Chapter 1

MULTI-SCALE PHASE MODULATIONS IN COLOSSAL MAGNETORESISTANCE MANGANITES

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Abstract  Extensive experimental results are presented on the multi-scale phase modulation phenomena observed in colossal magnetoresistance manganites. Two key types of phase inhomogeneities directly relevant to the colossal magnetoresistance (CMR) are discussed. The first type involves micrometer-scale coexistence of structurally and electronically different phases. We present extensive experimental data for a prototypical system exhibiting such a phase coexistence, (La,Pr)\textsubscript{5/8}Ca\textsubscript{3/8}MnO\textsubscript{3}. These data reveal that percolative transport phenomena play the key role in the metal-insulator transition in this system, and are largely responsible for the significant magnitude of the magnetoresistance. The phase
composition of the multiphase states is governed by both the electron correlations and the effects of martensitic accommodation strain. The second type of an inhomogeneous state is realized in the paramagnetic state commonly found in manganites at high-temperatures. In this state, nanometer-scale structural correlations associated with nanoscale charge/orbital ordered regions are observed. Experimental investigation of numerous manganite systems indicates that these correlations are generic in orthorhombic mixed-valent manganites, and that the correlated regions play an essential role in the CMR effect. This chapter is organized as follows. An introduction to the subject is given in Section 1. In Section 2, the phase diagram of (La,Ca)MnO$_3$ is presented. Electronic and structural properties of both the high- and low-temperature phases are discussed. Section 3 is devoted to the studies of the micrometer-scale multiphase states in (La,Pr)$_{3/8}$Ca$_{3/8}$MnO$_3$. In Section 4, high temperature nanoscale correlations are discussed. Extensive studies of electronic and thermal transport, and optical spectroscopy are presented. Section 5 focuses on x-ray scattering studies of the nanoscale correlations. Finally, Section 6 concludes this Chapter.

**Keywords:** colossal magnetoresistance manganites, multi-scale phase modulations, phase coexistence, charge/spin/orbital correlations, percolative transport, martensitic accommodation strain
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1. Introduction

The colossal magnetoresistance phenomena discovered in the early 90’s in mixed-valent manganites has stimulated world-wide research activities on the subject during the last decade [1, 2, 3]. Intense research has revealed many new aspects of this complex material system, which now turn out to be basic to the physics of correlated many-body systems. Several key phenomena observed in manganites, such as strong coupling among spin/charge/orbital degrees of freedom, competition among several order parameters, and the resulting inhomogeneous ground state, now appear to be broadly applicable to other correlated systems including high $T_c$ cuprates. Early experimental and theoretical results that uncovered many exciting physical properties are discussed in many excellent review articles (Ramírez, 1997 [4]; Coey, Viret, and von Molnar, 1999 [5]; Tokura and Tomioka, 1999 [6]), and in several edited books (Rao and Raveau, 1998 [7]; Tokura, 1999 [8]; Kaplan and Mahanti 1999 [9]). One of us (SWC) also reviewed early experimental progress in 1998 and 1999 [10, 11]. Early works on optical spectroscopy of the manganites were reviewed by Noh, Jung, and Kim [12], Okimoto and Tokura [13], and Cooper[14]. An experimental overview of structure and transport of the manganites was prepared by Salamon and Jaime, 2001 [15] and a theoretical review by Dagotto, Hotta, and Moreo, 2001 [16] on phase separation phenomena in manganites.

In this review, we cover the extensive progress made in understanding these interesting systems in the last about three years, with emphasis on multi-scale phase modulation phenomena. We include our recent experimental results that provided unambiguous evidence for multiscale charge/lattice/orbital inhomogeneity and the concomitant phase separation phenomena in the manganites. We begin with a discussion of the basic physics underlying these effects, and a brief summary of earlier relevant progress in the physics of the manganite system.

Roughly speaking, colossal magnetoresistance (CMR) results from a magnetic-field-induced shift of the ferromagnetic Curie temperature, and the accompanying metal-insulator transition. The initial extensive research on the origin of CMR effect revealed two important aspects of the intriguing system. First, it appears that charge carriers in the mixed-valent manganites are (Jahn-Teller-type) polaronic. In other words, charge carriers in the $e_g$ band of Mn$^{3+}$ tend to be localized by accompanying lattice distortions and to be strongly dressed by clouds of phonons. The lattice distortions accompanying the carriers probably resemble local Jahn-Teller distortions and the polaronic nature of charge carriers was much emphasized. However, it is noteworthy that the exact nature
(i.e., metallic or insulating) of the ground state of the many-polaron problem is still largely a mystery. The second important aspect, which is somewhat related to the Jahn-Teller polaron issue, is the unusually strong coupling among charge/spin/orbital degrees of freedom in manganites. For example, when charge carriers in the $e_g$ orbital can hop readily from one Mn site to another, the double exchange mechanism produces ferromagnetic coupling between localized $t_{2g}$ spins [17]. However, when charge carriers tend to localize, superexchange coupling becomes active. It turns out that the magnitude as well as the sign of this superexchange coupling depends on the orbital character of the localized charge [18]. For example, when the $e_g$ orbital electron of Mn$^{3+}$ faces the neighboring Mn$^{4+}$, the superexchange coupling between the Mn$^{3+}$ and Mn$^{4+}$ is ferromagnetic. Otherwise, the superexchange coupling is antiferromagnetic.

The prototypical manganite system is Ca-doped LaMnO$_3$, where the concentration of Mn$^{4+}$ is controlled by the doping level of Ca$^{2+}$ into La$^{3+}$ sites. The general trend of physical properties with concentration variation of Mn$^{3+}$ (or Mn$^{4+}$) can be summarized in the following way: (1) When there are more Mn$^{3+}$ than Mn$^{4+}$ (i.e., $x<0.5$ in La$_{1-x}$Ca$_x$MnO$_3$), the ground state tends to be metallic and ferromagnetic, probably induced by the double exchange mechanism. (2) When there are more Mn$^{4+}$ than Mn$^{3+}$ (i.e., $x>0.5$), the ground state often becomes charge-localized (insulating) and, in fact, charge-ordered with intriguing patterns. Magnetic coupling in this insulator is dominated by superexchange coupling, which is sensitive to orbital ordering. (3) Surprisingly, high temperature properties differ strongly from those of the ground state. At high temperatures, systems with $x<0.5$ tend to be more insulating than those with $x>0.5$. For example, the ground state of La$_{5/8}$Ca$_{3/8}$MnO$_3$ is ferromagnetic-metallic, but the system becomes insulating above the Curie temperature. Thus, we may conclude that the Jahn-Teller polaron nature is a controlling effect for $x<0.5$ at high temperatures. The details of these aspects are well discussed in various review papers [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16].

Recently, there has been an unexpected turn of events in manganite research. The steadily accumulating body of experimental results clearly indicates that the mixed-valent manganite system is electronically/magnetically inhomogeneous so that a Hamiltonian approach may have severe limitations. This inhomogeneity appears at various length scales as well as time scales. Trivial inhomogeneity such as chemical inhomogeneity through inappropriate synthesis of materials is partially responsible. However, there are non-trivial inhomogeneities not directly related to the origin of CMR effects. For example, in the low doping
range with $x\lesssim 0.1$ and $x\gtrsim 0.9$ in La$_{1-x}$Ca$_x$MnO$_3$, the system is a weakly doped antiferromagnet, with a tendency to exhibit very-small-scale (likely nano-scale) phase mixtures of an antiferromagnetic phase and a ferromagnetic phase. In fact, this is a general trend when carriers are introduced into antiferromagnetic (especially, Mott-type insulating) oxides.

There are, however, two important non-trivial inhomogeneities (or phase modulations) in mixed-valent manganites that can be relevant to CMR effects; these CMR-related phase modulations are the main theme of this chapter. One non-trivial phase modulation occurs at low temperatures with micro-meter length scales. For example, in Pr$^{3+}$-substituted La$_{5/8}$Ca$_{3/8}$MnO$_3$, ferromagnetic-metallic regions and charge-ordered insulating regions coexist at low temperatures with sub-micro-meter scales. The relative volume of the electronically/magnetically distinct regions varies with Pr substitution. Furthermore, this relative volume is sensitive to applied magnetic field (favoring the ferromagnetic-metallic state), which leads to huge negative magnetoresistance. It turns out that long-range strain, resulting from the significantly-different crystallographic structures of the metallic and insulating phases, plays an important role in producing large-length-scale phase coexistence in the system. This tendency resembles what generally happens in martensitic phase transformations. In martensitic systems, crystallographically-different phases can coexist at low temperatures to accommodate the significant long-range strain associated with martensitic transformation. Therefore, it appears that manganites are a wonderfully unique system in which martensitic effects and strongly-correlated physics both play critical roles.

The other important inhomogeneity is related to the presence of nano-scale charge/orbital correlated nano-clusters (or nano-scale charge/orbital ordering) in the background paramagnetic state above the Curie temperature. For example, above the Curie temperature of 275 K in La$_{5/8}$Ca$_{3/8}$MnO$_3$, nano-scale charge/orbital ordering has been observed. Furthermore, the nano-scale charge/orbital ordering is correlated with the insulating nature of the system above the Curie temperature. In fact, systematics of various manganites reveal that the insulating nature above the Curie temperature is always associated with the presence of charge/orbital correlated nano-clusters, existing only in the orthorhombic crystallographic structure. The theoretical reexamination of the exact role of Jahn-Teller polarons as well as polaron-polaron correlations in the insulator above the Curie temperature will be essential to understand the systematics.
To address the non-trivial phase modulations that are directly related to CMR properties in mixed-valent manganites, we organize this chapter as follows. A revisited phase diagram on (La,Ca)MnO$_3$ system covering high temperature structural transition boundaries is discussed in Section 2. Carrier-concentration-dependence of various electronic and thermal transport properties is also presented in this section to complete the phase diagram of this prototypical system. In Section 3, new experimental findings are discussed, especially relating to the phase separation phenomena with sub-micro-meter scales at low temperature. We focus on the (La,Pr,Ca)MnO$_3$ system produced with varying chemical pressure. Magnetotransport, electron microscopy, and optical conductivity studies are used to investigate extensively the nature of the low temperature phase separation. In Section 4, high temperature-nanoscale phase modulations are explored in (La,Ca)MnO$_3$ systems using various experimental approaches such as electronic/thermal transport and optical conductivity measurements. Section 5 focuses on the nanoscale phase coexistence problem studied with x-ray/neutron scattering measurements. Section 6 concludes this chapter.

2. Phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ manganites revisited

2.1 Construction of the phase diagram of (La,Ca)MnO$_3$

The perovskite manganite (La,Ca)MnO$_3$ is a prototypical system that exhibits various ground states as a function of carrier concentration. The Ca ionic size is almost identical to the La one, and thus a true solid solution forms in the entire range of Ca concentrations with minimal disorder effects, which might come from a size mismatch of the A-site ions in the ABO$_3$ perovskite structure. By varying relative ratios of La and Ca, we can explore the influence of carrier concentrations on the physical properties of this system.

To accurately obtain desired carrier concentrations, a large number of polycrystalline La$_{1-x}$Ca$_x$MnO$_3$ specimens with high density were prepared with similar synthesis conditions. The prepared Ca concentrations include $x=0.0, 0.03, 0.04, 0.05, 0.08, 0.1, 0.125, 0.15, 0.2, 0.21, 0.25, 0.3, 0.333, 0.375, 0.4, 0.45, 0.48, 0.5, 0.52, 0.55, 0.6, 0.625, 0.65, 0.666, 0.67, 0.7, 0.75, 0.8, 0.83, 0.875, 0.9, 0.95, and 1.0. The appropriate mixtures of pre-baked La$_2$O$_3$, CaCO$_3$, and MnO$_2$ underwent solid-state reaction at 1100-1400 °C in air for four days, and the samples were furnace-cooled. Because of the different vaporization rates of the starting constituent materials, initial low temperature calcining with frequent regrindings
was performed. In addition, the polycrystalline samples near the phase boundary such as ones near \( x = 0.5 \) (\( x = 0.485, 0.49, 0.495, 0.5, \) and 0.51) and near \( x = 0.20 \) (\( x = 0.185, 0.19, 0.195, 0.20, \) and 0.21) were synthesized. To get more accurate oxygen stoichiometry, the samples for \( x < \sim 0.2 \) were post-annealed in a flowing nitrogen gas, and the samples for \( x > \sim 0.8 \) in an oxygen for 12-60 hrs.

A previous study has focused on low temperature phase diagram based on the detailed measurements of magnetic susceptibility (\( \chi \)) (or magnetization) \[10\]. The data were still incomplete to understand detailed phase diagram. In this study, we extended our measurements to resistivity (\( \rho \)), thermal conductivity (\( \kappa \)) and thermoelectric power (\( S \)) at low temperatures to determine doping-dependent variations of electronic (charge) and phononic (lattice) degrees of freedom in the system. In addition, to complete the phase diagram, we also determined structural phase transition temperatures as a function of Ca concentrations through the high-temperature-dc resistivity measurements.

### 2.2 High temperature structural phase transitions

High temperature \( \rho \) was measured with a transport stick located inside a quartz tube in a furnace. Temperature was measured with a Pt and Pt-Rh thermocouple from 300 to \( \sim 1000 \) K. The thermocouple was pre-calibrated as a function of temperature. In each measurement, we used the conventional 4-probe technique with silver or gold pastes suitable for high temperature measurements. Depending on the carrier concentration, care was taken to flow a mixture of nitrogen and oxygen gases so that oxygen stoichiometry of a sample does not change while measuring resistivity at high temperatures above \( \sim 500 \) K. As explained above, when prepared in air, samples with \( x < \sim 0.2 \) tend to absorb oxygen, while samples with \( x > \sim 0.8 \) are susceptible to oxygen deficiency. Thus, larger amount of nitrogen gas were flown for low \( x \) samples while larger ratio of oxygen gas was required for high \( x \) samples. In all the measurements, we verified that both resistivity value and structural transition temperature of each sample are reproducible after several cooling and heating runs.

Fig. 1.2(top panel) shows that the Jahn-Teller distortion of \( x = 0.0 \) occurring around 758 K is accompanied by a sharp increase of \( \rho \). It is known that the Jahn-Teller distortion in a \( Mn^{3+} \) ion gives rise to a cooperative ordering of \( e_g \) orbitals in the orthorhombic \( ab \) plane. Structural analyses revealed that the orbital ordering for the \( x = 0.0 \) sample leads to an elongation of \( a- \) & \( b- \) axes and a shortening of \( c- \) axis, stabilizing the so-called \( O^\prime \)-structure \( (a > b > c / \sqrt{2}) \) below 758 K (754 K) for heat-
Figure 1.1. Phase diagram of La$_{1-x}$Ca$_x$MnO$_3$. There exist well-defined anomalies at commensurate concentration of $x=N/8$ (N=1, 3, 5, and 7) at low temperatures. PI: Paramagnetic Insulator, FMM: Ferromagnetic Metal, COI: Charge Ordered Insulator, AFI: Antiferromagnetic Insulator, FI: Ferromagnetic Insulator, and CAFI: Canted Antiferromagnetic Insulator. Structural transitions occur at high temperatures. R: Rhombohedral, $O^\prime$: Orthorhombic with Jahn-Teller distorted, and $O$: Orthorhombic with octahedron rotated.

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(We are using an orthorhombic $Pbnm$ notation, in which $a \sim \sqrt{2}a_c$, $b \sim \sqrt{2}a_c$, and $c \sim 2a_c$, where $a_c$ is the cubic perovskite lattice constant.) At those temperatures, there exists a sharp increase of $\rho$, as shown in Fig. 1.2 (top panel). As doping $x$ increases, the increase of $\rho$ at the transition becomes reduced and transition width becomes broad, indicating the Jahn-Teller structural transitions become more incoherent with carrier concentration $x$ increases. Furthermore, the transition temperature (arrows in the top panel of Fig. 1.2) decreases systematically. At $x=0.20$, this transition seems to be located at 35 K as indicated by a derivative of $\rho$ (the inset of Fig. 1.2). The structural distortion of $x=0.20$ at such a low temperature should be confirmed later with other techniques. Above the Jahn-Teller distortion temperatures, it is known that a normal orthorhombic structure ($O$ type; $a \approx b > c/\sqrt{2}$) is stabilized. The systematic evolution of the Jahn-Teller transition temperatures is summarized in Fig. 1.1 as crosses (+).
Figure 1.2. Upper panel: high temperature resistivity data of La$_{1-x}$Ca$_x$MnO$_3$ ($0.0 \leq x \leq 20$). Structural transition temperatures from rhombohedral (high temperature) to $O^\prime$-orthorhombic (low temperature) are indicated as arrows. The inset indicates that the structural transition temperature of $x=0.2$ is located around 36 K. Bottom panel: high temperature resistivity data of La$_{1-x}$Ca$_x$MnO$_3$ ($0.0 \leq x \leq 0.375$) showing evolution of another structural transition temperatures (arrows) from rhombohedral (high temperature) to $O$-orthorhombic (low temperature).

On the other hand, in the bottom panel of Fig. 1.2 and in the inset of Fig. 1.3, another structural phase transition is clearly identified at 1031 K (1028 K) for heating (cooling) in the $x=0.0$ sample. By monitoring temperatures where a sudden drop of $\rho$ occurs, we determined evolutions of the structural transition temperatures with increasing carrier concentrations. The arrows in the bottom panel of Fig. 1.2 show that the structural transition temperature decreases systematically down to 722 K as $x$ approaches 0.25 from 0.0. Radaelli et al [19] reported an orthorhombic ($Pbnm$) to rhombohedral ($R\bar{3}c$) transition near 725 K for La$_{0.7}$Ca$_{0.3}$MnO$_3$ from a neutron diffraction study. This result is consistent with the present transport studies. Therefore, this high temperature structural transition is attributed to be one from $O$-orthorhombic ($Pbnm$) to rhombohedral ($R\bar{3}c$) symmetry. As further shown in Fig. 1.3, the transition temperature again increases with $x$ until it reaches a broad maximum near 1000 K for $x \approx 0.80$, and finally decreases above
Figure 1.3. Upper panel: high temperature resistivity data of La\(_{1-x}\)Ca\(_x\)MnO\(_3\) (0.375\(\leq x \leq 0.80\)). Structural transitions from rhombohedral (high temperature) to O-orthorhombic structure are indicated as arrows. The inset shows that two high-temperature structural transitions of \(x=0.0\) have large thermal hysteresis, showing the first-order nature. Bottom panel: high temperature resistivity data for \(x=0.9\) and 1.0 exhibiting the structural transition temperatures (arrows). The inset shows derivative of resistivity of the \(x=0.9\) sample, indicating a structural transition around 980 K (arrow).

\(x=0.80\). The structural transition temperatures for both \(x=0.9\) and 1.0 are indicated the bottom panel of Fig. 1.3 and its inset. Systematic doping-dependence of the structural transition temperatures is summarized in the phase diagram of Fig. 1.1. It is noteworthy that the transition temperatures from \(O\)-orthorhombic (\(Pbnm\)) to rhombohedral (\(R\bar{3}c\)) structure display an interesting electron-hole symmetry as a function of carrier concentration. In other words, a minimum temperature for the structural transition occurs near \(x=0.25\) (hole doping), while a maximum exists near \(x=\sim 0.75\) (\(\sim 0.25\) electron doping). Those temperatures become lower below \(x=0.50\) and higher above \(x=0.50\), forming an asymmetric phase line centered at \(x=0.50\). It is an interesting question to be answered how the evolution of high temperature structural transition is linked to the ground state properties of the system.
2.3 Low temperature electronic/thermal transport and commensurate effects at \( x = N/8 \)

2.3.1 Low temperature phase diagram revisited: \( N/8 \) anomaly.

In a previous review by Cheong and Hwang [10], the phase diagram at low temperatures was constructed from detailed measurements of magnetic susceptibility primarily. The resulting phase diagram at low temperatures is summarized in Fig. 1.1. To characterize physical properties more extensively, dc resistivity (\( \rho \)), thermoelectric power (\( S \)), and thermal conductivity (\( \kappa \)) were measured in the \((La,Ca)MnO_3\) system. Temperature-dependent \( \rho \), \( S \), and \( \kappa \) are displayed in Fig. 1.4, 1.5, and 1.6, respectively, for various Ca concentrations (\( x \)) in \( La_{1-x}Ca_xMnO_3 \). The \( \rho \), \( S \), \( \chi \) (\( \equiv M/H \)), and \( \kappa \) values at 100 K and 300 K for various \( x \) are summarized in Fig. 1.7. The electronic/thermal transport data were measured in a closed-cycle cryostat equipped with a turbo-molecular pump. For \( S \) and \( \kappa \) measurements, a steady-state method was employed, using a radiation shield and a precalibrated type E-thermocouple. In particular, for \( \kappa \) measurements, high-density samples made with similar synthesis conditions were used to reduce thermal conductivity errors coming from the grain boundary scattering in polycrystalline specimens. Both perovskite \( LaMnO_3 \) and \( CaMnO_3 \) are antiferromagnetic insulators. The Mn valence in \( LaMnO_3 \) is +3 (\( t^{3}_{2g} e^{1}_{g} \)) and one in \( CaMnO_3 \) is +4 (\( t^{3}_{3g} \)) so that Mn ions in \( La_{1-x}Ca_xMnO_3 \) becomes mixed-valent. \( LaMnO_3 \) becomes a good insulator below the Jahn-Teller distortion temperature 758 K (see Fig. 1.2), because Mn\(^{3+} \) is a good Jahn-Teller ion, and the doubly degenerate \( e_g \) bands become split due to the Jahn-Teller distortion. In this special \( O^- \)-orthorhombic structure, \( LaMnO_3 \) is known to become an A-type antiferromagnet below 140 K, wherein ferromagnetic coupling exists in the orthorhombic basal plane and antiferromagnetic coupling perpendicular to the basal plane. Antiferromagnetic superexchange interaction between Mn\(^{4+} \) ions via an intervening oxygen makes \( CaMnO_3 \) a normal G-type antiferromagnet. Therefore, the initial Ca-substitution in \( LaMnO_3 \) produces hole carriers in the Jahn-Teller split \( e_g \) band, and the low doping of La in \( CaMnO_3 \) induces electrons in the empty \( e_g \) band. Consistent with this, thermoelectric power \( S \) data at high temperatures (Fig. 1.5) display large positive values for low hole doping samples and large negative values for low electron doping ones. The real hopping of \( e_g \) electrons between Mn\(^{3+} \) and Mn\(^{4+} \) through an oxygen ion produces a ferromagnetic coupling in the double exchange (DE) mechanism. Therefore, the increase of Ca-substitution produces the smaller resistivity and thermoelectric power values. However, the
Figure 1.4. Low temperature-resistivity data of La$^{1-x}$Ca$^x$MnO$_3$. At Curie temperature, each compound shows decrease of resistivity while resistivity increases at charge ordering temperature. Those ordering temperatures are consistent with the phase diagram shown in Fig. 1.1. See texts for details.

Figure 1.5. Temperature ($T$) dependent-thermoelectric power $S$ of La$^{1-x}$Ca$^x$MnO$_3$ at various doping ranges. At low temperature region of ferromagnetic metallic samples with $0.20 < x \leq 0.48$, $S$ value is very small, while at low temperature regions of charge ordered samples with $0.50 \leq x \leq 0.875$, $S$ becomes large negative. At high temperature region above ordering temperatures, $S$ shows a continuous evolution from positive to negative as doping $x$ increases. For $x \leq 0.20$, $S$ value is large positive at high temperature and decreases abruptly near $T_C$, and becomes large negative at lower temperatures.
low Ca doping samples with $0.0 < x < 0.2$, is still insulating even with ferromagnetic or canted antiferromagnetic coupling. Similarly, the samples with high Ca doping ($x > 0.875$), i.e., low La doping into CaMnO$_3$, produces insulating behaviour, possibly with a canted-antiferromagnetic coupling. Other interactions such as Jahn-Teller distortion and phase segregation tendency in the low-hole doping regime seem to overcome the DE mechanism, and produce the insulating behaviour even if a slight decreases of resistivity are observed near $T_C$ for both $x=0.15$ and 0.2 (Fig. 1.4). In addition, superexchange coupling between Mn$^{4+}$ and Mn$^{3+}$ ions can be either antiferromagnetic or ferromagnetic depending on the relative $e_g$ orbital orientation [18].

In samples with $0.2 \leq x \leq 0.5$, where the CMR has been observed, a paramagnetic insulating-to-ferromagnetic metallic transition occurs upon cooling due to the DE mechanism. At the transition, a sharp drop of $\rho$ is observed, as shown, for example, in the data of $x=0.375$ in Fig. 1.4. Then, $S$ values below $T_C$ become very small ($|S| < 1 \mu V/K$), consistent with the creation of the metallic carriers (See Fig. 1.5 and Fig. 1.7). For the higher doping range with $x \geq 0.5$, doped charge carriers localize and order with stripe modulations at a charge ordering temperature $T_{CO}$ [10], and an antiferromagnetic ordering occurs at lower temperatures (at the Neel temperature $T_N$). The charge ordering is accompanied by a sharp increase of resistivity for doping ranges $0.5 \leq x \leq 0.875$. At $T_{CO}$, $S$ values of these samples decrease sharply upon cooling to become more negative. The striped ordering of charge carriers reflects a generic tendency toward microscopic (nano-scale) electronic phase separation in the system, due to strong electron-lattice and electron-electron interactions.
The systematic behaviors of $\rho$ and $S$ observed in Fig. 1.2-1.5 are well summarized in Fig. 1.7, displaying the $\rho$ and $S$ data at 100 K and 300 K with varying $x$. The $\rho$ values at 100 and 300 K for low hole doping regions are quite larger than those for low electron doping regions. This indicates that the presence of Jahn-Teller distortion is responsible for the $\rho$ increase. For ferromagnetic metallic regions with $0.2 \leq x \leq 0.5$, both $\rho$ and $S$ become quite small. The $\rho$ and $S$ increases at 100 K for $0.5 < x \leq 0.875$ are consistent with localization of charge carriers with charge ordering. As is evident in the phase diagram, there are well-defined features at the commensurate carrier concentrations of $x = N/8$ ($N=1,3,4,5,$ and 7) in La$_{1-x}$Ca$_x$MnO$_3$. It is also found that there exist interesting electron-hole symmetry in the phase diagram; $T_C$ becomes maximum at $x = 3/8$ and $T_{CO}$ peaks at $x = 5/8$ with similar $T_C$ and $T_{CO}$ temperatures. As another interesting features at commensurate carrier concentrations, Fig. 1.7 reveals that a slight anomaly of $\rho$ values exists at 300 K near the $x = 0.50$ compound. In addition, $\chi$ values at $T = 300$ K display a strikingly sharp peak at $x = 3/8$ composition. These high temperature anomalous features observed for $x = 1/2$ and $3/8$ compounds will be discussed in detail in Section 4. Interestingly, the compound $x = 0.5$ is located at the $x$-dependent first-order phase-transition line between ferromagnetic (FM) metals ($x < 0.5$) and charge-ordered insulators ($x > 0.5$) at low temperature. The $x = 0.5$ sample exhibits both ferromagnetic and charge-ordering temperatures at 220 K and 180 K (warming), respectively. It turns out that the FM metallic and CO insulating phases coexist even at the lowest temperature. Therefore, as shown in the inset of $\chi$ plot in Fig. 1.7, the saturated magnetic moment $M$ estimated at $H = 5$ T and $T = 5$ K displays gradual decrease of ferromagnetic moment as the system crosses the first-order phase transition line to become a charge-ordered insulator.

**2.3.2 Thermal conductivity vs local lattice distortions.**

To gain further insights on $x$-dependent local lattice distortions, we measured $T$-dependent thermal conductivity ($\kappa$) of La$_{1-x}$Ca$_x$MnO$_3$ (Fig. 1.6: heating). The $\kappa$ values of La$_{1-x}$Ca$_x$MnO$_3$ are relatively small, showing about 1-3 WK$^{-1}$m$^{-1}$ at room temperature. Even the largest value observed in ferromagnetic samples reaches only about 4 WK$^{-1}$m$^{-1}$ at low temperatures. At $T$ above $T_C$ of ferromagnetic samples with $0.2 \leq x \leq 0.5$, $\kappa(T)$ increases linearly with increasing $T$, which is reminiscent of non-crystalline solids. A previous work on the FM manganites has attributed the anomalous behavior of $\kappa$, i.e., a linear increase above $T_C$ to the phononic $\kappa$, $\kappa_{ph}$, coupled with large anharmonic lattice distortions [21]. In addition, it has been known that an electronic thermal
Figure 1.7. Summaries of resistivity $\rho$, magnetic susceptibility $\chi$, thermoelectric power $S$, and thermal conductivity $\kappa$ values at $T=100$ (open squares) and 300 K (solid squares) for La$_{1-x}$Ca$_x$MnO$_3$. Solid (300 K) and open (100 K) circles represent the values measured in a previous study by Cohn et al.[22]. The inset of $\chi$ plot shows the saturated magnetic moment $M$, estimated at $H=5$ T and $T=5$ K.
conductivity, $\kappa_e$, of adiabatic small polarons, which might exist at $T$ above $T_C$ of the ferromagnetic samples, is also very small \[22, 23\]. For all the Ca concentrations in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $\kappa_e$ is negligible in the high temperature regions when it is estimated from the measured $\rho$ in Fig. 1.4 and the Wiedemann-Franz law. Even if $\rho$ values for single crystals are used, $\kappa_e$ is estimated to be only 20-40 % of total measured $\kappa$ \[15\]. Cohn et al.\[22\] found out that a magnon contribution to the observed $\kappa$ is also negligible. Furthermore, they found out that $\kappa$ values of either ferromagnetic or charge-ordered samples are inversely proportional to the degree of anisotropic lattice distortion of the corresponding compound, which can be estimated from neutron diffraction data. Thus, for all Ca doping ranges of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, it is concluded that the electronic contribution to $\kappa$ is also negligible, and that the phonon contribution, directly coupled to large anharmonic lattice distortion, dominates the measured $\kappa$.

From those previous findings and $x$-dependence of $\kappa$ values at 100 K and 300 K, summarized in Fig. 1.7, we can get interesting insights on $x$-dependent local lattice distortions of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. First of all, $\kappa$ values at both 100 and 300 K are quite enhanced at a commensurate hole-doping $x=3/8$. Even though further studies are necessary in samples with more fine doping spacing, Fig. 1.7 shows that a sharp increase of $\kappa$ at 300 K resembles that of $\chi$ in the $x=3/8$. This observation indicates that at the commensurate doping of $x=3/8$, local anharmonic lattice distortions are minimized while the ferromagnetic correlation is maximized at 300 K. It is already well known \[10\] that $T_C$ becomes maximal at $x=3/8$ and, thus, electron hopping does maximal in the DE mechanism. Therefore, in the context of existing strong electron-lattice coupling in the manganites, it can be inferred that the maximum electron hopping at $x=3/8$ is closely associated with the minimized local lattice distortions and maximized ferromagnetic correlation.

On the other hand, quite low $\kappa$ observed at low temperatures in the charge-ordered samples, can be also attributed to long-range anisotropic lattice strains, resulting from the cooperative Jahn-Teller distortion and orbital ordering. Furthermore, systematic decrease of $\kappa(100 \text{ K})$ observed when $x$ approaches 0.0 from 0.2, can be linked to the increased Jahn-Teller distortion and carrier localization. Therefore, inverses of the $\kappa$ values, summarized in Fig. 1.6 and 1.7, well represent the degree of local lattice distortions and closely related carrier-localization tendency in both high and low temperature regions of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. 
3. Phase separation in manganites

3.1 Percolation model between two electronic phases in La$_{1-y}$Pr$_y$Ca$_{3/8}$MnO$_3$

Extensive research on CMR in ferromagnetic manganites has established that magnetoresistance (MR) increases exponentially when $T_C$ is reduced by e.g., varying chemical pressure [3]. Thus, enormous MR can be realized in low $T_C$ materials. Since the CMR is realized only in such low $T_C$ materials, it is important to understand how $T_C$ is reduced from the optimum value of $\sim 375$ K in (La,Sr)MnO$_3$ system with chemical pressure. The chemical pressure can be varied without changing the valence of Mn ions by substituting trivalent rare earths with different ionic size into the A site of ABO$_3$ perovskites [3]. This chemical pressure modifies the local structural parameters such as Mn-O bond distance and Mn-O-Mn bond angle, which directly influence the electron hopping between Mn ions (i.e., electronic band width). Because ferromagnetic coupling between localized Mn $t_{2g}$ spins is mediated by the hopping of $e_g$ electrons via avoiding the Hund’s rule energy (the DE mechanism) [17], the band width ($t$) reduction by chemical pressure can be consistent with the decrease of $T_C$ in the DE mechanism. However, the detailed structural studies, combined with band structure considerations, clearly indicated that the $t$ change is too small to account for the large decrease of $T_C$ [10, 24, 25]. Furthermore, neutron scattering experiments on low-energy magnetic excitations in manganites with various $T_C$ showed that the spin wave stiffness, proportional to $t$ in the double exchange mechanism, changes little in different $T_C$ manganites [26].

As an alternative scenario, it was suggested that the electron-lattice coupling ($\lambda$), partially due to the Jahn-Teller effects, as well as $t$ plays an important role in manganite physics, in particular, in low $T_C$ materials with reduced bandwidth due to the chemical pressure effect. For instance, it was theoretically predicted that $T_C$ is a strong function of $t/\lambda$ [27, 28, 29]. Therefore, one might speculate that the increase of $\lambda$, in addition to the $t$ decrease, results in the large $T_C$ reduction by chemical pressure. However, the large change of $\lambda$ is not expected by the partial substitution of rare earths for the chemical pressure variation because $\lambda$ is basically a local physical parameter. Therefore, it was still puzzling in early 1999 why $T_C$ is so strongly reduced by chemical pressure, and why CMR is only realized in the reduced $T_C$ materials.

Systematic experimental results in this section will show that the puzzling question of manganites is a direct consequence of percolative electronic phase separation in broad compositional ranges. Electronic phase separation, in general, refers to the coexistence of two or more
phases with distinctly different electronic properties, which does not originate from chemical inhomogeneity or chemical phase separation. This electronic phase separation has also attracted considerable attention, particularly in the context of the high-$T_c$ superconducting cuprates \cite{30, 31}. Systematic investigations on the prototypical (La,Pr,Ca)MnO$_3$ system will unambiguously indicate that percolative transport through charge-ordered insulator and ferromagnetic metal mixtures, resulting from electronic phase separation, plays the principal role in the CMR phenomenon.

3.1.1 Magnetotransport study and percolative phase separation. In the phase diagram in Fig. 1.1 and in a previous study \cite{10}, $T_C$ is known to be optimized for $x=3/8$ in both La$_{1-x}$Ca$_x$MnO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$. In addition, in Pr$_{1-x}$Ca$_x$MnO$_3$ with $x$ near 3/8, long-range (l-r) charge ordering (CO), instead of ferromagnetic (FM) metallicity, occurs at low $T$. Interestingly, the resistivity ($\rho$) rise at the CO transition temperature ($T_{CO}$) in Pr$_{1-x}$Ca$_x$MnO$_3$ was found to be most pronounced at $x=3/8$ even though $T_{CO}$ changes monotonically near $x=3/8$. Therefore, the system of La$_{1-x-y}$Pr$_y$Ca$_x$MnO$_3$ with a commensurate carrier doping $x=3/8$ was chosen to investigate chemical pressure effects on the FM and CO instability in a series of samples.

Fig. 1.8 shows $T$-dependence of $\rho$ and MR of La$_{5/8}$Pr$_{y}$Ca$_{3/8}$MnO$_3$. First, $T_C$, defined as $T$ for the maximum slope of sudden $\rho$ drop, decreases slowly with increasing $y$ ($0.0 \leq y \leq 0.25$), but $T_{CO}$ ($\sim 210$ K), characterized by $\rho$ upturn, does not depend on $y$ ($\geq 0.3$). Surprisingly, $T_C$ is strongly suppressed down to $\sim 80$ K after $T_C$ coincides with $T_{CO}$ of $\sim 210$ K (see the $y=0.3$ data), indicating a competition between FM and CO states. The most striking aspect, however, is that enormously large residual $\rho$ (e.g., $\rho_o \approx 2 \times 10^4$ $\Omega$cm for $y=0.4$), much larger than the Mott metallic limit, develops for large $y$ even though $T$-dependence of $\rho$ is metallic-like below $T_C$. Another interesting feature in Fig. 1.8 is that a significant hysteresis develops when $T_C$ becomes lower than $T_{CO} \approx 210$ K. This hysteresis indicates the first-order-type transition in the system with two-phase coexistence. Even for $0.2 \leq y \leq 0.275$ where no CO transition is indicated in $\rho(T)$, the $\rho$ hysteresis is clearly observable, and this hysteresis behavior appears to correlate with a broad $\rho$ hump feature far below $T_C$. In the $y=0$ and 0.1 data, the $\rho$ hysteresis is negligible, but a very broad $\rho$ hump far below $T_C$ is clearly noticeable. This finding suggests the persistence of the two-phase coexistence even in La$_{5/8}$Ca$_{3/8}$MnO$_3$. All these observations naturally suggest the possibil-
Figure 1.8. Upper panel: temperature dependent $\rho$ for $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$. Both cooling (solid lines) and heating (dotted lines) curves are shown. Bottom panel: Magnetoresistance of $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ in 4 kOe with field cooling.

ity that FM metallic and CO phases coexist, and percolative transport through the metallic phase dominates the electronic conductivity.

To further investigate this possibility, saturation moment and magnetization of this system was measured as shown in Fig. 1.9. First, for $y>0.3$, the saturation moment below $T_C$ is significantly smaller than the full moment ($\sim 4 \mu_B$) for the optimum $T_C$ material of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x\approx3/8$ (see Fig. 1.9 (a)). In addition, the ratio of the saturation moment ($\sim 0.6 \mu_B$) for $y=0.4$, close to the critical concentration ($y_c$) for the metal-insulator transition, and the full moment of 4 $\mu_B$ is within the three-dimensional percolation threshold range of 10-25 % [32]. Furthermore, the M/H curves shown in Fig. 1.9 (b) clearly suggest that the metal-insulator (M-I) transition occurs at the percolation threshold value for each sample. The open circles in Fig. 1.9 (b) represent the M/H values at the metal-insulator (M-I) transition temperatures estimated from the $\rho$ curves in Fig. 1.8 (a). Interestingly, the average of those M/H values (dotted line) is about 17 % of 8.1 emu/mol, the saturated M/H value of $y=0.0$. Thus, with changing $T$, the M-I transition occurs when M of each sample becomes about 17 % of that of $y=0.0$, independent of $y$ value. If we assume that the $T$-dependent volume frac-
Figure 1.9. (a) Saturation moments at 5 K (closed squares) and 130 K (open squares) of La$_{5/8}$Pr$_{y}$Ca$_{3/8}$MnO$_3$ as a function of average ionic radius of La$_{5/8}$Pr$_{y}$Ca$_{3/8}$. Solid lines are drawn as guides for the eyes. The inset shows M(H) for $y=0.35$ at 130 K. The FM component is evident as indicated with a dashed line, and there exists a field-induced transition in high fields. (b) $T$-dependent M/H curves of La$_{5/8}$Pr$_{y}$Ca$_{3/8}$MnO$_3$ in $H=2$ kOe after zero field cooling. Open circles on the M/H curves depict the M-I transition temperatures determined from the $\rho$ data in Fig. 1.8. The dotted line represents an average of the M/H values at the metal-insulator transition temperatures, which is 17% of 8.1 emu/mole, the saturated M/H value of $y=0.0$. $T$-dependent volume fraction of the FM domains, $f(T)$, for each $y$, can be determined from $f(T,y) = M_y(T)/M_{0.0}(T)$.

tion $f(T)$ of the FM domain is proportional to M($T$) in $H=2$ kOe, the M-I transition with changing $T$ occurs when $f$ reaches $\sim$0.17, close to the three-dimensional percolation threshold ($f_c$).

MR of La$_{5/8}$Pr$_{y}$Ca$_{3/8}$MnO$_3$ is also consistent with two-phase coexistence and percolative electronic conduction. The MR of La$_{5/8}$Pr$_{y}$Ca$_{3/8}$MnO$_3$ was measured in the relatively low field of 4 kOe, low enough to minimize the change of the ground state (especially CO phase), but high enough to orient magnetic domains. As shown Fig. 1.8 (b), the MR peaks near $T_C$ result from the shift of $T_C$ to higher $T$ by applying field, MR increases with decreasing $T_C$, and MR becomes “colossal” in
low $T_C$ materials (particularly for $0.25 \leq y \leq 0.4$). One noticeable feature is the existence of a plateau in the MR for $0.25 \leq y \leq 0.375$ at $\sim 80 K \leq T \leq \sim 210 K$. This MR plateau is associated with the two-phase coexistence even at $T_C \leq T \leq T_{CO}$. The FM behavior at 130 K, between $T_{CO}$ and $T_C$, for $y=0.35$ is clearly visible in the M($H$) curve (inset of Fig. 1.9 (a)), and the change of this FM component at 130 K with $y$ is shown in Fig. 1.9 (a). The persistence of the FM component at 130 K for $y$ up to 0.41 indicates the two-phase coexistence even for $T_C \leq T \leq T_{CO}$. The saturation moment at 5 K in the same figure decreases sharply with $y$ ($\geq 0.3$) where $T_C$ is strongly suppressed below $\sim 80 K$, corroborating the earlier discussion that two phases coexist for $y \geq 0.3$ below $T_C$. It is noteworthy that the saturation moment at 5 K for $0 \leq y \leq 0.3$, including $y=0$, is also slightly suppressed from the optimum value of $\sim 4 \mu_B$ in La$_{1-x}$Sr$_x$MnO$_3$ ($x \approx 3/8$; $T_C \approx 375 K$). This suggests the presence of a small amount of CO phase even for $y=0$, consistent with the earlier speculation from $\rho$ hump.

3.1.2 Thermal and electronic transport properties vs two-phase model. Various aspects of above electronic transport results are consistent with the coexistence of FM and CO phases, whose relative volumes change with both $T$ and $y$, and the percolative M-I transition in FM-CO mixtures. $T$-dependent $\kappa$ and $S$ are also shown in Figs. 1.10 (a) and (b). In addition, the $\rho$ data in Fig. 1.8 is redrawn as conductivity vs $T$ in Fig. 1.10 (c). First, as explained in detail in Section 2, the measured $\kappa(T)$ for all $y$ has the dominant phonon contribution. With increasing $y$, $\kappa(T)$ shows smooth variation from that of $y=0.0$ to that of $y=0.625$, and the $\kappa$ increase at $T_C$ becomes smaller. Consistently, $\kappa$ vs. $M_y(T)/M_{0,0}(T)$ at 10 and 100 K (Fig. 1.11) shows that $\kappa$ varies monotonically from the maximum ($\kappa$ of $y=0.0$) to the minimum ($\kappa$ of $y=0.625$). In comparison with $\kappa$ (and $\sigma$), $S$ exhibits seemingly different behaviors with $y$. $S$ is very close to the metallic values even near $f_c$, where $\sigma$ (or $\kappa$) is still significantly smaller than $\sigma_M$ (or $\kappa_M$). $S$ vs. $M_y/M_{0,0}$ at 100 K (Fig. 1.11 (c)) clearly demonstrates this tendency; $S$ is close to zero (slightly negative), and is insensitive to $M_y/M_{0,0}$ as long as $M_y/M_{0,0} \geq \sim 10 \%$. In contrast, $\sigma$ at 100 K of $M_y/M_{0,0} = 10 \%$ is more than three orders of magnitude smaller than that of $M_y/M_{0,0} = 100 \%$ ($y=0$). In fact, $T$-dependence of $S$ near $T_C$ is also consistent with the metallic $S$ behavior near $f_c$. With decreasing $T$ near $T_C$, $S$ starts to decrease, i.e., becomes metallic at $T$ higher than those for $\sigma$ and $\kappa$ changes. For example, in the heating curves of $y=0.35$, $S$ starts to decrease around 130 K, significantly higher than $T$ ($\sim 100 K$) for abrupt $\kappa$ increase or $T$ ($\sim 110 K$) for $\sigma$ minimum. When thermal/electronic
Figure 1.10. (a) Comparison of the experimental data and theoretical predictions of $S(T)$ of La$_{5/8-\gamma}$Pr$_{\gamma}$Ca$_{3/8}$MnO$_3$. Crosses (+) represent cooling curves for $x=0.42$ and 0.35, and the others represent heating data. The solid lines show the theoretical predictions, using the Eq. (1), for $x=0.25$, 0.35, and 0.42 with heating. (b) $\kappa(T)$ of La$_{5/8-\gamma}$Pr$_{\gamma}$Ca$_{3/8}$MnO$_3$. Solid circles show $\kappa$ data with heating, and crosses (+) represent $\kappa$ data with cooling. (\(\kappa\) of $y=0.0$ and 0.625 with cooling were nearly the same with that with heating.) Solid lines show the theoretical predictions by using the generalized effective medium (GEM) equation (Eq. (2)) with $t=2$ & $f_c=0.17$. (c) $S(T)$ by the GEM equation (Eq. (2)). Solid squares are the experimental (heating) data redrawn from Fig. 1.8, and solid lines represent the theoretical predictions with $t=2$ & $f_c=0.17$ above ~80 K.

transport properties of the system are viewed as those of M-I mixtures, the above peculiar $S$ behavior is, in fact, consistent with the theoretical prediction of effective thermoelectric power $S_E$ by Bergmann and Levy [33]. For an isotropic M-I binary mixture, they showed that in terms of $\sigma$, $\kappa$, and $S$ of each component, $S_E$ is given by

$$S_E = S_M + (S_I - S_M)\left(\frac{\kappa_E/\kappa_M}{\sigma_E/\sigma_M} - 1\right) / \left(\frac{\kappa_I/\kappa_M}{\sigma_I/\sigma_M} - 1\right),$$

(1.1)

where the subscripts M and I refer to metallic and insulating components, respectively. $\kappa_E$ and $S_E$ refer to effective thermal and electric conductivity, respectively, of the binary mixture. This equation has
been successfully applied to explain $S$ behaviors of binary Al-Ge films [34]. When $\sigma_1/\sigma_M << \kappa_1 / \kappa_M <1$, which applies to our system, and for $f = f_c$, the above equation leads to $S_E \approx S_M$, which explains our experimental results noted above.

To quantitatively compare experimental results in Fig. 1.10 with Eq. 1.1, we calculated $\sigma_E$ at every $T$. In this comparison, experimental $\sigma$ and $\kappa$, shown in Fig. 1.10, were used for $\sigma_E$ and $\kappa_E$ and ($\sigma_1$, $\kappa_1$, and $S_1$) and ($\sigma_M$, $\kappa_M$, and $S_M$) are assumed to be identical with those of $y=0.0$ and 0.625, respectively. The solid lines in the bottom panel of Fig. 1.10 (a) depict the calculated $S_E$, using Eq. 1.1, for heating curves of $y=0.25$, 0.35, and 0.42. The calculated curves match with our experimental $S$ surprisingly well at all $T$ below $T_C$ or $T_{CO}$.

For $\sigma_E$ (or $\kappa_E$) of a binary M-I mixture, McIachlan [35] proposed the generalized effective medium (GEM) equation,

$$
(1 - f)(\frac{\sigma_1^{1/t} - \sigma_E^{1/t}}{\sigma_1^{1/t} + A\sigma_E^{1/t}}) + f(\frac{\sigma_M^{1/t} - \sigma_E^{1/t}}{\sigma_M^{1/t} + A\sigma_E^{1/t}}) = 0, \tag{1.2}
$$

where $A \equiv (1-f_c)/f_c$. The same equation also works for $\kappa$. The critical exponent $t$ is close to 2 in three dimension. This equation has been successfully applied to isotropic inhomogeneous media in wide $f$ regions including percolation regime [34, 35, 36].

By using above GEM equation, the $\kappa(T)$ for various $y$ can be calculated with the assumption that $\kappa_1(T) = \kappa(T)$ of $y=0.625$, $\kappa_M(T) = \kappa(T)$ of $y=0.0$, $t=2$, and $f_c=0.17$. The solid lines in Fig. 1.10 (b) represent the estimated $\kappa_E$ for $y=0.1$, 0.25, 0.35, and 0.42. In addition, the calculated $\kappa_E$ as a function of $M_y/M_{0,0}$ at 10 and 100 K is depicted as solid lines in Fig. 1.11 (b). Estimated $\kappa_E$ lines in Figs. 1.10 and 1.11 coincide with the experimental data well. In order to confirm self-consistency, $S_E$ at 10 and 100 K is evaluated by using the calculated $\sigma_E$ (see below) and $\kappa_E$ (solid lines of Figs. 1.10 (b) and (c)), and the Eq. 1.1. The calculated $S_E$ (solid lines of Fig. 1.11 (c)) with the variation of $y$ is in good agreement with the experimental values. To apply the GEM equation to $\sigma(T)$, we assumed that $f(T,y) = M_y(T)/M_{0,0}(T)$, $\sigma_M(T) = \sigma(T)$ of $y=0.0$, and $\sigma_1(T) = \sigma(T)$ of $y=0.625$. With the parameters $t=2$ & $f_c=0.17$, the calculated $\sigma_E$ for various $y$ are shown as solid lines in Fig. 1.10 (c). At $T \sim 80$ K, $\sigma_E(T)$ nicely matches the experimental $\sigma(T)$ even if $\sigma$ changes by 6 orders of magnitude with $T$ and $y$. However, this agreement does not hold at very low $T$. The calculated $\sigma_E(T)$ at $T < 80$ K with the same parameters $t=2$ & $f_c=0.17$ significantly deviated from the experimental $\sigma(T)$. We found that at $T < 80$ K, the calculated $\sigma_E(T)$ matches the experimental $\sigma(T)$ better when $t$ is increased to $\sim 4$. This anomalous critical exponent at zero-field becomes more evident in
the $y$ dependence of $\rho$ at 8 K. In Fig. 1.12 (a), log $\rho_o$ is plotted as a function of log $(y_c-y)$ with $y_c \equiv 0.41$. Surprisingly, there exists a linear region (0.4$\leq y \leq 0.275$) in the log $\rho_o$ vs. log $(y_c-y)$ plot where $\rho_o$ changes about 7 orders of magnitude. The slope ($\sim 6.9$) of the linear region turns out to be much larger than the three-dimensional percolation prediction ($\sim 1.9$). In other words, with the decreasing volume of FM phase, $\rho_o$ increases much faster than the simple percolation consideration. Furthermore, as seen in Fig. 1.12 (b), the slope still remains about $-4$ even when it is calculated from the log $\sigma_o$ vs. log $(f-f_c)$ plot with $f_c \equiv 0.17$, where $f$ and $f_c$ was determined from the FM volume fraction in the magnetization data of Fig. 1.9. [Note that the GEM theory reduces to a percolation equation $\sigma_M \sim (f-f_c)^t$ when $\sigma_I = 0$.] These observations demonstrate that $t$, normally close to a three-dimensional exponent of $\sim 2$, becomes $\sim 4$ at very low $T$. A similar, drastic increase of $t$ has been noted in the case of tunneling transport for M-I mixtures [34, 37], suggesting that a tunneling process between FM domains is important for $\sigma$ of our system at very low $T$ [38]. In other words, as will be also evident in a next section, the reduced electron conduction through FM regions can be responsible for the anomalous $t$ value at zero field when the magnetizations of neighboring FM regions are not aligned.
Figure 1.12. (a) log $\rho_o$ vs. log $(y_c-y)$ plot for zero field (closed circle) and 4 kOe (open circle) with $y_c=0.41$. For $0.275 \leq x \leq 0.4$, there exists a linear relationship with the slope of -6.9 for zero field (-2.5 for 4 kOe). The dotted line with the slope of -1.9 represents the prediction of a percolation theory $\rho_o \sim (y_c-y)^P$. (b) $\sigma_o$ vs. $(f-f_c)$ log scale plot redrawn from the data of (a), for zero field (closed circle) and 4 kOe (open circle) with $f_c=0.17$. Temperature-dependent volume fraction of the FM domains, $f(T)$, for each $y$, was determined from the relation of $f(T,y) = M_y(T)/M_{0.0}(T)$ and the data in Fig. 1.9 (b). The two solid lines represent the prediction of GEM theory with $\sigma_1=0$, $\sigma_3 \sim (f-f_c)^t$, with the critical exponents $t$, 2 and 4, respectively. Note the GEM equation reduces to the percolation equation when $\sigma_1=0$. 

\[ \log(\rho_o) = \log(y_c-y) \]

\[ \sigma_o \sim (f-f_c)^t \]
In summary, the unambiguous agreement between the measured thermal/electronic transport properties and the calculated values based on Eqs. 1.1 and 1.2 strongly indicates that: (1) transport properties are dominated by thermal/electrical conduction in M-I mixtures, (2) the relative volume of the (FM) metallic phase is proportional to the measured $M(T,y)$, and (3) the $T$-dependent transport and magnetic properties of metallic and insulating phases are always that of $y=0$ and $5/8$, respectively.

3.1.3 Electron microscopy study and colossal magnetoresistance. Direct evidence of the two-phase coexistence is provided by the change of the CO correlation length with $y$ and $T$ investigated by electron diffraction experiments. It is well established that superlattice peaks due to CO can be readily detected by electron diffraction [20, 39]. The dark-field image, obtained from a superlattice peak due to CO, at 20 K for $y=0.375$ in Fig. 1.13 (a) clearly exhibits the existence of CO regions even below $T_C$. The white domains are CO regions, and the dark domain (upper and middle part of the picture) is a charge-disordered, presumably, FM region. It was also unexpectedly found that the typical size of CO and FM regions at low $T$ is on the order of several thousand angstroms. This micro-scale mixture is commonly observed in other compositions at low $T$, and is in contrast with the nano-scale mixture of CO and FM phases in La$_{0.5}$Ca$_{0.5}$MnO$_3$ at $\sim 150 \text{K} < T < 220 \text{K}$.

In order to observe the $T$-evolution of CO, dark-field images at 17 K (Fig. 1.13 (b)) and 120 K (Fig. 1.13 (c)) are taken for $y=0.4$. It is found that the CO regions are micro-scale (a few thousand angstroms in size) domains at 17 K, similarly to those of $y=0.375$, and become short-ranged, nano-scale domains at 120 K, as can be seen from the white spotted areas in Fig. 1.13 (c). From the non-zero saturation moment at 130 K even for $y>0.25$ and the presence of nano-scale CO regions in the dark field image at 120 K for $y=0.4$, it is inferred that the nano-scale coexistence of CO and FM observed in La$_{0.5}$Ca$_{0.5}$MnO$_3$ is realized for $0.25 < y \leq 0.4$ at $\sim 120-130 \text{K}$. One more surprise in the electron diffraction results was the observation of the $x=1/2$-type superlattice peaks (not shown) in all our specimens with the carrier concentration of $3/8$ (i.e., the modulation wave length in orthorhombic basal planes is about $2 \times a$ with $a \approx 5.5 \text{A}$, indicating the strong stability of the $x=1/2$-type CO state.) In fact, the $x=1/2$-type CO for $x$ less than $1/2$ has been observed in earlier reports in, e.g., Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ [40]. In spite of the presence of the $x=1/2$-type CO state, the carrier concentration of CO regions is presumably close to $3/8$, because it must be difficult to break the charge neutrality on large length scale as large as thousands of angstroms. This
Figure 1.13. Dark-field images of electron microscopy, obtained by using one super-lattice peak caused by CO$_2$ for La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ with $y=0.375$ at 20 K (top), $y=0.4$ at 17 K (middle) and $y=0.4$ at 120 K (bottom). Bright regions are due to CO, and dark areas show charge-disordered regions. The river-like dark lines in bright regions are due to discommensurations.
difference in carrier concentration could be accommodated by charge
defects in the $x=1/2$-type CO state.

All of above experimental studies unequivocally suggest a clear physical
picture to understand the large $\rho_o$ and the large MR in reduced
$T_C$ manganites. Since micro-scale FM regions exist in these samples,
electron conduction between neighboring FM regions should be reduced
if their magnetizations are not aligned. This conduction reduction must
be particularly large in manganites where hopping electrons are strongly
aligned with the local orientation of magnetization (i.e. manganites are
the so-called half-metallic ferromagnet) [38]. The electron conduction
between neighboring FM regions could be dominated by tunneling if
adjacent FM regions are separated by this insulating region. The de-
gree of this magnetization misalignment will increases when the system
approaches the percolation threshold due to the increasingly poor con-
nection between the FM regions. Therefore, with decreasing volume of
FM regions, $\rho_o$ increases much faster than the prediction of simple per-
colation. It is then expected that when the FM regions are aligned in
applied fields, $\rho_o$ should once again follow the percolation prediction.
This appears to be consistent with our MR results. The variation of $\rho_o$
(open circles) in 4 kOe with $y$ is shown in Fig. 1.12 (a). The same plot
is also drawn as $\sigma_o$ vs $f$ (FM volume fraction) in Fig. 1.12 (b). The
slope of the linear region for $\rho_o$ and $\sigma_o$ in 4 kOe is about $\sim-2.6$ and 2
in Fig. 1.12 (a) and (b), respectively. Thus, both plots are showing the
exponents closer to the percolation prediction of $\sim-1.9$.

All of our findings can be summarized within the two-phase picture.
(1) When $T_C$ is above $\sim-210$ K, but less than the optimum value of
$\sim375$ K, there exists a long-range (l-r) FM state with a short-range
(s-r) CO phase. (2) When the $\rho$ upturn at $T_{CO}$ is clearly visible (for
$0.3\leq y\leq 0.4$), $T_C$ is strongly suppressed below $\sim80$ K. In this case, s-
r CO and s-r FM coexist at $T_C \leq T \leq T_{CO}$, and l-r FM with l-r CO
develops below $T_C$. This view, as well as the experimental values of
$T_C$ and $T_{CO}$, is summarized in the phase diagram of Fig. 1.14. Note
that the experimental values of $T_C$ and $T_{CO}$ are determined from our $\rho$
data, and they coincide with those from our $M(T)$ data in Fig. 1.9 (b).
Furthermore, our $M(T)$ data show a spin glass-like transition below
$\sim25$ K for $y\geq0.25$; there exists a slight difference between zero-field-
cooled and field-cooled $M(T)$ data below $\sim25$ K. Note that the average
ionic radius, $<r_A>$, was estimated from the tabulated values for twelve
coordination [41]. The initial slow $T_C$ decrease for small $y$ ($0.0\leq y\leq 0.25$)
may originate from the decrease of $t/\lambda$ by increasing Mn-O bond distance
and decreasing Mn-O-Mn bond angle, induced by the substitution of the
small Pr ions.
Figure 1.14. The phase diagram of La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ as a function of average ionic radius of La$_{5/8-y}$Pr$_y$Ca$_{3/8}$. $T_C$ and $T_{CO}$ are shown with closed circles (or triangles) and open circles, respectively. There exists a large thermal hysteresis at $T_C$ for $y^*=0.275$. The coexistence of long range (l-r) FM/short range (s-r) CO, s-r CO/s-r FM, or l-r CO/l-r FM is schematically shown in the phase diagram.

All of above results clearly indicate that the two-phase coexistence is directly associated with (1) CMR for low $T_C$ manganites, (2) the first-order-like $T_C$ for low $T_C$ manganites, (3) the sharp drop of $T_C$ with chemical pressure, (4) the $\rho$ hump far below $T_C$, and (5) the small saturation moment at low $T$ for reduced $T_C$ materials. Since the nature of the two-phase coexistence changes drastically with $T$, this coexistence is not the direct consequence of chemical inhomogeneity, but results from electronic phase separation. The possibility of electronic phase separation has been discussed theoretically between antiferromagnetic insulating and FM metallic states [16]. However, our results clearly indicate the electronic phase separation relevant to CMR at low temperature is the one between FM metallic and the $x=1/2$-type CO states.

In this section, one succinct picture was provided to explain the vast amount of earlier experimental results and ambiguities, as well as our own data. Basically, FM (metallic) and the $x=1/2$-type CO states coexist in a broad range of phase space through electronic phase separation in real space, and this two-phase coexistence is responsible for the anomalous behavior of low $T_C$ manganites. The subtle balance between these two states with distinctly different electronic properties can be readily influenced by varying physical parameters such as applied field, chemical (hydrostatic) pressure, and oxygen isotope, producing various “colossal” effects [1, 2, 3, 40, 42, 43].
3.2 Martensitic transformation and multiphase coexistence

3.2.1 Relaxation between charge order and ferromagnetism.

A simple percolation model between two phases of FM metallic and CO insulating states explains the experimental results above quite well in a broad sense. However, there are emerging experimental results that cannot be explained with a standard percolation model between the two electronic phases. The most surprising point is the existence of different structural phases as well as the distinct two electronic phases. The first can be intimately associated with the lattice degree of freedom, while the latter can be related to the spin and charge degree of freedom in the system. In view of the strong coupling among lattice, spin, and charge degrees of freedom in manganites, it is expected that these structural and electronic phase separations can be intimately linked to each other. P. B. Littlewood first suggested an idea that strain induced phase separation may exist in low temperature regions of (La,Pr,Ca)MnO$_3$ [44]. He pointed out that the FM and the CO phases have a large strain mismatch so that if part of a single FM crystallite nucleates into the CO phase, that domain is under a huge stress from the surrounding crystal that discourages further growth. Thus, the coexistence of CO and FM domains can produce random strain fields populated in each domain. To tackle the issue more systematically how structural (lattice) responses can be related to the electronic phase separation, we carefully studied the physical properties of La$_{1-x}$Ca$_x$MnO$_3$ (LCM) with $x$ near 1/2 and La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ (LPCM) with $y$ near 0.35, representing two important regions of manganite phase space. Magnetization study (not shown) clearly indicated that the ground state of LPCM is FM, and CO is a high-T state [45]. On the other hand, LCM shows the opposite way. Resistivity ($\rho$) data in Figs. 1.15 (a) and 1.16 (a) were consistent with the M($T$) results. In LPCM, CO transition, which is characterized by a sudden $\rho$ upturn, appears at a high $T$, and the abrupt $\rho$ downturn, indicating FM transition, occurs at a low-$T$ whereas the order of transitions is reversed in LCM (Fig. 1.16 (a)). There exists a large $\rho$ thermal hysteresis at the low $T$ transitions, indicating a first-order nature of the transition.

Thermodynamic view of these two systems in terms of free energy ($F=U-TS$; $U$: internal energy, $S$: entropy) is depicted in Fig. 1.17 (a) and (c). $U$ of FM ($U_{FM}$) is lower than the CO $U$ ($U_{CO}$) in LPCM with $x=3/8$, but $U_{CO}$ is lower than $U_{FM}$ in LCM with $x$ near 1/2. Now, the CE-type ($n_e=1$-$x$=1/2-type) CO state is commonly observed in the system with $n_e$ near 5/8, and excess electrons may be accommodated.
as charge defects or discommensurations in CO domains [39]. Thus, there ought to exist large configurational entropy associated with CO for \( n_e \) near 5/8. In LPCM with \( n_e = 5/8 \), CO state can be, thus, “softer” than FM state, i.e. the F line for CO decreases faster than that for FM with increasing temperature. U of paramagnetic (PM) state is higher than U_{FM} and U_{CO}, but PM state is softer than FM and CO states because of large entropy. In the case of LCM with \( x \) near 1/2, the system is near the phase boundary between FM and AFM states, and thus FM state can be susceptible to various thermally induced magnetic excitations. On the other hand, little configurational entropy exists for the CO state.
Figure 1.16. (a) Temperature-dependent resistivity $\rho$ for La$_{1-x}$Ca$_x$MnO$_3$ with $x=0.49$ and $x=0.495$ with various cooling rates. "q" and "vq" represents quick cooling within $\sim$20 and $\sim$1.5 minutes, respectively. (b) Time dependence of magnetization $M(t)$ at various, fixed temperatures after quick cooling for 5 minutes under 5 kOe for La$_{1-x}$Ca$_x$MnO$_3$ with $x=0.495$. $M(t)$ follows the stretched exponential form, $M_0 - M_1 \cdot \exp(-(t/\tau)^\beta)$. In this figure, log of the exponential part, log $((M_0-M_1)/M_1)$ $\propto -(t/\tau)^\beta$, is plotted as a function of square root of time. The inset shows the temperature dependence of relaxation time $\tau$, determined by fitting data to the stretched exponential form. The fitting results are as follows; $M_0=0.364, 0.359, 0.359, 0.357, 0.358$ and 0.378 emu/mol, $M_1=0.014, 0.027, 0.031, 0.047, 0.049$ and 0.058 emu/mol, $\tau=206, 112, 107, 48, 49$ and 29 min and $\beta=0.71, 0.51, 0.52, 0.38, 0.41$ and 0.39 at 80, 90, 105, 110 and 120 K, respectively.

of LCM with $n_e \sim 1/2$. Therefore, FM state is naturally softer than CO state in LCM. The free energy vs. $T$ plots constructed from these general observations are consistent with our various results shown in Figs. 1.14-1.16. For example, in LPCM, $T_{CO}$ and $T_C$ are the crossing points of the F lines for PM-CO and CO-FM, respectively. In LCM, $T_C$ and $T_{CO}$ correspond to the crossing points of the F lines between PM-FM and FM-CO, respectively.

Even though the transitions are evident, FM state in LPCM (or CO state in LCM) does not develop fully at low $T$. In LPCM, enormously large $\rho$ and reduced $M$ (full saturation $M_s = 4 \mu_B$) at low $T$ indicate
that CO phase remains partially at low T. Similarly, non-diverging $\rho(T)$ and significant magnitude of M in LCM at low T indicate that FM phase does not disappear completely at low T. The electron-diffraction study on La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ in the above section corroborates the two-phase coexistence with the length-scale associated $\sim 1/2 \mu$m.

Intimately associated with the origin of this large-scale coexistence of FM and CO phases, it was found that the two-phase situation can be influenced by cooling rate across $T_C$ and $T_{CO}$. As shown in Figs. 1.15 (a) and 1.16 (a), $\rho(T)$, especially at low T, is sensitive on the cooling rates across the transition temperatures. For example, solid line data in Fig. 1.15 (a) represent when the sample was cooled down to 150 K quickly for $\sim 20$ minutes, and then cooled down to 8 K slowly for 5 hours. The residual resistivity ($\rho_0$) changes more than a factor $\sim 100$ in $x=0.495$ and $\sim 10$ in $y=0.375$ by varying the cooling rate. In both LPCM and LCM, $\rho_0$ becomes smaller when the specimen was cooled slower through $T_C$ or faster through $T_{CO}$. Correspondingly, saturation M at 5 K becomes larger for slower (faster) cooling through $T_C$ ($T_{CO}$) (not shown). These findings indicate that the relative volume of FM with respect to the CO volume increases when the system was cooled slower (faster) though $T_C$, and the associated time scale is on the order of hours. This slow time-scale associated with the conversion between FM and CO suggests the involvement of the large-scale structure or lattice in the two-phase coexistence.

This slow dynamics is also reflected in the results of aging effect. The evolution of M was measured with time after quick cooling (for $\sim 5$ min.) from room T to various, fixed temperatures. In LPCM (see Fig. 1.15 (b)), M increases with time, and obeys the stretched exponential form $M_0 + M_1\exp(-\tau/t)\beta$ with the exponent $\beta$ near 0.5, indicating a wide distribution of relaxation process [46]. It is found that $\tau$ decreases from about $\sim 7.5$ (at 10 K) to $\sim 1$ (at 50 K) hour with increasing T, and the T dependence of $\tau$ is thermal-activation-type with the energy gap ($\Delta$) of $25\pm2K$ (see the inset of Fig. 1.15 (b)). In the LCM case, M, in contrast to M in LPCM, decreases with time, due to further development of CO phase. However, M even in LCM follows the stretched exponential form, and $\tau(T)$ is thermal-activation-type with $\Delta$ of $413\pm5 K$. Interestingly, this large difference of $\Delta$’s for LPCM and LCM is consistent with the fact that the strength of magnetic field to melt CO phase for LCM is much larger than that for LPCM ($\sim 15 T$ for LCM [47], $\sim 3 T$ for LPCM (inset of Fig. 1.9)).

Above experimental results lead us to construct a scenario for the two-phase coexistence with slow dynamics as well as large-length scales. In La$_{0.5}$Ca$_{0.5}$MnO$_3$, the system is quasi-cubic (slightly orthorhombic)
Figure 1.17. (a) Temperature- and (b) effective Pr doping $y^*$-dependence of the free energy for $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ and (c) temperature and (d) effective Ca doping $x^*$-dependence of free energy for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$.

at high temperatures, but the difference between $a \approx b$ and $c/\sqrt{2}$ of orthorhombic structure becomes very large (about 3\%) below $T_{CO}$ [19]. This large structural anisotropy originates from the cooperative Jahn-Teller distortions associated with CO [48]. During the nucleation of CO phase, this large structural anisotropy associated with CO cannot be readily accommodated in bulk materials, and results in large-scale anisotropic strain. Now, in the bulk specimen of LPCM, the concentration of small Pr ions, which can accommodate lattice distortions more easily than larger La ions, can fix or “clamp” the total anisotropic strain that the bulk system can sustain. In other words, Pr concentration fixes the relative volume of CO phase, and the non-CO regions may become FM, resulting in the two-phase coexistence. This large-scale strain can, naturally, show slow dynamics or relaxation, for example through slowly moving the two-phase interfaces [49]. When the specimen was cooled slowly through $T_{CO}$ ($T_C$), the strain is “annealed” so that CO (FM) develops better, leading to larger (smaller) $\rho_0$ and smaller (larger) $M$ at low $T$. This view in terms of strain for LPCM is schematically represented in Fig. 1.17 (b). Consistent with Fig. 1.17 (a), there are local
free energy minima for FM and CO states, $F_{\text{FM}}$ is lower than $F_{\text{CO}}$ at low $T (<T_{C})$, and $F_{\text{CO}}$ is lower than $F_{\text{FM}}$ at high $T (T_{C}<T<T_{\text{CO}})$. The $x$-axis represents the degree of the total anisotropic strain that the bulk system can accommodate, which is denoted as “effective” Pr concentration $y^*$. FM and CO phases correspond to small and large $y^*$, respectively. When Pr concentration is fixed in a specimen, the averaged $y^*$ is fixed for the bulk material. Therefore, the Maxwell construction provides the lowest total free energy state in bulk materials, leading to the coexistence of FM and CO [50]. As shown in Fig. 1.17 (b), the amount of FM and CO phases is fixed by the length of “C (dotted line)” and “F (solid line)”, respectively. (Note that the broad distribution of relaxation process, indicated from the stretched exponential form of $M(t)$, can be ascribed to a wide distribution of the energy barrier height between $F_{\text{CO}}$ and $F_{\text{FM}}$.) Similar free energy argument holds for LCM with $x\sim1/2$ as shown in Fig. 1.17 (d). CO and FM are the lowest free energy states at low $T (<T_{\text{CO}}$) and high $T (T_{\text{CO}}<T<T_{C})$, respectively. The $x$-axis is the “effective” Ca concentration $x^*$, similar with $y^*$ for LPCM. Here again, the Maxwell construction leads to the two-phase coexistence. This scenario for the two-phase coexistence resembles the origin of the so-called tweed structure formation in Martensitic systems [51, 52]. However, what is unique about manganite is that the two phases with the different structures, induced by strain, show distinct electronic properties (i.e., one FM metal and the other CO insulator). This can be referred as structural phase separation, in comparison with chemical or electronic phase separation.

In this section, a thermodynamic view combined with quasi-long-range strain consideration was proposed to explain the intriguing structural phase coexistence in manganites. This proposition naturally explains why the low-$T$ transition, independent from whether it is CO or FM transition, is always strongly first-order. Furthermore, the large-length-scale associated with the FM-CO-phase coexistence, and also the slow relaxation between FM and CO phases can be attributed to the quasi-l-r, anisotropic strain, resulting from the cooperative Jahn-Teller distortions associated with CO.

3.2.2 Accommodation of strain and the metal-insulator transition. Martensitic transformations, i.e. cooperative (diffusionless) motion of atoms resulting in a formation of different crystal structure within a parent crystal, have been known for more than a century [51, 52, 53]. In metals and alloys, important physical and metallurgical properties are determined by long-range strains associated with the structural distortion of martensitic phases. In transition metal oxides,
where strong electron-electron and electron-lattice interactions govern such phenomena as magnetic ordering, metal-insulator transition (MIT) and superconductivity, phase transitions are often accompanied by structural deformation [7, 8, 9]. However, the structural transformations are often considered as a secondary or even a cumbersome effect. Here another experimental evidence is summarized to support that the synergy of the martensitic accommodation strain and strongly correlated electrons can lead to the extraordinary electronic properties of manganites, and that martensitic accommodation strain, produced by the CO phase, plays an important role in the MIT [54].

The martensitic transformation is a structural phase transition of part of a parent crystal involving large structural distortions. This phase, structurally different from the parent structure, is called martensitic phase or martensite. Physical properties of martensitic alloys are governed by the long-range elastic or plastic deformation of the parent crystal lattice surrounding the martensitic particles, so called accommodation strain [51, 52, 53]. Growth of the accommodation strain with lowering $T$ below the temperature of the martensitic transformation dominates an establishment of the thermo-elastic equilibrium between the parent phase and the martensite. This type of strain is inherent to martensitic transformations as well as to the transformation twins and is produced at the martensite/parent boundary or at the twin faults [51]. In this respect, both the internal twinning and martensitic transformations are accompanied by the accommodation strain.

Applying the terminology of martensitic transformations to manganites, we refer to the orthorhombic CO phase as a martensite and to the high-$T$ cubic paramagnetic phase as a parent phase. Thus, for example, the CO transition in $(\text{Nd,Sm})_{1-x}\text{Sr}_x\text{MnO}_3$ ($x\approx1/2$) [55] and in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [56] could be described by martensitic phenomenology. Since martensitic transformation, such as charge ordering, takes place by cooperative motion of atoms, the growth of martensite crystals across the grain boundary is prohibited and the accommodation strain is expected to be very sensitive to the grain size of polycrystalline samples. In order to investigate the influence of grain boundaries on the accommodation strain and, therefore, on physical properties of manganites, systematic transport studies were conducted in single crystalline and polycrystalline samples with different average grain size $<d> = 3, 6, 9, 12$ and $17 \mu\text{m}$. All the polycrystalline samples were prepared from one high-quality $\text{La}_{0.275}\text{Pr}_{0.35}\text{Ca}_{0.375}\text{MnO}_3$ pellet, which was carefully grounded to become fine powder and then was sintered additionally at $1380^\circ\text{C}$ (and $1300^\circ\text{C}$) for different time periods $\Delta t$. 
Figure 1.18. Temperature-dependent resistivity in zero magnetic field $H = 0$ (upper panel) and in 5 kOe (lower panel) of the polycrystalline $\text{La}_{0.275}\text{Pr}_{0.35}\text{Ca}_{0.375}\text{MnO}_3$ samples with different grain size $<d> = 3 - 17$ nm and a single crystal of the same composition on cooling and heating. For simplicity, not all of the measured samples are presented in the figure. The upper inset shows the dependence of the insulator-metal transition temperature, $T_{\text{MI}}$, on $<d>$ for zero field cooling (closed circles) and for field cooling in 5 kOe (open circles). The lower inset shows the grain-size dependence of the magnetoresistance $\text{MR} = (\rho_{H=0} - \rho_{5\text{kOe}})/\rho_{5\text{kOe}}$ in 5 kOe at $T = 20$ K.

Remarkable dependence of the transport properties on grain size is revealed by the resistivity ($\rho$) and magnetoresistance ($\text{MR} = (\rho_{H=0} - \rho_{5\text{kOe}})/\rho_{5\text{kOe}}$) measurements of polycrystalline $\text{La}_{0.275}\text{Pr}_{0.35}\text{Ca}_{0.375}\text{MnO}_3$ (Fig. 1.18). Data for a single crystal of the same composition are shown for comparison. Although $T_{\text{CO}} \approx 210$ K is similar for all samples, $T_{\text{MI}}$, defined as the temperature of the maximum of $d(\log\rho)/dT$ taken on cooling, systematically decreases from 125 K to 30 K when $<d>$ is reduced from 17 to 6 $\mu$m, (the inset in Fig. 1.18). Finally, the specimen with the smallest grain size - 3 $\mu$m, does not exhibit the MIT down to 20 K, below which $\rho$ becomes too large to be measured reliably. Surprisingly, a change of the grain size by a factor of two is sufficient to switch the low-$T$ ground state of the same compound from metallic to insulating. The low-$T$ resistivity, $\rho_0 = \rho(20 \text{ K})$, appears to be the most grain-size-sensitive characteristic of the samples. For $<d> = 3 - 17$ $\mu$m, $\rho_0$ varies systematically over the range $0.1-10^8 \Omega\text{cm}$. 
Sensitivity of $\rho_0$ and $T_{\text{MI}}$ to $<d>$ becomes much less pronounced when a small magnetic field $H = 5$ kOe is applied (Fig. 1.18, the lower panel). First, this field induces the MIT in the sample with $<d> = 3 \mu m$. In fact, $\rho(T)$ for all $<d>$ becomes much more similar in $H = 5$ kOe, indicating that the sharp increase of $\rho_0$ observed in $H = 0$ cannot be attributed to the increasing contribution of topological defects and scattering at the grain boundaries to $\rho$ in the samples with small $<d>$. Second, low-field MR$_{5\text{kOe}}$ at $T = 20$ K varies systematically with $<d> = 3 - 17 \mu m$ over the range $1 - 10^8$ (see the inset). Extremely large low-field MR, up to $10^{10}$ %, in samples with small $<d>$ cannot be explained by the spin-polarized transport across magnetic domain boundaries, which has been shown to result in the $20-30$ % change of $\rho$ in polycrystalline films and epitaxial films grown on a bicrystal substrate [57, 58, 59]. The drastic suppression of the grain-size dependence of $\rho$ by a small magnetic field, observed here, supports the scenario of the MIT where the insulating phase responsible for the high $\rho_0$ is not the charge-ordered phase [60]. The magnetic field of 5 kOe is not strong enough to “melt” the CO phase [6].

Based on this transport measurement, a following scenario can be proposed for the MIT in manganites. The accommodation strain, introduced by the CO domains into the surrounding lattice at $T_{\text{CO}} \approx 210$ K, strongly affects the properties of the latter. When the parent phase is loaded with the strain, the FM transition becomes suppressed, e.g. $T_{\text{MI}}$ is shifted to a lower temperature. Therefore, it tends to retain properties of the high-$T$ paramagnetic phase, remaining charge-disordered and insulating (CDI) even at low $T$. It is known that with a decreasing grain size of a sample, it is more difficult to accommodate the martensitic strain [51, 52]. As a result, in the samples with a smaller grain size the amount of the strain-loaded phase, e.g. CDI, increases. The presence of a considerable amount of this insulating phase results in the unusually high $\rho_0$ and leads to the low temperature shift of the MIT with decreasing $<d>$. An experimental evidence for the existence of CDI phase at low temperatures will be provided in a next section, where optical conductivity probes at least three phases in a single crystal sample. Furthermore, recent $x$-ray and neutron scattering experiments [60] revealed that the volume fraction of the CO phase remains constant when the system is driven through the MIT, e.g. the CO phase is not involved in the MIT directly. Thus, the transition occurs within the parent phase, which is separated into the FM metallic and strain-stabilized CDI phases at $T \leq T_{\text{MI}}$. It’s worth mentioning, that the ability of strain to stabilize phases, which do not exist at all without the strain, is well known in martensites [53].
The results of this section show that sensitivity of the martensitic phase to the grain boundaries leads to the observed striking dependence of the transport properties of polycrystalline La$_{0.275}$Pr$_{0.35}$Ca$_{0.375}$MnO$_3$ samples on grain size. In contrast to the conventional insulator-to-metal transition, wherein the FM phase grows at the expense of the CO phase, e.g., La$_{0.5}$Ca$_{0.5}$MnO$_3$ under high magnetic field, the insulator-metal transition in La$_{0.275}$Pr$_{0.35}$Ca$_{0.375}$MnO$_3$ is suggested not to be a transition from the charge ordered into the ferromagnetic state. Instead, it is a transformation of the charge-disordered insulating phase into the ferromagnetic one. The former phase, charge-disordered insulating, is a result of the stabilization of the parent paramagnetic phase at low temperature by the martensitic strain. Typical signatures of martensitic transformations manifested by other manganites indicate the general applicability of the martensitic approach and phenomenology to the structural phase transitions in oxides with strongly correlated electrons.

3.3 Optical evidences of multiphase coexistence

3.3.1 Mid-infrared absorption peaks in La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$.

To provide further insights on the nature of the phase coexistence, temperature ($T$)- and magnetic field ($H$)-dependent optical conductivity $\sigma(\omega)$ of a La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ ($y=0.35$) (LPCMO) single crystal was investigated [61]. $T$-dependent $\rho$ data for the LPCMO, which is very similar to the single crystal data in Fig. 1.18, indicated that the sample undergoes a charge-ordering transition at $T_{CO} \approx 220$ K and then a relatively sharp insulator-metal transition around $T_C \approx 120$ K. The reflectivity spectra $R(\omega)$ was measured with increasing $T$ at $H=0$ T and with increasing $H$ at 4.2 K and the Kramers-Kronig transformation produced $\sigma(\omega)$ from the measured $R(\omega)$. Detailed techniques for the $R(\omega)$ measurements were described in our previous report [62].

Fig. 1.19 (a) shows $T$-dependent $\sigma(\omega)$ above $T_C$. As $T$ decreases from 300 K, the low frequency $\sigma(\omega)$ below 0.5 eV are systematically suppressed and an optical gap is clearly developed. Therefore, it is likely that the charge ordering (CO) phase is dominant at $T_{CO} < T < T_{CO}$ and that the broad band around 1.4 eV can be attributed to the characteristic optical response of the CO domains. The optical gap energy $2\Delta$ at $T \geq T_{CO}$, obtained from a crossing energy between a linear tangential line at the inflection point of $\sigma(\omega)$ and the $x$-abscissa, is shown as a dotted line in Fig. 1.19 (a). Figure 1.20 (a) shows the $2\Delta$ vs. $T$ plot. The $2\Delta$ just above $T_C$ is found to be as large as 0.38 eV. This value remains nearly the same between $T_C \leq T \leq 180$ K and slightly decreases near $T_{CO}$. It should be noted that the $2\Delta \approx 0.38$ eV at $T \approx 150$ K.
Figure 1.19. Temperature-dependent $\sigma(\omega)$ of a La$_{5/8}$Pr$_y$Ca$_{3/8}$MnO$_3$ ($y=0.35$) crystal (a) above and (b) below $T_C$. At $T_C<T$, the optical gap energy due to the CO phase is determined by drawing a linearly extrapolated line (dotted) at the inflection point of $\sigma(\omega)$. At $T \leq T_C$, at least two absorption bands appear in the mid-infrared region. The peak positions of the bands are indicated as asterisks.

is comparable to that of La$_{0.5}$Ca$_{0.5}$MnO$_3$ (i.e., $2\Delta(0)\approx0.45$ eV at the ground state). Since the CO phase in LPCMO is the La$_{0.5}$Ca$_{0.5}$MnO$_3$-type, i.e., the so-called CE-type, the large value of $2\Delta$ of LPCMO can be ascribed to a characteristic of the CE-type CO phase. The slightly smaller gap value of LPCMO might be related to the presence of small FM phase or carrier defects due to $x=3/8$ doping in the CE-type CO pattern. It is also noted in Fig. 1.20 (a) that $2\Delta \approx0.22$ eV at $T_{CO}$ and $2\Delta \approx0.1$ eV at 300 K. Thus, $2\Delta$ does not become zero at $T$ far above $T_{CO}$. This is an anomalous behaviour because many CO materials show nearly zero value of $2\Delta$ at $T_{CO}$. This nonzero $2\Delta$ behaviour indicates that there exists enhanced spatial and/or temporal fluctuation of CO correlation far above $T_{CO}$ in LPCMO. This enhanced CO fluctuation is regarded as a generic feature of LPCMO that has mixed-phases near the phase boundary where a phase separation occurs even when $T\rightarrow0$ K [63]. This subject will be discussed in Section 4 in detail.

Figure 1.19 (b) shows that as $T$ decreases below $T_C$, new absorption bands appear below $\sim0.4$ eV, and their strengths grow. As indicated by asterisks, $\sigma(\omega)$ at 10 K show at least two mid-infrared absorption bands, centered around 0.22 and 0.49 eV, respectively. As $T$ is lowered below
Figure 1.20. (a) Temperature dependence of the optical gap energy $2\Delta$ (solid circles). An open circle represents a $2\Delta$ at $T_C$. (b) Temperature-dependence of spectral weight $S_I$ (solid squares) and $S_{II}$ (crosses) at $T<T_C$. See, Fig. 1.21 and texts for definition. A solid line represents a normalized magnetization curve.

$T_C$, the former is located nearly at the same frequency, while the latter one shifts to a higher frequency from 0.35 eV at 120 K to 0.49 eV at 10 K, indicating that the origin of the lower frequency peak might be different with that of the higher frequency one. Note that the strength of a broad absorption band around 1.4 eV does not decrease even below $T_C$. This is in contrast with the $\sigma(\omega)$ behaviours of homogeneous FM metallic samples that show a significant spectral weight transfer from above 1.0 to below 1.0 eV [64, 65]. This observation suggests that the volume fraction of the CO phase does not change significantly below $T_C$.

Figure 1.21 (a) shows $H$-dependent $\sigma(\omega)$ at fixed $T=4.2$ K. It is found that, with increasing $H$, the spectral weight above 1.0 eV becomes strongly suppressed and transferred to a lower frequency region. Although the sample shows a metallic resistivity at 3 T, the corresponding optical spectrum has a very asymmetric mid-infrared band. At $H=12$ T, a clear Drude-like peak is observed with a saturated suppression of the absorption peak around 1.4 eV. This suggests that the CO insulating domains are melted to become the FM metallic ones and that the volume fraction of the FM metallic domains is increasing. The optical spectrum at 12 T is characterized as a single asymmetric absorption band below 1.5 eV, which is very similar to the shape of $\sigma(\omega)$ in some homogeneous FM metallic manganites at low temperature [64]. In addition, under the high $H$, the feature of two absorption bands in Fig. 1.19 (b) is not
Figure 1.21. (a) Temperature- and magnetic field-dependent $\sigma(\omega)$ of a La$_{5/8}$Pr$_{y}$Ca$_{3/8}$MnO$_{3}$ ($y=0.35$) crystal. (b) $\Delta\sigma(\omega,T) = \sigma(\omega,T) - \sigma(\omega,150 \text{ K})$ for various temperatures. The $\Delta\sigma(\omega,T)$ curves at $T<T_C$ are composed of an asymmetric absorption band and small additional bands (filled triangles). The spectral shape of the additional bands are very similar to the shape of $\Delta\sigma(\omega,T)$ at $T>T_{CO}$. The inset shows a $\Delta\sigma(\omega,10 \text{ K})$ curve and its fitting results using an asymmetric line shape (for Band I) and two Lorentzians (for Band II).

observed. Therefore, the $\sigma(\omega)$ at 12 T seems to represent the optical response of the dominant FM metallic phase.

To elucidate the origin of the two peak structure, the optical response of the CO phase needs to be subtracted from the measured $\sigma(\omega)$ at each temperature, $\sigma(\omega,T)$. It was assumed that $\sigma(\omega,150 \text{ K})$ could represent the $\sigma(\omega)$ of CO domains. Figure 1.21 (b) shows the results of $\Delta\sigma(\omega,T) = \sigma(\omega,T) - \sigma(\omega,150 \text{ K})$ at various temperatures. The $\Delta\sigma(\omega,10 \text{ K})$ curve is composed of an asymmetric absorption band peaked around 0.2 eV and a broad band with peaks around 0.4 and 0.8 eV. While the absorption band around 0.2 eV appears below $T_C$, the broad band with peaks around 0.4 and 0.8 eV already exists above $T_{CO}$.

To quantitatively estimate the $T$-dependent spectral weight of each absorption band, we fitted the $\Delta\sigma(\omega,T)$ below $T_C$ as a sum of an asymmetric band (Band I) around 0.2 eV and two Lorentzians (Band II) around 0.4 and 0.8 eV. The inset of Fig. 1.21 (b) shows the $\Delta\sigma(\omega,10 \text{ K})$ curve and its fitting results. It is found that Band I is very similar to $\sigma(\omega)$ at $H=3 \text{ T}$ in Fig. 1.21 (a). Especially, Band II is very similar to $\Delta\sigma(\omega,280 \text{ K})$ in Fig. 1.21 (b). These analyses strongly suggest that
Band I at low $T$ should be due to the FM metallic phase, while Band II can be attributed to another phase, of which physical properties are very similar to those of the high $T$ charge-disordered insulating (CDI) phase.

Based on these analyses, we estimated integrated spectral weights of Band I, $S_I$, and of Band II, $S_{II}$, below $T_C$. It is interesting to compare $T$-dependence of $S_I$ and $S_{II}$ with a normalized magnetization value, $M(T)/M(0)$. Figure 1.20 (a) shows $T$-dependences of $S_I$ (solid squares), $S_{II}$ (solid triangles), and $M(T)/M(0)$. It is found that $S_I$ is roughly proportional to $M(T)/M(0)$, indicating that Band I is linked to the FM spin ordering. However, rather gradual increase of $M(T)/M(0)$ is not consistent with the FM transition in a homogeneous system. Thus, $S_I$ can be attributed to the spectral weight of FM metallic domains in an inhomogeneous system. On the other hand, $S_{II}$ starts to increase near $T_C$, and continuously does below $T_C$ even when $M(T)/M(0)$ is saturated. This observation again supports that Band II is the absorption band of a CDI phase, of which volume fraction continuously increases with the development of the FM phase below $T_C$. How the CDI phase can be developed below $T_C$ will be discussed further below. In partial summary, all of above experimental findings unequivocally suggest that there exist at least three phases, i.e. the FM metallic, the CO insulating, and the CDI phases in LPCMO.

3.3.2 Implication of structural phase separation in optical conductivity spectra. In LPCMO with the charge ordering domains inside, anisotropic lattice strains can be developed due to the Jahn-Teller (JT) distortion and the concomitant orbital ordering. In particular, the anisotropic strain in the CE-type charge ordering is known to be quite large, due to a cooperative JT distortion and a $d^2_{xz}$ orbital ordering. In a nearly homogeneous FM metallic state, the JT distortion becomes small. If FM metallic domains appear below $T_C$ in the backbone of CO domains, the strain of this region will be released. Due to a large strain mismatch between the two phases, the interfacial region will have inhomogeneous strains larger than that of the FM domains, but smaller than that of the CO domains. This physical situation is quite similar to the case of ferroelastic materials with the martensitic transformation. This postulation suggests an appealing idea that at low $T$ region of LPCMO, each domain has different structural distortions so that electronic phase separation can be accompanied by structural phase separation.

As a result of a strong electron-phonon coupling, presence of a polaronic absorption band is another important spectral feature in the $\sigma(\omega)$
of manganites. However, in case of the manganites, the polaron absorption band is also strongly coupled to spin and orbital degrees of freedom [66]; a single polaron theory should be clearly extended further to include multi-polaron nature and many body effects in this compound. To our knowledge, theoretical understandings on the multi-polaron effects are still lacking. Thus, it should be noted that the discussion below is yet qualitative and based on a single polaron picture. With this in mind, the structural multiphase coexistence can still be well described by the existing single polaron theory. According to the polaron absorption theory [67, 68], the peak energy of the incoherent band is roughly proportional to the binding energy of a polaron that increases as the local lattice distortion increases. In the FM metallic manganites well below $T_C$, the mid-infrared polaron band becomes quite asymmetric and it is centered below $\sim0.3$ eV, which is close to the line shape of incoherent absorption of a large polaron [64, 67]. Above $T_C$, as local JT lattice distortions increase, the band becomes rather symmetric and the peak frequency shifts to a higher frequency. This polaron band can be close to the small polaron absorption band.

The asymmetric line shape of Band I indicates that the lattice distortion of the FM domains is not large. On the other hand, the $\sigma(\omega)$ of the CO domains with large strains showed a band centered $\sim1.4$ eV with a large $2\Delta \approx0.4$ eV. Most of the spectral weights of Band II appear in an energy region of $0.3 -1.0$ eV, indicating that the lattice strain of the CDI region can be larger than that of the FM metallic domains, but smaller than that of the CO domains. According to Fig. 1.19 (b) and Fig. 1.20 (b), both a lower peak frequency of Band II and $S_{II}$ increased as $T$ decreased below $T_C$. This seems to indicate that the volume fraction as well as the strain of the CDI domains, possibly located at the interface of FM and CO domains, increases with deceasing $T$. Therefore, the $\sigma(\omega)$ data suggest that the lattice strains and their interplay with $T$ inside the three main phases play a crucial role on the electronic and the magnetic properties of the LPCMO.

In this section, $T$-and $H$-dependent optical conductivity spectra of a La$_{5/8}$Pr$_{3/8}$Ca$_{3/8}$MnO$_3$ ($y\approx0.35$) single crystal revealed that at least two absorption bands newly appeared below $0.4$ eV at $T<T_C \approx 120$ K. The new absorption bands can be attributed to a FM metallic and a charge-disordered phase, coexisting with a charge-ordered phase. Quite different peak frequency of each absorption band suggests that the coexisting multi-phases can have different lattice strains. In addition, LPCMO had a rather large charge gap due to fluctuating charge-ordering correlation above $T_C$. This $\sigma(\omega)$ study supports that the structural as well as the electronic phase separation occurs in the LPCMO below $T_C$. 
4. High temperature charge-ordering fluctuation and nano-scale phase coexistence

In mixed-valent manganites, orbital degree of freedom associated with Mn$^{3+}$ ions, in addition to charge and spin degrees of freedom, plays an important role. The static charge/orbital ordering with stripe patterns is now well established, especially in La$_{1-x}$Ca$_x$MnO$_3$ with $x \geq 0.5$ at low $T$ region. CO in manganites occurs as periodic arrays of the sheet-like arrangement of Mn$^{3+}$ ions [39]. In this scheme, the CO state of La$_{0.5}$Ca$_{0.5}$MnO$_3$ is special in the sense that the density of Mn$^{3+}$-Mn$^{4+}$ pairs is the highest. In La$_{0.5}$Ca$_{0.5}$MnO$_3$, all of the charge, orbital and spin degrees of freedom freeze into the so-called CE-type stable configuration below 180 K (for heating) [11, 69].

One of the best examples of electronic phase separation, known from earlier research stage of manganites, was the nano-scale coexistence of an insulating phase with striped charge-order (CO) and a metallic phase with ferromagnetism (FM) in a narrow temperature ($\sim$180$< T <$220K) range of La$_{0.5}$Ca$_{0.5}$MnO$_3$ [20, 39]. An early study of synchrotron x-ray scattering for La$_{0.5}$Ca$_{0.5}$MnO$_3$ showed a drastic broadening of all the Bragg peaks in the FM region between $T_C$ and $T_N$ ($\approx T_{CO}$) [19]. After this discovery, an electron diffraction study showed that the fine scale ($\sim$100 Å) coexistence of CO and FM phases is responsible for the drastic broadening of x-ray Bragg peaks [20]. This coexistence is not due to chemical inhomogeneity because it disappears below $\sim$150 K. This nano-scale two-phase coexistence at $x=0.5$ at finite temperatures was thought to originate from the fact that $x=0.5$ is the phase boundary composition between FM ($x<0.5$) and CO ($x>0.5$) states. It was also presumed that the ground state of La$_{1-x}$Ca$_x$MnO$_3$ with $x=0.5$ becomes the CO state below $T_{CO} \approx$180 K.

This section will cover electronic/thermal transport, x-ray diffraction, and optical studies to investigate short-ranged, and/or dynamic CO correlation in the paramagnetic state of the half-doped manganite. The enhancement of $\rho$ up to 900 K in La$_{0.5}$Ca$_{0.5}$MnO$_3$ indicates that the spatial or dynamic CO fluctuation probably persists even at $T$-ranges much higher than long-range ordering temperature [70]. Furthermore, accumulated experimental and theoretical investigations now suggest that this robust charge fluctuation up to very high temperatures be intimately associated with the fact that the ground state of La$_{0.5}$Ca$_{0.5}$MnO$_3$ has, in fact, intrinsically two competing order parameters, i.e., FM metallic and CO insulating phases. This new view on the ground state of La$_{0.5}$Ca$_{0.5}$MnO$_3$ is quite consistent with the idea of electronic phase separation at zero temperature.
4.1 Transport and structural studies

Figure 1.22 shows the $\rho(T)$ curves for La$_{1-x}$Ca$_x$MnO$_3$ with $x$ near 0.5 from 4 to 900 K. For $x=0.48$, the FM metallic phase is dominant below 220 K even though a short-range CO phase probably coexists as indicated by a broad hump and small hysteresis at 100-180 K [71, 72]. However, with $x$ approaching 0.5 from below, the CO state stabilizes at low temperature. Thus, low temperature $\rho$ near $x=0.5$ increases systematically with $x$, and shows the insulating $T$-dependence when $x\approx0.485$. As shown in Fig. 1.23 (a), $\rho(100\ K)$ (open circles) shows such a systematic increase with $x$, consistent with a crossover from the FM metallic to the CO insulating states. If CO is stabilized at low temperature region for $x\approx0.5$, $\rho(100\ K)$ becomes insensitive on $x$.

It is interesting that in Fig. 1.23 (a), $\rho$ of La$_{0.5}$Ca$_{0.5}$MnO$_3$ at $T>T_{CO}$ is considerably larger than that of any neighboring compositions, and this behavior persists up to 900 K. This unexpected behavior was confirmed systematically in samples with fine spacing of $x$ near 0.5. The $\rho(300\ K)$ vs. $x$ plot in Fig. 1.23 (a) summarizes the results, showing a
Figure 1.23. (a) and (c) $\rho$ and $\kappa$ values at 100 and 300 K for La$_{1-x}$Ca$_x$MnO$_3$ near $x=0.5$, respectively. (b) The activation energy $E_a/k_B$ and prefactor $\rho_0$ vs. $x$ plot of adiabatic small polarons, obtained from the inset of Fig. 1.22. (d) The $x$-dependence of the peak width, $\Gamma$, and the center position of the (242) x-ray Bragg peak at 300 K, estimated from Gaussian fitting of the data in Fig. 1.24. The dotted and solid lines are guides for the eyes.

A previous study revealed that an adiabatic small polaron model, with $\rho=\rho_0 T \exp(E_a/k_B T)$, describes high temperature $\rho$ of La$_{1-x}$Ca$_x$MnO$_3$ in broad doping and temperature ranges ($0\leq x\leq 1$ and $\sim 300\text{K} \leq T \leq 1100\text{K}$) [73]. Here, $E_a$ represents the activation energy of small polarons, i.e. the potential barrier that polarons must overcome to hop to the next site. The inset of Fig. 1.22 shows that $\ln(\rho/T)$ vs. $1/T$ plot of our data at high $T$ region is almost linear, corroborating with the adiabatic small polaron model. Interestingly, $E_a$ is systematically enhanced at $x=0.5$ even if $\rho_0$ becomes maximum at $x=0.49$, slightly lower than 0.5, as shown in Fig. 1.23 (b). Therefore, the strong charge localization tendency at $x=0.5$ up to very high $T$, far above $T_{CO}$, is closely associated with the enhancement of polaron activation energy.

To gain further insights into understanding this surprising result, we measured $T$-dependent $\kappa$ (Fig. 1.22(b): heating). As pointed out in Section 2, the electronic $\kappa$ estimated from $\rho$ by using the Wiedemann-Franz law is negligible, and the anomalous behavior of $\kappa$, i.e., a linear increase above $T_C$, is related to the phononic $\kappa$ coupled with large anharmonic lattice distortions [21]. Thus, it is evident that at high $T$ region...
of La$_{1-x}$Ca$_x$MnO$_3$ ($x \approx 0.5$), phononic contribution dominates the measured $\kappa$. The abrupt $\kappa$ increase near $T_C$ in $\kappa(T)$ of $x=0.485$, 0.49, and 0.50 is due to the reduced lattice distortions in the FM-metallic state, and this $\kappa$ increase at $T_C$ becomes smaller with $x$ approaching 0.5. For $x \leq 0.5$, $\kappa$ tends to decrease at $T_{CO}$, which can be attributed to the large (JT-type) lattice distortion associated with CO. For $x > 0.5$, $\kappa$ shows only slight slope changes near $T_{CO}$, as seen in the data of $x=0.52$ and 0.55. As summarized in Fig. 1.23 (c), $\kappa$ at 100 K decreases systematically with $x$ approaching 0.5 (due to the stabilization of the CO state), and remains small when $x>0.5$. It is noted that even if the $\kappa$ values of $x=0.52$ and 0.55 are similar to that of $x=0.5$ at low $T$, they become considerably larger than that of $x=0.5$ for $T>T_{CO}$. This behavior is well illustrated in the $\kappa$(300 K) vs. $x$ plot (solid circles in Fig. 1.23 (c)), demonstrating a clear minimum at $x=0.5$. This suppression of $\kappa$(300 K) at $x=0.5$ correlates well with the $\rho$ peaking near 0.5 at 300 K. Therefore, the results in Figs. 1.22 and 1.23 show that the lattice thermal conductivity as well as electrical transport is suppressed in the high temperature region of the half-doped manganite.

Directly related to the suppression of phononic $\kappa$, there exists a slight, but noticeable broadening of the x-ray Bragg peaks for $x=0.5$ at room temperature. One example of the broadened x-ray peaks is shown in Fig. 1.24, displaying the compositional change of the (242) Bragg peak (in the orthorhombic $Pbnm$ notation) of x-ray powder diffraction at 300 K. The (242) Bragg peak, centered at $2\theta \approx 69.3^\circ$ for $x=0.5$, changes its position to higher angles as $x$ increases. The left and right sides of the (242) Bragg peak are due to the (004)-(400) peaks and $K_{\alpha 2}$ of the (242) and (004)-(400) peaks, respectively. As evident in Fig. 1.24, the peak width, $\Gamma$, of the central (242) peak is considerably broad at $x=0.5$. To extract $x$-dependence of $\Gamma$, the intensity profiles were fitted as a sum of three Gaussian peaks (by neglecting the weak $K_{\alpha 2}$ peaks of (004) and (400)). The solid squares and triangles in Fig. 1.23(d) represent fitting results for $\Gamma$ and the center position of the (242) peak, respectively. The center position increases almost linearly with $x$, indicating the linear lattice contraction with increasing $x$. On the other hand, $\Gamma$ shows a clear maximum at $x=0.5$. This broadening of $\Gamma$ indicates a slight distribution of lattice constants in La$_{0.5}$Ca$_{0.5}$MnO$_3$ at room temperature [19].

Based on the results from the synchrotron x-ray scattering study of La$_{0.5}$Ca$_{0.5}$MnO$_3$ that showed drastic broadening of all the Bragg peaks between $T_C$ and $T_N$ ($\approx T_{CO}$) [19], this new data indicate that the Bragg peak broadening for $x \approx 0.5$ persists even at room $T$, far above $T_C$ and $T_{CO}$. This observation strongly suggests that short-range CO exists in the paramagnetic state of the half-doped manganite. We cannot rule out
the possibility of dynamic correlation of CO at room $T$. Furthermore, the enhancement of $\rho$ up to 900 K in $La_{0.5}Ca_{0.5}MnO_3$ indicates that the spatial or dynamic CO fluctuation probably persists even at $T$ ranges much higher than long-range ordering $T$ [70]. Naturally, such a spatial variation of lattice constants, indicated by the Bragg peak broadening, will shorten phonon lifetime, and thus suppresses the phononic $\kappa$. It is emphasized that the observed Bragg peak broadening indicates various anomalous behaviors of $x \approx 0.5$ as bulk effects. In other words, the $\rho$ enhancement and the $\kappa$ suppression at $x \approx 0.5$ are not due to, for example, grain boundaries in the polycrystalline specimens. It is also noted that the findings are not consistent with La/Ca ionic ordering because the La/Ca ordering should reduce $\rho$.

Because CO correlation can influence magnetic correlation, the evolution of magnetic susceptibility ($\chi \equiv M/H$) was also investigated as a function of $x$ at room $T$ (above $T_C$). A few surprising results can be found in Fig. 1.25 (a). First, $\chi(T)$ above $T_C$ roughly follows the Curie-Weiss law, and the Curie-Weiss $T$ is FM for all $x$ studied. Consistent with earlier results, the $T_C$ vs. $x$ plot shows a broad bump near $x=3/8$ [10]. On the other hand, $\chi(x)$ at 300 K sharply peaks at $x=3/8$. This observation might be related to the fact that $T_C$ is maximized smoothly at $x=3/8$, and $\chi(T)$ is proportional to $1/T$ at high temperature. However, this pronounced peaking behavior of $\chi(x)$ above $T_C$ again corroborates that the commensurate carrier concentration of $x=3/8$ has a specially enhanced FM correlation. This observation naturally suggests an extraordinary possibility; the presence of short-range or dynamic correlation of charge/orbital ordering in such a way as to produce special FM coupling in addition to the double exchange-type FM coupling.

How can such a short-range charge correlation promotes FM coupling? In manganites, it has been well established that the CE-type CO
Figure 1.25. (a) The $x$-dependence of magnetic susceptibility $\chi$(closed squares) at 300 K (left axis). The open circles show the $T_C$ variation determined from $\chi(T)$ (right axis). (b) A schematic of FM zigzag chains, coupled antiferromagnetically each other. Open circles are Mn$^{4+}$ and the lobes show the $e_g$ orbitals of Mn$^{3+}$. $\sim$11 Å FM zigzag is shown with dark hue.

is very stable in broad $x$ ranges, at least at low temperature. For example, the CE-type CO has been commonly observed in La$_{1-x}$Ca$_x$MnO$_3$ and Nd$_{1-x}$Sr$_x$MnO$_3$ for $x \approx 0.5$. In addition, the CE-type CO has been reported even when $x$ deviates significantly from 0.5. For example, the CE-type CO occurs in Pr$_{1-x}$Ca$_x$MnO$_3$ with $0.3 < x \leq 0.5$, and also in (La,Pr)$_{5/8}$Ca$_{3/8}$MnO$_3$ at low $T$ [71]. Thus, it is appealing to assume that short-range or dynamic CO at high $T$ of La$_{1-x}$Ca$_x$MnO$_3$ ($0.2 < x \leq 0.5$) is also the CE-type. In the CE-type CO, there exist FM zigzag chains (Fig. 1.25 (b)), which couple to each other antiferromagnetically [69, 74]. It is conceivable that at high $T$, the CO correlation is so short that the short-range CO state may contain only one short FM zigzag (Mn$^{3+}$- Mn$^{4+}$- Mn$^{3+}$- Mn$^{4+}$- Mn$^{3+}$: shown with dark hue in Fig. 1.25 (b)) with $\sim$11 Å in length or one short FM “zig or zag” (Mn$^{3+}$-Mn$^{4+}$-Mn$^{3+}$) with $\sim$5.5 Å in length. Then, these extended objects can enhance FM correlation overall. The short FM zigzag can be considered as correlated polaron or a ferromagnetic polaron cluster, and may exhibit dynamic nature. Note that the carrier concentration of the short FM zigzag (zig or zag) corresponds to $x=0.4$ (1/3), which is close to $x \approx 3/8$ for the enhanced FM correlation. However, if the range of CO becomes slightly longer, then the zigzag may couple with the neighboring zigzags antiferromagnetically so that FM correlation can be
reduced. This effect can be significant at $x \approx 0.5$ where CO tendency is strong because carrier concentration matches the CE-type ordering. We also found that, in general, $\rho(300 \text{ K})$ for $x < 0.5$ (including $x \approx 3/8$ where $T_C$ is maximized) is larger than that for $x > 0.5$ (including $x \approx 5/8$ where $T_{CO}$ is optimized) even though the ground state is metallic (insulating) for $x < (>)0.5$, which corroborates with short-range CO at high $T$ for $x$ near or smaller than 0.5. This remarkable scenario remains to be confirmed by local probe measurements such as x-ray or neutron scattering experiments.

This section showed that the suppression of electronic conductivity as well as phononic thermal conductivity, and the broadening of Bragg peaks exist in a narrow composition range near $x=0.5$, but in a very broad temperature range up to 900 K. All these findings suggest the presence of spatial or temporal fluctuation of CO at high $T$. On the other hand, FM correlation is strongly enhanced for $x$ near 3/8, which can be related to the presence of FM zigzags that can be coupled or decoupled, depending on $x$. The “decoupled” short FM zigzag can enhance the overall FM correlation at $x$ near 3/8, and the AFM coupling of FM zigzags can progressively increase with $x$, and be maximized at $x \approx 0.5$ where charge localization tendency is strong.

4.2 Optical pseudogap and charge ordering fluctuation

Optical conductivity study has been one of unique tools to probe short-range fluctuating order parameters of solids. It has successfully revealed a phase-correlation time of superconducting order parameter in the normal state of the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ family and fluctuating charge-density-wave (CDW) order parameters of K$_{0.3}$MoO$_3$ and (TaSe$_4$)$_2$I at high temperature [75, 76]. However, up to this point, there are few optical conductivity studies to probe the short-range charge correlation above long-range charge ordering temperature, $T_{CO}$.

In parallel with the findings in Section 4.1, many recent experiments, such as Raman [77], neutron [78, 79], and x-ray [70] scattering studies, showed the existence of the spatial and/or temporal fluctuations of the CE-type CO in the FM metallic compounds above the Curie temperature $T_C$. In particular, the neutron scattering studies found dynamic ($\geq \sim 1 \text{ ps}$) or short-ranged ($\sim 10 \text{ Å}$) CE-type CO correlation above $T_C$. Recently, evidences for the existence of incipient charge ordering were observed in optical conductivity spectra of a FM bilayer manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_{7+}$, just above $T_C$ [80]. Based on the experimental results in the Section 4.1, the Ca-doped manganites including La$_{0.5}$Ca$_{0.5}$MnO$_3$
can be an ideal system to investigate the fluctuating CO through optical conductivity studies. Thus, optical conductivity spectra $\sigma(\omega)$ of the La$_{1-x}$Ca$_x$MnO$_3$ system ($0.48 \leq x \leq 0.67$) were systematically investigated to probe the fluctuating CO correlation [81]. For this purpose, high-density polycrystalline specimens of La$_{1-x}$Ca$_x$MnO$_3$ ($x=0.48$, 0.50, 0.52, 0.60, and 0.67) were investigated, of which characteristics are well described in Section 4.1. For $x=0.48$, a FM metallic state is dominant below $T_C \approx 220$ K with a possible short-range CO phase below 180 K. However, for $x \geq 0.52$, the antiferromagnetic long-range CO becomes stabilized at low $T$; $T_{CO}$ values of $x=0.52$, 0.60, and 0.67 were 190, 250, and 257 K, respectively. The $x=0.50$ sample has $T_{CO} \approx 180$ K and $T_C \approx 220$ K. Note that the $x=0.50$ sample can have coexistence of the FM metallic and the CO insulating states at lower $T$ as well as between $T_{CO}$ ($T_N$) and $T_C$.

Figure 1.26 (a) shows $\sigma(\omega)$ of the $x=0.48$, 0.50, and 0.52 samples at 10 K. $\sigma(\omega)$ of $x=0.48$ have a large absorption band centered at $\sim 0.5$ eV, which can be related to incoherent hopping motion of polarons from Mn$^{3+}$ to Mn$^{4+}$ sites [64, 82, 83]. On the other hand, an optical gap due to the long-range CO, namely, a charge gap is clearly observed in $\sigma(\omega)$ of $x=0.50$ and 0.52 at 10 K. A charge gap, $2\Delta$, an onset energy of the steeply rising part of $\sigma(\omega)$, can be determined from a crossing point be-
tween $x$-abscissa and a linear extrapolation line drawn at the inflection point of $\sigma(\omega)$. This procedure has been a common practice to evaluate $2\Delta$ of various CO materials [84], resulting in $2\Delta(10 \, K) \approx 0.45$ eV for both $x=0.50$ and 0.52 samples. The charge gap energy at the ground state, $2\Delta(0) \approx 0.45$ eV is the largest among numerous CDW systems [76] and charge-ordered oxides [84]. This large $2\Delta(0)$ can be a peculiar characteristic of the CE-type CO, indicating unusual stability of the special CO pattern.

Interestingly, $\sigma(\omega)$ of $x=0.50$ at 10 K show significant in-gap absorption below 0.5 eV, while in-gap absorption of $x=0.52$ is negligible at 10 K. One key finding from our experiments is that the spectral weight of the in-gap absorption is proportional to the amount of FM phase inside the samples. For example, decrease of M/H values at 10 K from $x=0.48$ to 0.52 (the inset of Fig. 1.26 (a)) is well correlated with decrease of spectral weight of $\sigma(\omega)$ below 0.5 eV at 10 K. In addition, the larger M/H values of $x=0.50$ than $x=0.52$ are consistent with the increased FM regions in $x=0.50$, located near the CO/FM phase boundary. Therefore, the in-gap absorption of $x=0.50$ is attributed to a FM phase coexisting with a CO phase at low temperature.

In Fig. 1.26 (b), $\sigma(\omega)$ of $x=0.50$ at 300 K reveal anomalous spectral features; $\sigma(\omega)$ below 1.0 eV are smaller than those of neighbouring compounds. Furthermore, $\sigma(\omega)$ increase steeply with $\omega$, showing a positive curvature at low photon energy, which is very similar to the gap-feature observed at 10 K. It is noted that this spectral response is not compatible with a single polaron absorption model [64]. Instead, the gap feature at 300 K suggests the presence of short-range CO or correlated multi-polarons even far above $T_{CO}$. It is noteworthy that it is not yet known if a theory for correlated multi-polaron absorption could account for the peculiar $\sigma(\omega)$ of $x=0.50$ above $T_{CO}$.

To understand further the anomalous $\sigma(\omega)$ of $x=0.50$, we systematically investigated $\sigma(\omega)$ of La$_{1-x}$Ca$_x$MnO$_3$ with $x=0.50$, 0.52, 0.60, and 0.67 (Fig. 1.27). It is found that $T$-dependence of the charge gap for $x=0.50$ is also peculiar; at 10 K $\leq T \leq 180$ K, large $2\Delta$ values are observed in $\sigma(\omega)$ of $x=0.50$. In particular, $2\Delta$ values at $T=250$ and 300 K still remain finite, remarkably having almost the same magnitude with $2\Delta$ at 200 K. The $\sigma(\omega)$ of $x=0.52$ with $T_{CO} \approx 190$ K also show that $2\Delta$ remains nonzero up to $T \approx 240$ K. These observations strongly suggest that the strong fluctuations of short-range CO (or correlated multi-polaron) can be responsible for the finite charge gap far above $T_{CO}$ in the $x=0.50$ and 0.52 samples.

Even at high $T>240$ K, where $2\Delta$ is no longer finite, there exists significant suppression of spectral weight below a photon energy of max-
Figure 1.27. $\sigma(\omega)$ of La$_{1-x}$Ca$_x$MnO$_3$ ($0.50 \leq x \leq 0.67$) at various temperature. The arrow for each $x$ represents an energy of maximum $\sigma(\omega)$, $\omega_m$, at 300 K. With decreasing $x$ from 0.67 to 0.50, $2\Delta$ at the lowest temperature increases (while $T_{CO}$ decreases), and the suppression of spectral weight below $\omega_m$, i.e., the optical pseudogap feature, is systematically enhanced.

Minimum $\sigma(\omega)$, $\omega_m$ (arrows in Fig. 1.27). This suppression of spectral weight is accompanied by a pseudogap in $\sigma(\omega)$, i.e., decreasing $\sigma(\omega)$ below $\omega_m$ at each $T$. This pseudogap is also observed in the $\sigma(\omega)$ of $x=0.60$ and 0.67 at temperatures up to at least 300 K, even if $2\Delta$ of $x=0.60$ and 0.67 becomes zero just above $T_{CO}$. Surprisingly, it is found that the pseudogap feature shows systematic doping dependence. First, $\omega_m$ at 300 K systematically increases as $x$ approaches 0.50 from above (See Fig. 1.27). Second, the suppression of spectral weight below $\omega_m$ at 300 K becomes more evident as $x$ approaches 0.50, which finally produces a nonzero $2\Delta$ even at 300 K. This systematic enhancement of the pseudogap feature and its proximity to the finite $2\Delta$ far above $T_{CO}$ near $x=0.50$ consistently suggest that the optical pseudogap can be attributed to the spatially fluctuating CO correlation of La$_{1-x}$Ca$_x$MnO$_3$ ($x \geq 0.50$) at high $T$ region.

To investigate the charge gap and its pseudogap developments quantitatively, we determined $T$-dependent suppressed spectral weight, $\Delta \sigma(T)=\sigma(\omega_m)\omega_m-\int_0^{\omega_m} \sigma(\omega)d\omega$ and $2\Delta(T)$ for each $x$, as shown in Fig. 1.28. Below $T_{CO}$, $\Delta \sigma(T)$ values of $x=0.50$ are smaller than those of $x=0.52$. The proximity to FM phase boundary at $x=0.50$ may be responsible for the reduction of $\Delta \sigma(T)$ of $x=0.50$ at low $T$. It is noted that high-$T$ $\Delta \sigma(T)$ values of all the samples are clearly nonzero up to at least 300 K. In particular, $\Delta \sigma(T)$ values at 300 K increase systematically as $x$ approaches 0.50. At the same time, $2\Delta(0)$ values in Fig. 1.28 (b) increase as $x$ approaches 0.50; $2\Delta(0) \approx 0.2$, 0.26, 0.45, and 0.45 eV for $x=0.67$, 0.60, 0.52 and 0.50, respectively. This increase of the $2\Delta(0)$ is well correlated with the
increase of $\Delta \sigma(T)$ at 300 K as $x$ approaches 0.50. These findings indicate that the strength of CO stability is clearly maximized for $x \approx 0.50$, being responsible for the enhanced CO fluctuation at high temperature. Because $T_{CO}$ of these compounds decreases as $x$ approaches 0.50, $2\Delta(0)/k_B T_{CO}$ values systematically increase: $2\Delta(0)/k_B T_{CO} \approx 9, 12, 28,$ and 30 for $x = 0.67, 0.60, 0.52$ and 0.50, respectively. The $2\Delta(0)/k_B T_{CO}$ up to 30, an unusually large value among many charge-ordered oxides, indicates strongly enhanced electron correlation near $x = 0.50$ [84, 85].

Related with the enhanced pseudogap feature and large $2\Delta(0)/k_B T_{CO}$ value for $x \approx 0.50$, $2\Delta(T)/2\Delta(0)$ vs $T/T_{CO}$ curves of $x = 0.50$ and 0.52 clearly deviate from the BCS functional form (Fig. 1.29). For example, $2\Delta(T)/2\Delta(0)$ values of $x = 0.50$ are still about 0.25 at $T/T_{CO} \approx 1.7$ ($T = 300$ K) and those values of $x = 0.52$ are nonzero up to at least $T/T_{CO} \approx 1.2$ ($T \approx 240$ K). These unique $2\Delta(T)/2\Delta(0)$ curves of non-BCS-type are quite consistent with the greatly enhanced spatial and/or temporal CO fluctuation near $x = 0.50$ at high temperature regions. However, as $x$ is increased, $2\Delta(T)/2\Delta(0)$ curves recover the BCS form for $x = 0.60$ and 0.67, as observed in most of CO materials [85].

To check how high temperatures this CO fluctuation survives, we studied high-$T$ resistivity of La$_{1-x}$Ca$_x$MnO$_3$ with $x \geq 0.50$ in Fig. 1.30 (a). The $x = 0.50$ sample shows insulating behaviour up to above $\sim 850$ K, where orthorhombic (low $T$) to rhombohedral (high $T$) structural transition occurs. Surprisingly, for $x \geq 0.52$, there exists a crossover from metallic to insulating states as $T$ decreases. Moreover, the crossover
temperature defined as, $T^*$, decreases systematically as $x$ increases from 0.50. This $T^*$ evolution with $x$ is well correlated to $2\Delta(0)$ and $\Delta\sigma(300 \text{ K})$ behaviours for $0.50 \leq x \leq 0.67$. Furthermore, in Fig. 1.30 (b), $T^*$ decreases as $T_{\text{CO}}$ does above $x=0.67$. Our previous study of $x=0.80$ showed $2\Delta(0) \approx 0.08 \text{ eV}$, indicating that both $T_{\text{CO}}$ and $2\Delta(0)$ decrease together above $x=0.67$ [86]. Therefore, $T^*$ of charge-ordered $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is clearly linked to $2\Delta(0)$. This observation supports that $T^*$ can be the temperature where high $T$-CO correlation starts and thus optical pseudogap appears.

Why is $2\Delta(0)/k_B T_{\text{CO}}$ so large near $x=0.50$? In a quasi-1-dimensional (D) CDW system, the CDW fluctuation, induced by low dimensionality, results in gap-like features in $\sigma(\omega)$ above the 3D long-range ordering temperature, $T_{\text{3D}}$ [76]. The mean field transition temperature of $T_{\text{MF}}$ (equiv $2\Delta(0)/3.5$) is usually quite larger than $T_{\text{3D}}$. Between $T_{\text{MF}}$ and $T_{\text{3D}}$, a crossover from 1-D to 3-D correlation occurs at $T^*$. These phenomena have some similarities with what observed in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x \geq 0.50$. However, it is not clear whether the striped charge and orbital ordering, and resultant effective low dimensionality can induce such unusually large charge fluctuation in 3-D materials. In addition, if the low dimensionality induced by striped charge/orbital ordering is the main source for the fluctuation, the samples near $x=0.67$ would have similar amount of charge fluctuations due to well-defined charge/orbital ordering at the commensurate case.

The more appealing origin for the enhanced CO fluctuation for $x \geq 0.50$, can be a competition of order parameters in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.50$). Obviously, the commensurate 1:1 ratio of Mn$^{3+}$ and Mn$^{4+}$ ions is compatible with the strong CO tendency at $x=0.50$. At the same time, the double exchange mechanism predicts that the strength of the FM cor-

![Figure 1.29. The $2\Delta(T)/2\Delta(0)$ vs $T/T_{\text{CO}}$ plot. The solid line represents the BCS functional form.](image)
relation in La$_{1-x}$Ca$_x$MnO$_3$ should be varied as $x(1-x)$ and optimized at $x=0.50$ [29]. Indeed, La$_{1-x}$Ca$_x$MnO$_3$ ($x=0.50$) has a thermodynamic bicritical point, where the FM metallic and the CO insulting states meet with the paramagnetic insulating state. Therefore, near the critical point, competing order parameters can lead to the suppression of ordering temperatures as well as increased spatial/temporal fluctuation among those phases. This scenario is further supported by a recent computational study, predicting that large charge fluctuations could be a generic feature of the mixed-phase systems at or near the regimes where a phase separation occurs as $T\rightarrow0$ K [63].

Finally, it will be interesting to check the time and the length scales of the fluctuating short-range order that can be observed at a $\sigma(\omega)$ study. The recent neutron scattering study indicated that CO fluctuations above $T_C$ occur with a time scale slower than 1 ps [87, 88, 89]. Thus, frequency-dependent optical spectroscopy can probe the presence of fluctuations, because 0.5-1 eV corresponds to time scales of 5-10 fs. Besides, an incoming light takes an average over a length scale of $\lambda/n$, where $\lambda$ is the wavelength of the light and $n$ is the refractive index of the medium. For the 0.5-1 eV energy ranges, $n \approx3$ and $\lambda/n \approx300-700$ nm.
Therefore, when the volume fraction of the CO domains is large, 10-100 nm scale CO correlations can be observed by $\sigma(\omega)$ study [84]. If the correlation length is too small, for example, $\sim 10 \text{ Å}$ for the La$_{1-x}$Ca$_x$MnO$_3$ ($x=0.30$) sample, the effects of the CO correlation on the $\sigma(\omega)$ might not be easily distinguished with a strong small polaron absorption band.

This section presented doping-dependent evolutions of charge-ordering gap and its pseudogap in La$_{1-x}$Ca$_x$MnO$_3$ ($0.48 \leq x \leq 0.67$) from systematic optical conductivity and transport studies. With decreasing $x$ from 0.67 to 0.50, the low temperature charge gap systematically increased while charge ordering temperature decreased. Simultaneously, the optical pseudogap, indicating charge-ordering fluctuation at high temperatures, is greatly enhanced as $x$ approaches 0.50. This $\sigma(\omega)$ study proves that short-range charge ordering fluctuation is anomalously strong in manganites.

5. X-ray scattering studies of high-temperature charge/orbital correlations

Because of the strong coupling between the electronic, magnetic, and structural degrees of freedom in manganites, charge/orbital fluctuations in these materials are always accompanied by local structural distortions. These distortions can be measured directly by x-ray and neutron diffraction techniques. In recent years, these techniques have been extensively utilized for the investigation of the local structural distortions in the high-temperature paramagnetic insulating (PI) phase of manganites [87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97]. In this section, we briefly outline some recent results of these studies, concentrating on x-ray diffraction and on three-dimensional perovskite manganites. We note that this is not a comprehensive review. In particular, layered manganites are not discussed here; the interested reader is referred to Refs. [87, 95, 97].

The importance of local structural distortions was first pointed out in connection to the anomalously large resistivity of the PI phase [27]. It was proposed that small lattice polarons are present in this state. A lattice polaron forms when an $e_g$ electron localizes on a Mn$^{3+}$ ion, and the surrounding oxygen octahedron distorts due to Jahn-Teller effect. Formation of the lattice polarons leads to the increase of the electrical resistivity. The polarons are strongly suppressed in the ferromagnetic metallic (FM) state, and therefore it was suggested that they play a key role in the CMR effect. Numerous experiments [83, 98, 99, 100, 101] have confirmed the presence of lattice polarons in the PI state including, in particular, diffuse x-ray scattering measurements [87, 90] and scattering measurements of the pair distribution function (PDF) [101].
An important step in understanding the nature of the PI phase was made in 1999 when it was realized that the local lattice distortion in this phase is not necessarily confined to the single oxygen octahedron surrounding a Mn ion. Neutron and x-ray diffraction measurements have shown that nanoscale structural correlations are present in the PI phase [88, 89, 90, 91, 92, 93, 94, 96]. These correlations were initially described as correlated polarons. It was also pointed out that in the $x=0.3$ compounds, these correlations occur at the same scattering vector as the charge/orbital peaks in the samples exhibiting long-range charge/orbital order of the CE type. Therefore, it was proposed that these correlations reflect the presence of nanoscale regions possessing charge and orbital order. Importantly, it was shown that the electrical resistivity and the intensity of the peaks due to the nanoscale correlations follow very similar temperature dependences [88, 89, 91]. The following picture therefore emerged: the PI state contains nanoscale insulating regions possessing charge/orbital order, and it is these regions that are responsible for the enhanced resistivity of the PI state. The nanoscale correlations, therefore, were concluded to play an important role in the CMR effect.

Since the original observation of the nanoscale correlations in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, they were found in a number of different manganite compounds [91, 92, 93, 94, 96]. It appears that these correlations are present in the PI state in a broad range of carrier concentration, which we tentatively define as $x=0.2-0.5$, provided that the lattice symmetry is of the orthorhombic $O$ type. Interestingly, the correlations are not significantly affected by the nature of the low-temperature ordered state. In particular, very similar nanoscale correlations were found in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ which exhibits the CE-type order at low temperatures, and in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, which is a ferromagnetic metal [91]. Nanoscale structural correlations, therefore, appear to be a generic feature of the orthorhombic PI state in hole-doped manganites.

Despite significant amount of research activity devoted to the local inhomogeneities in the PI state of the manganites, the exact structure of the correlated regions is still largely unknown. Moreover, recent studies indicate that the scenario described above, in which nanoscale charge/orbital ordered insulating regions are present in the PI state, is in all likelihood oversimplified. Below, we describe some recent x-ray scattering studies of the structural correlations in the PI state, discuss the implications of these experiments for the local structure of the PI state, and pose questions for future research.

We will focus our discussion on the properties of the $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, $x=0.3-0.5$ samples. These properties are representative of the manganites with the FM ground state; materials with the charge-ordered ground
state will be discussed later. The nanoscale correlations give rise to broad diffraction peaks at the $(0, k, 0)$, and $(h, 0, 0)$ reduced scattering vectors, with $h,k=0.35-0.55$ in different manganites \cite{88, 89, 90, 91, 92, 93, 94, 96}. (We are using the orthorhombic \textit{Pbnm} notation, in which $a \sim \sqrt{2}a_c$, $b \sim \sqrt{2}a_c$, and $c \sim 2a_c$, $a_c$ is the cubic perovskite lattice constant.) A representative overall scattering pattern is illustrated in Fig. 1.31. The broad peaks at $(4.5, 4, 0)$ and $(4, 4.5, 0)$ reflect the presence of the nanoscale correlations. The intensity of these peaks is believed to reflect the concentration of the correlated regions, and their width is inversely proportional to the region size \cite{96}. The position of the peaks defines the period of the lattice modulation in the correlated regions. The peaks are observed on top of the “butterfly-like” shaped background which is attributed to scattering from uncorrelated polarons, also known as Huang scattering, and to thermal-diffuse scattering \cite{87, 90}. To separate this background from the correlated peaks, scans along the $a$ or $b$ directions are taken, see Fig. 1.32. These scans are fitted to a Gaussian or Lorentzian line shape and a monotonically sloping background.

The parameters of the correlated peaks in the Nd$_{1-x}$Sr$_x$MnO$_3$ samples are shown in Fig. 1.33. The peak intensity is strongly reduced in the FM state and traces the behavior of the electrical resistivity over the entire temperature range in the PI and FM states. Interestingly, in many samples the structural correlations do not disappear completely below the Curie temperature even at the lowest temperatures. These results are consistent with the earlier PDF measurements \cite{101} indicating the presence of local Jahn-Teller distortions in the FM state. The data of
Fig. 1.32. $x$-ray scans along the $(4, 6+\Delta k, 0)$ direction ($x=0.45, 0.5$), and the $(4, 4+\Delta k, 0)$ direction ($x=0.3$). The temperatures are 210 K, 275 K, and 260 K for the $x=0.3$, 0.45, and 0.5 samples, respectively (reprinted from [96]).

Fig. 1.33 show that the correlations survive deep in the FM region of the phase diagram, indicating that the FM state is inhomogeneous.

Fig. 1.33 also illustrates two other important observations. First, the correlation length of the nanoscale regions is the same in all samples and is independent on temperature. The same correlation length is also found in other manganites, including $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.2, 0.3$) [88, 89], and $\text{La}_{0.75}(\text{Ca}_{0.45}\text{Sr}_{0.55})_{0.25}\text{MnO}_3$ [96]. Second, the period of the lattice modulation is also independent on temperature. It does depend on the sample composition, but in a very regular manner. In Fig. 1.34 we plot the period of the lattice modulation as a function of doping, $x$. Remarkably, all the results shown in Fig. 1.34 appear to fall on the same line, which begins at $x=0$ and $\delta=2/3$, and ends at $x=1$ and $\delta=0$.

In its mostly widely investigated form, the CMR effect is a field-induced transition from the PI to the FM phase. Since the nanoscale correlations are suppressed in the FM state, application of a magnetic field should also result in their suppression. The data of Fig. 1.35 show that this is indeed the case: as the magnetic field is applied, the electrical resistivity is reduced, and the intensity of the correlated peak is diminished, tracing the behavior of the resistivity [94]. Interestingly, a substantial correlated peak is still present at the highest magnetic field obtainable in this experiment. The field-induced transition is gradual. Assuming that the intensity of the correlated peak reflects the concentration of the correlated regions, one concludes that the field-induced state is very inhomogeneous. Finally, we note that the magnetic field affects neither the correlation length, nor the period of the lattice modulation in the ordered regions.
Figure 1.33. (a) Temperature dependence of the intensity of the peak due to the structural correlations in Nd\textsubscript{1−\textit{x}}Sr\textsubscript{\textit{x}}MnO\textsubscript{3}. The single-polaron background is subtracted. (b) The correlation length of the ordered regions. (c) The position of the peak relative to the nearest Bragg peak (the lattice modulation wave vector). Reprinted from [96].

Pseudo-cubic perovskite manganites exhibit a number of different structural phases, among them orthorhombic, rhombohedral, and tetragonal. The nanoscale correlations described above have thus far only been found in the orthorhombic \textit{O} phase. It remains to be seen whether they exist in other structural phases. Preliminary measurements suggest the possibility that the rhombohedral phase does not support the nanoscale fluctuations [102]. An example of the data supporting this claim is shown in Fig. 1.36 which shows temperature dependence of the correlated peak intensity and the electrical resistivity in La\textsubscript{0.75}(Ca\textsubscript{0.45}Sr\textsubscript{0.55})\textsubscript{0.25}MnO\textsubscript{3}. This compound exhibits a PI state for \( T > 300 \) K. With increasing temperature, the paramagnetic insulating state undergoes a structural transition from the orthorhombic \textit{O} state to a rhombohedral state. The data of Fig. 1.36 show that the nanoscale correlations abruptly disappear at the orthorhombic-to-rhombohedral transition. At the same time, the
Figure 1.34. The wave vector $\delta$ of the lattice modulation in the correlated regions as a function of doping $x$ (filled symbols). Open symbols show the wave vector of the structures with long range charge and orbital order observed in manganites with $x > 0.5$ (reprinted from [96]).

electrical resistivity is significantly reduced. These observations are in general agreement with the picture in which the correlations reflect the presence of insulating regions in the sample.

The above experimental results could be summarized as follows: (i) The nanoscale structural correlations are present in the orthorhombic PI state. They are suppressed (but not completely destroyed) on the transition to the FM state, independent on whether the transition is induced by changing temperature or magnetic field. (ii) The correlation length characteristic to the nanoscale regions is the same in all samples and does not depend on temperature or magnetic field. (iii) The period of the lattice modulation is the same linear function of the concentration of the divalent ion (doping level) $x$ in all the samples. Thus, it appears that the structure of the correlated regions in the manganites with the FM low-temperature state is defined by a single parameter, $x$.

We now turn to the interpretation of these data. We note that the precise determination of the structure of the correlated regions, similar to that carried out for the layered manganites [95], is yet to be done. At this stage, therefore, we can only present some current ideas on this subject. From the very beginning, the correlated regions were described as small regions possessing charge and orbital order [88, 89, 103]. This suggestion was made based on the observed scattering vectors of the maxima of the broad correlated peaks. In the case of $x = 0.3$, these peaks are observed at the same positions as the so-called orbital-ordering peaks in the CE-type charge/orbital ordered state. Thus, it was proposed that small regions with the CE-type order are present in the PI state. As $x$
Figure 1.35. Magnetic field-dependence of (a) the electrical resistivity, (b) the intensity of the (4, 4.5, 0) peak due to the correlated distortions, and (c) the correlation length of the ordered regions in \(\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\). All the data were taken at \(T=215\) K (reprinted from [94]).

deviates from 0.3, different charge/orbital ordered structures, possibly containing discommensurations, were speculated to be realized [96]. In particular, as \(x\) approaches 0.5, the lattice modulation period approaches 3, and one of the striped structures observed in highly doped manganites could be realized. It was also pointed out that if the ordered regions are well defined, their actual size could be significantly larger than the correlation length shown in Figs. 1.33 and 1.35, which was defined as inverse half-width at half-maximum of the peaks [96]. Thus, the charge and orbital ordered structures described above are compatible with the experimental results.

In the above scenario, the charge-ordered structures are observed at doping levels different from those of the corresponding long-range-ordered counterparts. The CE-type order, for example, is most stable at \(x=0.5\), and the striped structure with a period 3 is observed at \(x=2/3\) (see open symbols in Fig. 1.34). As a possible reason for this discrepancy,
it was proposed that charge-poor and charge-rich regions are formed in the sample [96]. The charge concentration in the charge-depleted regions could then be close to the ideal concentration needed for the formation of the charged-ordered structures with the observed periodicity. Several possible reasons for such variations of the charge density were proposed. First, it can result from chemical inhomogeneities. It is, however, difficult to see how chemical inhomogeneities would explain the observed common features in a variety of samples with quite different chemical compositions.

Second, even in the absence of chemical inhomogeneities, the formation of charge-rich and charge-poor regions is still possible. A number of theoretical calculations, in fact, predict such a phase separation [16]. Moreover, electronic phase separation appears to be a generic feature of almost any current theory describing mixed-valence manganites. Note, the usual argument that Coulomb interaction would prevent significant spatial charge segregation should not necessarily work in the case of nanoscale domains. This interaction could, of course, be one of the factors limiting the ordered region size.

It is interesting to note that manganites with the long-range CE-type and striped order exhibit the O-orthorhombic structure with the lattice
constants $c/\sqrt{2} < b \sim a$ [104, 105]. The $c$-axis contraction in these compounds reflects the Jahn-Teller distortion of the $\text{Mn}^{3+}\text{O}_6$ octahedra with the long axis lying in the $ab$ plane. Thus, on average, the long axes of the $\text{MnO}_6$ octahedra lie in the $ab$ plane in both the long-range charge ordered phase, and in the $O$ paramagnetic insulating state. In contrast, the $\text{MnO}_6$ octahedra are undistorted in the rhombohedral ($R\overline{3}c$) state [106]. It appears, therefore, that the average lattice distortion characteristic to the $O$ state promotes (or, possibly, reflects) formation of the nanoscale correlations. Since there is no a priori requirement that the local symmetry of the nanoscale ordered regions should match the average symmetry of the crystal lattice, this is quite an interesting observation.

Finally, we note that the case of the transition from the PI or FM phase directly to the charge-ordered phase, such as in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ or $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, is more complex. In such transitions, the periodicity of the lattice modulation and the correlation length vary on warming as the low-temperature, long-range charge order disappears and the high-temperature correlations arise [91, 92, 93]. The existing experimental data are not completely consistent, and it is unclear as to what extent they reflect the intrinsic properties of the PI state. Systematic measurements at temperatures much larger than the charge-ordering transition temperature are needed to answer this question.

Summing up, it appears that the important role of nanoscale structural correlations in manganites is currently quite well established. In particular, the presence of these correlations is one of the factors leading to the large magnetoresistance observed in these compounds. The correlations are found in a number of different manganite compounds, they show a systematic behavior, and, therefore, these correlations are not likely to be the artifacts resulting from unclean samples or secondary phases.

However, both the experimental investigation of the local structure of the phases exhibiting nanoscale correlations, and the theoretical work on the mechanism of their formation are still in their beginning stage. While the simple interpretation of the experimental data given above appears to be reasonable, there are several important problems with it. First, the integrated intensity of the correlated peaks is surprisingly small. Calculations based on the assumption that the magnitude of the lattice distortion in the correlated regions is the same as that in the corresponding long-range ordered phases produce extremely small estimates for the volume fraction of the charge-ordered regions in the PI state. Different authors give estimates for this fraction ranging from several percent [107] to a small fraction of 1 percent [102]. It is hard to see how such a small volume fraction could have a profound effect on
the transport properties. Second, the “uncorrelated polarons” and the “nanoscale correlations” are now often treated as two separate objects. In our opinion, this separation is not altogether justified, and both the $q=0$ and the $q\sim0.5$ signals might originate from the same object. Further studies of diffuse scattering in these materials, including energy-resolved studies, are clearly needed to address these problems.

The example of manganites clearly shows that local nanoscale inhomogeneities could have a great influence on the bulk properties. Numerous recent studies show that similar inhomogeneities are likely to play an important role in other correlated materials, cuprates and nickelates among them. Understanding the intriguing properties of the correlated materials, therefore, will require understanding details of their local structure. Experimental and theoretical studies addressing this issue will, therefore, play an important role in future work on correlated materials.

6. Conclusions

In this review chapter, we presented extensive experimental evidence to support the unambiguous existence of phase modulations in mixed-valent manganites. It is revealed that two important non-trivial inhomogeneities (or phase modulations) play an important role in producing colossal magnetoresistance in mixed-valent manganites, i.e., submicrometer-scale (macroscopic) and nano-scale (microscopic) phase coexistence/fluctuation. The first (macroscopic) phase separation is caused by the coexistence of mainly ferromagnetic metallic and charge-ordered insulating domains at low temperatures with micrometer length scales. Extensive experimental evidence for such a large-length-scale phase modulation was found in the Pr$^{3+}$-substituted La$^{3+}_{5/8}$Ca$^{2+}_{3/8}$MnO$_3$ system where the relative volume of the electronically- and magnetically-distinct regions varies with Pr substitution. However, it is important to note that both of the main two phases have the same charge densities but quite different long-range strains, resulting from the significantly different crystallographic structures of the metallic and insulating phases. It is this lattice strain that produces such large-length-scale phase coexistence at low temperature. This physical situation resembles what generally happens in martensitic systems, in which crystallographically-different phases can coexist at low temperatures to accommodate the significant long-range strain associated with the martensitic transformation. Even if many magnetotransport properties of the system can be understood within a percolation model between two different electronic phases, it is still necessary that martensitic-transformation-effects should be included to understand adequately many physical properties of the sys-
tem. For example, a martensite-like transformation can naturally bring another charge-disordered insulating phase with lattice strains different from those of the main two phases into play. Thus, extremely sensitive and huge magnetoresistance under an applied magnetic field at low temperature should be also associated with the special situation that structurally different phases can coexist and that they show avalanche-effects when they switch to a new phase under magnetic fields.

The other important phase modulation discussed in this chapter is caused by nano-scale charge/orbital correlated nano-clusters (or nano-scale charge/orbital ordering) in the background of the paramagnetic state above the Curie temperature (or charge ordering temperature). Experimental evidence from transport, magnetism, optical spectroscopy, and x-ray scattering studies were presented to show that microscopic phase fluctuation effects can exist over broad doping ranges of the prototypical $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ systems above the long-range ordering temperatures. In particular, those results revealed that unusually large fluctuation of the CE-type charge/orbital ordering exists in the samples near the special half-doped manganite $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Based on present and previous results, the high temperature CE-type correlations are expected to be dominant over a broad doping ranges of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.7$) and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$). In the future, it will be interesting to identify the exact nature of nano-correlation as a function of carrier concentration at high temperature in many ferromagnetic as well as charge/orbital-ordered manganites. Additionally, we have provided convincing experimental evidence for the existence of $T^*$, the cluster-forming temperature, in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, particularly with $x \geq 0.5$. The existence for $T^*$ in low-hole-doping manganites is still not clear yet because transport is always insulating-like up to structural transition temperatures. Future studies are quite necessary directed toward understanding the phase fluctuation effects in the low hole-doping regime of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. Finally, it is important to note that many systematic studies of various manganites now indicate that the insulating nature above the Curie temperature is always associated with the presence of charge/orbital correlated nano-clusters, existing only in orthorhombic crystallographic structures. Thus, the nano-clusters will play a key role in producing CMR near the insulator-metal transition of the manganites. In other words, sensitive collapse of nano-scale charge/orbital ordering under a small magnetic field will essentially produce a huge drop in resistivity, inducing large negative magnetoresistance just above the Curie temperature.

There remain several interesting unsolved questions. First, most of the competing interactions in manganites seem to produce fluctuations
of competing order parameters near its thermodynamic critical or bi-
critical points at finite temperatures according to the electronic/magnetic
phase diagram shown in Fig. 1.1. On the other hand, it remains to be
experimentally clarified whether the giant fluctuations of the half-doped
manganites are a direct consequence of the coexistence of competing
order parameters even at zero temperature as a theoretical model sug-
gests [16]. In this context, the role of quantum fluctuations should be
investigated more systematically to determine whether competition of
order parameters at zero temperature can play a key role in producing
nanoscale-phase coexistence/fluctuation in an unusual phase space in
perovskite manganites. Second, the long-range strain-induced phase co-
existence might be a generic feature in the manganites with strong Jahn-
Teller effects. However, local physics based on a Jahn-Teller electron-
phonon coupling alone doesn’t seem to be enough to describe the ob-
served unique phase modulation with micrometer length scale. The-
etical and experimental investigations directed toward understanding
the metal-insulator transition induced by long-range strain are impor-
tant. Third, it is still puzzling why ferromagnetism and metallicity are
optimized at the commensurate hole-doping \( x=3/8 \), where enhanced
electron-phonon coupling can be expected to result in localization of
carriers [10]. Enhanced metallicity exhibited for special commensurate
doping might be related to a dynamic nano-scale charge/orbital ordering
with stripe correlations. It is now well known that the high-\( T_c \) cuprates
have dynamic and short-ranged stripe correlations even in the super-
conducting regime. While static charge ordering is clearly compatible
with localization of carriers, the exact role of dynamic stripe correla-
tions on the metallicity or superconductivity is still not understood in
the cuprates. In this context, the role of dynamic stripe correlations
on the carrier mobility should be further investigated in manganites.
Finally, the discovery of two important phase-separation phenomena,
micro- and macro-scopic, increase our understanding of colossal magneto-
resistance found in the perovskite manganites at high and low temper-
atures, respectively. Phase-modulation phenomena, and related physics
established in manganites, however, will be broadly applicable to other
strongly correlated material systems, wherein two or multi-competing
interactions coexist.

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References

[1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).

[2] S. Jin et al., Science 264, 413 (1994).

[3] H. Y. Hwang, S.-W. Cheong, P. G. Radaelli, M. Marezio and B. Batlogg., Phys. Rev. Lett. 75, 914 (1995).

[4] A. P. Ramirez, J. Phys.: Condens. Matter 9, 8171 (1997).

[5] J. M. D. Coey, M. Viret, and S. von Molnar, Adv. Phys. 48, 167, (1999).

[6] Y. Tokura and Y. Tomioka, J. Mag. Mag. Mat. 200, 1 (1999).

[7] Colossal Magnetoresistance, Charge Ordering, and related Properties of Manganese Oxides, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998).

[8] Contribution to Colossal Magnetoresistance Oxides, edited by Y. Tokura (Gordon & Breach, Monographs in Condensed Matter Science, London, 1999).

[9] Physics of Manganites, edited by T. A. Kaplan and S. D. Mahanti (Kluwer Academic/Plenum Publishers, New York, 1999).

[10] S.-W. Cheong and H. Y. Hwang, Ferromagnetism vs charge/orbital ordering in perovskite manganites, in Colossal Magnetoresistance Oxides, edited by Y. Tokura (Gordon & Breach, London, 1999).

[11] S.-W. Cheong and C. H. Chen, Striped charge and orbital ordering in perovskite manganites, in Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998).
[12] T. W. Noh, J. H. Jung and K. H. Kim, Optical properties of colossal magnetoresistance manganites, in *Physics of Manganese*, edited by T. A. Kaplan and S. D. Mahanti (Kluwer Academic/Plenum, New York, 1999).

[13] Y. Okimoto and Y. Tokura, Journal of Superconductivity: Incorporating Novel Magnetism 13, 271 (2000).

[14] S. L. Cooper, Optical Sepectroscopic Studies of Metal-Insulator Transitions in Perovskite-Related Oxides, in *Structure and Bonding*, Vol. 98 (Springer-Verlag, Berlin 2001).

[15] M. B. Salamon and M. Jaime, Rev. of Modern Physics 73, 583 (2001).

[16] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. 344, 1 (2001).

[17] C. Zener, Phys. Rev. 82, 403 (1951); P. W. Anderson and H. Hasegawa, *ibid*. 100, 675 (1955); P. G. de Gennes, *ibid*. 118, 141 (1960); K. Kubo and N. Ohata, J. Phys. Soc. Jpn. 33, 21 (1972).

[18] J. B. Goodenough, Phys. Rev. 100, 564 (1955); J. Kanamori, Prog. Theor. Phys. 30, 275 (1963).

[19] P. G. Radaelli et al., Phys. Rev. Lett. 75, 4488 (1995); P. G. Radaelli, M. Marezio, H. Y. Hwang, S.-W. Cheong, and B. Batlogg, Phys. Rev. B 54, 8992 (1996).

[20] C. H. Chen and S-W. Cheong, Phys. Rev. Lett. 76, 4042 (1996).

[21] D. W. Visser, A. P. Ramirez, and M. A. Subramanian, Phys. Rev. Lett. 78, 3947 (1997).

[22] J. L. Cohn et al. Phys. Rev. B 56, R 8495 (1997).

[23] C. Wood, D. Emin, and P. E. Gray, *ibid*. 31, 6811 (1985).

[24] P. G. Radaelli et al., Phys. Rev. B 56, 8265 (1997).

[25] V. Laukhin et al., Phys. Rev. B 56, R10009 (1997).

[26] J. A. Fernandez-Baca et al., Phys. Rev. Lett. 80, 4012 (1998).

[27] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. 74, 5144 (1995).

[28] A. J. Millis, B. I. Shraiman, and R. Mueller, Phys. Rev. Lett. 77, 175 (1996).
REFERENCES

[29] H. Roder, J. Zang, and A. R. Bishop, Phys. Rev. Lett. 76, 1356 (1996).

[30] V. J. Emery & S. A. Kivelson, Physica C 209, 597 (1993).

[31] W. O. Putikka, M. U. Luchini & T. M. Rice, Phys. Rev. Lett. 68, 538 (1992).

[32] For example, B. I. Shklovskii & A. L. Efros, Electronic Properties of Doped Semiconductors, Springer-Verlag, New York (1984).

[33] D. J. Bergman and O. Levy, J. Appl. Phys. 70, 6821 (1991).

[34] G. Hurvits, R. Rosenbaum, and D. S. McLachlan, J. Appl. Phys. 73, 7441 (1993), and references therein.

[35] D. S. McLachlan, J. Phys. C 20, 865 (1987).

[36] N. Dupez, D. S. McLachlan, and I. Sigalas, Solid State Commu. 66, 869 (1988).

[37] I. Balberg, Phys. Rev. Lett. 59, 1305 (1987).

[38] H. Y. Hwang and S-W. Cheong, Chap. 9 in Colossal Magnetoresistance Oxides, edited by Y. Tokura (Gordon & Breach, Monographs in Condensed Matter Science).

[39] S. Mori, C. H. Chen, and S.-W. Cheong, Nature 392, 473 (1998); S. Mori, C. H. Chen, and S.-W. Cheong, Phys. Rev. Lett. 81, 3972 (1998).

[40] V. Kiryukhin et al., Nature 386, 813-815 (1997).

[41] R. D. Shannon, Acta Cryst. A32, 751 (1976).

[42] L. M. Rodriguez-Martinez and J. P. Attfield, Phys. Rev. B 54, R15622 (1996).

[43] G. M. Zhao, et al., Nature 381, 676 (1996).

[44] P. B. Littlewood, Nature 399, 529 (1999).

[45] M. Uehara and S.-W. Cheong, Europhys. Lett. 52, 674 (2000).

[46] R. H. Heffner et al., Physica B 230, 759 (1997).

[47] G. Xiao et al., Phys. Rev. B 54 6073 (1996).

[48] P. G. Radaelli et al., Phys. Rev. B 55, 3015 (1997).
[49] N. A. Babushkina et al., Phys. Rev. B 59, 6994 (1998).

[50] See, for example, P. Gordon, *Principle of Phase Diagrams in Materials Systems* (McGraw-Hill Series in Materials Science and Engineering).

[51] *Martensitic transformation*, Zenji Nishiyama, edited by M. Fine, M. Meshii, C. Wayman (Academic Press, New York, 1978).

[52] *International Conference on Martensitic Transformations: ICO-MAT 95, pt. 1, 2*, edited by R. Gotthardt and J. Van Humbeeck (Lausanne, Switzerland, August 20-25, 1995).

[53] *Physical Metallurgy Principles*, Robert E. Reed-Hill & Reza Abbaschian, 3rd edition (PWS-Kent Publishing Company, Boston, 1991) pp. 561-587.

[54] V. Podzorov, Europhys. Lett., 47, 371 (2001).

[55] H. Kuwahara et al., Phys. Rev. B 56, 9386 (1997).

[56] P. Levy et al., Phys. Rev. B 62, 6437 (2000).

[57] N. Mathur et al., Nature 387, 266 (1997).

[58] J. Klein et al., Europhys. Lett. 47, 371 (1999).

[59] A. Gupta et al. Phys. Rev. B 54, R15629 (1996).

[60] P. G. Radaelli et al. Phys. Rev. B 63, 172419 (2001); V. Kiryukhin et al., Phys. Rev. B 63, 024420 (2000).

[61] H. J. Lee, K. H. Kim, M. W. Kim, T. W. Noh, B. G. Kim, T. Y. Koo, S-W. Cheong, Y. J. Wang, and X. Wei., Phys. Rev. B 65, 115118 (2002).

[62] H. J. Lee, J. H. Jung, Y. S. Lee, J. S. Ahn, T. W. Noh, K. H. Kim, and S-W. Cheong, Phys. Rev. B 60, 251 (1999).

[63] A. Moreo, S. Yunoki, and E. Dagotto, Phys. Rev. Lett. 83, 2773 (1999).

[64] K. H. Kim, J. H. Jung, and T. W. Noh, Phys. Rev. Lett. 81, 1517 (1998).

[65] M. Quijada et al., Phys. Rev. B 58, 16 093 (1998); Y. Okimoto et al., ibid. 55, 4206 (1997).
REFERENCES

[66] M. W. Kim, J. H. Jung, K. H. Kim, H. J. Lee, T. W. Noh, J. Yu, and Y. Moritomo, Phys. Rev. Lett. 89, 016403 (2002).

[67] D. Emin, Phys. Rev. B 48, 13 691 (1993).

[68] A. S. Alexandrov and A. M. Bratkovsky, J. Appl. Phys. 87, 5016 (2000).

[69] J. B. Goodenough, Phys. Rev. 100, 564 (1955).

[70] M. v. Zimmermann et al., Phys. Rev. Lett. 83, 4872 (1999).

[71] M. Uehara, S. Mori, C. H. Chen, and S-W. Cheong, Nature (London) 389, 560 (1999).

[72] K. H. Kim, M. Uehara, C. Hess, P. A. Sharma, S.-W. Cheong, Phys. Rev. Lett. 84, 2961 (2000).

[73] D. C. Worledge, L. Miéville, T. H. Geball, Phys. Rev. B 57, 15 267 (1998).

[74] J. van den Brink, G. Khaliullin, D. I. Khomskii, Phys. Rev. Lett. 83, 5118 (1999).

[75] B. P. Gorshunov et al., Phys. Rev. Lett. 73, 308 (1994); A. Schwartz et al., Phys. Rev. B 52, 5643 (1995).

[76] G. Grüner, Density Waves in Solids (Addison-Wesley, New York, 1994), Chaps. 3 and 5.

[77] K. Yamamoto et al., Phys. Rev. B 61, 14 706 (2000).

[78] C. P. Adams, J. W. Lynn, Y. M. Mukovskii, A. A. Arsenov, and D. A. Shulvatev, Phys. Rev. Lett. 85, 3954 (2000).

[79] P. Dai, J. A. Fernandez-Baca, N. Wakabayashi, E. W. Plummer, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. 85, 2553 (2000).

[80] H. J. Lee, K. H. Kim, J. H. Jung, T. W. Noh, R. Suryanarayanan, G. Dhahenne, and A. Revcolevsch, Phys. Rev. B 62, 11320 (2000).

[81] K. H. Kim, S. Lee, T. W. Noh, and S.-W. Cheong, Phys. Rev. Lett. 68, 167204 (2002).

[82] K. H. Kim, J. H. Jung, and T. W. Noh, Phys. Rev. Lett. 81, 4983 (1998).

[83] K. H. Kim, J. Y. Gu, H. S. Choi, G. W. Park, and T. W. Noh, Phys. Rev. Lett. 77, 1877 (1996).
[84] H. L. Liu, S. L. Cooper, and S.-W. Cheong, Phys. Rev. Lett. 81, 4684 (1998).

[85] T. Katsufuji et al., Phys. Rev. B 54, R14 230 (1996); S. K. Park et al., ibid. 58, 3717 (1998); Y. Okimoto et al., ibid. 59, 7401 (1999); S. K. Park et al., ibid. 60, 10 788 (1999).

[86] S. Lee, Master thesis, Seoul National University, 1999.

[87] L. Vasiliu-Doloc, S. Rosenkranz, R. Osborn, S. K. Sinha, J. W. Lynn, J. Mesot, O. H. seek, G. Preosti, A. J. Fedro, and J. F. Mitchell, Phys. Rev. Lett. 83, 4393 (1999).

[88] P. Dai, J. A. Fernandez-Baca, N. Wakabayashi, E. W. Plummer, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. 85, 2553 (2000).

[89] C. P. Adams, J. W. Lynn, Y. M. Mukovskii, A. A. Arsenov, and D. A. Shulyatev, Phys. Rev. Lett. 85, 3954 (2000).

[90] S. Shimomura, N. Wakabayashi, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. 83, 4389 (1999).

[91] C. S. Nelson, M. v. Zimmermann, Y. J. Kim, J. P. Hill, Doon Gibbs, V. Kiryukhin, T. Y. Koo, S-W. Cheong, D. Casa, B. Keimer, Y. Tomioka, Y. Tokura, T. Gog, and C. T. Venkataraman, Phys. Rev. B 64, 174405 (2001).

[92] S. Shimomura, T. Tonegawa, K. Tajima, N. Wakabayashi, N. Ikeda, T. Shobu, Y. Noda, Y. Tomioka, and Y. Tokura, Phys. Rev. B 62, 3875 (2000).

[93] R. Kajimoto, H. Yoshizawa, Y. tomioka, and Y. Tokura, Phys. Rev. B 63, 212407 (2001).

[94] T. Y. Koo, V. Kiryukhin, P. A. Sharma, J. P. Hill, and S-W. Cheong, Phys. Rev. B 64, 220405 (2001).

[95] B. J. Campbell, R. Osborn, D. N. Argyriou, L. Vasiliu-Doloc, J. F. Mitchell, S. K. Sinha, U. Ruett, C. D. Ling, Z. Islam, and J. W. Lynn, Phys. Rev. B 65, 014427 (2002).

[96] V. Kiryukhin, T. Y. Koo, A. Borissov, Y. J. Kim, C. S. Nelson, J. P. Hill, D. Gibbs, and S-W. Cheong, Phys. Rev. B 65, 094421 (2002).

[97] D. N. Argyriou, J. W. Lynn, R. Osborn, B. Campbell, J. F. Mitchell, U. Ruett, H. N. Bordallo, A. Wildes, and C. D. Ling, Phys. Rev. Lett. 89, 036401 (2002).
REFERENCES

[98] C. H. Booth, F. Bridges, G. H. Kwei, J. M. Lawrence, A. L. Cornelius, and J. J. Neumeuer, Phys. Rev. Lett. \textbf{80}, 853 (1998).

[99] M. Jaime, H. T. Hardner, M. B. Salamon, M. Rubinstein, P. Dorsey, and D. Emin, Phys. Rev. Lett. \textbf{78}, 951 (1997).

[100] A. Machida, Y. Moritomo, and A. Nakamura, Phys. Rev. B \textbf{58}, R4281 (1998).

[101] D. Louca, T. Egami, E. L. Brosha, H. Roder, and A. R. Bishop, Phys. Rev. B \textbf{56}, R8475 (1997).

[102] V. Kiryukhin, T. Y. Koo, H. Ishibashi, J. P. Hill, and S-W. Cheong, unpublished.

[103] K. H. Kim, M. Uehara, and S-W. Cheong, Phys. Rev. B. \textbf{62}, R11945 (2000).

[104] R. Kajimoto, H. Yoshizawa, H. Kawano, H. Kuwahara, Y. Tokura, K. Ohoyama, and M. Ohashi, Phys. Rev. B \textbf{60}, 9506 (1999).

[105] Q. Huang, A. Santoro, J. W. Lynn, R. W. Erwin, J. A. Borchers, J. L. Peng, K. Ghosh, and R. L. Greene, Phys. Rev. B \textbf{58}, 2684 (1998).

[106] J. F. Mitchell, D. N. Argyriou, C. D. Potter, D. G. Hinks, J. D. Jorgensen, and S. D. Bader, Phys. Rev. B \textbf{54}, 6172 (1996).

[107] J. M. Zuo, and J. Tao, Phys. Rev. B \textbf{63}, 060407 (2001).