of a re-entrant spin glass system [7]. We note that the temperatures at which plateau region begins and ends (∼ 100 K to ∼ 175 K) at low fields nearly match the temperature of the two peaks $T_L \approx 90$ K and $T_H \approx 150$ K seen in our $\chi''$ of AC susceptibility [13]. At present the reason for an increase in both ZFC and FC magnetizations below 50 K (Fig. 2), which is more prominent in FC magnetization, is not clear to us. However, the appearance of magnetization minimum at $T_{min}$ can be attributed to different type of compensation effects, e.g., the compensation of antiferromagnetic interactions by ferromagnetic interactions [7,15]; the compensation of magnetization and anisotropy constants arising in multi cations (Ho$^{3+}$, Fe$^{3+}$ and Co$^{2+}$) system [16].

At fields $H \geq 10$ Oe, the following features: (i) magnetic irreversibility between FC and ZFC magnetization below a temperature $T_{irr}$ with a predominant magnetization maximum about $T_m$, and (ii) field dependence of both $T_{irr}$ and $T_m$ suggest spin glass behaviour [8] in our system. For spin glass system, $T_m$ and $T_{irr} \propto H^n$ [8]. Our data for $H \leq 100$ Oe, fits to a single value of $n = 0.46$ (Fig. 3 inset). For $H \geq 500$ Oe, $T_{irr} (H)$ deviates drastically from this exponent value, which may be due to occurrence of field induced ferromagnetism. Interestingly, the value 0.46 of the exponent is closer to the value 0.58 found for La$_{0.5}$Sr$_{0.5}$CoO$_3$ where cluster spin glass is suggested to coexist with ferromagnetic order [17], rather than those predicted by infinite range vector mean-field model $n = 0.67$ (for De Almeida-Thouless (AT) line) and $n = 1$ (for Gabay-Touless (GT) line) [18]. We have also analysed the $T_m (H)$ data and find the exponent $n = 0.023 \pm 0.002$ ($H \leq 100$ Oe). This value is even less than that found for $T_{irr} (H)$. Therefore, our system belongs neither to typical Heisenberg class (exhibits both AT and GT line) nor typical Ising class (exhibit only AT line). However, a randomly anisotropic Heisenberg SG has also shown to exhibit only AT line only at low field range [18]. Our fit value of $n$ (for $T_{irr} (H)$) is consistent with $n = 0.48 \pm 0.01$ seen for a short-range, including anisotropy effect, 3D Ising SG system [19]. Hence, we attribute the deviation of our $n$ values from those of infinite range vector mean-field predicted AT line or GT line, primarily, to the effect of field induced ferromagnetic order in its coexistence with spin glass state. The appearance of only AT type behaviour of $T_{irr} (H)$, we believe,
due to the anisotropy effect of Ho$^{3+}$ ions. The field induced effect on the magnetization minimum at $T_{\text{min}}$ (Fig. 3) can be quantified by taking the difference $\Delta\text{MFC}$ of FC magnetization at $T_m$ ($\text{MFC}_{\text{max}}$) and that at $T_{\text{min}}$ ($\text{MFC}_{\text{min}}$), normalized to $\text{MFC}_{\text{max}}$, i.e., $\Delta\text{MFC} = (\text{MFC}_{\text{max}} - \text{MFC}_{\text{min}})/\text{MFC}_{\text{max}}$. We find that $\Delta\text{MFC}$ decreases from 60% at 1 Oe to 1.2% at 1 Tesla. This clearly shows that the field induced ferromagnetic order, which dominates over the spin glass states in this system, also takes into account for increasing flatness of $M$ vs $T$ curve with increasing field [20].

Because of the field induced FM order, it is not easy to determine the magnetic ordering temperature ($T_C$) in a magnetically disordered system such as ours. From the first order derivative of the real part of AC susceptibility vs $T$ curve, we derived possible value of $T_C$ as $\sim$190 K [12]. However, the dc magnetization data (Fig. 2a inset) show magnetic irreversibility even up to 220K, suggesting $T_C$ is $\geq$ 220 K. We have attempted to estimate $T_C$ from Curie-Weiss law $\chi_{dc} = C/(T-\theta_p)$, from the dc susceptibility ($\chi_{dc}$) data at 100 Oe. We find that the data above 275 K gives a good fit (inset of Fig. 3) for Curie-Weiss law with Curie constant $C \approx 0.14$ and paramagnetic Curie temperature $\theta_p \approx 240$K. The positive value of $\theta_p$ confirms the dominant ferromagnetic interactions in our system.

**B. Field dependence of magnetization**

Fig. 4 shows the magnetic hysteresis of the sample over the field range -1.5 Tesla to +1.5 Tesla. The wide hysteresis loop at 10 K with a coercive field ($H_C$) $\sim$ 0.25 Tesla and a remanent magnetization ($M_R$) $\sim$ 32 emu/g confirm the presence of ferromagnetic interactions in this material at low temperature. The hysteresis loop area drastically reduces on increase of temperature with $H_C$ and $M_R$ becoming small above 50 K and no hysteresis loop is observed at $T \geq 250$K. The sharp increase of $H_C$ below 100K also takes into account the effect of coexisting spin glass state at low temperature. The small peak in $M_R$ around 170 K and small increase in $H_C$ around 160K are most probably related to anisotropy contribution of Ho$^{3+}$ ions [21].
Fig. 5 shows magnetization (M) vs field (H) data at selected temperatures with H upto 12 Tesla. In the temperature range 10-160K, the M shows an initial rapid increase, followed by slower increase with H which is a typical ferro or ferrimagnetic response of the sample. The lack of saturation of M upto 12 Tesla suggest that the sample is not an infinite long range order ferromagnet [15,22]. The isotherms can represent either a system with canted spin structure in the ferromagnetic cluster [17] or a system where ferromagnetic order coexists with superparamagnetic component [21]. In order to determine the spontaneous magnetization (M\textsubscript{S}) due to ferromagnetism, we applied Arrot plot (M\textsuperscript{2} vs H/M) (Fig. 5b). Although M(H) at 250 K and 305 K show non-linear increase, Arrot plot gives no M\textsubscript{S} for these temperatures, which indicate that at T ≥ 250 K, the system is in a paramagnetic regime mixed with short range interacting clusters. We fit M\textsubscript{S}(T) data to the functional form: M\textsubscript{S}(T) = K(T\textsubscript{C}-T)\textsuperscript{1/\gamma} for T < T\textsubscript{C}, as has been applied for disorder ferromagnet [4]. The best fit was obtained with K = 3.646, \gamma = 0.55±0.01 and Curie temperature T\textsubscript{C} = 225±5 K. The inset of Fig. 5b also shows that the obtained value of M\textsubscript{S} deviates and remain lower below 100 K than the fitted curve using above equation. This indicates the canted spin structure in those clusters which show low temperature spin glass freezing.

To verify the originality of the observed peak temperatures in AC susceptibility and dc magnetization data, the non-linear response of the sample is examined at low field (H ≤ 100 Oe). The dc susceptibility (\chi\textsubscript{dc} = M/H) consists of linear (independent of field) and non-linear (dependent on applied field) components as

\[
\chi\textsubscript{dc} = \chi_1 - \chi_3 H^2 + \chi_5 H^4.
\]  

The linear component (\chi_1) was obtained from \chi\textsubscript{dc} vs H plot at the zero field limit. \chi_3 and \chi_5 are the non-linear components of dc susceptibility. The non-linear susceptibility is defined as \chi\textsubscript{nl} = \chi_1 - \chi\textsubscript{dc}. The non-linear components were obtained by polynomial fit of \chi\textsubscript{nl}/H\textsuperscript{2} (y axis) vs H\textsuperscript{2} (x axis) plot at each temperature. For discussion, we neglect \chi_5 and higher non-linear components as their magnitudes are negligibly small. Fig. 6a shows a broad maximum in \chi_1 at ≈ 110 K and clear peak at ≈ 166 K. Eventhough, there are the signatures of two
peaks at $\approx 200$ K and 227 K, respectively, but they are of the order of the limit 10% error. However, the temperature dependence of $\chi_3$ (Fig. 6b) shows four clear peaks at $\approx 105$ K, 166 K, 200 K, 230 K, respectively. The low temperature peak at $\approx 105$ K may be associated with the cluster spin freezing below $\approx 120$ K [13]. Some specific features of $\chi_3$ at 105 K, i.e., more divergence than other three peaks and rapid decrease of $\chi_1$ below 105 K suggest low temperature re-entrant magnetic phase, as predicted in Ising model [18]. The fourth one at $\approx 230$ K is close to the Curie temperature ($T_C \approx 225 \pm 5$ K) obtained from Arrot plot (Fig. 5b) and, so associated with the paramagnetic to ferromagnetic phase transition of the sample. The $\chi_3$ peak at $\approx 166$ K is close to the high temperature $\chi''$ peak at $T_H \approx 160$ K [13] and we suggest its origin from the domain rotation effects [18] of "super-ferromagnetic" clusters. Finally, the $\chi_3$ peak at $\approx 200$ K is near to the value of $T_C \sim 190$ K obtained from the first order derivative of $\chi'$ vs T data [12] and its origin is not clear at present.

C. Time dependence of magnetization

To study the time response of the magnetic clusters at different temperatures below 250 K, we cooled the sample from 300 K under ZFC and FC mode. In view of the unusual increase of TRM above 150 K and with peak at $\sim 170$ K (see next section, Fig. 8) in this sample, we have investigated time response of magnetization at 153 K (ZFC) and 160 K (FC) to see if the increase in TRM has any effect on the time response also. 160 K is chosen with the exception that it would not make much difference with respect to 153K, and if at all it would show some effect, a slightly higher temperature is taken to ensure the effect, if any, of the TRM maximum. The sample was waited for 300 sec at 153 K (ZFC) and at 160 K (60 Oe FC) prior to application and removal of 60 Oe field, respectively. Fig. 7a shows that the magnetization at 153 K in the presence of field achieves equilibrium quite fast and remains constant during the observation time upto $5 \times 10^4$ sec. On the other hand, the remanent magnetization ($M_R$) at 160 K decreases with time (Fig. 7a) following power law behavior.
\[ M_R = M_0 t^{-\alpha} \] (2)

where \( t \) is the time of observation and \( \alpha \) is the exponent. Thus, in the time dependence, we did not observe any effect of maximum in TRM vs T. Before confirming about no effect of maximum in TRM, we have applied almost identical condition to the sample for \( M_R \) vs \( t \) measurement at 160 K which was given during TRM vs T measurement. In this process, the sample was field cooled (60 Oe) from 300 K to 38 K. Then field was removed and \( M_R(t) \) was recorded for \( 6 \times 10^3 \) sec. After measurement, sample was slowly warmed up to 160 K in the absence of external field and the \( M_R(t) \) was observed for \( 4.5 \times 10^4 \) sec. Eventhough the condition is identical, \( M_R \) does not increase with time (Fig. 7a), as observed with temperature (Fig. 8). Fig. 7a also shows that the \( M_R \) at 160 K, after thermal cycling, is lower in comparison with earlier data at 160 K (Fig. 7a). Interestingly, \( M_R \) still follows power law, but with larger value of exponent. Therefore, inspite of the fast equilibrium at 153 K (ZFC), the magnetic relaxation at 160 K suggests that a fraction of clusters, out of ferromagnetic state, are blocked in this temperature regime and showing relaxation effect.

The time dependence of \( M_R \), after direct 60 Oe field cooling, for all other temperatures in the range 20 K to 250 K (data not shown) also follow power law behaviour. The values of fit parameters are shown in Fig. 7b. The decrease of \( M_0 \) with increase of temperature is expected due to thermally activated processes. The application of power law decay and almost linear decrease of exponent \( \alpha \) below 100 K indicates that spin glass state of the sample is of Ising type [23]. The decrease of the exponent below 100 K implies that magnetic relaxation becomes very slow due to freezing of clusters, whereas the decrease of the exponent above 100 K is well explained by the blocking of a fraction of clusters in the ferromagnetic state. The ferromagnetic clusters quickly reach to its equilibrium magnetization because of very small coercive field (inset of Fig. 4b), where as the clusters in the blocking state slowly relax. Above 250 K the system is in the paramagnetic state and all magnetic clusters instantly reach its equilibrium value (\( M_0 \)) and hence \( \alpha \) again tends to zero value.
D. Thermoremanent magnetization

Thermoremanent magnetization (TRM) vs temperature (T) has been measured by cooling the sample from 300 K to 10 K in presence of constant magnetic field and after reducing the cooling field to zero value. The unusual observation of a maximum in the TRM(T) data at $T_{trm}^{max} \approx 170$ K (for 30 Oe cooling field) [13] has generated further interest for the present sample. To observe the effect of higher applied fields ($\sim 500$ Oe, 1 kOe and 1 Tesla) on TRM vs T, SQUID magnetometer was employed. Care was taken to ensure that the remanent field of superconducting magnet is as close to zero as possible, by measuring the remanent field with a known paramagnetic sample and then applying a compensating field during TRM measurement. The TRM data (normalized by colling field: $H_{FC}$) (Fig. 8) show a maximum about 180 K and a minimum about 125 K for $H = 500$ Oe. It is also observed that the maximum in TRM is suppressed with increasing cooling field to 1 Tesla. Consequently, the minimum in TRM about 125 K transform into a plateau in the temperature range 100 K to 175, which is a character of re-entrant magnetic behaviour [24]. It is also found for 500 Oe that the increase of TRM at 180 K with respect to TRM at 125 K is only 0.4% of the decrease of TRM at 10 K with respect to TRM (125 K). This confirms that a spin glass state, coexisting with ferromagnetic state, at low temperature sharply decreases above 125 K and a superparamagnetic state of a fraction of clusters (super-ferromagnetic) develops in the ferromagnetic state above 125 K which we postulated in this sample [13]. Eventhough the contribution of superparamagnetic type clusters is about 0.4 %, but their existence in the sample is intrinsic. We suggest that the minimum in TRM about 125 K arises due to the competition effects between spin glass component and super-ferromagnetic component of the clusters. The ”super-ferromagnetic” clusters, even, show spontaneous magnetization in absence of external field due to their strong internal field ($H_i = 2K/M_S$) and below 180 K these clusters are more relaxed (blocked) in different local anisotropy axes related to Ho$^{3+}$ ions. In Ref. [13], we demonstrated the freezing of ”super-ferromagnetic” clusters due to the antiferromagnetic inter-cluster interactions. The larger negative TRM
with asymmetry behaviour for $H_{FC} = -1 \text{kOe}$ with respect to that taken for $+1 \text{kOe}$ (inset of Fig. 8) indicates that really, blocking of the ”super-ferromagnetic” clusters along its local anisotropy axes prefers antiferromagnetic direction with respect to the ferromagnetic order of large number of small clusters. We, further, suggest that the magnetic behaviour of the ”super-ferromagnetic” clusters will be governed by Ho$^{3+}$ moment due to its large magnetic moment and anisotropy. If we consider the ”super-ferromagnetic” cluster as single domain particle, the effective spin of this cluster may add Ising nature to the sample [23] which is reflected in time dependence of field cooled remanent magnetization and in $T_{irr} (H)$ fit. At this stage, we suggest that the re-orientation effect of Ho$^{3+}$ spins [15,21] below 125 K are the cause of ferromagnetic increase of magnetization below 50 K (Fig. 2 and Fig. 3). Since the magnetic order of ”super-ferromagnetic” cluster is local anisotropy effect, this effect is very prominent in low field magnetization data (Fig. 2) and TRM vs T data (Fig. 8) and in high field measurement this effect is suppressed by the global effect of small size clusters (see Fig. 3 and Fig. 8 for 1 Tesla).

At this juncture, we would like to add a note of caution for measurements performed in magnetometers using superconducting magnets, which have remanent field due to trapped flux when magnet current is made zero. The remanant field would be large (usually about -50 G and could be even higher) in high field (12 Tesla) magnetometers such as VSM using Nb$_3$Sn magnets. If sufficient caution is not exercised during application of such magnetometer, one might get negative magnetisation at low field values. An example of such an observation encountered by us is shown in Fig. 9. Therefore, sufficient care should be taken [25] to ensure that the field is truly zero by applying compensating field of exact magnitude for the magnetic response in delicate systems such as spin glass.

IV. CONCLUSIONS

On the basis of dc magnetic measurements of Co$_{0.2}$Zn$_{0.8}$Fe$_{1.95}$Ho$_{0.05}$O$_4$ spinel oxide, we made the following conclusions:
(i) The antiferromagnetic B sublattice superexchange ($J_{BB}$) interactions are strongly modified into dominant ferromagnetic interactions due to random B site occupancy of Ho$^{3+}$ ions. Consequently, the B site clusters are grouped into ”super-ferromagnetic” clusters with Ho$^{3+}$ moments and small clusters without Ho$^{3+}$ moments.

(ii) ”Super-ferromagnetic” clusters, a fraction in number of total B site clusters, show super-paramagnetic blocking below 180 K along different local axes determined by anisotropy contribution of Ho$^{3+}$ and contribute ferromagnetic order below 50 K due to spin re-orientation effect of Ho$^{3+}$. On the otherhand, small clusters show spin glass behaviour below $\approx$ 120 K. In presence of high magnetic field (even at very low field FC magnetization) the local effect of Ho$^{3+}$ is suppressed by the field induced ferromagnetic order. As a result, the sample shows re-entrant magnetic behaviour with paramagnetic to ferromagnetic state below $T_C \approx 225\pm 5$ K and ferromagnetic to cluster spin glass state below $T_f \approx 120$K.

(iii) The random distribution and competition between superexchange interactions amongst various magnetic moments (Fe$^{3+}$, Co$^{2+}$ and Ho$^{3+}$) shows spin glass behaviour in the sample, where as the dominant ferromagnetic order inside the ”super-ferromagnetic” clusters and spin canting effect inside the small clusters show field induced (not infinite long range) ferromagnetic order in the sample.

(iv) The existence of cluster size distribution and competition of different magnetic order deviate the spin glass dynamics of the sample both from typical character of vector mean-field predicted Ising and Heisenberg SG. However, the single domain nature, along with anisotropy effect, of the ”super-ferromagnetic” clusters show the sample to be close to Ising SG or randomly anisotropic Heisenberg SG.

(v) Finally, the unusual TRM maximum about 170 K is attributed to the competition between ferromagnetic order and superparamagnetic blocking related to anisotropy effect of Ho$^{3+}$ moments in ”super-ferromagnetic” clusters.

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Figure Captions

Fig. 1 M vs T data at 30 Oe in ZFC mode for Co$_{0.2}$Zn$_{0.8}$Fe$_{1.95}$Ho$_{0.05}$O$_4$ sample. The left and right arrow indicates the magnetization (M) axis.

Fig. 2 a) ZFC, b) FC magnetization of Co$_{0.2}$Zn$_{0.8}$Fe$_{1.95}$Ho$_{0.05}$O$_4$ sample at 0.2 Oe to 5 Oe. Inset of a) shows the ZFC and FC magnetization at 0.2 Oe.

Fig. 3 ZFC and FC magnetization vs T at different fields. $T_m$: MZFC peak temperature, $T_{irr}$: temperature below which MFC shows irreversibility with terpect to MZFC, $T_{min}$: temperature where MFC shows minimum. Inset shows $T_{irr}(H)$ (left scale) and H/M vs T data (right scale).

Fig. 4 Inset shows temperature dependence of coercive field $H_C$ (left scale) and remanent magnetization $M_R$ (right scale). The main panel shows the hysteresis data at different temperatures.

Fig. 5 a) M vs H data at different temperatures. solid lines guide to eye. b) Arrot plot ($M^2$ vs H/M) at different temperatures. Inset (b) shows the spontaneous magnetization ($M_S$), obtained from Arrot plot and fit data (solid line).

Fig. 6 Temperature dependence of linear and first component of non-linear dc susceptibility, obtained from M vs H (0 Oe to 100 Oe) data, for Co$_{0.2}$Zn$_{0.8}$Fe$_{1.95}$Ho$_{0.05}$O$_4$ spinel oxide. Note the scale factor for $\chi_3$ and the arrows indicate the possible transition temperatures. data are plotted with 10% error.

Fig. 7 a) Time dependence of magnetization (ZFC: 153K, FC: 160K). b) Temperature dependence of the $M_0$ obtained by fitting the relaxation data. Inset shows the temperature dependence of the $\alpha$ obtained by fitting.

Fig. 8 TRM vs T data for 500 Oe to 1 Tesla cooling field. The measurement was performed using SQUID with compensating field +10 Oe. Inset shows TRM vs T data measured at +1 Tesla and -1 Tesla cooling field.

Fig. 9 TRM vs T data measured at different cooling field ($H_{FC}$) using VSM magnetometer.
REFERENCES

[1] E.L. Nagaev, Phys. Rep. 346, 387 (2001); M.B. Salamon and M. Jaime, Rev. Mod. Phys. 73, 583 (2001)

[2] J.A. Alanso, J.L. Martinez, M.J. Martinez-lope, M. T. Casais, Phys. Rev. Lett. 82, 189 (1999)

[3] G. Blasse, Philips Res. Rep. (suppl.) 64, 33, 45, 51, 52 (1964)

[4] A. Belayachi, J.L. Dormann and M. Nogues, J. Phys. Condens. Matter. 10, 1599 (1998)

[5] J.L. Dormann, M. Nogues, J. Phys.: Condens. Matter 2, 1223 (1992)

[6] M. Gabay and G. Toulouse, Phys. Rev. Lett. 47, 201 (1981)

[7] J. Dho, W.S. Kim and N.H. Hur, Phys. Rev. Lett. 89, 027202 (2002)

[8] J. A. Mydosh, Spin glasses: An experiemntal Introduction (Taylor & Francis, 125 (1993)

[9] N. Rezlescu, E. Rezlescu, C. Pasnicu, M. Craus, J. Phys.: Condens. Matter 6, 5707 (1994)

[10] C. Yan, F. Cheng, Z. Peng, Z. Xu, C. Liao, J. Appl. Phys. 84, 5703 (1998)

[11] R. N. Bhowmik and R. Ranganathan, J. Magn. Magn. Mater. 248, 101 (2002)

[12] R. N. Bhowmik and R. Ranganathan, J. Alloys. Comp. 326, 128 (2001)

[13] R. N. Bhowmik and R. Ranganathan, J. Magn. Magn. Mater. 247, 83 (2002)

[14] Anindita Ray, A. Chakravarty and R. Ranganathan, Rev. Sci. Instrum. 67, 7891996

[15] J. Gal, I. Yaar, E. Arbaboff, H. Etedgi, F.J. Litterst, K. Aggarwal, J.A. Pereda, G.M. Kalvius, G. Will and W. Schäfer, Phys. Rev. B 40, 745 (1989)

[16] S. Ohkoshi, Y. Abe, A. Fujishima and K. Hashimoto, Phys. Rev. Lett. 82, 1285 (1999)

[17] D.N.H. Nam, K. Jonason, P. Nordblad, N.V. Khiem and N.X. Phuc, Phys. Rev. B 59,
[18] J.H. Zhao, H.P. Kunkel, X.Z. Zhou and G. Williams, Phys. Rev. B 66, 184428 (2002)

[19] G. C. DeFotis, G.S. Coker, J.W. Jones, C.S. Branch, H.A. King, J.S. Bergman, S. Lee and J.R. Goodey, Phys. Rev. B 58, 12178 (1998)

[20] J. Hesse, C. Böttger, A. Wulfes, J. Sievert and H. Ahlers, Phys. Stat. Sol. (a) 135, 343 (1993)

[21] J. Geshev, L.G. Pereira, J.E. Schmidt, and M. Mikhov, J. Appl. Phys. 90, 6243 (2001)

[22] J.Mira, J. Rivas, M. Vazquez, J. M. Garcia-Beneytez, J. Arcas, R.D. Sanchez and M.A. Senaris-Rodriguez, Phys. Rev. B 59, 123 (1999)

[23] W. Kinzel, Phys. Rev. B 19, 4595 (1979)

[24] K. Muraleedharan, J.K. srivastava, V.R. Marathe and R. Vijayaraghavan, J. Phys. C: Solid state Phys. 18, 5355 (1985)

[25] see Fig. 2 for example, how a very small field can make a large difference to the magnetization. This measurement performed in a air core copper magnet having no remanent field.
Fig. 1 $M$ vs $T$ data at 30 Oe in ZFC mode for $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_{2-x}\text{Ho}_x\text{O}_4$ sample.

The left and right arrow indicates the magnetization ($M$) axis.
Fig. 2 a) ZFC, b) FC magnetization of $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_{1.95}\text{Ho}_{0.05}\text{O}_4$ sample at 0.2 Oe to 5 Oe. Inset of a) shows the ZFC and FC magnetization at 0.2 Oe.
Fig. 3 ZFC and FC magnetization vs T at different fields. $T_m$: MZFC peak temperature, $T_{irr}$: temperature below which MFC shows irreversibility with respect to MZFC, $T_{min}$: temperature where MFC shows minimum. Inset shows $T_{irr}(H)$ (left scale) and $H/M$ vs $T$ data at 100 Oe (right scale).
Fig. 4 Inset shows temperature dependence of coercive field $H_C$ (left scale) and remanent magnetization $M_R$ (right scale). The main panel shows the hysteresis data at different temperatures.
Fig. 5 a) $M$ vs $H$ data at different temperatures. Solid lines guide to eye.

b) Arrot plot ($M^2$ vs $H/M$) at different temperatures. Inset in (b) shows the spontaneous magnetization ($M_S$), obtained from Arrot plot and fit data (solid line).
Fig. 6 Temperature dependence of linear and first component of non-linear dc susceptibility, obtained from $M$ vs $H$ (0 Oe to 100 Oe) data, for $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_{1.95}\text{Ho}_{0.05}\text{O}_4$ spinel oxide. Note the scale factor for $\chi_3$ and the arrow indicate the possible transition temperatures. Data are plotted with 10% error.
FC down to 38K, reducing the field to zero value remanent magnetization were recorded at 38K during 6000 s, heated upto 160K in absence of field, remanent magnetization were recorded at 160K with time.

FC down to 160K, reducing the field to zero value remanent magnetization were recorded at 160K.

Fig. 7 a) Time dependence of magnetization (ZFC : 153K, FC : 160K).
b) Temperature dependence of $M_0$ obtained by fitting the relaxation data. Inset shows the temperature dependence of $\alpha$ obtained by fitting.
Fig. 8 TRM vs T data for 500 Oe to 1 Tesla cooling field. The measurement was performed using SQUID with compensating field = +10 Oe. Inset shows TRM vs T data measured at +1 Tesla and -1 Tesla cooling field.
Fig. 9 TRM vs T measured at different cooling field ($H_{FC}$) using VSM magnetometer.