Valence electronic structure of Mn in undoped and doped lanthanum manganites from relative K x-ray intensity studies

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Abstract

Relative K x-ray intensities of Mn in Mn, MnO₂, LaMnO₃ and La₀.⁷B₀.³MnO₃ (B = Ca, Sr, and Ce) systems have been measured following excitation by 59.54 keV γ-rays from a 200 mCi ²⁴¹Am point-source. The measured results for the compounds deviate significantly from the results of pure Mn. Comparison of the experimental data with the multiconfiguration Dirac-Fock (MCDF) effective atomic model calculations indicates reasonable agreement with the predictions of ionic model for the doped manganites except that the electron doped La₀.⁷Ce₀.³MnO₃ and hole doped La₀.⁷Ca₀.³MnO₃ compounds show some small deviations. The results of MnO₂ and LaMnO₃ deviate considerably from the predictions of the ionic model. Our measured Kβ/Kα ratio of Mn in La₀.⁷Ca₀.³MnO₃ cannot be explained as a linear su-
perposition of $K\beta/K\alpha$ ratios of Mn for the end members which is in contrast to the recent proposal by Tyson et al. from their Mn $K\beta$ spectra.

I. INTRODUCTION

The variety of physical properties of $ABO_3$ oxides with perovskite structures has made them a lively area of research in the last decade. Among these compounds, the hole doped $La_{1-x}B_xMnO_3$ ($B = Ca, Sr,$ and $Ba$) and electron doped $La_{1-x}Ce_xMnO_3$ compounds have attracted much attention recently due to the discovery of colossal magnetoresistance effects [1–5]. Both end members of the above compounds behave like paramagnetic insulators at higher temperatures and antiferromagnetic insulators at low temperatures, but when trivalent $La$ is replaced by divalent $Ca, Sr$ or $Ba$ (hole doped) or tetravalent $Ce$ (electron doped) in the range of $0.2 \leq x \leq 0.4$ the material becomes a metallic ferromagnet below the transition temperature [5,6]. From electronic point of view the doped compounds below the transition temperature are mixed valent systems with a disordered distribution of $Mn^{3+}$ and $Mn^{4+}$ ions in hole doped and $Mn^{2+}$ and $Mn^{3+}$ in electron doped compounds. The Hund coupled $t_{2g}$ electrons may be considered as a single localised spin with $S = \frac{3}{2}$ while the $e_g$ electrons are strongly hybridized with oxygen $2p$ states. In divalent doping a corresponding number of Mn ions are converted into quadrivalent $Mn^{4+}$ ($t_{2g}^3$) i.e. the divalent dopants introduce holes in the $e_g - 2p$ band near the Fermi energy. The strong coupling between the magnetic ordering and the electrical conductivity is explained by the double exchange model [7,8], in which the holes in the $e_g - 2p$ band are the electrical carriers that move on a background of $Mn^{4+}$ ($t_{2g}^3$) ions in hole doped compounds whereas in electron doped compounds electrons in the $e_g - 2p$ band are electrical carriers.

There is much conflicting data on the valence of Mn in $La_{1-x}B_xMnO_3$ ($B = Ca, Sr,$ and $Ba$). The work of Hundley and Neumeier [9] on thermoelectric power (TEP) experiments finds that more holelike charge carriers or alternatively fewer accesible Mn sites are present than expected for the value $x$. They suggest a charge disproportionation model based on
the instability of $Mn^{3+} - Mn^{3+}$ relative to $Mn^{2+} - Mn^{4+}$. This transformation provides excellent agreement with doping-depend trends exhibited by both TEP and resistivity. The electronic paramagnetic resonance (EPR) measurements of Oseroff et al. \cite{10} suggest that below 600 K there are no isolated Mn atoms of $2^+, 3^+, \text{or} 4^+$. However they argue that EPR signals are consistent with a complex magnetic entity composed of $Mn^{3+}$ and $Mn^{4+}$ ions. $Mn\, 2p$ x-ray photoelectron spectroscopy (XPES) and $O\, 1s$ absorption studies of Park et al. \cite{11} suggest the double exchange theory with mixed valence $Mn^{3+/4+}$ ion. They were able to obtain approximate spectra of the intermediate doping XPES spectra by linearly combining the end-member spectra – consistent with a linear change of spectral features with doping. However, the significant discrepancy between the weighted spectrum and the prepared spectrum (for given $x$) suggests a more complex doping effect. Subias et al. \cite{12} examined the valence state of $Mn\, K$-edge x-ray absorption near edge spectra (XANES) and found a large discrepancy between intermediate doping spectra and linear combination of the end members. Tyson et al. \cite{13} from their high resolution $Mn\, K\beta$ spectral studies show that the $LaMnO_3$ and $CaMnO_3$ to be covalent $Mn^{3+}$ and $Mn^{4+}$, respectively, by a clear comparison with $Mn^{3+} - Mn_2O_3$ and $Mn^{4+} - MnO_2$ covalent oxide standards. For $La_{1-x}Ca_xMnO_3$ (0.3 $\leq x \leq$ 0.9) their $Mn\, K\beta$ emission results are consistent with a mixed valent $Mn^{3+/4+}$ while mixed spectra are well represented by linear superposition of end spectra in direct proportion to $x$.

Millis et al. \cite{14} showed that the double exchange model cannot explain the CMR effect in $La_{1-x}Sr_xMnO_3$ and proposed that polaron effects due to a strong electron-phonon interaction arising from Jahn-Teller splitting of the $Mn\, d$-levels play an important role.

The study of Dessau et al. \cite{15} suggested that changes in the density of states at the Fermi level play a dominant role in the "colossal" conductivity changes which occur across the magnetic ordering temperature. This contrasts with the typical explanations (such as double exchange or Anderson localization) in which the most dominant cause for the conductivity is a change in the carrier mobility.

The purpose of the present study is to determine the electronic structure of valence
states of $Mn$ in various manganese oxide compounds including the CMR materials above the transition temperature. The study mainly deals with a measurement of $K\beta/K\alpha$ x-ray intensity ratios of $Mn$ in which the atomic-type $K\beta$ transition is sensitive to the valence electronic structure of $Mn$. The change in the $K\beta/K\alpha$ x-ray intensity ratio is caused by a change in the $3p$ electron screening due to a change in the localized $3d$ electron population. Earlier studies on the influence of chemical effect in the $K\beta/K\alpha$ ratios of $3d$ metals in their compounds by Brunner et al. [16] had shown that $3d$ electron delocalization of the transition metal causes changes in the $3p$ electron screening which is responsible for the change in the $K\beta/K\alpha$ ratio. In many compounds transfer of electrons from the ligand atom to the $3d$ state of the metal or vice versa [17-19] can also cause a change in the $3d$ electron population of the metal which will cause a change in the $K\beta/K\alpha$ ratio.

II. EXPERIMENTAL DETAILS

Bulk ceramic samples were prepared through conventional solid state reaction route starting from $La_2O_3$, $CaCO_3$ ($SrCO_3$) and $MnO_2$ for the hole doped samples and $La_2O_3$, $CeO_2$ and $Mn_2O_3$ for the electron doped cerium compound. Stochiometric amounts of the various compounds were mixed, ground and heated in air for 18 hrs at 900 °C for divalent doped samples and heated at 1100 °C for $Ce$ doped sample. The reacted powder is then reground, pelletized and sintered for 15 hrs at 1450 °C in oxygen flow, cooled down to 1000 °C at 10 °C / min kept for 10 hrs in oxygen flow, and cooled to room temperature at 10 °C / min. The samples were characterized through x-ray diffraction (XRD) and energy dispersive x-ray microanalysis (EDX). The cell constants were calculated using the XLAT software. The composition was found to be nearly identical to the starting composition within the accuracy of 3% of EDX.

The $\gamma$-ray fluorescence experiments were carried out on pelletized samples of the size 15mm dia $\times$ 3mm thick. Gamma rays of 59.54 keV from a 200 mCi $^{241}Am$ point-source have been used to ionize the target atoms and the emitted x-rays following the ionization
were detected by a 30 mm$^2 \times$3mm thick Canberra Si(Li) detector having a 12.7 $\mu$m thick beryllium window. The resolution of the Si(Li) detector was $\approx$165 eV [full width at half maximum (FWHM)] for a 5.9 keV x-ray peak. Details of the experimental arrangements can be found in an earlier paper [20].

Pulses from the Si(Li) detector preamplifier were fed to an ORTEC-572 spectroscopy amplifier and then recorded in a Canberra PC based Model S-100 multichannel analyzer. The gain of the system was maintained at $\approx$16 eV/channel. The counting was continued until the counts under the less intense $K\beta$ peak were around $4.5 \times 10^4$. Two sets of measurements were carried out for each sample and an average of the two measurements is found for the $K\beta/K\alpha$ x-ray intensity ratio which is reported.

III. DATA ANALYSIS AND CORRECTIONS

All the x-ray spectra were carefully analyzed with the help of a multi-Gaussian least-square fitting programme [21] incorporating a non-linear background subtraction. No low energy tail was included in the fitting as its contribution to the ratio was shown to be quite small [21]. The $K\beta/K\alpha$ x-ray intensity ratios were determined from the fitted peak areas after applying necessary corrections to the data. A typical x-ray spectrum of $LaMnO_3$ is shown in Fig. 1.

In the experiment it was found that the $L\gamma$ x-rays of $La$ and $Ce$ interfere in the $K$ x-ray peaks of $Mn$. In order to make suitable corrections to the measured $K\alpha$ and $K\beta$ x-ray intensities of $Mn$ from $L\gamma$ x-ray peaks of $La$ and $Ce$ we have recorded the $L$ x-ray spectra of $La$ and $Ce$ in $La_2O_3$ and $CeO_2$ samples which are shown in Figs. 2 and 3, respectively. A typical $K$ x-ray spectrum of $Mn$ for the sample $LaMnO_3$ is shown in Fig. 4 in which the fitted spectrum is also shown.

Corrections to the measured $K\beta/K\alpha$ ratios come from the $L\gamma_{15}$ x-rays of $La$ and $Ce$ interfering with the $K\alpha$ peak of $Mn$ and $L\gamma_{23}$ x-ray peak of $Ce$ interfering with the $K\beta$ peak of $Mn$. We did not find any $L\gamma_{23}$ peak in the $L$ x-ray spectrum of $La$ (see Fig. 2) and hence its interference to the $K$ x-ray spectrum of $Mn$ is assumed to be negligible and
not considered for the correction. The interference correction was made by measuring the $L_{\gamma 15}/L_{\alpha}$ and $L_{\gamma 23}/L_{\alpha}$ intensity ratios of $La$ and $Ce$ in their $L$ x-ray spectra in $La_2O_3$ and $CeO_2$ samples and equating these ratios for the CMR samples.

The interference of $L_{\gamma 15}$ x-ray peak of $La$ in the $K\alpha$ x-ray peak of $Mn$ was estimated by using the following equation:

$$\left(\frac{I_{La}^{L_{\gamma 15}}}{I_{La}^{L_{\alpha}}}\right)_{La_2O_3}C_1 = \left(\frac{I_{La}^{L_{\gamma 15}}}{I_{La}^{L_{\alpha}}}\right)_{i}C_i$$

where $i$ stands for $LaMnO_3$, $La_{0.7}Ca_{0.3}MnO_3$, and $La_{0.7}Sr_{0.3}MnO_3$ samples, $C_1$ corresponds to self absorption correction for the ratio $\left(\frac{I_{La}^{L_{\gamma 15}}}{I_{La}^{L_{\alpha}}}\right)$ in $La_2O_3$ and $C_i$ ’s are the self-absorption corrections for the ratio $\left(\frac{I_{La}^{L_{\gamma 15}}}{I_{La}^{L_{\alpha}}}\right)$ in respective lanthanum manganite samples. For the estimation of $L_{\gamma 15}$ and $L_{\gamma 23}$ x-ray peak intensities in $K\alpha$ and $K\beta$ x-ray peaks of $Mn$ in $La_{0.7}Ce_{0.3}MnO_3$, respectively, we have used the following equations:

$$\left(\frac{I_{La}^{L_{\gamma 15}}}{I_{La}^{L_{\alpha}}}\right)_{La_2O_3}C_1 = \left(\frac{I_{La}^{L_{\gamma 15}}}{I_{La}^{L_{\alpha}}}\right)_{La_{0.7}Ce_{0.3}MnO_3}C_3$$

$$\left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)_{CeO_2}C_2 = \left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)_{La_{0.7}Ce_{0.3}MnO_3}C_4$$

where $C_2$, $C_3$, and $C_4$ are self absorption corrections for the ratio $\left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)$ in $CeO_2$ sample, $\left(\frac{I_{La}^{L_{\gamma 15}}}{I_{La}^{L_{\alpha}}}\right)$ in $La_{0.7}Ce_{0.3}MnO_3$ sample, and $\left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)$ in $La_{0.7}Ce_{0.3}MnO_3$, respectively. The interference of $L_{\gamma 23}$ x-ray peak of $Ce$ in the $K\beta$ x-ray peak of $Mn$ has been obtained by using,

$$\left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)_{CeO_2}C_5 = \left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)_{La_{0.7}Ce_{0.3}MnO_3}C_6$$

where $C_5$ corresponds to the self absorption correction of $\left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)$ ratio in $CeO_2$ sample and $C_6$ corresponds to the self absorption correction of $\left(\frac{I_{Ce}^{L_{\gamma 23}}}{I_{Ce}^{L_{\alpha}}}\right)$ ratio in $La_{0.7}Ce_{0.3}MnO_3$ sample. For the sample $La_{0.7}Ce_{0.3}MnO_3$ the $La\alpha$ peak is a composite one consisting of $La\alpha$ x-rays of $La$ and $Ce$ whose intensities were obtained by making a two Gaussian fit to the composite $La\alpha$ peak. Using the above equations we have estimated the intensities of $L_{\gamma 15}^{La}$ and $L_{\gamma 23}^{Ce}$ which interfered with the $K\alpha$ peak of $Mn$ and $L_{\gamma 15}^{Ce}$ which interfered with the $K\beta$ peak of
Mn. After correcting for the interference the $K\beta/K\alpha$ ratios are further corrected for the difference in the $K\alpha$ and $K\beta$ self attenuations in the sample, difference in the efficiency of the Si(Li) detector and air absorption on the path between the sample and the Si(Li) detector window. The efficiency of the detector is estimated theoretically as mentioned in our previous paper [20]. Our theoretically estimated efficiency was shown to be in good agreement with the measured efficiency [22]. It has been found that discrepancy between the measured and theoretical efficiency at the energy region of present interest is less than 1%.

The self absorption correction in the sample and the absorption correction for the air path are determined as per the procedure described before [14]. For the estimation of these corrections and absorption factors in equations 1, 2, 3 and 4 we used the mass attenuation coefficients compiled in a computer programme XCOM by Berger and Hubbell [23]. The mass attenuation coefficients for the compounds are estimated using the elemental values in the following Bragg’s-rule formula [24]:

$$\frac{\mu}{\rho} = \sum w_i \frac{\mu_i}{\rho_i}$$

(5)

where, $w_i$ is the proportion by weight of the $i^{th}$ constituent and $\mu_i/\rho_i$ is the mass attenuation coefficient for the $i^{th}$ constituent. The measured ratios after all the corrections are presented in Table I. The errors quoted for the results given in Table I are statistical only. They are calculated by the least-square fitting programme [21].

IV. RESULTS AND DISCUSSION

The experimental results for the $K\beta/K\alpha$ x-ray intensity ratios of Mn in various materials along with the theoretical results based on the multi configuration Dirac-Fock (MCDF) theory [25] are presented in Table I. The theoretical calculations are made assuming atomic configurations based on the valencies of Mn in various compounds. The formal $d$ electron numbers of Mn in various materials based on the manganese valency are presented in the
second column of Table II. The $d$-electron occupation numbers obtained by comparing the experimental $K\beta/K\alpha$ intensity ratios with the theoretical results for different $3d^n$ ($n = 3 - 7$) configurations of $Mn$ are presented in the fourth column of the same table.

As is seen from Table I, the experimental $K\beta/K\alpha$ ratio of $Mn$ is in agreement with the theoretical ratio obtained for the $3d^54s^2$ valence electronic configuration of manganese metal. However, the results for $MnO_2$ and $LaMnO_3$ are not consistent with the $d^4$ and $d^3$ valence electronic configurations of $Mn$. In an earlier electronic structure study \cite{26} of early first-row transition metal oxides it was also shown that the net $d$-electron occupation $n_d$ differed by about one unit from the $d$-occupation number obtained from the valency.

Our measured $K\beta/K\alpha$ ratio for $MnO_2$ is found to be in very good agreement with the one reported earlier by Mukoyama \textit{et al.} \cite{27}. The inferred minimum $d$-electron occupancy in this case is 5.26 (see the last column of Table - II) which is 2.26 more than the formal $d$ electron occupation number of 3. In the case of $LaMnO_3$, our result suggests a minimum $d$-electron occupancy of 6.5 which is about 2.5 more than the formal $d$ electron occupation number of 4. In fact in this case almost all the $4s$ electrons of $Mn$ are transferred to the $d$-band and there is almost no transfer of electrons from manganese to the oxygen atom.

When we look at our results for the doped lanthanum manganites they are reasonably in good agreement with the theoretical results assuming various valence electron configurations based on the valency of $Mn$. The experimental result for $La_{0.7}Ce_{0.3}MnO_3$ shows a lower $d$-electron occupation than expected from the ionic model. However, this $d$-electron discrepancy can, to some extent, be accounted as arising due to a mixture of $Mn^{2+}$ and $Mn^{3+}$ ions in $CeMnO_3$ as per the $Ce$ valency between 3 and 4 suggested by Tranquada \textit{et al.} \cite{28}.

We also see that our $K\beta/K\alpha$ ratio results for doped lanthanum manganites cannot be explained as a superposition of results for its end members because the result of $LaMnO_3$ is unusually lower than the value that could be obtained for a $d^4$ valence state of $Mn$. So without having the result for $CaMnO_3$ we can confidently say that the $K\beta/K\alpha$ ratio result of $La_{0.7}Ca_{0.3}MnO_3$ cannot be explained as a linear superposition of the results of
LaMnO$_3$ and CaMnO$_3$. However, Tyson et al.\cite{13} from their Mn K$\beta$ spectra suggested that doped lanthanum manganite can be considered as a linear superposition of its end members which is not borne out by our measured $K\beta/K\alpha$ intensity ratio results. It appears that $La_{0.7}Ca_{0.3}MnO_3$ is not just a mixed compound of $LaMnO_3$ and $CaMnO_3$ in its true sense but some electronic rearrangement takes place in the formation of the doped compound. Similar arguments hold good for the other doped compounds of lanthanum manganite.

\section*{V. CONCLUSION}

Our results for the doped lanthanum compounds suggest that Mn has a mixed valency of Mn$^{3+}$ and Mn$^{4+}$ for Ca and Sr doped compounds whereas for Ce doped compound it is of the type Mn$^{3+}$ and Mn$^{2+}$. The $d$ electron occupations of Mn in MnO$_2$ and LaMnO$_3$ suggest that they are more like covalent compounds. Our results for the doped compounds suggest that the physical properties of doped CMR compounds cannot be considered as a linear superposition of their end members.

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FIGURES

FIG. 1. $L$ x-rays of $La$ and $K$ x-rays of $Mn$ in $LaMnO_3$.

FIG. 2. $L$ x-ray spectrum of $La$ in $La_2O_3$.

FIG. 3. $L$ x-ray spectrum of $Ce$ in $CeO_2$.

FIG. 4. Experimental (○) and fitted (---) $K$ x-ray spectrum of $Mn$ in $LaMnO_3$. The solid line corresponds to fitted background.
TABLE I.  $K\beta/K\alpha$ x-ray intensity ratios of Mn in pure Mn metal, MnO$_2$ and undoped and doped lanthanum manganites. The quoted errors correspond to counting statistics in the measurements.

| Element | Chemical constitution | Experimental $K\beta/K\alpha$ | Theoretical $K\beta/K\alpha$ |
|---------|------------------------|-----------------------------|-----------------------------|
| Mn      | Mn metal               | 0.1344 ± 0.0009             | 0.1342                      |
| MnO$_2$ |                        | 0.1316 ± 0.0008             | 0.1456                      |
| LaMnO$_3$ |                     | 0.1250 ± 0.0025             | 0.1397                      |
| La$_{0.7}$Ca$_{0.3}$MnO$_3$ |   | 0.1364 ± 0.0019             | 0.1415*                     |
| La$_{0.7}$Sr$_{0.3}$MnO$_3$ |   | 0.1412 ± 0.0018             | 0.1415*                     |
| La$_{0.7}$Ce$_{0.3}$MnO$_3$ |   | 0.1422 ± 0.0019             | 0.1382*                     |

* These correspond to average $K\beta/K\alpha$ ratio taken over the mixed valence states of Mn in the doped compounds as given in column - 3 of Table II.
TABLE II. The formal 3d-electron occupancy numbers of Mn based on the valence considerations are compared with the experimental findings deduced by comparing the experimental $K\beta/K\alpha$ ratios with the theoretical results of MCDF calculation.

| Chemical constitution | Formal electron | Valency | Average d-electron occupation taken into account the formal mixed valency of Mn in the doped compounds. |
|-----------------------|-----------------|---------|--------------------------------------------------------------------------------------------------|
| Mn                    | 5               | –       | 4.84 ± 0.18                                                                                      |
| $MnO_2$               | 3               | $4^+$   | 5.44 ± 0.18                                                                                      |
| $LaMnO_3$             | 4               | $3^+$   | 7.70 ± 1.20                                                                                      |
| $La_{0.7}Ca_{0.3}MnO_3$ | 3.7 *           | $3^+, 4^+$ | 4.46 ± 0.36                                                                                    |
| $La_{0.7}Sr_{0.3}MnO_3$ | 3.7 *           | $3^+, 4^+$ | 3.62 ± 0.29                                                                                    |
| $La_{0.7}Ce_{0.3}MnO_3$ | 4.3 *           | $3^+, 2^+$ | 3.46 ± 0.30                                                                                    |

* These correspond to average d-electron occupancy taking into account the formal mixed valency of Mn in the doped compounds.