Abstract. The colossal magnetoresistance (CMR) effect in perovskite manganites is a magnetic-field-induced transition from a paramagnetic insulating (PI) to a ferromagnetic metallic state. The large electrical resistivity of the PI state lies at the heart of the CMR effect. This enhanced resistivity stems, in part, from strong electron–lattice coupling and the associated local lattice distortions. Both uncorrelated local distortions (Jahn–Teller polarons) and correlated distortions are present in the PI state. The latter are believed to signal the presence of nanoscale orbital correlations. In this paper, we describe recent x-ray and neutron-scattering studies of the orbital correlations in pseudocubic manganites $\text{Ln}_{1-x}\text{B}_x\text{MnO}_3$. Possible microscopic structures giving rise to these correlations are discussed. It is found that the correlations are ubiquitous in the orthorhombic PI phase of hole-doped manganites, and that their properties are defined by a single parameter—the doping level $x$. The correlations, however, are absent in the other paramagnetic phase exhibited by the manganites—the rhombohedral phase. The latter phase is metallic in the doping range in which the CMR effect is observed. Since the uncorrelated lattice distortions are present in both these phases, the insulating character of the PI state in CMR manganites results from the presence of the correlated lattice distortions. The orbital correlations, therefore, play the key role in the CMR effect.
1. Introduction

Strongly correlated systems are a major research subject in modern condensed matter physics. Perovskite manganites are, arguably, among the few most widely investigated correlated compounds [1]–[3]. The large magnetoresistance values exhibited by some manganites were the reason for the initial research activity in the field. However, these compounds continue to attract significant attention because of a large number of their other interesting properties. Indeed, these systems are extremely complex, and exhibit a number of interesting phases that are subject of intense current research activity [4]. Perhaps even more importantly, studies of manganites gave rise to several new conceptual approaches in physics of correlated systems. It is recognized, for example, that intrinsic electronic inhomogeneities play a key role in manganites [3]. The extreme sensitivity of these compounds to changes in the external conditions (magnetic field, pressure, exposure to light) is directly related to the presence of the inhomogeneities. Similar intrinsic inhomogeneities have been found recently in other important correlated systems [3]. The inhomogeneous states possess unusual properties and are often quite susceptible to external perturbations, giving rise to various interesting effects. Intrinsically inhomogeneous systems are now commonly considered an important subject in the physics of correlated systems.

In this paper, we discuss x-ray and neutron scattering studies of the nanoscale inhomogeneities in magnetoresistive manganites of the chemical formula Ln$_{1-x}$B$_x$MnO$_3$. We concentrate on one specific type of the correlations which plays an especially important role in the colossal magnetoresistance (CMR) effect. To present a complete picture, some of our previously published data are discussed first, and then new data are described. We believe that the data presented here allow us to make several important conclusions about the microscopic properties of the insulating phase and, consequently, about the mechanism of the magnetoresistance in the manganites.

Mixed-valence manganites exhibit a large variety of different states. As an example, figure 1 shows phase diagram of La$_{1-x}$Ca$_x$MnO$_3$. This variety stems from the presence of various competing and cooperating interactions involving the charge, orbital, spin and lattice degrees of freedom. These interactions are conventionally described using the Mn 3d orbitals and a simple ionic picture. In this picture, the Mn$^{4+}$ ion contains three electrons in the $t_{2g}$ state (the $xy$, $xz$ and $yz$ 3d orbitals), which are localized and have collinear spins because of the large Hund’s coupling. When the system is doped, the extra electron goes into the $e_g$ orbitals. There is also a large Hund’s coupling between the $e_g$ electron and the immobile $t_{2g}$ spin. As a consequence, the metallic ground state in manganites is also ferromagnetic [5]. It is important to note that the
Figure 1. Phase diagram of La$_{1-x}$Ca$_x$MnO$_3$: FM, ferromagnetic metal; CO, charge-ordered insulator; O', paramagnetic insulating phase with no long-range JT order. Courtesy of Uehara et al [4].

Because of the large Hund’s coupling, the paramagnetic state in manganites is expected to have an increased electron scattering rate and, consequently, increased electrical resistivity. Experimentally, the paramagnetic state in hole-doped manganites ($x < 0.5$) is indeed an insulator [1]. However, its resistivity is significantly larger than anything that can be explained by the effects of the increased spin scattering [6]. It is this increased resistivity that lies at the heart of the celebrated CMR effect (see figure 2 for an example). The CMR effect is a magnetic-field-induced transition from the paramagnetic insulating (PI) state, shown in white in figure 1, to the ferromagnetic metallic (FM) state, shown in red in the same figure. Understanding the physical mechanism responsible for the increased resistivity of the PI phase is, therefore, essential for understanding the CMR effect.

2. Experimental procedures

Single crystals of the manganite compounds discussed below were grown using the floating zone technique. Polycrystalline samples were prepared using standard solid-state reaction techniques. Synchrotron x-ray measurements were carried out at beamline X22C at the National Synchrotron Light Source, as discussed in detail in [7]. Neutron scattering experiments were performed at
the NIST centre for neutron research. Single-crystal measurements were performed using the BT-2 thermal triple-axis spectrometer. 60°-40°-S-40° collimation and fixed final energy of 14.8 meV were used. Powder diffraction measurements were performed using the BT-1 powder diffractometer. A Cu (311) monochromator, $\lambda = 1.5403(2)$ Å, and 15°-20°-S-7° collimation were utilized. The samples were mounted in a closed-cycle refrigerator (30–400 K). Crystal structure refinements were carried out using the GSAS program [8]. In this paper, we use the orthorhombic Pbnm notation, in which the $a$, $b$ and $c$ axes run along the (1, 1, 0), (1, $-1$, 0) and (0, 0, 1) cubic perovskite directions, respectively.

3. Nanoscale orbital correlations

It is now well established that electron–lattice coupling plays a key role in the PI state [1]–[3], [6]. This coupling gives rise to local lattice distortions (static or dynamic) and leads to increased electrical resistivity. There is a large body of experimental evidence that Jahn–Teller (JT) polarons are present in the PI state [2], [9]–[11]. In the Mn orbital description mentioned above, a JT polaron forms when an $e_g$ electron localizes on a Mn$^{3+}$ ion, and the surrounding oxygen octahedron distorts due to the JT effect. The $t_{2g}$ electrons are JT-inactive, and Mn$^{4+}$ O$_6$ octahedra are undistorted. Until recently, the polarons were believed to be chiefly responsible for the enhanced resistivity of the PI state.

Numerous measurements of transport, thermodynamical and optical properties in manganites indicate that the actual microscopic structure of the PI state is, in fact, more complex [2, 3]. To interpret the properties of the PI phase, various scenarios have been proposed, including presence of charge/orbital correlations [7, 12, 13], a pseudogap state [2, 4] and a Griffiths phase [14]. A common feature of all these scenarios is the presence of finite-length electronic or structural correlations. With the benefit of hindsight, one can note that some kind of structural correlations should have been expected in the PI state in CMR manganites. Indeed, in the vicinity of the ‘optimal’ doping $x \approx 0.3$, at which the CMR effect is large, the nominal concentrations of the Mn$^{3+}$ and Mn$^{4+}$ ions are comparable. The JT polaron concentration should be considerable.
Figure 3. The x-ray intensity around the (4, 4, 0) Bragg peak in the PI state (\(T = 230\) K) in Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\).
with $x \sim 0.5$. It is therefore natural to propose that the correlations arise due to the presence of nanoscale regions exhibiting the CE-type charge and orbital order. Importantly, such an assumption would be consistent with the enhanced resistivity of the PI state.

The nature of the CE-state itself was the subject of debate recently. Thus, an appropriate clarification is due here. The original model of the CE-state [16] was proposed by Goodenough for manganites with $x = 0.5$. It involves a checker-board order of Mn$^{3+}$ and Mn$^{4+}$ ions, a specific order of the Mn d orbitals (see figure 4) and also a complex low-temperature antiferromagnetic order. The charge-ordered state is also observed for $x > 0.5$ (see figure 1), and the Goodenough model can easily be extended for these doping levels. An example of such a structure exhibiting Mn$^{3+}$ stripes running along the $a$-axis for $x = 2/3$ is shown in figure 4. XANES experiments have shown, however, that only a small charge disproportionation (if any) can be present in the ‘charge-ordered’ state [17]. New models for the CE-state, not involving charge or orbital order, were then proposed [18]. Recent resonant x-ray diffraction measurements show, however, that the basic topology of the Goodenough structure is correct [19]. Specifically, the spatial order of the JT-distorted and -undistorted MnO$_6$ octahedra is the same as that of the Goodenough model. In agreement with the XANES measurements, it is found that there is no full charge separation. The lattice sites can, therefore, be described as Mn$^{3+}$ and Mn$^{4+}$-like, with the $3x^2 - r^2$ and $3y^2 - r^2$ orbitals partially occupied in the former, and the $x^2 - y^2$ orbitals in the latter sublattice. This picture is also supported by theoretical calculations [20]. It appears, therefore, that the CE-state can still be described as orbitally ordered, even though the charge order may only be partial, if present at all in this state.

We now proceed to the description of the basic properties of the structural correlations. Figure 5 shows the intensity of the correlated peak, the correlation length extracted from the peak width and the electrical resistivity as functions of temperature in zero field (a–c), and magnetic field at $T = 215$ K (d–f) in Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ [21]. As in other manganites [7, 12, 13],

Figure 4. A sketch of the orbitally ordered state in manganites for $x = 0.5$, and for $x = 2/3$. The properties of the different Mn sites are described in the text.
Figure 5. Temperature dependence of (a) the electrical resistivity, (b) the intensity of the correlated peak and (c) the correlation length in Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ in zero magnetic field. (d)–(f) Magnetic field dependence of the same quantities at $T = 215$ K [21].

The intensity of the peak traces the electrical resistivity. The correlations survive over only a few unit cell lengths. The correlation length and the period of the lattice modulation (not shown) do not exhibit any significant dependence on either temperature or the magnetic field [7, 21]. These observations are consistent with a scenario in which the correlations stem from the presence of nanoscale regions exhibiting the CE-type orbital order [7, 12, 13]. Interestingly, these regions have an essentially constant size. The intensity of the correlated peak can, therefore, be considered to be proportional to the concentration of the correlated regions. Another important observation is that the correlations survive in the FM state, thus possibly being a factor determining the resistivity of this state. The FM state is, therefore, also inhomogeneous in this particular sample.

Numerous experiments with other orthorhombic manganites of different chemical compositions and doping levels ($0.2 < x < 0.5$) reveal the same basic pattern [7]. The structural properties of the correlations (the modulation wavevector and the correlation length) do not depend on temperature significantly, and the intensity of the correlated peak traces the behaviour of the resistivity. Within the experimental errors, the correlation length is found to be the same in all the samples. The correlated regions possess, therefore, a certain intrinsic size. The period of the lattice modulation within the correlated regions, on the other hand, is different in different samples. It was found that this period is, in fact, uniquely defined by the doping level $x$ [7].
Figure 6. The wavevector $\delta$ of the lattice modulation in the correlated regions as a function of doping $x$ in various manganites (solid symbols). The corresponding chemical compositions are given in [7]. Open symbols show the high-temperature values of $\delta$ for the critical fluctuations of charge/orbital order measured in samples with charge-ordered ground states. As discussed in the text, some of the open symbols show only an upper bound for $\delta$. Blue—Pr$_{1-x}$Ca$_x$MnO$_3$, electron diffraction [24]; red—La$_{1-x}$Ca$_x$MnO$_3$, electron diff. [24]; green—Bi$_{1-x}$Sr$_x$MnO$_3$, x-ray diff. Dashed line shows the wavevector of the low-temperature structures with long-range charge/orbital order.

Figure 6 shows dependence of the lattice modulation wavevector $\delta$ on the doping level in the pseudocubic manganites studied so far (solid symbols). Interestingly, all the experimental points appear to fall on a straight line connecting $\delta \approx 2/3$ at $x = 0$ with $\delta \approx 0$ at $x = 1$.

This behaviour clearly resembles the behaviour of the lattice modulation vector in the charge-ordered phase, which is shown as a dashed line in figure 6. Thus, it is reasonable to assume that the correlated regions possess the same striped orbitally ordered structures as those found in the manganites exhibiting long-range charge-ordered states (see figure 4). However, the slopes of the two linear dependences shown in figure 6 are quite different. Therefore, if this proposal is correct, the correlated regions must be electron-depleted. For example, in the samples with $x = 0.3$, $\delta$ is approximately equal to 0.5, indicating that the $x = 1/2$ structure shown in figure 4 is realized in the correlated regions. The doping level in these regions should therefore be $x = 0.5$, rather than $x = 0.3$, and the rest of the sample should have an increased electron concentration. Such segregation of charge was, in fact, predicted in numerous theoretical calculations, in which several different Hamiltonians with terms including electron hopping, Hund’s coupling, superexchange and electron–lattice interaction were considered [3]. It is difficult to include long-range Coulomb forces in such calculations. It is important to note that the Coulomb forces should not prevent the formation of nanoscale charge-depleted regions, even though they can be one of the factors limiting the regions size. Thus, it appears that the intrinsic instability of manganites towards electronic phase separation accompanied by charge segregation is a key factor leading to the formation of the nanoscale structural correlations.

There are other factors that can also affect the formation of the correlated regions. Firstly, effects of quenched disorder might be very important [3], especially because such a disorder is always present in doped manganites as they are solid solutions. It is worth noting, however, that the
correlations are found to disappear upon the orthorhombic-to-rhombohedral transition that occurs within the paramagnetic phase in certain manganite samples [22]. Since the quenched disorder does not change in such a transition, it cannot be the only major driving force responsible for their formation. Another factor to be considered is possibility of cation clustering. Since manganites with quite different chemical compositions and doping levels exhibit similar correlations [7, 12, 13], the clustering cannot be a major factor too. Finally, the linear dependence of the lattice modulation vector on the doping level suggests that the Fermi surface nesting effects might also be responsible for the formation of the correlations. Currently available calculations indicate that such a scenario is unlikely for the three-dimensional pseudocubic manganites [23].

Another interesting piece of experimental evidence suggesting connection between the long-range charge-ordered phases and the nanoscale correlations comes from electron diffraction experiments. These experiments can be done in manganites exhibiting the striped charge-ordered states found for \( x > 0.5 \), most of which can only be prepared in polycrystalline form and are not suitable for x-ray or neutron experiments. The electron diffraction experiments show [24] that as the charge-ordered state disappears on heating across the phase transition to the high-temperature state, its lattice modulation wavevector \( \delta \) continuously decreases from its low-temperature value of \( 1 - x \). Unfortunately, all these measurements are done only in a limited temperature range above the transition temperature, and the limiting value of the wavevector cannot be established in all the cases. It appears, however, that these high-temperature values of \( \delta \), shown as open symbols in figure 6, fall on the same line as those of the nanoscale correlations discussed above. These data suggest that the nanoscale correlations found in the PI state for \( x < 0.5 \) are indeed closely related to the fluctuations of the striped charge/orbital order, thus providing additional evidence for the model discussed above.

More work is needed to establish unambiguously whether the observed lattice correlations indeed reflect presence of local orbital order of the CE-type. Direct measurements of the local structure giving rise to the observed correlations are yet to be made. In addition, calculations assuming the CE-type structure of the nanoscale regions predict significantly larger intensity of the diffuse peaks than what is actually observed in x-ray experiments [22]. Thus, the amplitude of the lattice distortions in the correlated regions is, in all likelihood, significantly smaller than that in the long-range charge-ordered structures.

Summing up, the PI state in hole-doped CMR manganites exhibits nanoscale structural correlations. (A more precise statement about the presence of the correlations in the paramagnetic state is given in the next section.) The structure of the correlated regions appears to be determined by a single parameter—the doping level \( x \). The lattice modulation wavevector values show a common linear dependence on the doping level. The experimental data are consistent with a model in which the correlations reflect presence of nanoscale regions exhibiting doping-dependent charge and orbital order (stripes), and in which the correlated regions are electron-depleted. In the framework of this model, the intrinsic instability of manganites towards electronic phase separation (amplified, perhaps, by quenched disorder) is a key factor leading to the formation of the nanoscale structural correlations.

4. Orbital correlations and uncorrelated JT polarons

Until now, we have avoided discussing two very important questions. Firstly, do correlations always exist in the high-temperature phase in manganites in the range of dopings relevant to the
CMR effect ($0.2 < x < 0.5$)? And secondly, what are the respective roles of the uncorrelated polarons and the orbital correlations? These questions are addressed in this section.

The JT polarons have long been thought to be responsible for the enhanced electrical resistivity of the PI state [1, 2]. They are strongly suppressed in the FM state, and their concentration exhibits temperature-dependent behaviour similar to the behaviour of the correlated peak of figure 5(b) [12]. It is, therefore, possible that the correlations discussed above are simply a by-product of the large number of interacting JT polarons in the sample. In this case, the polaronic correlations would play only a secondary role in the CMR effect. Below, we discuss experimental evidence showing that the nanoscale correlations, in contrast, play a key role in the CMR manganites.

In hole-doped CMR manganites ($0.2 < x < 0.5$), the high-temperature paramagnetic state exhibits two different pseudo-cubic perovskite structures: an orthorhombic (O*) and a rhombohedral (R) phase [1, 25, 26]. The MnO₆ octahedra in the O* phase are distorted, reflecting, perhaps, strong electron–lattice coupling and JT effect [26]. The MnO₆ octahedra in the average R structure are not distorted [25]. However, local JT distortions are known to be present in the R phase [10, 25, 26]. Interestingly, the nanoscale correlations have so far been detected only in the O* phase [22]. In fact, the experimental data available now suggest that the correlations are always present in the paramagnetic O* phase, at least at moderate temperatures [7, 12, 13].

It is, therefore, possible to investigate properties of the paramagnetic state both in the presence and in the absence of the correlations. Moreover, such studies can be done using the same sample, provided that the material undergoes an O*–to–R transition in the paramagnetic phase. A convenient series of compounds for such studies is La$_{1-y}$(Ca$_{1-y}$Sr$_y$)$_y$MnO$_3$ with $x \approx 0.3$. A schematic phase diagram for this series [27] is shown in figure 7. As $y$ increases from 0 to 1, the system undergoes an O*–to–R transition at $y \approx 0.5$. The nanoscale correlations are clearly present in the $y = 0$ compound [12], and were not detected for $y = 1$ [22]. In a certain range of
y values, the system undergoes an O*-to-R transition within the paramagnetic phase. Below, we discuss one such sample, La$_{0.75}$(Ca$_{0.45}$Sr$_{0.55}$)$_{0.25}$MnO$_3$. This compound undergoes a transition from the low-temperature FM phase to the paramagnetic O* state at $T_c \approx 300$ K, and a structural transition from the O* state to the high-temperature paramagnetic R state at $T_s \approx 360$ K.

Figure 8 shows x-ray intensity in the vicinity of the (4, 4, 0) Bragg peak at $T = 300$ K (O* phase) and $T = 400$ K (R phase). X-ray scans through the correlated peak positions are shown in figure 9. As was reported in [22], the correlations are only present in the paramagnetic O* state. The temperature dependence of the signal due to the correlations has been characterized in detail in [22]. The data of figure 8 also show that the uncorrelated polarons remain in the R phase, as indicated by the butterfly-like scattering pattern observed at $T = 400$ K. This scattering, however, has not been characterized quantitatively in this system so far.

In order to determine the relative roles of the correlations and the uncorrelated polarons in the paramagnetic state, it is necessary to characterize their temperature-dependent properties.
Figure 10. Energy scans at $q=(4, 0.45, 0)$ at various temperatures in La$_{0.75}$(Ca$_{0.45}$Sr$_{0.55}$)$_{0.25}$MnO$_3$. The scans are displaced vertically by 400 counts with respect to each other for clarity. The solid lines are results of fits, as described in the text.

separately. For this purpose, it is more convenient to use neutron scattering, as it allows us to distinguish the correlated and the uncorrelated polarons using their differences in both the spatial properties ($q$-scans), and their dynamics. In addition, the temperature-dependent background due to phonons can be easily eliminated in neutron measurements.

We have carried out neutron scattering measurements using single crystal and powder samples of La$_{0.75}$(Ca$_{0.45}$Sr$_{0.55}$)$_{0.25}$MnO$_3$. Figure 10 shows energy scans at several temperatures for $q=(4, 0.45, 0)$. Because of the proximity of a strong Bragg peak, significant scattering from the uncorrelated polarons should be present at this $q$. Also, the signal from the correlated distortions, which in this sample, peaks at the reduced wavevector of $(0, 0.5, 0)$ (see figure 9), is expected at this position. On the other hand, no contribution from the Bragg peak tail, and no $\lambda/2$ contamination should be present in the scans of figure 10. For $T<T_c$, these scans show only an elastic peak at $E=0$, and a resolution-limited transverse acoustic (TA) phonon peak at $E \approx 8$ meV. This scattering pattern changes significantly as temperature is increased above $T_c$: a broad quasielastic signal appears, and the TA phonon peak broadens. To analyse these data, the scans were fitted to a sum of a resolution-limited elastic peak, a Lorentzian quasielastic peak and a TA phonon peak. The fits were convoluted with the instrumental resolution. The energy, height and the Lorentzian width of the phonon peak were fitted at all temperatures. The width $\Gamma = 5.5(5)$ meV of the quasielastic peak was determined at $T=300$ K and then kept fixed for larger temperatures. The obtained fits are shown as solid lines in figure 10.
Figure 11. Temperature dependence of (a) the energy-integrated quasielastic scattering due to the uncorrelated polarons at $q=(4, 0.45, 0)$, (b) the intensity of the x-ray peak due to the correlated lattice distortions and (c) the electrical resistivity of La$_{0.75}$(Ca$_{0.45}$Sr$_{0.55}$)$_{0.25}$MnO$_3$. The data shown in (b) and (c) are taken from Kiryukhin et al [22].

The temperature dependence of the integrated intensity of the broad quasielastic feature is shown in figure 11(a). This intensity does not show any significant anomaly at $T_s$. In contrast, the energy-integrated correlated scattering measured in the x-ray experiments of Kiryukhin et al [22] abruptly disappears upon the O*-to-R transition at $T_s$ (see figure 11(b)). The quasielastic scattering of figure 11(a), therefore, does not contain any significant contribution from the correlated distortions. Thus, we conclude that this scattering originates from the uncorrelated polarons.

The data of figure 11(a) clearly show that both the O* and the R paramagnetic phases exhibit the dynamic uncorrelated polarons. In other words, fluctuating nanoscale structural inhomogeneities are present in the both of these structural paramagnetic states. The physical properties showing anomalous behaviour in both the O* and the R states should, therefore, be associated with the effects of the dynamic uncorrelated polarons. One such property is damping of the acoustic phonon modes which can readily be observed in the data of figure 10. For $T > T_c$, the TA phonons acquire a finite lifetime $\hbar/\Gamma_{TA} \sim 300–400$ fs, where $\Gamma_{TA}$ is the Lorentzian width of the phonon peak determined from the fits of figure 10. Because acoustic phonons provide a major contribution to the thermal conductivity in manganites [2, 28], this damping may be an important factor leading to its strong reduction in the paramagnetic phase [29]. We note that an even more significant damping of the optical JT phonon modes in related manganite compounds...
All these phonon anomalies are, of course, natural consequences of the presence of local inhomogeneities in the crystal lattice. In fact, similar phonon anomalies have been observed in several other systems exhibiting nanoscale inhomogeneities such as, for example, relaxor ferroelectrics [32].

Other transport properties should also be affected by the presence of the dynamic polarons and the polaronic correlations. The electrical resistivity is, clearly, of special importance in manganites because of the CMR effect. We now turn to the key question addressed in this section: the separate effects of the structural correlations and the uncorrelated polarons on the resistivity. Figure 11(c) shows temperature dependence of the resistivity in $La_{0.75}(Ca_{0.45}Sr_{0.55})_{0.25}MnO_3$. It exhibits an abrupt decrease in the O*-to-R transition temperature $T_s$. Since the uncorrelated polarons do not show any significant anomaly at $T_s$ (figure 11(a)), this decrease can either be explained by the disappearance of the structural correlations, or by the changes in the average crystallographic structure upon the structural transition at $T_s$.

To characterize the structural changes at $T_s$, we have determined the average crystallographic structure for $T = 340$ K (paramagnetic O* state), and for $T = 400$ K (paramagnetic R state) using neutron powder diffraction. The results of the structural refinement are shown in table 1. To provide a quantitative estimate of the possible effects of this structural change on the electrical resistivity, we note that the electronic bandwidth in manganites is proportional to $\cos \omega/d^{3.5}$, where $\omega = (\pi - \langle Mn-O-Mn \rangle/2)$, $d$ is the Mn–O bond length and $\langle Mn-O-Mn \rangle$ is the Mn–O–Mn angle [33]. Using the structural data shown in table 1, we find that the difference in the bandwidths of the R and O* states due to their structural differences is smaller than 0.3%. While this argument is not strict in the case of the nonmetallic paramagnetic state, it does show that the structural changes that take place at $T_s$ have a negligible effect on the overall electronic band structure.

Therefore, the larger electrical resistivity of the O* state stems from the presence of the correlated distortions. This is the central result of this section. To understand the significance of this result, we refer to the phase diagram of figure 7. This system exhibits two paramagnetic states: the O* state possessing the polaronic correlations, and the R state with no correlations present. We find that the changes in the single polaron concentration at the structural O*-to-R transition are minor, and the corresponding structural changes are not large enough to have a significant effect on the transport properties. The differences in the properties of the O* and the R paramagnetic states should, therefore, be attributed to the presence of the polaronic correlations in the O* state.

Further experiments are needed to establish whether these results can be generalized to all the perovskite manganites. We believe, however, that there is sufficient evidence in hand to warrant a proposal for the microscopic mechanism explaining the observed variation in the properties of the paramagnetic phase in optimally doped ($x \sim 0.3$) manganites. In figure 12, a sketch of the general phase diagram of $x \sim 0.3$ perovskite manganites is shown [34, 35]. As the tolerance factor (defined as $t = d_{Ln-O}/\sqrt{2d_{Mn-O}}$) increases, the system undergoes a structural transition from the orthorhombic to the rhombohedral phase. Extensive measurements of bulk properties [35] indicate that electron–lattice coupling effects play a much more significant role on the orthorhombic side of the phase diagram. A large number of anomalous properties, such as large volume and magnetic entropy changes at $T_c$, high magnetostriction, and the largest values of magnetoresistance (CMR) are observed in the orthorhombic phase. These anomalies are absent or strongly reduced in the rhombohedral state [35]. Correlated lattice distortions have been found in a large number of orthorhombic perovskite manganites with different compositions [7, 12, 13]. No significant lattice correlations have been reported so far in the rhombohedral state [22]. These
observations cover a significant part of the phase diagram of figure 12, from the narrow-bandwidth Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ ($t \approx 0.905$) to the large-bandwidth La$_{0.7}$Sr$_{0.3}$MnO$_3$ ($t \approx 0.93$). In addition, our results clearly show that it is the correlated distortions, and not single polarons, that distinguish the R and O$^*$ states on the microscopic level. We believe that these observations allow us to propose that the observed drastic differences between the properties of the paramagnetic O$^*$ and R states in hole-doped manganites stem from the presence of the correlated lattice distortions in the O$^*$ phase.

Thus, the correlated lattice distortions play the key role in the CMR effect. When they are absent in the paramagnetic state, that is, when the paramagnetic state is rhombohedral, the

Table 1. Refined structural parameters from neutron powder diffraction data for La$_{0.75}$(Ca$_{0.45}$Sr$_{0.55}$)$_{0.25}$MnO$_3$. For $T = 340$ K, space group is Pbnm. The atomic positions are Mn: (0.5, 0, 0); La/Ca/Sr, O(1): (x, y, 0.25); O(2): (x, y, z). For $T = 400$ K, space group is R3c. The atomic positions are Mn: (0, 0, 0); La/Ca/Sr: (0, 0, 0.25); O(1): (x, 0.25).

|                  | $T = 340$ K  | $T = 400$ K  |
|------------------|--------------|--------------|
| $a$ ($\text{Å}$) | 5.51785(6)   | 5.51729(3)   |
| $b$ ($\text{Å}$) | 5.48206(6)   | 5.51729(3)   |
| $c$ ($\text{Å}$) | 7.7524(1)    | 13.3539(1)   |
| Mn $u_{iso}$ ($\text{Å}^2$) | 0.0054(3) | 0.0066(2) |
| La/Ca/Sr $x$     | -0.0031(5)   | 0            |
|                  | 0.0142(5)    | 0            |
| S $u_{iso}$ ($\text{Å}^2$) | 0.0086(2) | 0.0110(2) |
| O(1) $x$         | 0.0604(6)    | 0.44869(9)   |
|                  | 0.4938(6)    | 0            |
| $u_{11}$ ($\text{Å}^2$) | 0.0093(5) | 0.0166(2) |
| $u_{22}$ ($\text{Å}^2$) | 0.0212(9) | 0.0160(3) |
| $u_{33}$ ($\text{Å}^2$) | 0.0123(7) | 0.0177(2) |
| $u_{12}$ ($\text{Å}^2$) | 0.0003(8) | 0.0080(2) |
| $u_{13}$ ($\text{Å}^2$) | 0          | -0.0022(1)  |
| $u_{23}$ ($\text{Å}^2$) | 0          | -0.0044(3)  |
| O(2) $x$         | 0.7331(4)    | -            |
|                  | 0.2683(3)    | -            |
|                  | 0.0314(5)    | -            |
| $u_{11}$ ($\text{Å}^2$) | 0.0129(5) | -            |
| $u_{22}$ ($\text{Å}^2$) | 0.0131(5) | -            |
| $u_{33}$ ($\text{Å}^2$) | 0.0145(4) | -            |
| $u_{12}$ ($\text{Å}^2$) | -0.0034(4) | -            |
| $u_{13}$ ($\text{Å}^2$) | 0.0008(6)  | -            |
| $u_{23}$ ($\text{Å}^2$) | 0.0008(5)  | -            |
| $R_{WP}$ (%)     | 6.08         | 5.41         |
| $\chi^2$ (%)     | 1.748        | 1.343        |
magnetoresistance is relatively small. In fact, the rhombohedral state is usually considered to be a metal in the optimally doped manganites ($x \sim 0.3$) [1, 2], [25]–[27]. Therefore, the experimental data available at this stage are consistent with the scenario in which the presence of the correlations distinguishes the metallic and the insulating paramagnetic states in manganites. This intriguing possibility clearly deserves further investigation.

Finally, we note that while the extant experimental work points to the importance of the average crystallographic symmetry in manganites [22], detailed theory explaining why the correlations are observed only in the O* state has not been developed yet. The importance of the average long-range structure stems from the fact that the significant lattice distortions associated with the correlated regions give rise to long-range anisotropic strain [15]. A possible explanation of the experimental observations discussed here will, therefore, likely invoke the effects of the favourable elastic response of the O* structure to these long-range strains. Even though interesting theoretical results on the role of long-range strains in manganites have recently been achieved [36, 37], realistic models taking into account the long-range elastic effects are yet to be developed.

Summing up the results discussed in this section, the orthorhombic PI state in hole-doped ($0.2 < x < 0.5$) manganites exhibits nanoscale structural correlations, while the correlations are absent in the rhombohedral state. Uncorrelated JT polarons are present in both of the structural paramagnetic states. The correlations are responsible for the increased electrical resistivity of the paramagnetic O* state, thus playing the key role in the CMR effect.

5. Conclusions

In summary, we report x-ray and neutron-scattering studies of nanoscale structural distortions in magnetoresistive manganites. The obtained results can be summarized as follows. (i) The
O*-orthorhombic paramagnetic insulating state in hole-doped pseudocubic manganites (0.2 < x < 0.5) exhibits nanoscale structural correlations. The correlations are absent in the rhombohedral paramagnetic phase R. (ii) The experimental data are consistent with a model in which the correlations reflect the presence of nanoscale regions exhibiting doping-dependent charge and orbital order, and in which the correlated regions are electron-depleted. The structure of the correlated regions appears to be determined by a single parameter—the doping level x. The orbital order within the correlated regions is likely to be related to the CE-type and striped orbital structures found in the long-range charge/orbitally ordered states in manganites for x ≥ 0.5. (iii) Uncorrelated polarons are present in both the orthorhombic and rhombohedral phases. They affect the dynamics of the crystal lattice, as manifested by the phonon damping effects, and should therefore affect various transport properties. We do not find any significant anomaly in the polaron concentration at the O*-to-R transition. (iv) The increased electrical resistivity of the orthorhombic paramagnetic state should be attributed to the presence of the correlated structural distortions. Because the increased resistivity of this state is responsible for the CMR effect, the orbital correlations play the key role in this effect. The other structural paramagnetic phase found in the pseudocubic manganites—the R phase—lacks the correlations, is metallic in the relevant doping range and exhibits much smaller magnetoresistance values than those found in the O*-state. The general phase diagram of the CMR manganites reflecting these findings is shown in figure 12. (v) Based on these results, as well on previously published work, we propose that the insulating character of the orthorhombic paramagnetic phase in CMR manganites stems from the presence of the correlated structural distortions.

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