Ferromagnetic to spin glass cross over in (La,Tb)$_{2/3}$Ca$_{1/3}$MnO$_3$

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In the series La$_{2/3-x}$Tb$_x$Ca$_{1/3}$MnO$_3$, it is known that the compositions are ferromagnetic for smaller values of $x$ and show spin glass characteristics at larger values of $x$. Our studies on the magnetic properties of various compositions in the La$_{2/3-x}$Tb$_x$Ca$_{1/3}$MnO$_3$ series show that the cross over from ferromagnetic to spin glass region takes place above $x \approx 0.1$. Also, a low temperature anomaly at 30 K, observed in the ac susceptibility curves, disappears for compositions above this critical value of $x$. A mixed phase region coexists in the narrow compositional range $0.1 \leq x \leq 0.125$, indicating that the ferromagnetic to spin glass cross over is not abrupt.

I. INTRODUCTION

There has been a wide interest in the study of the substituted perovskite-type manganites, La$_{1-x}$A$_x$MnO$_3$, in order to understand the different aspects of the complex magnetic behaviour exhibited by these compounds. The double exchange interactions involving Mn$^{3+}$ and Mn$^{4+}$ ions give rise to ferromagnetism in the substituted manganites. The changes in the Mn-O-Mn bond angle, from structural distortions, are very crucial in determining the strength of the ferromagnetic interactions. Highest Curie temperature in the La$_{1-x}$Ca$_x$MnO$_3$ series is obtained for $x \approx 1/3$ and hence there are many studies reported for the composition La$_{2/3}$A$_{1/3}$MnO$_3$. Many interesting new magnetic behaviors are observed when La$^{3+}$ is partially substituted by other trivalent rare-earth ions in La$_{2/3-x}$Ca$_x$MnO$_3$, though there are no changes in the Mn$^3$/Mn$^4$ ratio after substitution. Hwang et al. found a direct correlation between the Curie temperature and the average ionic radius of the La-site ions, where the Curie temperature decreases with decreasing average ionic radius in La$_{0.7-x}$R$_x$Ca$_{0.3}$MnO$_3$ (R = Pr, Y), indicating the role of lattice effects in determining the ferromagnetic properties. Partial substitution of La by smaller ions leads to a decrease in the Mn-O-Mn bond angle and this affects the long range ferromagnetic exchange interactions.

For La$_{0.67-x}$Tb$_x$Ca$_{0.33}$MnO$_3$ (in the reports, the chemical composition is used as (La$_{1-x}$Tb$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$), a gradual decrease in the Curie temperature is observed with increasing concentration of Tb. This is also associated with a broadening of the magnetic transition and ultimately a spin glass behaviour is observed at larger concentrations of Tb. In La$_{0.67-x}$Tb$_x$Ca$_{0.33}$MnO$_3$, the evolution of a spin glass (SG) or a cluster glass (CG) state is thought to be due to the competing interactions of ferromagnetic (FM) and antiferromagnetic (AFM) types or the random distribution of Mn-O-Mn bond angle which suppresses the exchange strength between the Mn ions significantly. At sufficiently large values of $x$ ($x \approx 0.22$), short range ordered magnetic clusters are formed with typical magnetic coherence length of around 18 Å, at low temperatures.

The reported studies on La$_{0.67-x}$Tb$_x$Ca$_{0.33}$MnO$_3$ are performed on ferromagnetic compositions ($x \leq 0.1$) or spin glass compositions ($x > 0.15$) and therefore no information is available on the changeover region from ferromagnetic to spin glass characteristics. In order to explore the critical concentration of the Tb ions which results in the formation of magnetic clusters leading to spin glass characteristics, a series of compositions with very close values of $x$ between 0.1 and 0.15 in La$_{0.67-x}$Tb$_x$Ca$_{0.33}$MnO$_3$ have been studied. The critical concentration is found to be $x \approx 1/8$, and interesting magnetic properties are observed for compositions close to the cross over region.

II. EXPERIMENTAL

The polycrystalline La$_{0.67-x}$Tb$_x$Ca$_{0.33}$MnO$_3$ compositions were synthesized by the conventional solid state route from La$_2$O$_3$, Tb$_2$O$_7$, CaCO$_3$ and MnO$_2$ by mixing these oxides in the required stoichiometry for $x = 0$, 0.03, 0.07, 0.1, 0.11, 0.12, 0.125, 0.13, 0.15, 0.2, and 0.25. The well-mixed powders were initially heated at 1273 K for 48 h, and subsequently at 1473 K for 48 h, 1573 K for 48 h and finally at 1623 K for 24 h, with intermediate grindings at every 24 h steps to ensure the sample homogeneity. Finally the powder samples were pelletized and sintered at 1673 K for 24 h. The samples were characterized by powder X-ray diffraction using Cu Kα radiation and Ni filter. The Mn$^{4+}$ contents in the compounds were estimated by the iodometric titration method. The magnetization measurements were performed on a vibrating sample magnetometer. Temperature variation of the ac magnetic susceptibility of the samples was measured by the mutual inductance method in a field of 2 Oe and at a frequency of 210 Hz.

III. RESULTS AND DISCUSSION

The samples were characterized for their phase purity by X-ray diffraction. All samples showed single phase nature and the diffraction patterns were indexed on the distorted orthorhombic structure with space group Pbnm. The lattice parameters were obtained by least squares refinement of the diffraction patterns and found to be
comparable for those of the corresponding compositions reported previously. The Mn$^{4+}$ content was found to be matching with the expected value of 33\% for all the compositions.

The ac susceptibility curves of the unsubstituted and some Tb-substituted compositions are shown in Fig. 1. With increasing concentration of Tb, the magnetic transition temperature is decreased, and the susceptibility curves show a cusp-like feature when the concentration is increased beyond $x = 0.1$. The shapes and features of the ac susceptibility curves of the Tb-substituted compositions (for $x \leq 0.1$ and $x > 0.15$) are similar to that reported earlier. Although well-defined magnetic transitions are observed for the samples with low concentrations of Tb, there is a distinct anomalous feature in the susceptibility curves of these compositions at low-temperatures. A decrease in the susceptibility is observed below $\sim 30$ K, as soon as a small amount of Tb is incorporated ($x = 0.03$).

As shown in Fig. 2 for $x = 0.1$, a small step in the susceptibility curve is observed below the main magnetic transition. For $x = 0.11$, there is a cusp like feature observed at a higher temperature which is succeeded by the normal flat curve, and finally a drop in the susceptibility below 30 K. This is a complex feature and is not commonly reported for the manganite compositions. As the concentration of Tb ions is further increased, it can be seen that the cusp-like feature becomes more prominent, the flat region gradually vanishes, but a dip in susceptibility is still observed at 30 K for the compositions up to $x = 0.125$. For $x > 0.125$ there is only a cusp-like feature in the ac susceptibility curve as observed for spin glass systems. The composition with $x = 0.33$ is reported to show spin glass behavior. Neutron diffraction studies have indicated ferromagnetically ordered state for $x = 0.067$ at low temperatures, whereas short range ordered clusters are found for $x = 0.2$ (the authors have used the chemical formula as $(La_{1-x}Tb_x)_{2/3}Ca_{1/3}MnO_3$, so that $x = 0.1$ and 0.3, respectively, correspond to $x = 0.067$ and 0.2 in $La_{0.67-x}Tb_xCa_{0.33}MnO_3$). These clusters show spin glass-type of behavior due to competition between FM and AFM types of exchanges.

For the compositions with $x > 0.125$, there is a gradual shift of the cusp towards lower temperatures as the value of $x$ is increased. Also, it was found that the relative susceptibility value also decreased with the increasing Tb concentration. These observations point out the evolution of short range ordering due to the decreasing Mn-O-Mn bond angle and consequent formation of magnetic clusters as the concentration of Tb is increased. This clustering is likely to be due to the breaking or weakening of the double exchange closer to the Tb-sites caused by the local structural distortion and the spin glass like feature originates from the formation of such clusters. The decreasing temperature corresponding to the cusp, identified as $T_g$ henceforth, suggests the confinement of magnetic clusters to shorter length scales as the number of Tb centers is increased (increasing values of $x$).

As shown in Fig. 3 for $x = 0.11$, the ferromagnetic transition temperature decreases almost linearly with increasing $x$, up to $x = 0.125$. For the compositions showing both ferromagnetic and spin glass characteristics ($0.1 \leq x \leq 0.125$), $T_c$ and $T_g$ are determined as illustrated in the inset of Fig. 3 for $x = 0.11$. Here, the $\chi$-T data for $x = 0.15$ (spin glass composition) is shifted towards the right side and that of $x = 0.07$ (ferromagnetic composition) is shifted towards the left side along the $x$-axis, to match with the observed data of the mixed phase composition and the curves are normalized with respect to the maximum values. $T_c$ is taken as the mid point of the magnetic transition. $T_g$ changes abruptly around $x = 0.125$ and varies from 66 K for $x = 0.13$ to 43 K for $x = 0.25$. $T_g$ has been found to be almost independent (40-50 K) of $x$ for higher Tb concentrations. Thus, the lowest value of
at intermediate values of \( x \), the Tb ions form a \( \text{TbMnO}_0 \) separated whose size decreases with increasing \( x \). Thus, the feature at 30 K for 0.03 \( x \leq 0.125 \) is larger than the temperature (30 K) where a decrease in the ac susceptibility is observed for 0 < \( x \leq 0.125 \).

The decrease in the susceptibility below 30 K as soon as a small amount of Tb is incorporated in the lattice of \( \text{La}_{3/3}\text{Ca}_{1/3}\text{MnO}_3 \) has been ascribed to spin glass behavior.\(^2\) However, neutron diffraction studies showed ferromagnetic ordering for \( x = 0.067 \) down to 7 K.\(^{11}\) Thus, the feature at 30 K for 0.03 \( x \leq 0.125 \) is not likely to be spin glass transition. It is possible that at small concentrations the \( \text{Tb}^{3+} \) ions are randomly distributed in the lattice, the double exchange is disturbed around the Tb centers and therefore tiny magnetic clusters are formed with reduced Mn-O-Mn angle. These tiny magnetic clusters remain isolated until \( x = 0.125 \) (1/8) above which larger magnetic clusters are formed due to the breaking or considerable weakening of the three dimensional long range ordering. Thus, the temperature at which a decrease in the susceptibility is observed, due to these small clusters, remains the same until \( x = 1/8 \). The three dimensional ordering is affected when \( x > 1/8 \).

However, there is another possibility that, at small concentrations, the Tb ions form a \( \text{TbMnO}_3 \) like local environment in the lattice of \( \text{La}_{0.67-x}\text{Tb}_x\text{Ca}_{0.33}\text{MnO}_3 \). For \( \text{TbMnO}_3 \), an incommensurate-commensurate phase transition, which is accompanied by a ferroelectric transition, associated with a lattice modulation, is observed close to \( \sim 30 \) K and large magnetic field controlled polarization effects are reported at this temperature.\(^{13,14}\)

A local phase separation exists in the \( x = 0.1 \) sample, as evidenced by a small step- like magnetic transition, indicating that ferromagnetic clusters are started forming at this value of \( x \). It is possible that, above this value of \( x \), some magnetic clusters with short range ordering are separated whose size decreases with increasing \( x \). Thus, at intermediate values of \( x \), the lattice is consisting of larger ferromagnetic clusters with sufficiently long range ordering and smaller short range ordered clusters. Also, for the larger long range ordered part, the magnetic transition temperature decreases due to the decrease in the Mn-O-Mn bond angle. Thus, the clustering may be seen to start when \( x = 0.11 \), where a cusp is also observed along with the normal magnetic features.

Fig. 3 shows the dc magnetization curves of different compositions, measured at 12 K, up to a maximum field of 15 kOe. The magnetization is saturated above 10 kOe for \( x \leq 0.1 \). The variation of the magnetization at the maximum measured field of 15 kOe, as a function of \( x \) in \( \text{La}_{2/3}\text{Tb}_x\text{Ca}_{1/3}\text{MnO}_3 \), is shown in the inset of Fig. 3. The magnetization remains almost the same up to \( x = 0.1 \) and then decreases above this value of \( x \). Also, the magnetization is not saturated for \( x > 0.1 \) in the measured field range. Recent studies suggest the existence of quantum critical point (QCP) effect in \( \text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3 \).\(^{15}\) QCP is defined as a second order transition accompanied by the change of a non-thermal parameter. The observation of QCP in \( \text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3 \) system is as predicted by the theoretical calculations and the QCP in this system was expected for a value of 10-20% of Ga substitution.\(^{15}\) The substitution of a nonmagnetic ion like Ga at the Mn-sublattice of the perovskite-type oxide causes the localization of the electronic states suppressing the double exchange mechanism. For \( \text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3 \), the spontaneous magnetic moment calculated from the experimental neutron diffraction patterns recorded at 1.5 K decreased for \( x > 0.1 \) and vanished for \( x > 0.16 \), indicating electron localization which suppresses the double exchange mechanism. The present dc magnetization data on \( \text{La}_{2/3-x}\text{Tb}_x\text{Ca}_{1/3}\text{MnO}_3 \) shows almost a similar trend, except for the finite value of the magnetization at higher values of \( x \), suggesting the possible existence of QCP in this system also. However, this needs to be ver-
FIG. 5: The virgin magnetization (red curves) and part of the hysteresis loop (blue curves) of $x = 0.125, 0.13, 0.15, \text{ and } 0.2$ in La$_{0.67-x}$Tb$_x$Ca$_{0.33}$MnO$_3$. Note that the $H$ scale is different for $x = 0.125$.

Another interesting behavior observed in the low temperature $M - H$ measurements for the compositions immediately above $x = 1/8$ is an irreversible jump to a ferromagnetic state at higher magnetic fields, as shown in Fig. 5. This is observed only for the virgin magnetization measurements. Up to $x = 0.125$, a normal feature is observed, where the virgin magnetization curve lies inside the hysteresis loop. For $x = 0.2$, the behaviour is similar to that observed for some typical spin glass systems, where the virgin magnetization curve initially lies outside the loop and then merges with the loop at higher fields. On the other hand, for $x = 0.13$ and 0.15, the entire virgin magnetization curve lies outside the hysteresis loop above a certain small field (this small crossing field is observed for $x = 0.2$ and 0.25 also, and increases with $x$), and an anomalous step-like feature is observed in the virgin magnetization curve, similar to that of a metamagnetic transition. However, this transition is completely irreversible. The field above which a broad step is observed is larger for $x = 0.15$ compared to that for $x = 0.13$. After the magnetic field is increased in the negative direction to -15 kOe and when brought back to +15 kOe through $H = 0$, the transition is not observed. This is an irreversible ferromagnetic transition in the sense that the step-like feature is never obtained when the measurements were repeated immediately or even after a time gap of 30 minutes. In the subsequent measurements, the first part of the curve always lies inside the hysteresis loop, like that for the compositions for $x \leq 0.125$. It appears that an irreversible magnetic field induced phase transition is occurred. Similar characteristics were reported for some Pr-based substituted manganite compositions. Do and Hur explained this behavior in terms of the reorientation of the Mn spins pinned by localized Pr moments, whereas Woodward et al. explained the observations in terms of an avalanche behavior. It may be noted that the first part of the virgin curve is similar to that of the spin glass composition $x = 0.2$, in the present case, and therefore, it is possible that the second jump is due to a field induced growth of the larger ferromagnetic clusters. Once the clusters are grown, it is not possible to revert back to the original state due to the unavailability of sufficient thermal energy. The original state is found only when the temperature is raised above the peak temperature and then cooled back in zero field.

IV. CONCLUSIONS

The present studies made on a series of close compositions in La$_{0.67-x}$Tb$_x$Ca$_{0.33}$MnO$_3$ indicate that single phase ferromagnetic compositions are possible for $x < 0.1$, mixed long range ordered ferromagnetic and short range ordered magnetic clusters coexist for $0.1 \leq x < 0.125$ and spin glass like phases are formed for larger values of $x$. The ferromagnetic clusters present in the compositions immediately above the cross over region show magnetic field induced growth and give larger magnetization at higher fields. Further detailed studies are required to understand the complex magnetic behavior shown by these Tb substituted manganite compositions at the intermediate and the cross over regions.

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