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Abstract

Studies aimed at the nature of magnetic interactions in Fe and Cr substituted lanthanum deficient manganites, $La_{0.88}Mn_{1-x}Fe_xO_3$ ($x = 0$–0.15) and $La_{0.88}Mn_{1-y}Cr_yO_3$ ($y = 0$–0.175) are reported. The oxides order ferromagnetically for the entire range of x- and y-values. A decrease in the Curie temperature T_c with increasing substitution is observed for both compounds, but the decrease in T_c is large for Fe substitution. A large decrease was also seen in the low-temperature magnetic moment of Fe substituted samples. The data indicate possible ferromagnetic ordering of Cr and antiferromagnetic ordering of Fe moments in the oxides. Ferromagnetic resonance studies indicate (i) strong spin–lattice effects in the paramagnetic state, (ii) valence-exchange effects in the ferromagnetic state, and (iii) possible microscopic inhomogeneities in Cr-substituted samples

Keywords: Lanthanum deficiency; Fe and Cr substitution; Ferromagnetic resonance

1. Introduction

Lanthanum manganites when substituted with a divalent ion D = Ca, Sr or Ba show ferromagnetism (FM) and metallic conduction [1]. The observation of colossal magnetoresistance (CMR) in such LDMO compounds is of importance for possible applications in sensor technologies. On the other hand, it is not necessary to have divalent substitution in manganites in order to realize FM and CMR. For example, the lanthanum deficient compound, $La_{1-\delta}MnO_3$ (LMO) is reported to show both FM and CMR (for extensive reference see Ref. [2]) [3–6]. For $\delta = 0.1$, the oxide is expected to behave similar to a LDMO system in which 30% of La is replaced with a divalent ion since charge neutrality requires the conversion of 30% of Mn^{3+} to Mn^{4+} in both compounds. Our earlier studies did reveal ferromagnetism with a Curie temperature T_c of 270 K for LMO with $\delta = 0.15$ [6]. Since the ionic radius for Ca and La are approximately of the same magnitude and that the T_c for LDMO with 30% Ca is on the order of 260 K, it is reasonable to conclude that the double exchange between Mn ions [7] is relatively strong in lanthanum deficient LMO compounds. Further insight into the nature of magnetic interactions could be obtained by studies on manganites in which Mn is partially replaced with magnetic or nonmagnetic ions. Results of our studies on Fe and Cr substituted LMO compounds are presented

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here. Although Fe and Cr have ionic radii that are comparable to Mn, the 180° Fe–O–Mn super-exchange is expected to be antiferromagnetic whereas the Cr–O–Mn interaction is predicted to be ferromagnetic [8]. With these in mind, we report here on the preparation and physical properties of polycrystalline samples of $La_{0.88}MnO_3$, $La_{0.88}Mn_{1-x}Fe_xO_3$ ($x = 0$–0.15) and $La_{0.88}Mn_{1-y}Cr_yO_3$ ($y = 0$–0.175). Our data on the Curie temperature and saturation magnetization indicate antiferromagnetic ordering of Fe moments and ferromagnetic ordering of Cr. The overall changes in T_c with x or y were found to be smaller than the values reported for similar substitutions in LDMO compounds [9–13]. In addition, ferromagnetic resonance linewidth data were obtained for information on the g-value, magnetic transitions and the chemical homogeneity of the compounds. Details on these measurements and results are provided in the following sections.

2. Experimental techniques

Polycrystalline samples of $La_{0.88}MnO_3$, $La_{0.88}Mn_{1-x}Fe_xO_3$ ($x = 0$–0.15) and $La_{0.88}Mn_{1-y}Cr_yO_3$ ($y = 0$–0.175) were prepared by repeated mixing and sintering of the required quantities of oxides. The final sintering was done in air at ~ 1350°C for 24 h and all the samples were annealed in the flowing oxygen at 850°C for 24h. Phase purity was checked by X-ray diffraction (XRD) analyses (CuK_α, 40 kV, 20 mA). Magnetisation was measured as a function of temperature and magnetic field using a commercial SQUID magnetometer. Low field magnetoresistance measurements were done in a field of 0.3 T applied parallel to the sample plane using the van der Pauw configuration. Ferromagnetic resonance studies were carried out at 9.2 GHz as a function of temperature. Spheres with a diameter of 0.2–1 mm were prepared from the polycrystalline pellets and placed at the bottom of a TE_{102} reflection-type cavity. The first derivative of the FMR absorption was obtained with a modulation field of 10 Oe at 100 Hz. The resonance field H_r and the peak-to-peak linewidth ΔH were measured over the temperature range 77–292 K.

3. Results

3.1. Lattice parameter, magnetization and magnetoresistance

The XRD pattern of the sample $La_{0.88}MnO_3$ indicated a rhombohedral symmetry with no extra phase and the lattice parameters were found to be $a_R = 5.475 \pm 0.002$ Å and $\alpha = 60.57°$. Comparing our data with those published earlier [5] we estimate the oxygen content to be ~ 2.98. For x(Fe) = 0.05 to 0.1, there was hardly any change in the lattice parameters whereas the values of a_R (α) increased slightly to 5.483 (60.58°) and 5.486 (60.58°) for $x = 0.05$ and 0.175, respectively. A minor impurity peak was also seen for the $x = 0.175$ sample. On the other hand, the value of a_R stayed almost constant for y(Cr) < 0.1 but decreased to 5.472 for y(Cr) = 0.175 with a small increase in α to 60.59° but no impurity phase was seen. Magetisation of all the samples were measured as a function of temperature in $H = 0.01$ T. As an example, data are shown in Fig. 1 for the samples, $La_{0.88}MnO_3$, $La_{0.88}Mn_{0.85}Fe_{0.15}O_3$ and $La_{0.88}Mn_{0.825}Cr_{0.175}O_3$. Sharp transitions were observed for the non-doped and the Cr substituted samples reflecting the quality of the samples. The para-ferromagnetic transition temperatures T_c as a function of x(Fe) and y(Cr) substitutions are shown in Fig. 2. Also shown are the values of T_c in the case of Fe

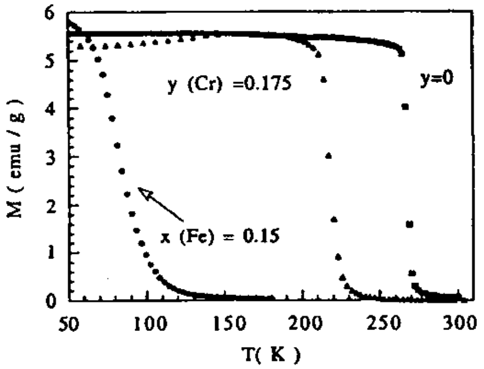

Fig. 1. Magnetisation ($H = 0.01$ T) of $La_{0.88}MnO_3$, $La_{0.88}Mn_{0.85}Fe_{0.15}O_3$ and $La_{0.88}Mn_{0.825}Cr_{0.175}O_3$ as a function of temperature.

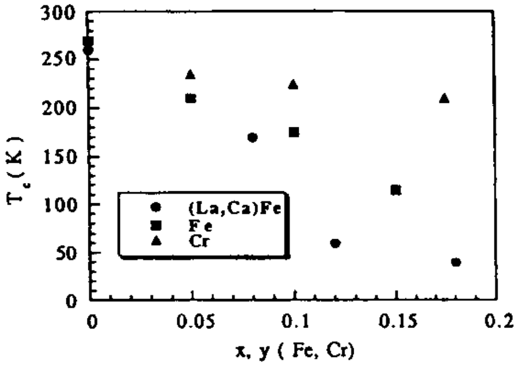

Fig. 2. T_c as a function of x(Fe) and y(Cr) substituted in $La_{0.88}MnO_3$.

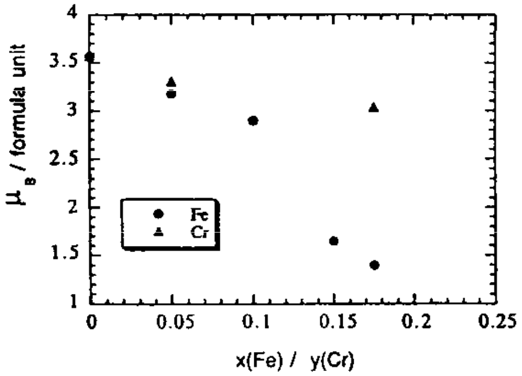

Fig. 3. Magnetic moment per formula unit (5 K, 5 T) as a function of x(Fe) and y(Cr) substituted in $La_{0.88}MnO_3$.

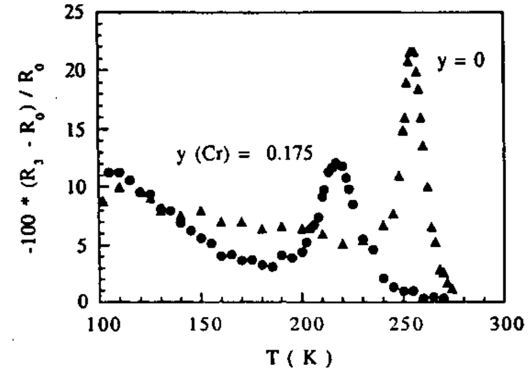

Fig. 4. CMR of $La_{0.88}MnO_3$ ($y = 0$) and $La_{0.88}Mn_{0.825}Cr_{0.175}O_3$ ($y = 0.175$) as a function of temperature.

substituted in $La_{0.63}Ca_{0.37}MnO_3$ (LCMO) taken from Ahn et al. [9]. Three important features can be noted form this figure. First, the depression of T_c caused by the substitution of Fe ($dT_c/dx = 1000$ K/Fe) is larger compared to that caused by Cr substitution ($dT_c/dy = 340$ K/Cr). Second, the depression is much more when Fe was substituted in $La_{0.63}Ca_{0.37}MnO_3$ than when it was substituted in $La_{0.88}MnO_3$. Third, whereas Jian-Wang Cai et al. [10] reported spin-glass behaviour in the 0.1 Fe substituted LCMO; our samples for similar substitution are strongly ferromagnetic. The influence of Fe and Cr on the magnetic moment obtained at 5 K in a field of 5 T is shown in Fig. 3. In the case of Fe, the magnetic moment decreased rapidly. The low field (0.3 T) colossal magnetoresistance, CMR, defined as $[-100*(R_H - R_0)/R_0]$ is shown as a function of temperature for the non-doped and y(Cr) = 0.175 substituted samples in Fig. 4. In the case of the former, a maximum value of 21% was observed at T close to T_c and in the case of the latter, the value was ~ 14% also located at T close to T_c. For $T < T_c$, for both the samples showed, the CMR was around ~ 10% which reflects the grain boundary tunneling magnetoresistance [3]. Other samples also showed similar values of CMR close to T_c.

3.2. Ferromagnetic resonance

The temperature dependence of H_r and ΔH for the $La_{0.88}MnO_3$ (LMO) sample is shown in Fig. 5. At room temperature the linewidth was 280 Oe and the absorption occurred for an applied field corresponding to $g = 2.05$. On cooling the sample, H_r remained constant and ΔH increased until the Curie temperature was reached. Below T_c, in addition to the primary absorption ($H_{r1}, \Delta H_1$), we observed the evolution of a low field resonance ($H_{r2}, \Delta H_2$). The intensity of the low field resonance was found to increase with decreasing temperature, but disappeared below 135 K. The resonance fields showed variations with T only at the lowest temperatures and the linewidths remained temperature independent in the ferromagnetic state.

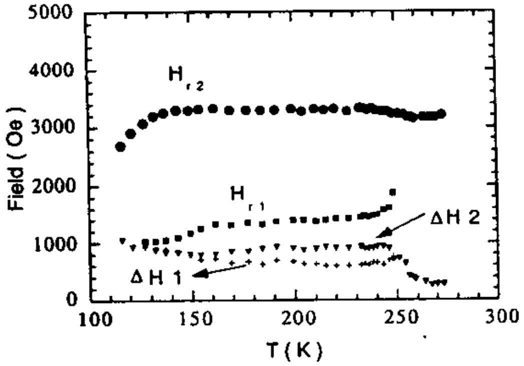

Fig. 5. Temperature dependence of the ferromagnetic resonance (FMR) field H_r and peak-to-peak linewidth ΔH for a 1 mm dia sphere of polycrystalline $La_{0.9}MnO_3$. The Curie temperature for the sample is 270 K. A single resonance with $g = 2.05$ is observed above T_c. Two resonance absorptions are observed below T_c.

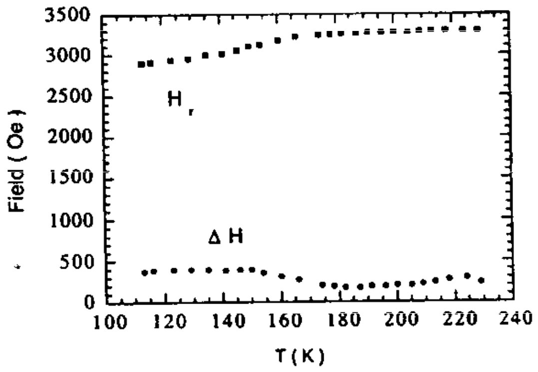

Fig. 6. Resonance field and linewidth as a function of temperature for $La_{0.88}Mn_{0.9}Fe_{0.1}O_3$.

Similar FMR measurements were performed on spheres of the Fe and Cr substituted samples. Figs. 6 and 7 respectively show data for the Fe and Cr substituted samples. Consider the data in Fig. 6 for $La_{0.88}Mn_{0.9}Fe_{0.1}O_3$. A well-defined symmetric FMR absorption was observed in this system. As the temperature was increased from 100 K, H_r was found to increase and ΔH remained constant. The ferromagnetic to paramagnetic transition at T_c was accompanied by a constant H_r and a drop in ΔH. The g-value in the paramagnetic state was 2.00. The linewidth increased with increasing T in the paramagnetic state. Consider now the data in Fig. 7 for $La_{0.88}Mn_{1-y}Cr_yO_3$, for $y = 0.175$. The data are qualitatively similar to the observation for Fe-substituted samples except for the peak in ΔH at the magnetic transition temperature. We also noticed a series of well-defined narrow absorption lines for temperatures close to T_c which are most likely the Walker modes expected for spheres of ferromagnetic samples. The g-value estimated from the room temperature H_r was 1.99 for this sample.

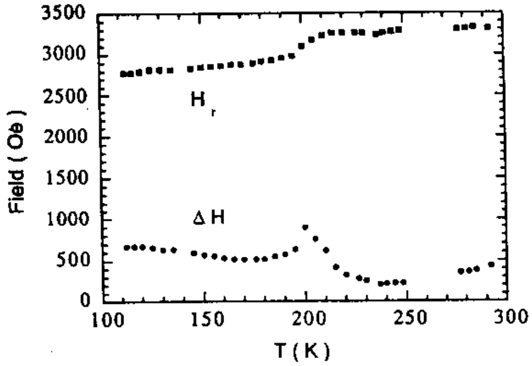

Fig. 7. Resonance field and linewidth as a function of temperature for $La_{0.88}Mn_{0.825}Cr_{0.175}O_3$.

4. Discussion

The appearance of ferromagnetism in the divalent substituted LMO was ascribed to the double exchange mechanism by Zener [7]. The divalent substitution induces a change in the valency of Mn and thus the 30% substituted compound is expected to have 30% Mn^{4+} and 70% Mn^{3+}. The e_g electron from Mn^{3+} can hop to the e_g band of the Mn^{4+} via oxygen by hopping and this double exchange mechanism mediates ferromagnetism also resulting in a semi-conductor to metal transition (SMT). In the La deficient compound ($La_{0.9}MnO_3$), too, the charge balance requires the presence of mixed valent Mn and thus one can account for the observed para-ferromagnetic transition accompanied by a SMT [3–6]. Now, when we substitute Mn by Fe, we note that Fe and Mn have almost the same size. Hence, the lattice parameters do not vary very much as observed and further the valency of Fe is expected to be 3 + [1]. As suggested by Ahn et al. [9], the double exchange may be weakened by the depopulation of the hopping electrons resulting in a reduction of T_c. However, we note that the reduction of T_c is more pronounced in the case of Fe substituted LCMO compared to Fe when substituted in LMO. We note that the LCMO samples are orthorhombic [12] whereas our samples retain their rhombohedral symmetry. However, neutron diffraction data are required to quantitatively interpret our data. Another cause may also be ascribed to the relative effect of oxygen stoichiometry in LCMO and LMO. Next, we note that the depression of T_c is larger in the case of Fe substitution compared to Cr when substituted. This may be explained as follows. It is known that the Fe–O–Mn exchange is anti-ferromagnetic whereas Cr–O–Mn is ferromagnetic. This also explains why the magnetic moment reduced faster in the case of Fe substitution.

Consider the FMR data in Figs. 5–7. We discuss first the paramagnetic g-value and ΔH. For the non-substituted LMO at room temperature the g-value estimated from the resonance field in the paramagnetic state is 2.05. Since the trivalent and the tetravalent Mn-ions are in octahedral crystal fields, the theoretical g-values are 1.994 and 2.2, respectively, for the $3d^3$ (Mn^{4+}) and $3d^4$ (Mn^{3+}) ions [14]. Since the oxide contains 30% Mn^{4+} and 70% Mn^{4+}, the measured g-value is in excellent agreement with the theoretical value of 2.055. Upon substitution of either Fe^{3+} ($g = 1.99$) or Cr^{3+} for Mn^{3+}, the g-value is expected to decrease and is in agreement with the measured values of 1.99–2.00. For $T > T_c$, ΔH in Figs. 4–6 are of comparable magnitude. Both spin–spin and spin–lattice interactions contribute to the linewidth. A dominant spin–spin interaction in a magnetically concentrated system is predicted to result in a temperature independent ΔH. A strong spin-lattice interaction, however, results in phonon modulation of the exchange interactions and crystal fields and leads to a linear increase in ΔH with T [15]. For $T > T_c$, the observed increase in ΔH with increasing T for the oxides is indicative of the strong spin-lattice coupling in the manganites. Next, we discuss the temperature dependence of H_r and ΔH in the ordered state. Consider first the variation of the resonance field. The transition from paramagnetic to ferromagnetic order results in contributions to H_r due to crystalline anisotropy, porosity, and eddy currents [16]. The data in Fig. 5 for LMO are indicative of negligible contributions from porosity, anisotropy and similar effects to H_r since the resonance field for the primary resonance at $g = 2.05$ shows insignificant shift through the paramagnetic to ferromagnetic transition. One of the significant observations in this study is the low field resonance in LMO. The resonance appears just below T_c at $g = 3.6$, and H_{r2} decreases with decreasing temperature. The origin of this absorption which disappears below 135 K cannot be due to some impurity phases. Even though high-resolution electron microscopy in manganites show cubic regions in a rhombohedral matrix leading to microscopic inhomogeneities [17], since the intensity of the low field resonance line is comparable to the primary resonance at $g = 2.05$, any impurity concentration of such levels could easily be identified with X-ray diffraction studies. Srivastava et al. [14] reported the observation of a similar low field resonance in LMCO. Based on the g-values they attributed the primary resonance ($g = 2.05$) to ferromagnetic clusters of Mn^{3+}–Mn^{4+} and the low field resonance to antiferromagnetic clusters of Mn^{3+}–Mn^{3+}. However, the presence of a large fraction of antiferromagnetically coupled trivalent Mn in our compound is not evident from low temperature saturation magnetization data. Any suggestions on the origin of the low field absorption must also account for its absence in Fe or Cr substituted samples. Data on H_r versus T in Figs. 6 and 7 for substituted samples show features similar to the observation for LMO. One observes a downward shift in H_r through the paramagnetic to ferromagnetic transition due to contributions from porosity and other effects mentioned earlier. The shift in H_r, relative to the paramagnetic resonance field, is on the order of 10%. We consider now, the temperature dependence of the linewidth in the ordered state. In the ferromagnetic state, an increase in ΔH is predicted due to several possible causes including spin wave scattering due to surface pits in a sphere, valence–exchange which involves the transfer of electron between $Mn^{3+}$and Mn^{4+} that leads to double-exchange and ferromagnetism in manganites, and slow or fast relaxing impurities. Additional contributions arise due to porosity, anisotropy, and eddy currents [16]. The eddy current contributions are quite small even in metals and can be ignored in the oxides. Thus the paramagnetic to ferromagnetic transitions in polycrystals are generally accompanied by an enhancement in ΔH.

Recently, the data on FMR linewidth as a function of temperature was used to extract information on the chemical homogeneity of lanthanum manganite films and polycrystals [18,19]. Any chemical defects can be modeled as a spread in T_c and M. The linewidth is then the sum of three terms; the intrinsic part, broadening due to a spread in T_c and spread in M. The second term manifests as a peak in ΔH at the average T_c and the third term is linearly proportional to M.

Data on ΔH in Figs. 5–7 show enhanced values relative to the paramagnetic linewidth. The largest increase in ΔH through paramagnetic to ferromagnetic transition is observed for LMO. In the ordered state, however, ΔH for both resonance absorption remained temperature independent for LMO. Since chemical defects are suggested to lead to a rapid decrease in ΔH with increasing T (the term proportional to M) and a peak at T_c (due to spread in T_c) the data are clear evidence for the chemical homogeneity of the sample. The smallest ΔH, data in Fig. 6, is observed for the sample substituted with Fe. The linewidth data is indicative of good sample quality. In Fig. 7 one notices a decrease in ΔH with increasing T and a peak at T_c, quite likely due to microscopic impurities. Further FMR studies are essential for an understanding of contributions to ΔH from valence–exchange and the presence of Mn^{4+} and Fe or Cr which could behave as fast or slow relaxing impurities.

In conclusion, evidence for a relatively strong magnetic interaction in La-deficient manganites were obtained from magnetization and Curie temperature studies on Fe and Cr substituted LMO. In particular, we found a smaller decrease in T_c for Fe substituted in LMO compared to that in LCMO indicating that double exchange was less affected in our samples. Ferromagnetic resonance linewidth data are indicative of possible line broadening due to valence–exchange. The possible presence of microscopic chemical inhomogeneities in Cr substituted samples is inferred from the linewidth data.

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