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La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> and their correlation with electrical transport  
behaviour**

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# Doping and bond length contributions to Mn K-edge shift in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and their correlation with electrical transport behaviour

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The experimental Mn K-edge x-ray absorption spectra of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ,  $x = 0 - 0.7$  are compared with the band structure calculations using spin polarized density functional theory. It is explicitly shown that there is a correspondence between the inflection point on the absorption edge and the centre of gravity of the unoccupied Mn  $4p$ -band. This correspondence has been used to separate the doping and size contributions to edge shift due to variation in number of electrons in valence band and Mn-O bond lengths, respectively when Sr is doped into  $\text{LaMnO}_3$ . Such separation is helpful to find the localization behaviour of charge carriers and to understand the observed transport properties and type of charge carrier participating in the conduction process in these compounds.

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In recent years, hole-doped manganese oxides have been the subject of intense research because of their various interesting properties: colossal magnetoresistance (CMR), charge ordering, orbital ordering, phase separation, *etc.* [1, 2, 3]. The compounds under present study  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ,  $x = 0 - 0.7$  also show these interesting properties for specific range of  $x$  [4]. In this doping range the resistivity behaves in a non-monotonic fashion, first decreasing as  $x$  increases up to 0.4 and then increasing as  $x$  further increases, see upper inset in Fig. 1. This behaviour is not very well understood. Although double exchange mechanism is commonly employed, it is known to be inadequate [5]. Qualitatively, by considering Jahn-Teller splitting of  $e_g$  band of the Mn and invoking strong Hund coupling it is seen that Sr doping corresponds to adding holes in the system. Thus as  $x$  increases the resistivity should decrease for low  $x$ . Experimentally also it is well established that the conduction is predominantly by holes for  $x < 0.5$  [6, 7, 8] and electron like for  $x > 0.5$  [6, 7]. The electron- or hole-like behaviour is also sensitive to electron-phonon interaction and orbital degeneracy [9]. Naively one would expect the resistivity to have a minimum at  $x = 0.5$ ; however, the detailed interactions involved in conduction phenomenon could alter this situation. Besides adding holes to the system, Sr doping would also change the lattice parameters due to its different ionic radius as compared to La. The changed overlap integrals would modify the local electronic densities and localization of electrons and holes at different sites in the lattice, thus affecting the transport properties.

X-ray absorption (XA) edge represents the transition of electron from a core level to the low lying unoccupied states of appropriate symmetry. The shift in its energy position depends on electronic state of absorbing atom reflected by its effective charge and arrangement of surrounding atoms [10]. There are many works in the literature reporting the XA spectra at Mn K-edge in man-

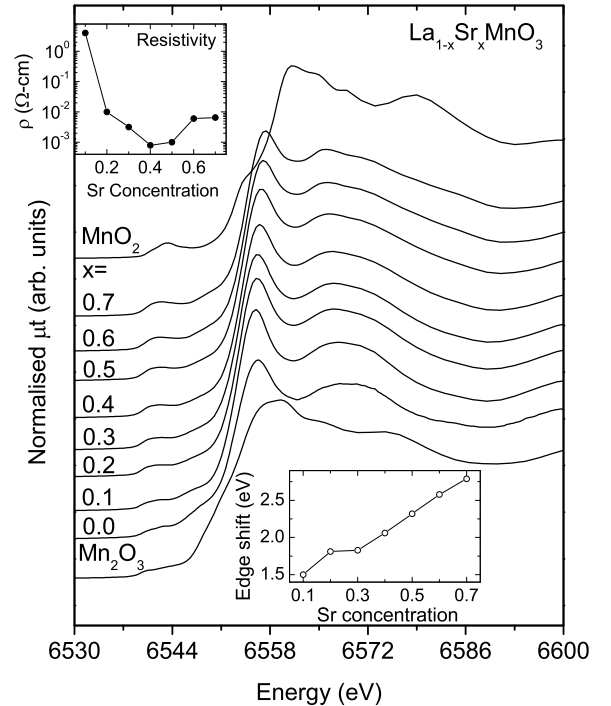


FIG. 1: Experimental Mn K-edge x-ray absorption spectra for  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$  and  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ,  $x = 0 - 0.7$ . Resistivity at 300 K (from [4, 23]) and edge shift in Mn K-edge with respect to  $\text{LaMnO}_3$  for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  are shown in the upper and lower insets, respectively.

ganites [11, 12, 13, 14, 15, 16]. Almost all this work is concentrated on  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  and the change in the edge shift is correlated with the change in the electronic state of Mn ion on Ca doping. There are only a few studies [13, 14, 15] in which the effect of lattice distortion has been correlated with the Mn K-edge absorption spectra. Ignatov *et al.* [13] calculated the XA spectra for orthorhombic and rhombohedral  $\text{LaMnO}_3$  and observed

that for rhombohedral structure the K-edge is shifted by about 1.5 eV with respect to that for orthorhombic one. They also observed an increase in the intensity of the first peak immediately after the absorption edge. A similar observation was made by Qian *et al.* [15]. Bridges *et al.* [14] used band structure calculations of Elfimov *et al.* [17] to understand the experimentally observed single absorption edge inspite of different Mn-O bond lengths in Jahn Teller distorted  $\text{MnO}_6$  octahedra. Though these studies bring out the lattice and band structure effects on the absorption edge, estimation of different contributions to the edge shift and their relation with various physical properties of manganites which depend on the coupling between the spin, charge and lattice degrees of freedom have not yet been done.

In this report we show using experimental XA spectra and electronic structure calculations that shift in Mn K-edge position taken as the first inflection point on it corresponds to the changes in the centre of gravity (CG) of the unoccupied Mn  $4p$ -band. This correspondence is then used to show that there are two contributions to the edge shift, one from changed number of valence electrons due to doping and the other from changes in bond lengths due to difference in ionic radii of La and Sr, which we denote as doping and size effects, respectively. The CG of Mn  $4p$  band is obtained by doing a full band structure calculation. As remarked earlier, doping involves addition of holes to the system and such holes when localized on the absorbing atom (Mn) would contribute to effective charge on it. There would be further contribution to the effective charge from localization of other valence electrons in the system. Our attribution of the edge shift to separate doping and size effects permits us to monitor the localization of the doped holes on the Mn site and that helps in interpretation of electrical transport properties.

Polycrystalline samples of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ,  $x = 0.0 - 0.7$  were prepared by solid state route. XA spectra were recorded at room temperature on beamline X-18 B using a Si(111) channel cut monochromator at the National Synchrotron Light Source, Brookhaven National Laboratory. The details of sample preparation and experiments are given elsewhere [18, 19]. As shown in our earlier EXAFS work on  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  [19],  $\text{MnO}_6$  octahedron is distorted throughout the series and four Mn-O bonds have same bond length and other two have different bond lengths. Therefore, for the purpose of band structure calculations, the local structure is represented by a tetragonal lattice in the whole range  $x = 0$  to 0.7 with interchange of lattice parameters  $a$  and  $c$  at  $x = 0.4$  to account for the change in local structure around  $x = 0.4$ . Lattice parameters taken for obtaining the muffin-tin radii are two times of these Mn-O bond lengths. Spin polarized electronic structure calculations were carried out using LMTART 6.61 [20]. For calculating charge density, full-potential LMTO method working in plane wave representation was used. The charge density and effec-

tive potential are expanded in spherical harmonics up to  $l = 6$  inside the sphere and in a Fourier series in the interstitial region. The exchange correlation functional of the density functional theory was taken after Vosko, Wilk, and Nussair and the generalized-gradient approximation scheme of Perdew *et al.* [21] was also invoked. (6, 6, 6) divisions of the Brillouin zone along three directions for the tetrahedron integration were used to calculate the density of states. Self-consistency was achieved by demanding the convergence of the total energy to be smaller than  $10^{-4}$  Ry/cell.

The experimental XA spectra at Mn K-edge (6539 eV) for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ,  $x = 0 - 0.7$  together with the ones for  $\text{Mn}_2\text{O}_3$  ( $\text{Mn}^{3+}$ ) and  $\text{MnO}_2$  ( $\text{Mn}^{4+}$ ) are shown in Fig. 1. The edge-height for all the spectra is normalized to unity. The edge energy  $E_0$  has been taken as the energy position of the first inflection point on the absorption edge. It is evident from the figure that inflection points of all the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  spectra lie between the inflection points for the absorption edge of  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  with Mn in  $3+$  and  $4+$  valence states, respectively. This indicates that for all these compounds, the effective charge on Mn is in between  $3e^+$  and  $4e^+$ . All the absorption spectra also exhibit three pre-edge features; these will be discussed elsewhere.

The edge shift for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ,  $x = 0 - 0.7$  measured from the absorption edge position of parent compound  $\text{LaMnO}_3$  is shown in the lower inset of Fig. 1. As seen from the figure this edge shift increases monotonically with increase in Sr concentration. As remarked earlier these shifts depend on both doping and size effects; below we discuss how these two effects can be separated using band structure calculations. In order to do so, we first establish that the inflection point of the absorption edge can be related with the CG of the Mn  $4p$  band contributing to the absorption edge. Then we establish that the total shift in CG is sum of shifts in CG due to doping and size contributions explicitly for  $x = 0.5$  compound, as it is computationally less demanding. This additive character of doping and size contributions to the edge shift is used to obtain the doping contribution from the experimental edge shift and calculated size contribution for all other compounds of the series. Then we discuss how these contributions are used to understand the transport behaviour of these compounds in a simple manner.

In Fig. 2, the upper panels show the experimental Mn K-edge absorption spectra for  $\text{LaMnO}_3$ ,  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  and  $\text{SrMnO}_3$ , and the lower two sets of panels show the calculated Mn  $4p$  and O  $2p$  partial density of unoccupied states (PDOS) per formula unit for these compounds. The calculated PDOS matches well with the reported ones by Ravindran *et al.* [22]. The PDOS of only  $p$  symmetric states is shown since for K-edge only  $s \rightarrow p$  transition is dipole allowed and thus is relevant for the present discussion. The contribution of O  $2p$  unoccupied

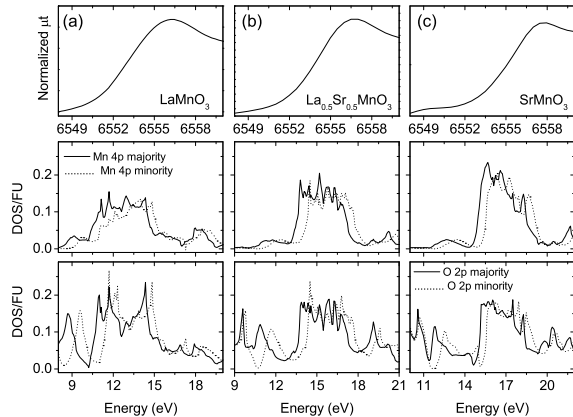


FIG. 2: Experimental Mn K-edge x-ray absorption edge (top panel), calculated spin polarized partial density of states per formula unit for Mn 4p (middle panel) and O 2p (lower panel) of (a) LaMnO<sub>3</sub>, (b) La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> and (c) SrMnO<sub>3</sub>.

states is minimal to the absorption edge as it involves a matrix element with wave functions centred on spatially separated atoms; therefore, we discuss only about the CG of Mn 4p band. The edge position corresponds to the difference between 1s and 4p levels; we note that 1s energy with respect to Fermi level hardly changes ( $\sim 0.02$  eV) with  $x$ , and the edge shift is given by that in 4p band only. The value of average of CG of Mn 4p majority and minority bands for these three compounds is 12.99, 15.65 and 16.94 eV, respectively. Thus the shift in CG for La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> and SrMnO<sub>3</sub> with respect to LaMnO<sub>3</sub> is 2.66 and 3.95 eV, respectively. Similarly, the Mn K-edge energy for these compounds is 6551.88, 6554.22 and 6555.67 eV with corresponding shifts in  $E_o$  for 50% doped and SrMnO<sub>3</sub> compounds being 2.34 and 3.79 eV, respectively. The shift in CG is thus approximately same (within  $\sim 0.3$  eV) as the shift in absorption edge energy. Such behaviour is also seen for shifts in average CG and  $E_o$  for CaMnO<sub>3</sub> with respect to LaMnO<sub>3</sub>. This indicates that the edge shift can be understood in terms of the shift in the CG of Mn 4p band contributing to the main Mn K-edge and thus CG can be used to monitor the changes in the edge shift. Further, our calculations show that the total shift in average CG is less than 0.2 eV when different magnetic ordering (*i.e.* FM, C-AFM, A-AFM) are considered. This would indicate that edge shift does not depend much on type of magnetic ordering in conformity with earlier results [13]. Henceforth, correspondence of  $E_o$  with CG obtained from the calculations for the FM phase only is considered.

We now show using La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> that the shift in CG can be used to separate out the doping and size contributions to the edge shift. For  $x = 0.5$  such calculation can be readily done by taking a doubled unit cell. How-

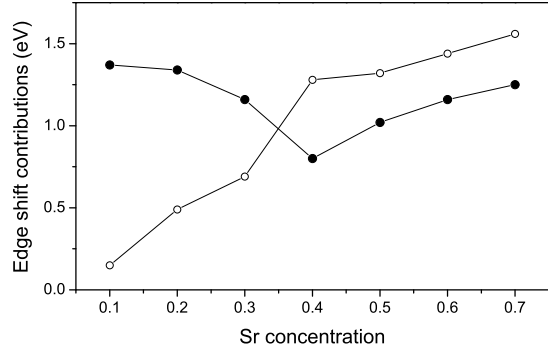


FIG. 3: The contributions due to doping (close circles) and size effects (open circles) to the x-ray absorption Mn K-edge shifts with respect to LaMnO<sub>3</sub>.

ever, for other values of  $x$ , it is rather involved as the necessary unit cell would be too big and contain a much larger number of atoms. The band structure calculations for  $x = 0.5$  compound were done using following three lattice models to separate out the doping and size contributions: (a) using Mn-O bond lengths of  $x=0.5$  compound obtained from EXAFS thus representing the size effect with respect to the parent compound LaMnO<sub>3</sub>, (b) using the Mn-O bond lengths of LaMnO<sub>3</sub> and replacing 50% of La atoms by Sr thus representing the doping effect with respect to LaMnO<sub>3</sub> and (c) using bond lengths corresponding to La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> and replacing 50% La atoms by Sr by doubling the unit cell, thus considering both doping and size effects together. The shift in average CG of Mn 4p band with respect to that of LaMnO<sub>3</sub> obtained from (a) and (b) are 1.32 and 1.28 eV, respectively. The summation of these two shifts is 2.60 eV, approximately equal to a shift of 2.66 eV obtained from (c). This indicates that such a strategy could be adopted to determine these two contributions to the edge shift. The validity of this was also noted with the compound SrMnO<sub>3</sub> corresponding to  $x = 1$ . Therefore, we now calculate the size contributions for rest of the compounds and estimate the doping contribution by subtracting it from the edge shift observed experimentally.

In Fig. 3, the shifts in CG with respect to the CG of LaMnO<sub>3</sub> due to size contributions are shown by open circles and that due to doping contributions by solid circles. From this figure it is evident that the size contribution increases monotonically with Sr concentration. The doping contribution first decreases up to  $x = 0.4$  and then it increases as  $x$  is increased to 0.7. This result is surprising as one would have expected the doping contribution to increase with  $x$  as the number of holes increases with increase in Sr doping. The magnitude of size contribution to edge shift is much less than that of the doping contribution for  $x < 0.3$ . This trend is reversed for  $x \geq$

0.4 with crossover point at  $\sim 0.35$ . Further, beyond  $x = 0.4$  these two contributions have roughly same rate of increase with Sr doping.

This behaviour of doping and size contributions to the edge shift can be directly related with the transport properties of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  compounds. One is essentially doping holes into the parent compound when some of the trivalent La ions are replaced by divalent Sr. Thus doping contribution is basically representing the effect of hole doping on edge shift. A decrease in edge shift due to this contribution would thus indicate a decrease in effective charge and increase in delocalization of holes at Mn sites. The size contribution has been estimated using observed changes in the Mn-O bond lengths with composition. The change in Mn-O bond length would then correspond to the change in the extent of overlap of Mn  $3d$  and O  $2p$  orbitals. In our calculations we have kept Mn-O-Mn bond angle fixed at  $180^\circ$ . Therefore, decrease in the Mn-O bond length represents an increase in this overlap and thus increase in the delocalization of electrons which in turn corresponds to an increase in the positive effective charge on the Mn ion. Thus, changes in size contribution can be considered as representative of change in electron localization with composition. The observed behaviour of these two contributions shown in Fig. 3 would then mean that both electrons and holes delocalize up to  $x = 0.4$ . However, it is mainly the hole delocalization that is governing the transport behaviour of these compounds for  $x < 0.35$ , because the corresponding contribution to the edge shift is more in comparison to that due to electron delocalization. Holes indeed dominate the transport behaviour of manganites in this range of doping as is evident from the Hall effect measurements [6, 7, 8]. Since delocalization of both electrons and holes increases up to  $x = 0.4$ , such a delocalization should result in increase in conductivity as has been observed experimentally by Urushibara *et al.*[23] (see Fig. 1, upper inset).

For  $x > 0.4$ , the holes start localizing at Mn sites as is evident from the increase in doping contribution to edge shift. This would imply that for higher compositions hole localization and electron delocalization compete with each other. As seen from Fig. 3, the hole localization appears to be more than the electron delocalization when  $x$  increases from 0.4 to 0.5, and thus the resistivity should increase. This is in conformity with the observed increase in room temperature resistivity [4]. As one goes from 0.6 to 0.7, electron delocalization and hole localization changes by almost same amount indicating that the resistivity of these compounds should be about the same as is evident from the upper inset of Fig. 1. Further, in these compounds the magnitude of size contribution is more than that of doping contribution. This would indicate that now the majority charge car-

riers must be electrons as has been observed by Gordan *et al.* [6]. Thus these results indicate that the observed transition from metallic to insulating ground state at  $x > 0.5$  may be due to hole localization.

In conclusion we have shown using a simple model based on first principle calculations that it is possible to separate out the contributions due to doping and size effects, which are related with the localization of holes and electrons, respectively, from the absorption edge shifts and use them to understand the electrical transport phenomenon in manganites. These contributions may also be helpful in further understanding of various other phenomena, like metal insulator transition with temperature, charge and orbital ordering, *etc.* where charge localization plays an important role, in manganites and other similar systems.

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