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Transition-element doping effects in $La_{0.7}Ca_{0.3}MnO_3$

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The influence of transition element (TE) doping on the magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ is studied for the entire transition element series (TE=Cr, Fe, Co, Ni, Cu, Zn) for a fixed (5% at Mn sites) dopant concentration. The systematics of different properties such as the metal-insulator transition temperature T_p, the Curie temperature T_c, $\rho(T_p), \rho(5\,\mathrm{K})$, and the maximum value of magnetoresistance (MR), with respect to lattice parameter and the ionic radii of dopants, are examined. The important findings include an interesting correlation between the maximum MR, the lattice parameter, and the ionic radii, and some distinct features exhibited by Fe, Cu, and Zn dopants. [S0163-1829(98)01146-1]

Observation of colossal magnetoresistance (CMR) in the perovskite manganite systems of the form $RE_xA_{1-x}MnO_3$ (RE=rare earth, A=Ca, Sr, Ba) (Refs. 1–4) has spurred considerable interest in the study of these compounds during the past few years. The early work on the structural, magnetic, and transport properties of these compounds was carried out in the fifties.[5–7] These and other subsequent studies[8–10] had revealed the significance of the Mn^{3+}-O-Mn^{4+} network in an unusual interplay of transport and magnetism displayed by these materials. Specifically, Zener[6] had proposed the double exchange model to explain the concurrent occurrence of ferromagnetism and metallic transport in these compounds. The recent detailed research of the properties of these compounds has, however, shown that much still remains to be understood about the structure-property correlations in these materials, especially the complex nature of the interplay of the spin, charge, and lattice systems.[1–4,11–17] These studies have highlighted the competing role of the Jahn-Teller distortion associated with the Mn^{3+} ion as well as charge ordering effects in the attendant phenomena. There is growing evidence to suggest that the so-called double exchange model is insufficient to explain the rich variety of phenomena found in these compounds. Among other issues, it is now clear that lattice strain and deformations, which affect the Mn^{3+}-O-Mn^{4+} bond angle and length, have dramatic consequences for the properties of these systems.[18–22]

An interesting way to modify the crucial Mn^{3+}-O-Mn^{4+} network is to dope at the Mn site itself.[23] Some such studies have been undertaken during the past few years.[24–31] Blasco *et al.*[24] studied the structural, magnetic, and transport properties of the $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_{3-\delta}$ compounds, wherein the Al doping at the Mn site was shown to decrease the Curie temperature T_c and the metal-insulator transition temperature T_p rapidly with the Al concentration for $x<0.05$ without affecting the MR significantly. At higher x values spontaneous loss of oxygen was found with a concurrent enhancement of MR. Several authors have studied the effects of Fe doping at the Mn site on the properties of CMR perovskites.[25–31] Righi *et al.*[25] examined a 5% Fe-doped $La_{0.7}Ca_{0.3}MnO_3$ compound and found a 50-K decrease in T_c and a 10–15% decrease in the average moment measured at 1 T. Pissas *et al.*[26] studied the lightly (2%) Fe-doped $La_{0.75}Ca_{0.25}MnO_3$ compound by Mossbauer spectroscopy and suggested the existence of ferromagnetic clusters in the sample with a size distribution. Ahn *et al.*[27] observed that replacement of Mn by Fe favors insulating character and antiferromagnetism opposing the effects of double exchange. These authors argued that the nonparticipation of Fe^{3+} in the double exchange results purely due to the electronic structure considerations. The absence of any signatures of Fe^{4+} and Fe^{5+} in the Mossbauer spectra in Fe-doped samples further supports this conclusion. Consequently the Mn e_{g1} band alone is electronically active, with the carrier hopping occuring between the Mn^{3+} and Mn^{4+} ions. Cai *et al.*[28] examined the properties of $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ and confirmed the occurrence of spin-glass behavior therein. Their data also suggested the presence of, and competition between, ferromagnetic and antiferromagnetic clusters in the system. Gayathri *et al.*[29] also studied the properties of the $La_{0.7}Ca_{0.3}Mn_{1-x}Co_xO_3$ system for $0.05<x<0.5$. They suggested that substitution of Mn by Co dilutes the double exchange and transforms the long range ferromagnetic order to a cluster-glass-type FM order.[28] M. Rubinstein *et al.*[30] studied the effects of Gd, Co, and Ni doping in $La_{2/3}Ca_{1/3}MnO_3$ for high dopant concentrations (>10%). These authors pointed out that on the basis of the Goldschmidt tolerance factor considerations and the phase diagram of Hwang *et al.*[18] one would expect an increase of T_c by almost 100 °C for a dopant concentration of ~10%. However, the results showed that T_c dropped by ~30 K for this dopant concentration. They attributed this drop to the absence of double exchange interaction between the dopant (Co, Ni) and the Mn ion leading to the dominance of the antiferromagnetic superexchange interaction. Ogale *et al.*[31] studied the Fe concentration dependence of the properties of the $La_{0.75}Ca_{0.25}Mn_{1-x}Fe_xO_3$ compound and discovered the occurrence of a localization-delocalization transition in the sys-

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tem at a critical dopant concentration. Based on their observations, these authors argued that a quasiparticle of a finite dimension (few unit cells) should be associated with the carrier transport in CMR materials.

Since most of the work on doping at the Mn site is focussed primarily on the use of Fe as a dopant, there appears to be a need to explore and compare the effects of different members in the family of transition elements on the CMR properties. The work reported here is intended to be a step in this direction.

The ceramic samples ($La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}TE_{0.05}O_3$ with TE=Cr, Fe, Co, Ni, Cu, and Zn) used in our study were prepared by the standard ceramic route, employing sintering at a temperature of 1300 °C.[30,31] Fine powders of the oxides of the required elements of high purity (>99.99%) were taken in stoichiometric proportions. The powders were mixed thoroughly using a mortar and pestle for several hours. After dry mixing, propanol was added to the mixture and again the mixture was ground so that the particle size was reduced and the mixture became homogeneous. The homogeneous mixture was put in a platinum crucible and heated for over 24 h in air at 900 °C. The calcined powder thus obtained was reground and a small quantity of binder poly vinyl acetate (PVA) was added to it. The mixture was reground until it was completely dry. After mixing the binder, the mixture was pelletized under a pressure of 5 tons/cm^2. Such pellets were heated for over 48 h in air at 1300 °C. The resistivity and magnetoresistance (at fields up to 8 T) were measured following the usual procedures. It was confirmed that our data for the undoped system compare very well with the best results reported by other groups. This ensures the quality of our sample processing conditions and procedures.

Structural information was obtained from powder x-ray diffraction studies. To see the variation of the lattice constant we collected the x-ray data in the 2Θ range of 10–90° with a step size of 0.02°, and long exposure time (>24 h). To eliminate the error in the Θ values we used standard silicon powder for all the samples. X-ray powder diffraction data confirmed the monophase character with (pseudo)cubic structure in all the samples. The individual lines showed structures that reflect the presence of orthorhombic or tetragonal distortions as pointed out by Rubinstein *et al.*[30] However, within the accuracy of the measurement and analysis available to us, it is perhaps not appropriate to analyze and compare these distortions in quantitative terms for different dopants. The lattice constants were calculated using least-square refinement of the powder diffraction data.

Magnetization of all the samples was measured with a SQUID (Quantum Design Inc., model MPMS) magnetometer. To determine the magnetic transition temperature the temperature dependence of the magnetization data were obtained with small applied magnetic field (2 Oe). The magnetic field was applied well above the magnetic transition temperature. The samples were field cooled from 300 to 5 K. Then during heating, the temperature dependence data were collected. We have taken the T_C to be the midpoint of the transition.

In Fig. 1(a) are shown the data for the dependence of resistivity on temperature for the undoped and the different transition element doped samples. It can be readily noted that the case of Fe doping stands out clearly from the rest of the data for a significant downward shift in T_p as well as a broadening of the temperature dependence on the ferromagnetic metallic side. The cases of Cu and Zn doping also stand out for remarkably sharp drops in resistance on the ferromagnetic side (large temperature coefficient of resistance). We shall discuss the special features about these three elements (Fe, Cu, Zn) in the context of the transport problem in the course of the analysis of the entire data. In Fig. 1(b) are shown the data for the dependence of magnetization on temperature measured in a field of 2 Oe for the undoped and the different transition element doped samples. The lower shift in T_C is small for Cu- and Zn-doped samples, slightly larger for the Cr-doped sample, significant for the Ni- and Co-doped samples, and very large for the Fe-doped sample.

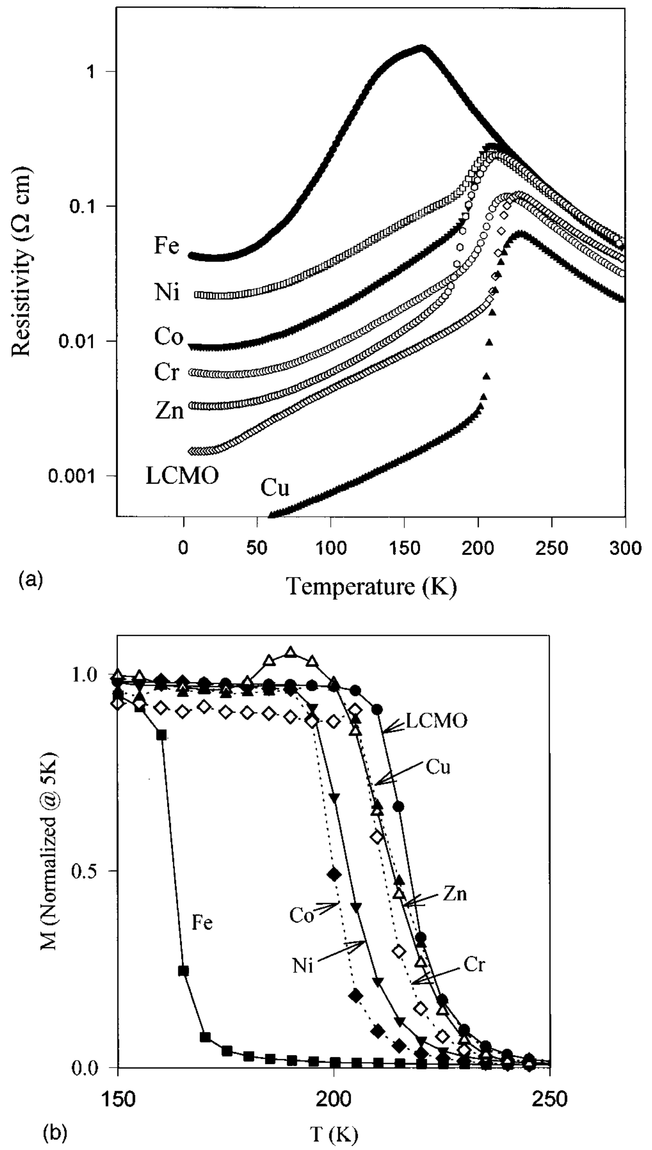

FIG. 1. (a) Dependence of resistivity on temperature for undoped and transition element doped $La_{0.7}Ca_{0.3}Mn_{0.95}(TE)_{0.05}O_3$ samples. (b) Dependence of the magnetization measured in a magnetic field of 2 Oe on temperature for undoped and transition element doped $La_{0.7}Ca_{0.3}Mn_{0.95}(TE)_{0.05}O_3$ samples.

In Fig. 2 are shown the nature of the dependence of the metal-insulator transition temperature T_p and the Curie tem-

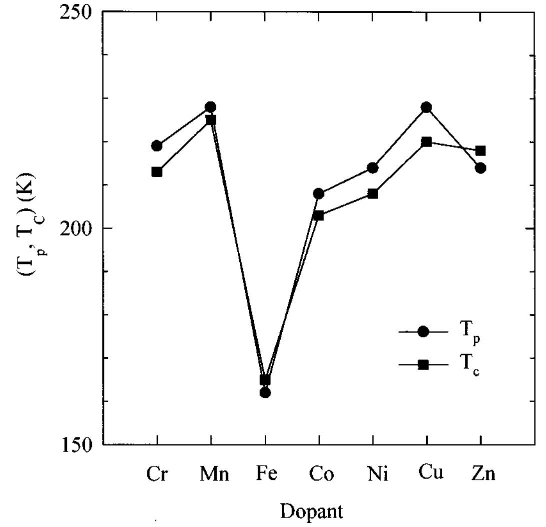

FIG. 2. Dependence of the metal-insulator transition temperature T_p and the Curie temperature. T_c on TE for $La_{0.7}Ca_{0.3}Mn_{0.95}(TE)_{0.05}O_3$ samples doped with different elements in the transition metal series.

perature T_C for $La_{0.7}Ca_{0.3}MnO_3$ doped with different transition elements. It can be seen that there is a sharp valley at the location of Fe dopant and the values for the Cr-, Cu-, and Zn-doped samples are close to that for the pure $La_{0.7}Ca_{0.3}MnO_3$(LCMO) sample. The values for Co- and Ni-doped samples are intermediate between the low T_p, T_C values for the Fe-doped sample and the highest values for pure LCMO.

In Fig. 3 are shown the systematics of the dependence of the resistivity value at the metal-insulator transition temperature $\rho(T_p)$ and at low temperature ρ(5 K) for $La_{0.7}Ca_{0.3}MnO_3$ doped with different transition elements. It is interesting to note that these data have an almost exact inverse correlation to the data shown in Fig. 2.

In Fig. 4 is shown the nature of the dependence of the percent departure of the lattice parameter a(Å) from the value for undoped LCMO, and the maximum value of magnetoresistance (MR) obtained at a field of 8 T for $La_{0.7}Ca_{0.3}MnO_3$ doped with different elements in the transition-metal series. It is interesting to note that there is a significant degree of correlation between these two quantities, although there appears to be a departure in the correlation in the case of Mn (which of course is the parent compound) and Co. The correlation between the lattice parameter (which is a function of strain and oxygen stoichiometry) and MR (which is a function of the the properties of the Mn^{3+}-O-Mn^{4+} bond) further emphasizes the coupling of spin, charge, and lattice in this system. This can be brought out with even greater clarity by examining the ionic radii of different transition element dopants. These are shown in Fig. 5. The Mn ionic radius is used as the average over the radii for Mn^{3+} and Mn^{4+} ions in the ratio 70:30. All other radii are compared to this $r(Mn_{av})$ and are represented as percentage departure from this value. Since it is demonstrated that Fe holds its valence state at 3+ in the system because of the absence of exchange with Mn ions in the matrix, we have used the radius of the Fe^{3+} ion in the plot. From similar considerations and for charge neutrality condition we have used 3+ radii also for Cr, Co, and Ni for which such a charge state is known to exist. However, for Zn the 3+ state does not occur and for Cu it is rare; hence the radii for the 2+ state are used in the plot for these two ions. When the plot in Fig. 5 is compared to that in Fig. 4 one can see a very clear correlation between the maximum MR and the ionic radii. This undoubtedly brings out the fact that strain plays a central role in controlling the magnetotransport in this system. Note, however, that the scale for ionic radii for 2+ species (Cu, Zn) is significantly different from that for the 3+ ions. Thus the jumps in MR as we go from Ni to Cu and from Cu to Zn do not strictly reflect the jumps in the ionic radii. These two ions are 2+ and should affect the carrier concentration as well, in addition to their implications for strain.

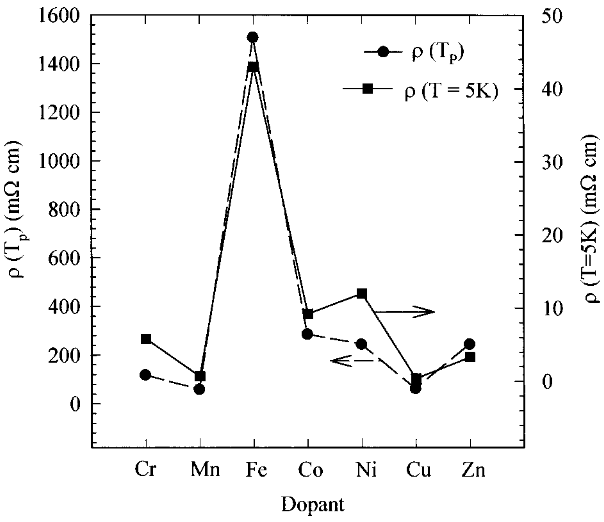

FIG. 3. Systematics of the dependence of the resistivity value at the metal-insulator transition temperature $\rho(T_p)$ and low temperature ρ(5 K) for $La_{0.7}Ca_{0.3}Mn_{0.95}(TE)_{0.05}O_3$ doped with different elements in the transition-metal series.

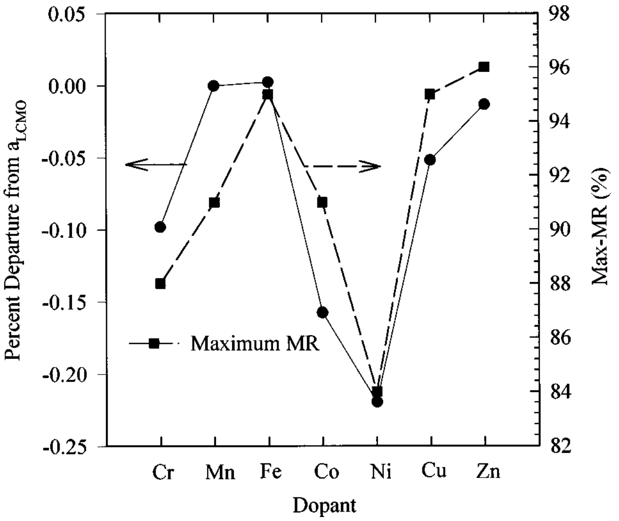

FIG. 4. Dependence of the percent departure of lattice parameter from a_{LCMO} and the maximum value of MR obtained at a field of 8 T for $La_{0.7}Ca_{0.3}Mn_{0.95}(TE)_{0.05}O_3$ doped with different elements in the transition-metal series.

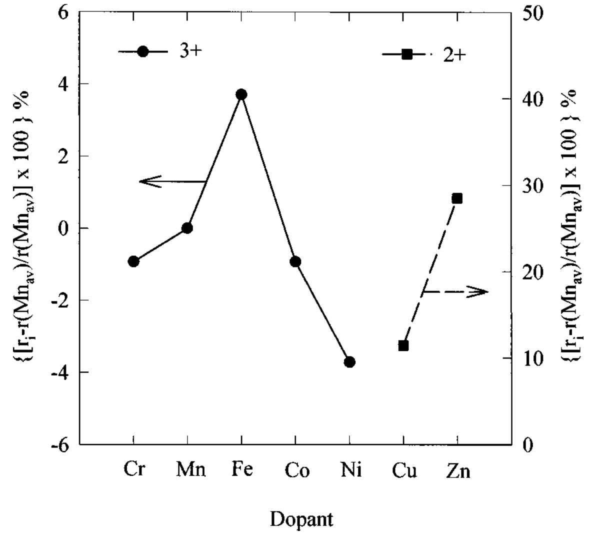

FIG. 5. Percentage departure of ionic radii of different transition element dopants (Cr^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Cu^{2+}, Zn^{2+}) from the Mn ionic radius averaged over Mn^{3+} and Mn^{4+} contributions in the ratio 70:30.

The early indications that strain is a critical consideration in the analysis of the properties of CMR manganites came from the work of Hwang *et al.*,[18] who examined the lattice effects on the magnetoresistance in doped $LaMnO_3$. For a fixed carrier concentration they found a direct correlation between the Curie temperature T_C and the average ionic radius of the La site $\langle r_A \rangle$, which was varied by substituting different rare-earth ions for La. These results showed that the changes in the Mn-Mn electron hopping parameter due to the changes in the bond angle must be incorporated in the double exchange picture.

Neumeier *et al.*[12] and Hwang *et al.*[32] examined the effects of hydrostatic pressure on the magnetoresistance properties of manganite perovskites. Neumeier *et al.*[12] found that pressure strongly decreases ρ and drives T_C up at rates as high as +37 K/Gpa for a $x=0.21$ specimen of $La_{1-x}Ca_{x-}MnO_3$. The effects are relatively weaker, though significant even at other concentrations. These authors emphasized that the observed dT_C/dP values in manganites are significantly larger than in conventional ferromagnets, and that the Mn-O-Mn bond angle θ, which upon its decrease from 180° is observed to reduce the magnetic exchange and electron hopping, is perhaps the most crucial factor in determining T_C. Hwang *et al.*[32] have compared the effects of external hydrostatic pressure and the internal chemical pressure caused by the substitution of La by a smaller Pr ion. In the latter case they found a decrease in T_C, which they attributed to the rotation of MnO_6 octahedra leading to $\theta < 180°$.

Rodriguez-Martinez and Attfield[19] studied the cation disorder and size effects in the CMR manganites ($A_{0.7}B_{0.3}MnO_3$, $A=$La, Pr, Nd, Sm, $B=$Ca, Sr, Ba) and found evidence for large cation disorder effects originating from the size differences between the A-site 3+ ions and B-site 2+ ions. Their analyses indicated that the Jahn-Teller distortions assist electron localization near the metal-insulator transition temperature. Yeh and co-workers[20,21] studied the CMR properties of epitaxial $La_{0.7}Ca_{0.3}MnO_3$ thin films deposited on substrates with a range of lattice constants and compared the corresponding properties with those of $La_{0.5}Ca_{0.5}CoO_3$ films. Based on the systematics reflected by the data these authors argued that lattice polaron conduction associated with the Jahn-Teller coupling is essential for the occurrence of CMR, the lattice distortion causing a further enhancement of the CMR effect. Kwon *et al.*[22] have also emphasized the role of lattice effects in the context of the CMR properties based on their analysis of the metal-nonmetal transition data on mixed valence manganites in terms of the tolerance factor ($t=d_{A\text{-O}}/\sqrt{2}d_{\text{Mn-O}}$) and the standard deviation (σ) of the rare-earth site cation radius. All these studies collectively indicate that the CMR properties of manganite systems are closely related to the topological features of the Mn^{3+}-O-Mn^{4+} network and their influence on the carrier transport.

While the present study confirms the importance of strain on the nature of transport across the Mn^{3+}-O-Mn^{4+} network, it is important to distinguish between the effects caused by indirect means, such as substrate-induced strain or strain due to doping at the rare-earth site, from the effects caused by the direct incorporation of the dopant in the Mn^{3+}-O-Mn^{4+} bond itself. The manifestation of strain could be entirely different in the case of doping at the Mn site, which may be the reason for an apparent inapplicability of tolerance factor based considerations in the case of Co and Ni dopant effects at high concentrations as examined by Rubinstein *et al.*[30] The departure from the average Mn radius $[r(\text{Mn})_{\text{av}}]$ at the dopant site would subject the neighboring Mn-O bonds to a centric push or pull thereby causing local distortions leading to unequal Mn-O bond lengths in the surrounding unit cells. This distortion would lift the degeneracy of the e_g electron states leading to a lowering of one of the two e_g levels and thereby causing trapping of the carrier. This should lead to a decrease of T_c and increase of resistivity. Among the 3+ ions, the departure is highest for the case of Fe doping; hence the reduction in T_p (or T_c) and enhancement of ρ is also seen to be maximum.

The case of 2+ ions (Cu and Zn) is distinctly different for some specific reasons. First, there would be a local change in the lattice constant caused by the incorporation of a significantly bigger ion. This is similar to the internal pressure situation discussed by Hwang *et al.*[32] except for the fact that in their case the pressure resulted via doping at the rare-earth site. While a bigger ion at the Mn site should compress some Mn^{3+}-O-Mn^{4+} bonds radially, it would also lead to bond angle distortion. Thus the transport will be radially hastened and tangentially impeded in the neighborhood of the ion. Secondly, there is a possibility that the presence of a 2+ ion, which is unable to acquire higher valence, would induce a higher residence time of the higher valence state of Mn, namely, Mn^{4+} in its immediate neighborhood. Since Mn^{4+} is a smaller ion, the suggested local charge ordering would straighten out the Mn^{3+}-O-Mn^{4+} bonds releasing the strain in the system. This appears to be the cause of an improved quality of transition (TCR) in the Cu- and Zn-doped samples.

It may further be noted that the resistivity for the Cu-doped sample is lower as compared to all the other samples over the entire temperature range. The origin of this effect may possibly lie in the electronic nature of the grain boundary in the Cu-doped case being distinctly different with respect to that in the other samples, in addition to the release of strain within the grain due to local charge ordering, as indicated above. Since Cu and Zn have substantially large ionic radii as compared to the average Mn radius, such ions in the proximity of the grain boundary may be attracted towards the boundary in order to release the local strain; thereby modifying the electronic states responsible for grain boundary conduction. Whether the decorating ion poisons or heals the grain boundary electronically depends upon the details of the electronic structure, which is unknown at this time. It seems that Cu (d^9) improves the grain boundary conduction thereby reducing the overall resistivity, while Zn (d^{10}) does not.

In conclusion, transition element doping effects in $La_{0.7}Ca_{0.3}MnO_3$ have been investigated. It is observed that dopant-size-induced local strain effects are dominant in controling the magnetotransport in this CMR material. The case of Fe stands out among the 3+ dopants due to the largest departure of its ionic radius from $r(\mathrm{Mn_{av}})$, the radius of Mn ion averaged over the Mn^{3+} and Mn^{4+} radii. The cases of 2+ dopants, namely, Cu and Zn, appear to yield considerably higher TCR in the system presumably due to strain relief caused by local charge rearrangement.

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