Magnetic and High Pressure Magnetotransport Properties of Cesium Substituted Lanthanum Calcium Manganites

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ABSTRACT

The nature of the double exchange (DE) interaction in lanthanum manganites is studied through chemical substitutions, Cs for La, and high pressure measurements. Static and high frequency magnetic measurements and high pressure electrical transport studies were carried out on bulk polycrystalline and radio frequency sputtered thin films of \( \text{La}_{0.7-x}\text{Cs}_x\text{Ca}_{0.3}\text{MnO}_3 \) for \( x = 0-0.1 \). The samples are found to be cubic. Curie temperature \( T_c \) measurements provide evidence for bond length related weakening of DE as \( x \) is increased from 0 to 0.03. For higher \( x \), the bond angle related changes lead to an increase in the strength of DE. High-pressure mangetoresistance data indicate both bond length and bond angle related increase of 10–20 K/GPa in \( T_c \) with pressure, with the largest increase measured for \( x = 0.03 \). The rate of increase in the Curie temperature with pressure decreases with increasing \( T_c \). Anomalies are observed in the magnetic parameters for \( x = 0.03 \). The Cs-concentration dependence of the low temperature saturation magnetization show a minimum close to \( x = 0.03 \). Ferromagnetic resonance studies at x-band reveal a 5% decrease in the g-value for \( x = 0.03 \) relative to the end members (\( x = 0 \) and 0.1). The low field magnetostriction for \( x = 0.03 \) indicate a relatively strong electron-phonon-spin coupling compared to neighboring compositions.

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1. Introduction

The observation of colossal magnetoresistance in La-based manganites has renewed interests in these ferromagnetic oxides for useful technologies [1, 2]. The oxides are ferromagnetic for specific compositions and temperatures due to the double exchange (DE) interaction between Mn\(^{3+}\) and Mn\(^{4+}\) [3]. Two important tools for studies on the nature of DE interactions are (i) chemical substitutions and (ii) application of an external hydrostatic pressure. There have been several studies in the past on the influence of substitutions on the strength of DE interactions [4-7]. For example, substitution of smaller (divalent or trivalent) ions for La is expected to lead to a decrease in the bond length and, therefore, an increase in the strength of the double exchange interaction. But a decrease in the Curie temperature $T_C$ was measured for such substitution and was attributed to a decrease in the Mn-O-Mn bond angles [4, 5]. This observation was in agreement with results of structural studies on manganites with trivalent rare-earth substitutions that revealed significant changes only in the Mn-O-Mn bond angle [6]. Thus chemical substitutions lead to competing structural changes that tend to weaken the DE interactions, for example, with smaller rare-earth substitution for La.

The application of an external hydrostatic pressure, however, results in significant changes both in the bond angle and bond distance. With the external pressure as a parameter, one can introduce a controlled decrease in the Mn-O bond length and an increase in the Mn-O-Mn bond angle [8]. Both these changes lead to strengthening of the DE interactions and an increase in the magnetic ordering temperature [6-10]. In addition, pressure and external magnetic field influence the crystal structure and transport properties in a similar way. Since chemical substitutions and high pressure have different influence the magnetic interactions, studies on
high-pressure effects on a manganite with a specific but varying amount of chemical substitution are therefore ideal for an understanding of the nature of the ferromagnetic double exchange.

In this study monovalent Cs (ionic radius on the order of 0.162 nm) was substituted for La (ionic radius = 0.122 nm) in La$_{0.7-x}$Cs$_x$Ca$_{0.3}$MnO$_3$ ($x=0-0.1$). A liquid pressure cell was used for measurements at pressures as high as 1.2 GPa. The resulting changes in the magnetic interactions were inferred from magnetic and high pressure electrical transport studies on bulk polycrystalline and radio frequency (rf) sputtered thin films. X-ray diffraction data indicate an impurity free cubic phase for the samples, with the lattice constant increasing by 0.3% over the range $x=0$ to 0.1. The ferromagnetic Curie temperature determined from ac susceptibility and magnetization shows the expected bond length related decrease in $T_c$ with increasing $x$ only for $x=0-0.03$. For higher $x$, the data indicate an increase in $T_c$ that could only be attributed to bond angle changes. Under the influence of an external pressure, however, we obtained clear evidence for both bond length and bond angle related increase in $T_c$. Magnetoresistance data reveal an increase of 10-20 K/GPa for the magnetic ordering temperature with pressure, with the largest increase for $x = 0.03$. Anomalies are observed in magnetic parameters for the sample with $x = 0.03$. Ferromagnetic resonance (FMR) measurements at 9.4 GHz indicate a 5% decrease in the $g$-value for $x=0.03$ relative to the end members, $x = 0$ and 0.1. The low field magnetostriction is found to be larger for $x = 0.03$ than for the neighboring compositions. Details on these results are provided in the following sections.
2. Sample Preparation and Structural Studies

Polycrystalline samples with $x = 0.1$ were prepared by standard ceramic techniques that consist of mixing and ballmilling oxides or carbonates of La, Mn, Ca and Cs, several presinterings at 1300-1400 K, and final sintering at 1500 K. Thin films were deposited by the technique of radio frequency (rf) sputtering. We used sintered polycrystalline targets of parent materials. It was necessary to tailor the target composition to obtain stoichiometric films. A 2-inch diameter magnetron gun modified for the deposition of magnetic films was used. Films were sputtered on silicon substrates in a sputter down configuration. The sputtering conditions included rf power of 50 W, pressure of 10 mTorr and a mixed argon-oxygen atmosphere. Films with a thickness of 1 μm were obtained for deposition duration of 24 hrs.

An x-ray diffractometer (XRD) was used for structural characterization. A cubic structure free of any impurity phases was determined for all the compositions. The thin films on Si were polycrystalline with a lattice constant in agreement with the bulk polycrystalline values. Figure 1 shows the variation of the lattice constant with $x$. As $x$ is increased, a gradual increase in the lattice constant is observed for $x \leq 0.04$ and is followed by a rapid increase in the parameter for higher $x$. A 0.3% increase in the lattice constant is observed when $x$ is increased from 0 to 0.1. With the introduction of Cs for La, electrical neutrality requires the conversion of two Mn$^{3+}$ to two Mn$^{4+}$. For increasing $x$ one therefore expects an increase in the average radius of the La-site ion and a decrease in the average radius of Mn-site ions. The data in Fig. 1 is indicative of an overall increase in the unit cell dimension with Cs substitution. For samples with higher $x$, XRD data indicated peaks corresponding to impurity phases. Impurities in samples with $x > 0.1$ were also evident from magnetization data.
3. Magnetic and Electrical Transport Characterization

For magnetic characterization, an ac susceptometer, Faraday magnetic balance and a SQUID magnetometer were used. Ferromagnetic resonance studies were carried out at 9.2 GHz. Low field magnetostriction on specific compositions was measured with a strain gauge. A liquid pressure cell was used for high pressure (0-1.2 GPa) resistivity and low field (5 kOe) magnetoresistance measurements. Most of these studies were performed from liquid nitrogen temperature to 292 K.

3.1 Curie Temperature and Magnetization

The ferromagnetic ordering temperature $T_c$ was determined from data on low field magnetization (10-40 Oe) with a Faraday balance and a SQUID magnetometer. For samples with $x > 0.1$, the data indicated discontinuities in the magnetization for temperatures close to 50 K that were reminiscent of magnetic transitions associated with Mn$_3$O$_4$ [11]. Thus results on samples with $x > 0.1$ need further investigation and are not reported here. The Curie temperature was also determined, for comparison, from data on the real part the complex ac susceptibility $\chi$ vs temperature measured for a field of 0.6 Oe and a frequency of 100 Hz. The Curie temperature corresponds to the temperature at which $d\chi/dT$ is maximum and was found to be in very good agreement with values obtained from low field magnetization. Figure 2 shows the variation of $T_c$ with the concentration of Cs for bulk samples. The data show a substantial decrease in $T_c$ with increasing $x$, from 260 K for $x = 0$ to 245 K for $x=0.03$. With further increase in $x$, a sharp rise in $T_c$ is seen in Fig. 2 and remains constant for $x = 0.07$-0.1. It is clear from Figs. 1 and 2 that there is overlap of the regions in which both the lattice constant and $T_c$ show the onset of a rapid increase with increasing $x$. 

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The low temperature saturation magnetization for the bulk polycrystalline samples were obtained using a Faraday Balance for a static magnetic field of 5 kOe and are shown in Fig.3 as a function of x. The magnetization $n_B$ per formula unit is expressed in Bohr magneton. The measured values are compared in Fig. 3 with the expected moment of $(3.7 - 2x)\mu_B$, calculated based on the assumption that the substitution of one Cs ion results in the conversion of two Mn $^{3+}$ to two Mn $^{4+}$ and spin-only contributions for the moment. Although one expects a linear decrease in the moment with increasing $x$, the data indicate variations that essentially track the changes observed in $T_c$ and is of significance. The moment is relatively small for $x$ values for which $T_c$ is also small. The $n_B$ value ranges from a minimum of 3.42 $\mu_B$ for $x = 0.02$ to a maximum of 3.72 $\mu_B$ for $x = 0.10$.

Similar Curie temperature and magnetization measurements were performed on thin films with three specific compositions, $x = 0.03, 0.05, 0.10$, i.e., the sample with the lowest $T_c$, and compositions that correspond to the region of sharp increase in $T_c$ with $x$ in Fig. 2. The thin film $T_c$ values were in excellent agreement with bulk polycrystalline values in Fig. 2, but the $M$-values were 10% smaller than for bulk polycrystalline samples.

Consider the Curie temperature data in Fig. 2. In a stoichiometric compound, the substitution of Cs for La could lead to the formation of Mn$^{4+}$ ions. To our knowledge, such a state for Mn has not been reported in any manganites. The other possible effect of Cs substitution is the conversion of two Mn $^{3+}$ to two Mn $^{4+}$ for each Cs-ion, resulting in an increase in the average valence for Mn. The overall strength of the double exchange is expected to be sensitive to relative concentration of trivalent and tetravalent Mn. It is therefore reasonable to compare the data in Fig.2 with reported $T_c$-dependence on Mn $^{4+}$ concentration in La-Ca-Mn-oxides. The expected concentration of Mn $^{4+}$ in Cs substituted compounds is $(0.3+2x)$. Figure 2
also shows the variation of $T_c$ with Mn$^{4+}$ concentration based on data reported in Refs. 3 and 12. Assuming a similar effect in the Cs-substituted oxide, $T_c$ is expected to decrease with increasing $x$. It is clear from the data that the observed $T_c$ dependence on $x$ cannot be due to the enhancement in the concentration of tetravalent Mn. Studies on similar manganites with monovalent substitutions, such as Na or K, do not show any correlation between the average valence for Mn and $T_c$ [6].

Two important factors that contribute to changes in the strengths of DE interactions and $T_c$ are the Mn-O bond distance, $d_{\text{Mn-O}}$, and Mn-O-Mn bond angles, $\theta$. A clear $d_{\text{Mn-O}}$ dependence of $T_c$ for low $x$ is obvious in Fig. 2 which shows a decrease in $T_c$ with increasing $x$ for $x = 0.00-0.03$. As $x$ increases both the average radius for the La-site $<r_\alpha>$ and $d_{\text{Mn-O}}$, as indicated by XRD data, increase leading to weakening of DE interactions and a reduction in $T_c$. A similar $T_c$ vs. bond length behavior was reported for lanthanum manganites [6]. Another important aspect of the data in Fig. 2 is the dramatic increase in $T_c$ with $x$ for $x = 0.03-0.10$. Such a behavior could only be due to the influence of bond angles on DE interactions as evident from the study by Hwang, et al. [5]. Their study revealed a direct relationship between $<r_\alpha>$ and $T_c$; the Curie temperature was observed to increase with increasing $<r_\alpha>$. Although $<r_\alpha>$ will have direct impact on $d_{\text{Mn-O}}$, it is suggested to have a greater impact on the strength of DE through bond angle changes with substitutions. The hopping of electron between Mn-ion that leads to ferromagnetism and metallic conductivity is dependent sensitively on $\theta$. With increasing $<r_\alpha>$ (and the tolerance factor), the increase in $\theta$ is the dominant factor that leads to strengthening of the DE interaction and an enhancement in $T_c$ [5]. In the present system, any change in $\theta$ for $x = 0.00-0.03$ is probably too small to influence the ordering temperature. With increasing $x$ and $<r_\alpha>$, $\theta$ increases which in turn enhances the probability of electron hopping between Mn-ions and consequently the
strength of the DE interaction. Thus for large x the key factor that contributes to the increase in Tc is the θ dependence of ferromagnetic DE interactions. To summarize, Cs-substitution leads to bond-length related weakening of DE interactions for low x and a bond-angle related strengthening for high Cs concentrations. The effect of an external hydrostatic pressure on the magnetic interactions, however, was found to be substantially different from the changes associated with the substitution and is discussed next.

3.2 High Pressure Magnetotransport

We investigated the effect of external hydrostatic pressure by magnetoresistance (MR) studies in the Cs-substituted compounds. A Cu-Be liquid pressure cell was used to achieve pressures as high as 1.2 GPa. A calibrated strain gauge was used for pressure determination. The magnetoresistance, defined as MR = [R(0)-R(H)]/R(0) for the samples were measured for H = 5 kOe. The electrical resistance R was measured using the standard four-probe method and an ac (10 Hz) excitation current. Data on R vs. T showed the typical behavior observed in most DE ferromagnetic manganites; a metallic conduction below a characteristic temperature Tp, a peak in R at Tp and an activated type conduction above Tp. Figure 4 shows MR vs. T data for zero external pressure for the sample with x=0.05. A very sharp peak in MR is observed at Tp and Tc correlated very well with Tc for all the samples. The largest MR was measured for the sample with x = 0.05. The maximum MR close to Tc ranged from 7 to 31% for the Cs-substituted compounds.

The pressure dependence of the Curie temperature was determined from MR vs. T data. The change in Tp was measured as a function of the pressure P. Figure 5 shows the measured variation of Tp (∼ Tc) with P for a representative composition, the bulk sample with x = 0.01. A
linear increase in $T_c$ with $P$ is evident from the data, with the slope $dT_c/dP = 17 \text{ K/GPa}$. Similar pressure dependence of MR measurements were performed for other Cs substitutions and the variation of $dT_c/dP$ is plotted as a function of $x$ in Fig.6. With increasing $x$, the rate of increase in $T_c$ with $P$ increases for $x = 0.01-0.03$. The largest change in $T_c$ with $P$ occurs for $x = 0.03$. The pressure induced change in $T_c$ is relatively small for $x > 0.03$.

An external hydrostatic pressure affects both the bond length $d_{\text{Mn-O}}$ and the bond angle $\theta$. High pressure studies on LaNiO$_3$ show compression of the bond distance and increase of the bond angle with increasing pressure [13]. In a recent study, Laukhin, et al., [6] proposed a simple model in which the pressure dependence of $T_c$ is primarily due to the variation of the bandwidth for itinerant $e_g$ electrons with three parameters: $d_{\text{Mn-O}}$, $\theta$, and the strength of electron-phonon coupling. This model predicts a linear $(1/T_c)\ dT_c/dP$ vs $T_c$ behavior. With nominal values for bond-length and bond-angle compressibilities [15], the theoretical estimates for the sign and magnitude for $dT_c/dP$ were found to be in reasonable agreement with experimental values [6]. The inset in Fig.6 shows a plot of $(1/T_c)\ dT_c/dP$ as a function of $T_c$ for the present system; the variation is linear as predicted by the theory. In summary, a large substitution of Cs ion for La or an external pressure has similar effect on the strength of the ferromagnetic interaction and $T_c$. However, for very low concentration of Cs we observe a weakening of the double exchange related to bond length effects.

In addition to relatively small $T_c$ and magnetization and large $dT_c/dP$ for Cs substitution of 0.03, we observed anomalies in the ferromagnetic resonance $g$-value and magnetostriction, which are discussed next.
3.3 Ferromagnetic Resonance

Ferromagnetic resonance (FMR) studies were carried out at 9.2 GHz. For bulk polycrystalline samples, we used spheres with a diameter of 0.5 mm. For thin films, 4 mm² samples on silicon substrates were used. The samples were placed at the bottom of a TE₁₀₂ 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 \( \Delta H \) were measured over the temperature 77-292 K.

Figure 7 shows the temperature dependence of \( H_r \) and \( \Delta H \) for a representative sample, the film with \( x = 0.03 \). At room temperature the linewidth is 280 Oe and the absorption occurs for an applied field corresponding to \( g = 2.066 \). On cooling the sample, \( H_r \) remains constant and \( \Delta H \) initially decreases, but a rapid increase is evident at temperatures close to \( T_c \) and reaches a peak value at the Curie temperature. Below \( T_c \), both the resonance field and the linewidth drop rapidly with decreasing \( T \). For \( T < 230 \text{ K} \), one observes a gradual decrease in \( H_r \) and an increase in \( \Delta H \) with decreasing \( T \).

Similar resonance measurements were carried out on films and spheres of other compositions. Since the manganites are paramagnetic at room temperature, Fig.8 shows the composition dependence of the room temperature g-value estimated from the measured resonance field for the entire series. We discuss first the paramagnetic g-value in Fig. 8, which ranges from 2.066 to 2.082 with the minimum value observed for \( x = 0.03 \). These values are in general agreement with reported values that range from 1.99 to 2.04 [14,15]. The wide variation in the reported g values could be due to variations in the average valence for Mn for samples prepared under at different conditions. 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
(Mn⁴⁺) and 3d³ (Mn³⁺) ions [16]. Since the sample with $x = 0$ must have 30% Mn⁴⁺ and 70% Mn³⁺, the calculated $g$-value is 2.13. Upon substitution of Cs for La³⁺ and assuming subsequent conversion of two Mn³⁺ to Mn⁴⁺, the $g$-value is expected to decrease linearly with increasing $x$.

In contradiction to the predicted linear dependence of $g$ on $x$, the data do not show any systematic variation. The most important observation is the minimum in $g$ for $x = 0.03-0.04$ and might be indicative of local distortion of the Mn-O octahedron due to Cs substitution. It is significant that the minimum in $g$ occurs for the compositions for which both $T_c$ and the saturation magnetization are also small.

We consider next the paramagnetic linewidth and resonance field data in Fig. 7 for the film with $x = 0.03$. For $T > T_c$, $\Delta H$ is of comparable magnitude to reported linewidths in similar compounds [15]. In a paramagnet both spin-spin and spin-lattice interactions contribute to $\Delta H$. A dominant spin-spin interaction in a magnetically concentrated system is predicted to result in a temperature independent $\Delta H$. A strong spin-lattice interaction, however, results in phonon modulation of the exchange interactions and crystal fields and leads to a linear increase in $\Delta H$ with $T$ [15]. For $T > 255$ K, the observed increase in $\Delta H$ with increasing $T$ for the oxides is indicative of the strong spin-lattice coupling in the manganites.

Now we discuss the temperature dependence of $H_r$ and $\Delta H$ in the ordered state. Consider first the variation of the resonance field. The magnetic phase transition from paramagnetic to ferromagnetic order results in contributions to $H_r$ due to the demagnetizing field, crystalline anisotropy, porosity, and eddy currents [16]. The resonance field data in Fig. 7 shows significant shift through the paramagnetic to ferromagnetic transition primarily due to the shape anisotropy. Any additional contributions from porosity, anisotropy and similar effects to $H_r$ are proportional
to the sample magnetization. Although such contributions are likely to be small, the observed
decrease in \( H \) with decreasing \( T \) in Fig. 7 is indicative of such effects in the film [16].

Next we consider the temperature dependence of the linewidth in the ordered state. The
resonance linewidth data for the ordered state in Fig. 7 show enhanced values relative to the
paramagnetic state. As the sample is warmed up, \( \Delta H \) remains temperature independent for
temperatures up to 175 K. Further increase in \( T \) leads to increasing \( \Delta H \) and a peak in \( \Delta H \) is
observed at \( T_c \). In the ferromagnetic state, an increase in \( \Delta H \) is predicted due to several possible
causes. These include spin wave scattering due to defects and inhomogeneities, valence-
exchange which involves the transfer of electron between \(^{3+}\text{Mn}^+\) and \(^{4+}\text{Mn}^+\) 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 \( \Delta H \) as observed in Fig. 7.

Recently Bhagat and others used the data on FMR linewidth as a function of temperature to
extract information on the chemical homogeneity of lanthanum manganite films and
polycrystalline samples [17]. 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, and broadening due to a spread in
\( T_c \) and spread in \( M \). The second term manifests as a peak in \( \Delta H \) at the average \( T_c \) and the third
term is linearly proportional to \( M \). The data in Fig. 7 is probably indicative of chemical
inhomogeneities in the films, in agreement with the observation of 10\% reduction in the
saturation magnetization compared to bulk polycrystalline samples.
3.4 Magnetostriction

Temperature dependent low field magnetostriction measurements were made on selected compositions to obtain further insight into the origin of anomalously low magnetic parameters for compositions around $x = 0.03$. The measurements were made on three compositions, the sample of importance $x = 0.03$ and the neighboring compositions $x = 0.02$ and 0.04. The standard strain gauge method was used to measure the magnetostriction parallel ($\lambda_{//}$) and perpendicular ($\lambda_\perp$) to the in-plane applied magnetic field. It is worth noting that saturation magnetostriction measurements for manganites require very high fields, on the order of 100-120 kOe [18]. Since the present study is aimed at comparison of $\lambda$ for $x = 0.02$-0.04, measurements were done for a field of 5 kOe.

Figure 9 shows the variation of $\lambda_{//}$ and $\lambda_\perp$ with temperature for the sample with $x = 0.03$. At temperatures well below $T_c$, the magnetostriction is positive for parallel fields and is negative for directions perpendicular to the field. The change in the sample dimension at low temperatures is due to domain rotation and domain growth along the field direction. The net change in the sample volume due to the field is quite small at low temperatures as expected. As the sample is warmed up, both $\lambda_{//}$ and $\lambda_\perp$ become negative at temperatures close to $T_c$ indicating a decrease in the sample volume. Figure 10 shows the volume magnetostriction $\omega = \lambda_{//} + 2 \lambda_\perp$, for the three compositions of interest. The volume magnetostriction is quite small at low temperatures since $H$ is expected to have a relatively minor effect on the sample magnetization. Since the magnetic field has the strongest effect on magnetization close to $T_c$, $\omega$ has the largest value for temperatures close to $T_c$ and is a measure of electron-phonon-spin coupling in the manganites. The peak in $\omega$ coincides with the ferromagnetic ordering temperatures for the three
compositions. The most important inference from the data in Fig.10 is that $\omega$ and therefore the electron-phonon coupling is much stronger for $x = 0.03$ than for the neighboring compositions.

4. Conclusion

In conclusion, the introduction of chemical pressure accomplished with Cs in lanthanum calcium manganites leads to both bond distance and bond angle related changes in the magnetic ordering temperature. The bond length influence is dominant at low substitutions where as the bond angle induced enhancement of the double exchange and the ordering temperature occurs for high substitutions. Studies under an external hydrostatic pressure provided evidence for the strengthening of the magnetic interactions that could be attributed to decreasing bond length and increasing bond angle and phonon-electron coupling. For samples with compositions around $x=0.03$, the Curie temperature, saturation magnetization and paramagnetic g-value are relatively small. Further, magnetostriction data show evidence for strong electron-phonon-spin coupling for $x = 0.3$. Detailed structural studies are essential for an understanding of the anomalies observed in the composition dependence of these magnetic parameters.

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Caption for figures

Fig. 1: Lattice constant as a function of Cs-concentration \( x \) for \( \text{La}_{0.7-x}\text{Cs}_x\text{Ca}_{0.3}\text{MnO}_3 \). X-ray diffraction measurements indicate cubic structure for the manganites.

Fig. 2: The Cs-concentration \( x \) dependence of the ferromagnetic Curie temperature \( T_c \) determined from ac susceptibility and low field magnetization data for bulk polycrystalline and thin films of the manganite. The anticipated concentration of \( \text{Mn}^{4+} \) in \( \text{La}_{0.7-x}\text{Cs}_x\text{Ca}_{0.3}\text{MnO}_3 \) is \( 0.3+2x \). The broken line is the reported variation of \( T_c \) with the concentration of \( \text{Mn}^{4+} \) in lanthanum calcium manganites (Refs. 3 and 12).

Fig. 3: The variation with Cs concentration of the low temperature saturation magnetization (in Bohr magneton) measured at 77 K with a Faraday balance for a field of 5 kOe. The solid line is the calculated moment of \((3.7-2x)\ \mu_B\), assuming the conversion of 2 \( \text{Mn}^{3+} \) to 2 \( \text{Mn}^{4+} \) for each Cs ion and spin only moments for the Mn ions.

Fig. 4: Temperature dependence of the magneto-resistance \( \text{MR} = [R(0)-R(H)]/R(0) \) for \( \text{La}_{0.60}\text{Cs}_{0.05}\text{Ca}_{0.3}\text{MnO}_3 \) (\( x = 0.05 \)) for zero applied pressure. The values are for an applied magnetic field of 5 kOe. The arrow indicates the Curie temperature. The temperature \( T_c \) corresponding to the maximum in MR correlated well with \( T_c \) for all \( x \)-values.
Fig. 5: The variation of $T_c$ with the applied hydrostatic pressure. The Curie temperature as a function of pressure for the sample with $x = 0.05$ were obtained from the peak position in MR vs. $T$ data as in Fig. 4. The MR measurements were done with a liquid pressure cell for pressures up to a maximum of 1.2 GPa.

Fig. 6: The rate of change in $T_c$ with pressure for $La_{1-x}Cs_xCa_{0.3}MnO_3$ for $x = 0.01$. Data on $dT_c/dP$ were obtained from the pressure dependence of $P$ as in Fig. 5. The inset shows the change in $(1/T_c) dT_c/dP$ with $T_c$.

Fig. 7: Ferromagnetic resonance linewidth $\Delta H$ and resonance field $H_r$ at 9.4 GHz for a 1 $\mu$m thick radio frequency sputtered film with $x = 0.03$ on silicon substrate. The arrow indicates the Curie temperature.

Fig. 8: Room temperature $g$-value as a function of Cs concentration $x$.

Fig. 9: Temperature dependence of the parallel ($\lambda_\parallel$) and perpendicular ($\lambda_\perp$) magnetostriction for a bulk polycrystalline sample with $x = 0.03$. The measurements were done using the standard strain gauge technique and a field of 5 kOe.

Fig. 10: Variation with temperature of the volume magnetostriction $\omega = \lambda_\parallel + 2 \lambda_\perp$ for bulk polycrystalline samples with $x = 0.02, 0.03$ and 0.05. The volume magnetostriction was measured for a field of 5 kOe and from data as in Fig. 9.
Fig. 1
Saturation Magnetization (Bohr magneton)

Fig. 3
Fig. 4