在 Pr_{0.65}Ca_{0.35-x}Sr_xMnO_3 中電荷與自旋有序的相互影響

Interplay of charge and spin ordering in Pr_{0.65}Ca_{0.35-x}Sr_xMnO_3
Abstract

The manganites of the type RMnO$_3$ (R=La, Nd, Pr, Sm) are antiferromagnetic and the end (n=∞) members of the so-called Ruddlesden-Popper series, R$_{n+1}$Mn$_n$O$_{3n+1}$. These oxide materials illustrate many interesting properties like colossal magnetoresistance (CMR)\textsuperscript{1-13}, charge ordering (CO)\textsuperscript{14-21}, magnetic field induced structural and ferromagnetic transitions\textsuperscript{22-24} when R is partially substituted by divalent cation A (=Ca, Sr, Ba, Pb) as R$_{1-x}$A$_x$MnO$_3$. According our results of resistivity ($\rho$) and specific heat (C) on the Pr$_{1-x}$Ca$_x$MnO$_3$ series, we confirmed the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ is the good choice to investigate the interplay of double exchange (DE) interaction and charge(CO)/orbital(OO) ordering.

A systematic study of $\rho$, magnetization (M) and C on polycrystalline Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0-0.35) perovskite manganites has been reported. The T-x phase diagram presenting their electrical and magnetic properties is prevailed. The Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ (for x=0.1) sample is particularly unique showing a CO transition at $T_{CO}$ ~ 200K, an antiferromagnetic (AFM) ordering transition at $T_N$ ~ 175K, a metal-insulator (MI) transition at $T_{MI}$ ~ 80K and a ferromagnetic (FM) ordering transition at $T_C$ ~ 45K in the absence of magnetic fields. However, the C data of it do not show any anomaly at $T_{MI}$ for MI transition but illustrates a much smaller anomaly than expected one at $T_C$ and is suppressed by magnetic fields. This may indicate that the FM ordering in it, commonly related to MI transition, is of meta-stable characteristic and is ascribed to electronic and magnetic instability induced by spin fluctuations. This is established from the T-H phase diagram, as well as the thermal and magnetic hysteresis in $\rho$, M and C.
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Chapter one: Introduction

1.1 Physical properties of R_{1-x}A_xMnO_3:

Since the discovery of the high-temperature superconductivity, there has been renewed interest in mixed-valence perovskite 3d-transition-metal systems with strong electron correlations. Among the perovskite compounds, hole-doped manganese oxide systems have attracted great attention because of their diverse range of electronic, magnetic and structural properties with the prospect of application in various fields like spin valve devices, magnetic storage in hard disks and floppy disks etc. Such as R_{1-x}A_xMnO_3, these materials exhibit CMR^{1-13}, CO^{14-21}, phase separation^{25-27}, phase transition^{25-28}, and magnetic field induced structure change^{22-24}. CMR is the magnetoresistance associated with ferromagnetic-to-paramagnetic phase transition. The typical CMR compounds are derived from the parent compound, perovskite LaMnO_3. It is realized that the MR associated with the correlation between M and ρ can be very large. The resistivity is directly related to the DE^{29-31} mechanism between Mn^{3+} and Mn^{4+} ions, when the spins of their respective d-shells point in the same direction. As suggested by Jonker and Van Santen, it is the migration of these Mn^{4+} ions, accomplished by a Mn^{4+} ion capturing an electron from a neighbor Mn^{3+} ion, that gives rise to electrical conductivity. However, the DE interaction is not sufficient to explain the MR. When x=0.2-0.4 a strong electron-phonon interaction arising from the Jahn-Teller splitting of the outer Mn d level plays a crucial role^{32}. Recently, in addition to the interest in the ferromagnetic (FM) state, more attention has been given to the CO state typically observed for x >0.3. The CO transition has been observed which the doped carriers are ordered in the real space. It is found that the CO and orbital ordering (OO) occur simultaneously at a transition temperature higher than that.
of the spin ordering. The CO is always accompanied with a structural phase transition and pointed out by S. Uhlenbruck etc. The band-filling (1-x) and the effective one electron band width (W) are the key parameters to control their transport properties. W depends on the tilting of the MnO₆ octahedral and related to the Goldschmidt tolerance factor \( t = (r_A + r_O)(r_B + r_O)^{2/3} \) where \( r_A, r_B, \) and \( r_O \) are the ionic radii of the elements A, B and O respectively in ABO₃ perovskites. The Mn-O-Mn bond also plays an important role in the DE mechanism. The deformation of crystal structure results in the tolerance factor \( t \) and modifies the Mn-O-Mn bond and bond distance. This influences the electron hopping probability and DE interaction. Since the hopping electron retains information of its spin state before hopping, the resistivity becomes the function of its inherent magnetic order. Consequently the core magnetic spin of the manganese is correlated to the itinerant electron taking part into electrical conduction. DE mechanism generates the localization of electrons resulting in dynamic Jahn-Teller distortion that provides strong electron-phonon coupling and lifts the double degeneracy of the energy orbital preserving the total energy. In general, the material shows metallic behavior in ferromagnetic states and insulator like in paramagnetic states. The hopping of electron from Mn³⁺ to Mn⁴⁺ via O²⁻ critically depends on the relative alignment of Mn core spins. Thus the electrical resistivity is extremely sensitive to external magnetic fields. According to DE model, the application of magnetic field increases the transfer interaction.

1.2 (Pr, Ca, Sr)MnO₃:

The complicated phase diagram in CMR materials, \( R_{1-x}A_xMnO₃ \), takes place due to the interplay of DE interaction and CO. It is well established that the DE interaction prefers the FM metallic state and the CO results in AFM insulating state via the super-exchange interaction. It is found that the competition among the
interactions is strong for $x=0.5$ where the manganese ions are of equal amount and the coexistence of FM and AFM domains are observed. This competition also compels the system to have some interesting phenomena like magnetic and thermal hysteresis of resistivity and magnetization.

CMR systems with rare earth Pr have been widely studied. CO phase has been observed in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ for a wide range of $x$ ($0.3 \leq x \leq 0.75$). Magnetic field induced MI transitions in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ are reported with $x\approx 0.45$. Actually the interplay of DE interaction and CO can be tuned by changing the value of $x$ which in turn alters the ratio of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$, varying the radius of rare/alkaline earth metal, applying magnetic fields on the material. The T-H phase diagram of the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system exits the hysteresis region and the field-induced MI transition is irreversible in the region. In addition, the specific heat of polycrystalline $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ exhibits a large contribution linear in temperature ($\gamma T$) even though the compounds are insulator. But it is interesting that the $\gamma$ term decreases with applying magnetic field. The FM metallic states induced by the melting of AFM and CO insulating states have been perceived in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ through the application of magnetic fields. Therefore, it will be interesting to choose a suitable system and systematically investigate the interplay of CO/AFM insulating and FM metallic states by studying the transport, magnetic and thermal properties.

According our systematic study on $\rho$ and $C$, we confirmed the $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ is the good choice to investigate the charge ordering. Because the charge ordered state is much weaker than $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and the phase transition of the CO is very clear. The Sr substitution of Ca has the same effect of applying magnetic field.

In this article, we report the interplay of CO/AFM insulating and FM metallic states in polycrystalline $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ ($x=0$-0.35) manganites. Special
emphasis has been given on the discussion of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$, in which a charge ordering (CO) transition at T$_{CO}$ $\sim$ 200K, an antiferromagnetic ordering transition at T$_N$ $\sim$ 175K, a metal-insulator (MI) transition at T$_{MI}$ $\sim$ 80K and a ferromagnetic ordering transition at T$_C$ $\sim$ 45K are observed and unusual compared to others of the series. This is very unique to clearly observe the CO, AFM, MI and FM transitions in one sample at zero magnetic field. The T-x phase diagram for Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ and T-H phase diagram for Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ have been drawn on the basis of the temperature and magnetic field dependence of $\rho$, M and C. About 35K apart of MI from FM transition temperature is found at zero magnetic field in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$. In addition, a much smaller specific heat anomaly than expected one is observed in it at T$_C$ and is suppressed by magnetic fields. Through detailed study on $\rho$, M, and C, the electronic and magnetic instability due to spin fluctuations is concluded as the origin of an unusual FM state below T$_{MI}$ in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ at low magnetic fields.
Chapter two: Theory

2.1 Double Exchange:

The parent antiferromagnetic insulator LaMnO$_3$ contains Mn$^{3+}$ ions with $t_{2g}^3e_g^1$ (spin quantum number $S=2$) configuration. The $t_{2g}$ electrons are localized and so can be viewed as local spins with $S=3/2$. In contrast, the $e_g$ electrons are strongly hybridized with the oxygen $2p$ states and change from a localized to itinerant character with oxidation of the MnO$_3$ lattice. An important feature is that strong intra-atomic ferromagnetic (Hung) coupling acts between the $t_{2g}$ spin and $e_g$ electrons, which gives rise to a parallel alignment of their spins. Chemical substitution of La$^{3+}$ by Ca$^{2+}$ introduces holes into the $e_g$ orbitals, that are mobile and mediate an interatomic ferromagnetic interaction between the Mn atoms; the $e_g$ electrons gain kinetic energy through this double-exchange interaction. As suggested by Jonker and Van Santen, it is the migration of these Mn$^{4+}$ ions, accomplished by a Mn$^{4+}$ ion capturing an electron from a neighbor Mn$^{3+}$ ion, that gives rise to electrical conductivity$^{19}$. In compliance with Hund’s rule, the Mn ion is in its configuration of highest multiplicity. Defining $\psi_1$ and $\psi_2$ as follow, the integral is no vanishing only if the spins of the two $d$-shell are parallel.

\[
\begin{align*}
\psi_1: & \text{ Mn}^{3+}\text{O}^2\text{-Mn}^{4+} \\
\psi_2: & \text{ Mn}^{4+}\text{O}^2\text{-Mn}^{3+}
\end{align*}
\]

The lowest energy of the system thus corresponds to a parallel alignment of the two transition of the system corresponds to a parallel alignment of the spins of the two transition metal ions. Now a stationary state is represented by the two linear combinations of $\psi_1$ and $\psi_2$.

\[
\begin{align*}
\psi_+ &= \psi_1 + \psi_2, \\
\psi_- &= \psi_1 - \psi_2.
\end{align*}
\]
\[ \int \psi_1^*(H-\varepsilon_0) \psi_2 d\tau \quad (3) \]

Depending upon the sign of the exchange integral (3), the double exchange raises the energy associated with \( \psi_+ \), lowers the energy with \( \psi_- \), or vice versa. Thus, the energy of one of these two stationary states is lowered by the double exchange which takes place when the \( d \)-shell spins are parallel.

This scheme was proposed by de Gennes as a microscopic origin of the ferromagnetic metallic states in the hole-doped LaMnO\(_3\) perovskite. Very recently, such a strongly spin-charge coupled state has been extensively revisited in light of the observation of a colossal negative magnetoresistive effect. Near the ferromagnetic ordering temperature (\( T_C \)), and external magnetic field can align more or less disordered local spins ferromagnetically. The forcedly spin-polarized conduction electrons (holes) then suffer less from the scattering by local spins and become more itinerant.
2.2 Superexchange Interaction:

Superexchange may be defined as the exchange mechanism taking place in transition-metal salts in which the ions are fairly well separated by normally diamagnetic group, and in which conduction is poor at all normal temperature. Superexchange interaction is always antiferromagnetic and shown to be closely related to the poor conductivity in agree with experiment. In ground state, Mn^{2+} \((3d)^{5}\) and O^{2-} \((2p)^{6}\), the oxygen ions cannot interact with the Mn ions on either side, nor would be the interaction between the two Mn^{2+} ions cause the great distance. By means of crystal field theory, the lattice parameters determining superexchange can be estimated, the exchange integral can be evaluated with accuracy of several tens of percents. There is certain probability of transferring one of the p electrons of oxygen to the Mn^{2+}. In excited state, Mn^{2+} \((3d)^{6}\) and O^{2-} \((2p)^{6}\), the unpaired electrons can interact with Mn^{2+} ions on account of the overlap of the p-orbital with the d-orbital of Mn^{2+}. Spins of magnetic cation are counted indirectly through intervening anions. Superexchange interaction predicts antiferromagnetic phenomena.
Chapter Three: Experimental Details

3.1 Sample preparation:

All samples were prepared by standard solid-state reaction method under identical condition. High-purity powders of Pr$_6$O$_{11}$, SrCO$_3$, CaO and MnO$_2$ were mixed in appropriate proportion. The mixed powders were calcined in air at 900°C for 12 hours, and reground and fired in air at 1200°C for 12 hours. Then, the obtained powder was pressed into pellets and sintered in air at 1350°C for 48 hours. The pellets were taken out and reground and sintered in air at 1350°C for 48 hours with intermediate grindings for two times. Then we got the high quality samples. The flow chart of sample preparation is given in Fig. 3-1.
3.2 Sample Characterization:

X-ray was discovered in 1895 by the Roentfen and were so named because their nature was unknown at the time. It was not until 1912 that the exact nature of X-rays was established, in that year the phenomenon of X-ray diffraction by crystals proved the wave nature of X-rays and provided a new method for investigating the fine structure of matter. The subject of this section is to simply introduce our X-ray system and structural analysis.

We used X-ray diffraction instrument of Siemens D5000 model to characterize the lattice structure of samples. It was carried out $2\theta$ from 20° to 80° at a scanning rate of 0.6° per min by powder X-ray diffraction using Cu Kα radiation. Structure parameters were refined by the Rietvld method, using the program GSAS. Fig. 3-2 is the flowing chart of operating X-ray diffraction measurement. Rocking curve and Detector Scan were used to check and correct the systematic errors each three months.

Lattice parameters were determined using computer program "Generalized Structure Analysis System (GSAS)" with input the X-ray diffraction data. GSAS can work with multiple data sets simultaneously, including mixed powder and single-crystal data. Both soft and hard constraints can be used. It provides for separate determination of crystallite size and microstrain parameters on the basis of order dependence and also model anisotropy in the effects.

During the program running the refined result is better or worse we can know from some indicators listed below.

(1) The Weighted Profile R-Factor:
\[ R_{wp} = \sqrt{\frac{\sum_i \delta_i |I_i(\text{obs}) - I_i(\text{cal})|^2}{\sum_i \delta_i I_i(\text{obs})^2}} \]

(2) The profile R-Factor:

\[ R_p = \frac{\sum_i I_i(\text{obs}) - I_i(\text{cal})}{\sum_i I_i(\text{obs})} \]

(3) The R-expected pattern:

\[ R_E = \sqrt{\frac{N - P + C}{\sum_i \delta_i I_i(\text{obs})^2}} \]

From a purely mathematical point of view, \( R_{wp} \) is the most meaningful of these R’s because the numerator is the residual being minimized. For the same reason, it is also the one that best reflects the progress of the refinement. Another useful numerical criterion is the ‘goodness of fit’, \( \chi^2 \). It is the ratio of \( R_{wp}/R_E \) and a measure of how well the fitted model accounts for the data. A \( \chi^2 \) factor greater than about 2.5 is a strong indication of an inadequate model or a false minimum. In general, we use the value of \( \chi^2 \) to do the judgement.
### 3.3 Electrical resistivity:

We used standard four-probe method (Fig. 3-3) to measure the electrical resistivity from 10K to 300K. We cut a piece of the sample by the diamond cutter and rubbed by abrasive paper to be a rectangular parallelepipeds of approximate dimensions 0.5×1.5×5 mm³. The Pt electric leads were attached on the samples with silver paint contacts. The samples were attached to copper sample holder with thin double face tape to ensure good thermal conductivity and electrical insulation between sample and sample holder.

The cooling system consists of CTI closed cycle refrigerator (10K to 300K) and a RMC-CRYOSYSTEMS series 4000 temperature controller accompanying with D19683-E silicon diode temperature sensor. The measurements were made by constant ac (16 Hz) current with rms amplitude of 0.1-1 mA to eliminate thermoelectric effect. The ac signal is feedbacked by Linear Research LR-400 main autobalance circuits. Resistance data were automatically recorded in PC files by using a PC-LR400 adapter. We used formula of $R=\rho*(l/A)$ to get the resistivity from resistance. Fig. 3-4 is the flowing chart of resistivity measurement.
3.4 High temperature specific heat:

The flowing chart of the measuring processes is shown in Fig.3-6. We will have some illustrations about the details.

(1) Preparation before measurement:

A spot welder was used to make thermocouple junctions and flattened the thermocouple to increase the contact area. We should prepare several pairs of thermocouple and at least one sample holder beforehand. The structure of sample holder is displayed in Fig. 3-5(a). The bases of the four junctions are sapphires that are adhered to the copper ring with dilute GE 7031 varnish (GE 7031 varnish is diluted by 50% methanol and 50% toluene). Both the sapphires and GE 7031 varnish have good thermal conductance, but are electric insulators. Then, we should make sure that the four junctions are all electric insulated to the copper ring. In addition, we should cut and sand the sample into proper size. The thickness of the sample is about 0.1mm to ensure one-dimensional heat flow through the sample.

(2) Sample mounting:

The sample is adhered on the junction of two pairs of thermocouples by applying a little bit amount of glue (GE 7031 varnish or silver paint, usually $< 5 \mu g$). Following, we weld the set of sample and thermocouple on the four junctions of the sample holder with indium. Check the four junctions are electric conducting each other, but insulated to the copper ring one more time. Following, we evaporate a PbS film on the sample front surface. We lock the prepared sample holder to the end of the ac calorimeter probe, and weld the four enamel-insulated wires to the four metallic pins on the annulus with tin solder. Then, checking the four metal pins are electric conducting to each other, but all insulated to the probe. Finally, we vacuum the chamber of the ac calorimeter by mechanical pump for a period of time to increase the
vacuum as better as we can. Last, we put in a little bit of helium gas as exchange gas and by adjusting the vacuum valve, we maintain the gas pressure of the probe about 200 mTorr.

(3) Parameters of the electronic instruments:

a. Function generator: We chose a square wave output to drive the stepping motor.

b. Halogen lamb housing: We can adjust the four adjustments on the lamb housing (shown in the Fig. 3-7.) until the ac signal that shown on the monitor of the lock-in amplifier arrives maximum.

c. Keithley 182: When we turn on the power, we set the Range on Auto.

d. Lock-in amplifier (SR830): Following is the parameters of the measurement.

   Time constant: 3s, 12dB, sync
   Sensitivity: 500 μV (It can be adjusted with the magnitude of V_{AC})
   Signal Input: A channel, DC, Float
   Reserve: Low noise
   Filters: line (for 60Hz), 2xline (for 120Hz)
   Channel One: R, X
   Channel Two: \( \theta \), Y
   Reference: Freq, NEG EDGE (or POS EDGE)

e. Computer (Labview software): Setting cooling or warming and adjusting the increment (0.05,0.1 or 0.2 K/point) as we need. General speaking, we chose 0.1K/point as the increment as measuring condition, but if there is phase transition existed, we should take denser data in the vicinity of the temperature that phase
transition happened, so we chose 0.05K/point.

(4) By adjusting the chopping frequency f, we should find the proper range of chopping frequency so that \( f \cdot V_{AC} = \) constant for our measurements.

(5) Formulas of the collected data and the relative specific heat \( C_P \):

Because the thermoelectric power of thermocouple has different temperature dependence, we divide the temperature range into three portions: \(< 40K, 40K\sim100K \) and \( > 100K \). When we get the average increment of sample temperature, \( V_{DC} \), from Keithley 182, we substitute the data into the formulas,* and we get the real temperature increments \( T_{DC} \). By the same token, \( V_{AC} \), the vibration of the sample temperature reading from lock-in amplifier can be transformed into real temperature difference, \( T_{AC} \). Hence, the temperature of the sample \( T_S \) is equal to the summation of \( T_B \) (reading from the temperature controller ITC503), \( T_{DC} \) and \( T_{AC} \). From the definition of specific heat, we can get the relative specific heat \( C_P \). \( (C_P = \frac{0.001}{T_{AC}}) \)

*The formulas of the transformation: \( (D_V \) is the thermoelectric power of thermocouple.)

\[ \begin{align*}
\text{T}_B < 40K: & \quad D_V = 0.00095452451 + 1.5 \times 0.00062137836 \times T^2 + 2 \times 0.00013234848 \times T + \\
& \quad 1.1139668 \times 10^{-23} \times \exp(T)
\end{align*} \]

\[ \begin{align*}
\text{40K} < \text{T}_B < \text{100K}: & \quad D_V = 0.068685698 + 3 \times 1.242889 \times 10^{-7} \times T^2 - 0.5 \times 0.0610023 \times T^3 + 1.2053819 \times 10^{-1}
\end{align*} \]

\[ \begin{align*}
\text{T}_B > 100K: & \quad D_V = 0.022640596 + 2.5 \times 0.000082627279 \times T^{1.5} - 3 \times 0.00000025168507 \times T^2 - \\
& \quad 0.5 \times 8.6780185 \times T^{-1.5}
\end{align*} \]

\[ \begin{align*}
\text{T}_{DC} = \frac{V_{DC}}{D_V}, \quad T_{AC} = \frac{V_{AC}}{D_V}, \quad T_S = T_B + T_{DC} + T_{AC}, \quad C_P = \frac{0.001}{T_{AC}}
\end{align*} \]
3.5 X-ray absorption near-edge structure spectra (XANES) technique

There are ultimate outstanding characters for synchrotron radiation for X-ray absorption spectrum including continuous wavelength, wild and modified photon energy range, high photon flux, well focused, and accurate aligned photon source. X-ray absorption near edge structure spectra (XANES) using synchrotron radiation is a powerful tool for the investigation of unoccupied electronic states in complex materials. XANES spectra can give information on local intensity also.

Our X-ray absorption measurement were recorded using 6-m high-energy spherical grating monochromator (HSGM) beamline of Synchrotron Radiation Research Center (SRRC) in Hsing-Chu, Taiwan. The general design feature of 6m-HSGM beamline is accessible for high photon flux around 1000eV photon energy region. The measured photon flux is shown in Fig. 3-8 with both slit (S1 and S2) 100 \( \mu \) m open for four separated grating density( 400, 700, 1200, 1800 1/mm). We measured Mn 2p-edge (635~665ev) an absorption spectrum with 1200 1/8mm grating density and slit 40x40 in this work. The designed parameters and accessible experiments for 6m-HSGM beamline are listed in table [3.1].
3.6 Low temperature specific heat System:

The aim of this section is to describe the principles and procedures associated with a He$_3$ relaxation calorimeter using the heat-pulse technique. At first, the principle of operation will be discussed in general terms. Second part is the detailed process of mounting and demounting samples, which is the most important procedure in order to obtain the best results. Following is the structure of sample platform, then is thermometry by far the most important experimental aspect of calorimetry. Finally, we talk about the measurement process and troubleshooting of the calorimeter.

Figure. 3-9 is the setup of the specific heat system.

Figure. 3-10 is the schematic diagram of the insert of the calorimeter.

I. Principle of operation

Traditional (adiabatic) calorimeter involves supplying a thermally isolated sample with a known amount of heat and measuring the change in its temperature. The heat capacity is then directly obtained as the quotient of the temperature change and the heat input, $C = \frac{\Delta T}{\Delta \Theta}$. The measurement requires that the sample is sufficiently well isolated that heat losses are small enough to be ignored, or at least corrected for, on the time scale of the measurement. This condition is generally impracticable at cryogenic temperatures and alternative techniques must be employed.

The calorimetry technique used here is known as the time-constant or relaxation method. It consists of changing step-wise the power supplied to the sample. Associated with the new power level is a new equilibrium temperature at which the rate of heat loss to the surroundings again matches the rate of heating. The chip temperature will decay exponentially towards this new level according to

$$T = T_1 + \Delta T_0 (1 - e^{-\frac{t}{\tau}}),$$

where $T_1$ is the initial temperature, and $T_1 + \Delta T_0$ is the final equilibrium temperature. Alternatively, this can be written as
\[ \Delta T = \Delta T_0 \left(1 - e^{-\frac{t}{\tau}} \right) \]

where \( \Delta T \) is the change in temperature, \( T - T_1 \).

The variations of heater power and chip temperature are sketched in figure 3-8. The time, \( \tau \), is the product of the heat capacity of the chip and the effective thermal resistance between the sample and its surroundings.

\[ \tau = R_{TH} C \]

The thermal resistance is obtained from the relation

\[ R_{TH} = \frac{\Delta T_0}{\Delta P} . \]

Note that this quantity, considered infinite in the adiabatic case, now becomes an integral part of the measurement. The heat capacity can then be calculated as

\[ C = \frac{\tau}{R_{TH}} . \]

If the temperature increment is small compared with \( T_1 \), then the heat capacity is approximately that of the sample at the initial temperature, \( T_1 \). In order to perform this measurement, it is necessary to have a means of supplying heat to the sample and of measuring its temperature. In addition, the sample must be reasonably well isolated thermally from its surroundings so that its thermal time constant is not too small. The heater and thermometer should have a small heat capacity compared with that of the sample in order to minimum errors due to addenda subtraction. They must also be in intimate thermal contact with the sample so that they all act as one thermal unit.
3.7 Magnetoresistance and Magnetization:

The measurements of Magnetoresistance (MR) and Magnetization (M) were performed in National Chiao Tung University by the commercial superconducting quantum interference (SQUID) magnetometer between room temperature (300K) and 10K with applied magnetic fields up to 8T. I very appreciate the help of S. J. Liu in Department of Electrophysics, National Chiao Tung University, and P. C. Chung and Dr. J. -Y. Lin in Institute of Physics, National Chio Tung University.
Pr₆O₁₁, SrCO₃, CaO, MnO₂ were mixed in appropriate proportions, and grinding.

Calcine the powder in air at 900°C for 12 hours.

Grind and calcine the powder in air at 1200°C for 12 hours.

Grind and press into a pellet, the calcine the pellet in air at 1350°C for 48 hours.

Grind and press into a pellet, the calcine the pellet in air at 1350°C for 48 hours. Repeat one time.

Cool down to room temperature at the rate of 4 °C per min.

Fig. 3.1 Flowing chart of sample preparation.
Load the lattice structure and the element composition

Prepare X-ray diffraction sample

Simulate CMPR program in computer

Operate the X-ray diffraction instrument

Standard lattice structure

X-ray diffraction pattern

Compare the diffraction plane (h k l) and diffraction angle (2θ)

Refined the structure by GSAS program

If ERROR FIT < 2.5 then output the result

Fig. 3-2. Flowing chart of operating X-ray diffraction measurement and parameters calculation.
Fig. 3-3. Schematic diagram of resistivity specimen.
Fig. 3-4. Flowing chart of resistivity measurement.
Fig. 3-5. The structure of sample holder.
Vacuum Dewar flask
Weld thermocouple
Cut and sand sample

Adhere sample on thermocouple

Prepare sample holder

Mount sample and thermocouple on sample holder

Lock the prepared sample holder to the end of ac calorimeter and vacuum it

Put in the exchange gas (He) and maintain vacuum about 200mTorr

Put the probe into Dewar flask and connect all of the

Transfer liquid helium into Dewar flask

Adjust the strength of helogen light to the $V_{AC}$ maximum

Choose the proper chopping frequency for $f \cdot V_{AC} = \text{constant}$

Start measurement with zero magnetic field

Apply magnetic field

Start measurement

Fig. 3-6. Flowing chart of specific-heat measurement.
Fig. 3-7. One can slide the inner lens barrel forward or backward to adjust
Fig. 3-8. The measured photon flux of 6m-HSGM beamline
Fig. 3-9. Schematic diagram of instruments in the Specific-Heat.
Fig. 3-10. Schematic diagram of the insert of the calorimeter.
Table 3.1 General design feature and accessible experiments of 6m-HSGM beamline in SRRC.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arm Length S1 - G (cm)</td>
<td>172.0</td>
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<tr>
<td></td>
<td>G - S2 (cm)</td>
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<tr>
<td>Horizontal Acceptance Angle (mrad)</td>
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<tr>
<td>Total Power (W)</td>
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</tr>
<tr>
<td>Slits' Width S1 (µm)</td>
<td>5 - 2000</td>
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<tr>
<td></td>
<td>S2 (µm)</td>
</tr>
<tr>
<td>Gratings</td>
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</tr>
<tr>
<td>Groove Density (l/ mm)</td>
<td></td>
</tr>
<tr>
<td>Scanning Range λ (Å)</td>
<td></td>
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<tr>
<td>E (eV)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 - 110</td>
</tr>
<tr>
<td></td>
<td>110 - 310</td>
</tr>
<tr>
<td>Resolution (S1 = S2 = 10 µm)</td>
<td></td>
</tr>
<tr>
<td>Δλ (Å)</td>
<td>0.014 - 0.020</td>
</tr>
<tr>
<td>ΔE (meV)</td>
<td>21 - 106</td>
</tr>
<tr>
<td>Throughput (max) x 10⁹ (photons/sec,mrad,200mA,0.1%BW)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(S1 = S2 = 10 µm)</td>
</tr>
<tr>
<td>Beam Size at Sample (mm x mm)</td>
<td>&lt; 1.5 x 1.0 (S1 = S2 = 10 µm)</td>
</tr>
<tr>
<td>Accessible Experiments</td>
<td>Absorption Spectroscopy</td>
</tr>
<tr>
<td></td>
<td>Photoemission</td>
</tr>
<tr>
<td></td>
<td>Microscopy</td>
</tr>
<tr>
<td></td>
<td>* EXAFS Spectroscopy</td>
</tr>
<tr>
<td></td>
<td>** SXES</td>
</tr>
</tbody>
</table>

* EXAFS : Extended X-ray Absorption Fine Structure
** SXES : Soft X-ray Emission Spectroscopy
Chapter Four: Experimental results

We investigated the Pr$_{1-x}$Ca$_x$MnO$_3$ perovskite manganites to know which composition is the best choice to interplay of DE interaction and charge/orbital ordering. Finally we confirmed the Pr$_{0.65}$(Ca$_{0.35-x}$Sr$_x$)MnO$_3$ is the answer. With the systematic study, the bandwidth controlled system revealed many interesting phenomenon about the competition of DE and CO. Special emphasis has been given on the discussion of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ which is very unique to observe the CO, AFM, MI and FM transitions in one sample at zero magnetic field.

4.1 Pr$_{1-x}$Ca$_x$MnO$_3$ system:

In order to study the CO transition, we performed the resistivity ($\rho$) and heat capacity (C) measurements as a function of temperature of the Pr$_{1-x}$Ca$_x$MnO$_3$ system. The data of resistivity was obtained by the standard four-terminal method. The relative specific heat data is taken by ac calorimetry. The sample is sanded to a thickness of about 0.2mm to ensure one-dimensional heat flow through the sample.

The powder X-ray diffraction (XRD) patterns for Pr$_{1-x}$Ca$_x$MnO$_3$ system with 0.3 and 0.4 are shown in Fig. 4-1. All samples were identified to be single phase within our experimental resolution. X-ray diffraction data was consistent with an orthorhombic cell, space group Pbnm. The temperature dependence of $\rho$ and C are shown in Fig. 4-2 and Fig. 4-3.

4.2 Pr$_{0.65}$(Ca$_{0.35-x}$Sr$_x$)MnO$_3$ system:

Figure. 4-4. shows the XRD patterns of Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0-0.35) samples. The structures of the series show a single phase within our experimental resolution. XRD data were consistent with an orthorhombic cell, space group Pbnm. The
refinement of the XRD patterns was carried out by the GSAG program. The plot of the observed (crosses) and fitted (solid curves) diffraction patterns for Pr\textsubscript{0.65}Ca\textsubscript{0.35-x}Sr\textsubscript{x}MnO\textsubscript{3} (x=0-0.35) samples are shown in Fig. 4-5 to Fig. 4-14. The structural parameters vs. Sr-concentration for Pr\textsubscript{0.65}Ca\textsubscript{0.35-x}Sr\textsubscript{x}MnO\textsubscript{3} are plotted in Fig. 4-15, the lattice parameters a, b, and c* vs. Sr-concentration is displayed with different symbols, where c*=c/\sqrt{2}.

Temperature variation of $\rho$ and C of Pr\textsubscript{0.65}Ca\textsubscript{0.35-x}Sr\textsubscript{x}MnO\textsubscript{3} (x=0-0.35) perovskite manganites is illustrated in Fig.4-16 and Fig. 4-17. The profiles of the magnetization vs. temperature of x=0, 0.5, 0.1, and 0.35 are shown in Fig. 4-18 (a) to Fig. 4-18 (d).

Figure. 4-19 shows the Mn 2p-edge (635~665ev) spectrums of the Pr\textsubscript{0.65}Ca\textsubscript{0.35-x}Sr\textsubscript{x}MnO\textsubscript{3} (x=0, 0.05, 0.1, 0.15, and 0.35) together with Mn\textsuperscript{3+} and Mn\textsuperscript{4+}.

The magnetoresistance of the polycrystalline of Pr\textsubscript{0.65}Ca\textsubscript{0.35-x}Sr\textsubscript{x}MnO\textsubscript{3} (x=0, 0.05 , 0.075, 0.1, 0.0125, 0.2, and 0.35) series for cooling process has been investigated in the range of 10$\leq$T$\leq$300K and 0$\leq$H$\leq$8T that is shown in Fig.4-20 to 26.

The magnetoresistance of the polycrystalline of Pr\textsubscript{0.65}Ca\textsubscript{0.35-x}Sr\textsubscript{x}MnO\textsubscript{3} (x=0, 0.05 , 0.075, 0.1, 0.0125, 0.2, and 0.35) series for cooling and warming processes has been investigated in the range of 10$\leq$T$\leq$300K and 0$\leq$H$\leq$5T that is shown in Fig.4-27 to 33.

The temperature dependence of magnetization (M) under 0.1T and 8T of the x=0, and 0.05 samples are shown in Fig. 4-34 and Fig. 4-35The CO of x=0.05 sample is completely melted under 8T from the result of magnetization.

The profiles of magnetization vs. H at the constant temperature (T=10, 70, and 300K) of the x=0 sample are shown in Fig. 4-36(a) to (c).

The profiles of magnetization vs. H at the constant temperature (T=10, and 300K) of the x=0.05 and x=0.1 samples are shown in Fig. 4-37 and 38.

Finally we compared the $\rho$(H) and M(H) of x=0, 0.05, and 0.1 samples at 10K in
In order to compare with the behavior of typical ferromagnetic CMR like the Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ sample. We measured the magnetization as a function of temperature for cooling process at different magnetic fields (H=0, 0.1, 1, 2, 3, and 5T) of the Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ sample and presented in Fig.4-42. Basically, the sample does not have any hysteresis. Figure. 4-43 shows that the $\rho(H)/\rho(0)$ vs. H bellow 0.3Tesla at different temperature (T=290, 295, 300K).

4.3 Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ :

The Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ sample is the most interesting one in the Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ system. We performed the magnetization vs. temperature in the range of $0 \leq H \leq 8$T show that in Fig. 4-44. The M vs. T of ZFC and FC under 100Oe is shown in Fig. 4-45. Figure. 4-46 shows that the M vs. T for $H_{DC}$ is 0Oe and $H_{AC}$ is 1Oe and the frequency is 500Hz. We performed relative specific heat data as a function of temperature under magnetic fields and the results are shown in Fig. 4-47. The absolute low temperature specific heat data below 60 K was taken by heat pulse calorimetry. We combined the result with the high temperature relative specific heat data the C vs. T from 0.6K to 300K at zero field is shown in Fig. 4-48. Figure.4-49 shows the C/T vs. T curves for Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ sample at different magnetic fields (0-2T). The FM transition temperature ($T_C$) and the data during cooling and warming are indicated by arrows. The inset shows the absolute C/T vs. T of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ sample measured by HPTR calorimeter at zero field.

Figure.4-50 shows the $\rho(H)/\rho(0)$ vs. H bellow 0.3Tesla at different temperature (T=70, 75, 90K).

Finally we measured the hydrostatic pressure (P) dependent ac magnetic susceptibility
$(\chi_{ac})$ for Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ sample at warming temperature from 80 to 280K and show that in Fig. 4-51.
Fig. 4-1. The powder X-ray diffraction patterns for the \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \) system (\( x=0.3-0.4 \)).
Fig. 4-2. The temperature dependence of resistivity of the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system ($x=0.3-0.4$).
Fig. 4-3. The temperature dependence of C of the Pr$_{1-x}$Ca$_x$MnO$_3$ system (x=0.3-0.4).
Fig. 4-4. The powder X-ray diffraction patterns for the Pr$_{0.65}$(Ca$_{0.35-x}$Sr$_x$)MnO$_3$ system (x=0-0.35).
Fig. 4-5. Refine of the XRD pattern of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$. 
Fig. 4-6. Refine of the XRD pattern of Pr_{0.65}Ca_{0.3}Sr_{0.05}MnO_{3}.
Fig. 4-7. Refine of the XRD pattern of Pr_{0.65}Ca_{0.275}Sr_{0.075}MnO_3.
Fig. 4-8. Refine of the XRD pattern of $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$. 
Fig. 4-9. Refine of the XRD pattern of Pr$_{0.65}$Ca$_{0.225}$Sr$_{0.125}$MnO$_3$.
Fig. 4-10. Refine of the XRD pattern of $\text{Pr}_{0.65}\text{Ca}_{0.22}\text{Sr}_{0.15}\text{MnO}_3$. 
Fig. 4-11. Refine of the XRD pattern of $\text{Pr}_{0.65}\text{Ca}_{0.15}\text{Sr}_{0.2}\text{MnO}_3$. 
Fig. 4-12. Refine of the XRD pattern of Pr$_{0.65}$Ca$_{0.1}$Sr$_{0.25}$MnO$_3$. 
Fig. 4-13. Refine of the XRD pattern of Pr$_{0.65}$Ca$_{0.05}$Sr$_{0.3}$MnO$_3$. 
Fig. 4-14. Refine of the XRD pattern of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$. 
Fig. 4-15. The lattice parameters $a$, $b$, and $c^*$ vs. $x$ of the $Pr_{0.65}(Ca_{0.35-x}Sr_x)MnO_3$ ($c^* = c/\sqrt{2}$).
Fig. 4-16. The temperature dependence of resistivity of the 
$Pr_{0.65}(Ca_{0.35-x}Sr_x)MnO_3$ $(x=0-0.35)$ system.
Fig. 4-17. The temperature dependence of specific heat of the Pr$_{0.65}$(Ca$_{0.35-x}$Sr$_x$)MnO$_3$ (x=0-0.35) system.
Fig. 4-18. The profiles of the magnetization vs. temperature of
Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0, 0.05, 0.1, and 0.35).
Fig. 4-19. Mn 2p-edge Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0, 0.05, 0.1, 0.15, and 0.35)
Fig. 4-20. Magnetoreistance vs. T of the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ in the range of 0≤H≤8T for cooling process.
Fig. 4-21. Magnetoreistance vs. T of the Pr$_{0.65}$Ca$_{0.3}$Sr$_{0.05}$MnO$_3$ in the range of 0≤H≤8T for cooling process.
Fig. 4-22. Magnetoreistance vs. $T$ of the $\text{Pr}_{0.65}\text{Ca}_{0.275}\text{Sr}_{0.075}\text{MnO}_3$ in the range of $0\leq H \leq 5\text{T}$ for cooling process.
Fig. 4-23. Magnetoresistance vs. T of the Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ in the range of 0≤H≤8T for cooling process.
Fig. 4-24. Magnetoresistance vs. T of the Pr$_{0.65}$Ca$_{0.225}$Sr$_{0.125}$MnO$_3$ in the range of 0≤H≤5T for cooling process.
Fig. 4-25. Magnetoreistance vs. T of the Pr₀.₆₅Ca₀.₂Sr₀.₁₅MnO₃ in the range of 0 ≤ H ≤ 5T for cooling process.
Fig. 4-26. Magnetoreistance vs. T of the Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ in the range of 0≤H≤5T for cooling process.
Fig. 4-27. MR vs. T of the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ for cooling and warming processes (H=0, and 5T).
Fig. 4-28. MR vs. T of the $\text{Pr}_{0.65}\text{Ca}_{0.3}\text{Sr}_{0.05}\text{MnO}_3$ for cooling and warming processes ($H=0$, 2, 3, and 5T).
Fig. 4-29. MR vs. T of the Pr$_{0.65}$Ca$_{0.275}$Sr$_{0.075}$MnO$_3$ for cooling and warming processes (H=1, 2, 3, and 5T).
Fig. 4-30. MR vs. T of the Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_{3} for cooling and warming processes (H=0, 1, 2, and 3T).
Fig. 4-31. MR vs. $T$ of the Pr$_{0.65}$Ca$_{0.225}$Sr$_{0.125}$MnO$_3$ for cooling and warming processes ($H=0$, 0.5, 1, and 2T).
Fig. 4-32. MR vs. T of the Pr$_{0.65}$Ca$_{0.2}$Sr$_{0.15}$MnO$_3$ for cooling and warming processes (H=0, 0.5, 1, and 2T).
Fig. 4-33. MR vs. T of the \( \text{Pr}_{0.65}\text{Sr}_{0.35}\text{MnO}_3 \) for cooling and warming processes (H=0, 0.5, 1, and 2T).
Fig. 4-34. M vs. T of the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ for cooling processes (H=0.1, and 8T).
Fig. 4-35. $M$ vs. $T$ of the Pr$_{0.65}$Ca$_{0.3}$Sr$_{0.05}$MnO$_3$ for cooling processes ($H=0.1$, and 8T).
Fig. 4-36. $M$ vs. $H$ of the $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ for $T=10$, 70, and 300K.
Fig. 4-37. $M$ vs. $H$ of the $\text{Pr}_0.65\text{Ca}_{0.3}\text{Sr}_{0.05}\text{MnO}_3$ for $T=10$, and $300\text{K}$. 
Fig. 4-38. M vs. H of the Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ for T=10, and 300K.
Fig. 4-39. M and log$p$ vs. $H$ of the $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ at $T=10$K.
Fig. 4-40. $M$ and $\log \rho$ vs. $H$ of the $\text{Pr}_{0.65}\text{Ca}_{0.3}\text{Sr}_{0.05}\text{MnO}_3$ at $T=10\text{K}$. 
Fig. 4-41. M and $\log p$ vs. H of the Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ at T=10K.
Fig. 4-42. The temperature dependence of magnetization of the Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ sample for H=0.1, 1, 2, 3, and 5T.
Fig. 4-43. $\rho(\mathcal{H})/\rho(0)$ vs. $\mathcal{H}$ of the Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ for $T=290$, 295, 300K.
Fig. 4-44. The magnetization vs. temperature in the range of 0≤H≤8T of Pr$_{0.65}$Ca$_{0.35}$Sr$_{0.1}$MnO$_3$. 
Fig. 4-45. The magnetization vs. temperature under ZFC and FC under 100Oe of Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$. 
Fig. 4-46. The $M$ vs. $T$ for $H_{DC}$ is 0Oe and $H_{Ac}$ is 1Oe and the frequency is 500Hz of $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$. 
Fig. 4-47. C vs. T under magnetic fields (H=0, 1, 2, 2.5, 3, 4, and 8T) of $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$. 
Fig. 4-48. C vs. T at zero-field in the range of $0.6 \leq T \leq 300$K of $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$. 

$\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$
Fig.4-49. C/T vs. T curves for Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3 sample at different magnetic fields (0-2T). The FM transition temperature (T_C) and the data during cooling and warming are indicated by arrows. The inset shows the absolute C/T vs. T of Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3 sample measured by HPTR calorimeter at zero field.
Fig. 4-50. $\rho(0)$ vs. $H$ bellows 0.3 Tesla at the temperature $(T=70, 75, 90\text{K})$ of $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$. 
Fig. 4-51. Hydrostatic pressure (P) dependent ac magnetic susceptibility ($\chi_{ac}$) for $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$ sample measured at warming temperature from 80 to 280K.
Chapter Five: Discussions

We investigated the temperature dependence of resistivity and specific heat of Pr_{1-x}Ca_xMnO_3 and showed that in Fig. 4-2 and Fig. 4-3. When x = 0.4–0.35, the corresponding T_{CO} is 227–215K and the T_N is 165~160K. The behavior of the CO transition in specific heat of the x=0.325 sample is very weak and the peak is not obvious as the samples of x≥0.35. When x deceases to 0.3, there is not any distinguishable transition observed in the C data. We know that the CO state is most stabilized for x=0.5^{27} and destabilizes with the decreasing of x. When x≤0.3, the CO transition will vanish, and it means that x=0.3 is the boundary of the CO transition. With a carefully inference, we confirm that the x=0.35 is the best choice to study the interplay of DE interaction and charge/orbital ordering. Because the behavior of the CO and AFM transitions of Pr_{0.65}Ca_{0.35}MnO_3 are very clear in C and ρ, and the CO is not so strong as x≥0.35. We can study the interplay of CO and DE by Sr-substitution or applying magnetic field.

5.1 Pr_{0.65}(Ca_{0.35-x}Sr_x)MnO_3:

In order to unravel the mystery of the unusually CMR materials, arises due to the interplay of DE interaction and charge/orbital ordering, we should distinguish the contribution of the size effect from the valence effect. From the point of view of single-band conduction, the two parameters defining this relationship are band filling and band width (W). Substitution of Ca by Sr in Pr_{0.65}Ca_{0.35}MnO_3 increases the one electron bandwidth in terms of the lessening of lattice distortion and maintains the ratio of the Mn^{4+}/Mn^{3+}. The lattice parameters a, b, and c(c^*) are presented in Fig. 4-15. The average ionic radii of (R, A) increase with the increase of the Sr
concentration in the $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ perovskites, the Mn-O-Mn bond angle distortion decreases and accordingly the one electron bandwidth should increase. The behavior may be explained on the basis of the tolerance factor, defined as $(r_A + r_O)/2(r_B + r_O)$, where $r_A$, $r_B$, and $r_O$ are, respectively, the ionic radii of the A, B cations and oxygen in the ABO$_3$ structure. The tolerance factor increases with the raising x. An increase in the tolerance factor amounts to a decreasing distortion in the structure.

Figure 4-19 shows the Mn 2p-edge X-ray absorption near edge structure (XANES) for the $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ (x=0, 0.05, 0.1, 0.15, 0.35) samples. For comparison, the XANES spectra of MnO$_2$ (Mn$^{4+}$) and Mn$_2$O$_3$(Mn$^{3+}$) are also plotted in the figure. All spectra show two broad multiple structures separated by the Mn 2p$_{3/2}$-Mn 2p$_{1/2}$ spin-orbit splitting. The chemical shift is caused by the changes in the electrostatics energy at Mn site driven by the variation of the ion valence in the compounds. Based on our results, the position of Mn 2p$_{3/2}$ peaks of $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ samples are between those of Mn$^{3+}$ and Mn$^{4+}$, and the positions were independent of x. This result proves that the Mn$^{4+}$/Mn$^{3+}$ ratio of $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ samples is independent of Sr-concentration.

Figure 4-16 shows the logρ vs. T curves for the $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ (x=0-0.35) perovskite manganites in absence of external magnetic fields. The change from an antiferromagnetic charge/orbital ordered insulator at x=0 to a double exchange ferromagnetic metal at x=0.35 is observed. The samples for x=0-0.075 demonstrate the semiconducting behavior at all the temperature range. While the remaining samples (for x=0.1-0.35) reveal semiconducting behavior first and is followed by a metallic one due to MI transition with the decrease of temperature. The MI transition temperature (TMI) increases with the increase of x. Samples of x=0 to 0.15 exhibit CO
insulating state having a decrease of $T_{CO}$ with the increase of $x$. An abrupt drop of resistivity is perceived due to MI transition in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ (for $x=0.1$) at $T_{MI} \approx 80$K. Similar MI transitions are also observed in Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ at high magnetic fields of 5T which is shown in Fig. 4-20. According to the DE mechanism, the MI transition temperature $T_{MI}$ coincides with the ferromagnetic transition temperature $T_C$, and these transition temperatures are controlled by the Mn valence. However, recent experimental results have shown that $T_C$ and $T_{MI}$ do not necessarily coincide in some CMR compounds$^{32}$. Figure 4-18 shows the temperature dependence of magnetization ($M$) of Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ for $x=0$, 0.05, 0.1 and 0.35 at a fixed magnetic field of 1000 Oe. For $x=0$ to 0.1, the peaks of charge ordering and antiferromagnetic transitions are similar to the results of $C$ vs. $T$. The ferromagnetic transition ($T_C \approx 290$K) of $x=0.35$ in magnetization is also corresponding to the peak of FM transition in $C$ data. Most of these results are consistent, besides the $T_{MI}$ of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ manganite. The $T_{MI}$ does not coincide with the temperature of saturation in magnetization at $H=0.1$T. As the temperature is decreased, the $M$ starts increasing at $T_{MI}$ and becomes saturated below $T_C$. The changes of $M$ for $x=0.1$ and 0.35 samples (Figs. 4-18c and d) are considerably large ($0$ to 29 emu/g for $x=0.1$ and 0 to 50 emu/g for $x=0.35$) because of ferromagnetic transitions. However, it should be noted that the proliferation of $M$ at low temperatures for samples of $x=0$ and 0.05 (Figs. 4-18a and b) may not be associated with a commonly ferromagnetic ordering since the changes of $M$ are too small ($0.2$ to 0.75 emu/g for $x=0$ and 0.4 to 1.9 emu/g for $x=0.05$) compared to those of $x=0.1$ and 0.35 samples. This is moreover confirmed from the magnetic field dependent resistivity of these samples where MI transitions are not attained with the application of such a low magnetic field (1000 Oe) at all temperatures. The variation of specific heat ($C$) with temperature (80-300K) in the absence of magnetic...
field for Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0-0.35) perovskites is demonstrated in Fig. 4-17. There are clearly two groups among the curves i.e. one for x=0-0.125 and the other for x=0.15-0.35. In the former group, both CO and AFM anomalies are clearly detected and are shifted correspondingly towards lower and higher temperatures with the increase of x. Conversely, only the FM anomalies are detected in the latter group which moves towards higher temperatures with the rise of x. Here it should be mentioned that though the sample with x=0.1 shows sharp MI transition at $T_{M1}$ ~ 80K (Fig. 4-16), no pronounced anomaly in C at $T_{M1}$ is detected (for clarity, see Fig. 4-48).

The phase diagram (T-x) for the Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ series is drawn shown in Fig. 5-1, on the basis of the temperature variation of $\rho$, M and C (Fig. 4-16 to 18), where paramagnetic insulating (PMI), charge-ordered insulating (COI), antiferromagnetic insulating (AFMI) and ferromagnetic metallic (FMM) regions are clearly indicated. We denote FM*M as an unusual FMM state in the range of 0.1≤x≤0.15. Because the existence of shaded area (unusual ferromagnetic metallic state) at zero magnetic field is quite unique, the particular sample in this region with x=0.1 (Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$) is specially chosen for further studies to investigate its uniqueness from others of the series as followings.

The advantage in our experiments is that the ac calorimetry can directly investigate the phase transition from the relative specific heat. Actually this is the first evidence of phase transition and we can make sure the temperature of transition directly.

After an advanced study on cooling processes of magnetoresistance (MR) of the Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0, 0.05, 0.075, 0.1, 0.125, 0.2, and 0.35) series, the MR vs. T under different magnetic field are shown in Fig. 4-20 to 26. First of all, we reexamine our thorough data on resistivity of Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ samples to show
its magnetoresistance ratio, \( \text{MRR} = -[\rho(H) - \rho(0)]/\rho(0) \), with \( \rho(0) \) and \( \rho(H) \) being the resistivities at 0 and H magnetic fields respectively. It is fascinating that the maximum MRR for it at \( T=70 \text{K} \) (near its \( T_{\text{MI}} \)) is very high at low magnetic fields and is 50, 80 and 99% correspondingly at 0.1, 0.2 and 0.5 T. To demonstrate how an enormous enhancement of MRR happens in this particular sample at low magnetic fields below its MI transition temperature, we plot \( \text{MRR}_{\text{max}} \) vs. \( x \) in Fig. 5-2 for the Pr\(_{0.65}\)Ca\(_{0.35-x}\)Sr\(_{x}\)MnO\(_3\) series at low magnetic fields of 0.1, 0.2 and 0.5T. It evidently shows that the highest \( \text{MRR}_{\text{max}} \) occurs at the vicinity of \( x \sim 0.1 \) at all magnetic fields. For supplementary performing the comprehensive of magnetoresistance data at low magnetic fields, the resistivity ratio vs. low magnetic fields for samples Pr\(_{0.65}\)Ca\(_{0.25}\)Sr\(_{0.1}\)MnO\(_3\) and Pr\(_{0.65}\)Sr\(_{0.35}\)MnO\(_3\) near their respective MI transition temperatures 70 and 295K is shown in Fig. 5-3. The resistivity ratio of the former decreases (i.e. MRR increases) rapidly with the increase of magnetic fields while that of the latter (typical CMR is observed at high magnetic fields \( \sim 5\text{T} \)) changes very little. This may be explained by that the Pr\(_{0.65}\)Ca\(_{0.35}\)MnO\(_3\) exposes an insulating behavior (with \( T_{\text{CO}} \sim 215\text{K} \)) at all temperatures while Pr\(_{0.65}\)Sr\(_{0.35}\)MnO\(_3\) reveals the metallic behavior with MI transition near room temperature, \( T_{\text{MI}} \sim 290\text{K} \) (Fig. 4-16). Thus a competition of a charge ordered insulating state and a ferromagnetic metallic state is accomplished in Pr\(_{0.65}\)Ca\(_{0.35-x}\)Sr\(_{x}\)MnO\(_3\). Hence by means of appropriate doping, a particular unstable mixing phase of a weak CO insulating at high temperatures and an unusual ferromagnetic metallic (FM\(^*\)M) at low temperatures is obtained for samples with \( x \sim 0.1 \). Therefore, the application of a low magnetic field (\( \leq 0.5\text{T} \)) on the sample with \( x=0.1 \) is enough to partially melt the charge ordering phase and enhance the ferromagnetic metallic state. Hence, the large enhancement of MRR for Pr\(_{0.65}\)Ca\(_{0.25}\)Sr\(_{0.1}\)MnO\(_3\) indicates its electronic and magnetic instability below its \( T_{\text{MI}} \) at
low magnetic fields.

As we mentioned before, the interplay of DE interaction and charge/orbital ordering can be tuned by changing the radius of rare/alkaline earth metals and applying electric/magnetic fields. Through out the magnetoresistance of the polycrystalline of Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ shown in Fig.4-20 to 26 and the temperature dependence of M of the x=0, 0.05, 0.1, 0.35 samples shown in Fig. 4-34, 35, 42, and 44, we can confirm the effect of Sr-doping is equivalent to application of magnetic field. In order to have a clearly comparison, we combine the magnetoresistance of x=0-0.1 for cooling process in Fig. 5-4. This picture makes us realize the Sr-doping destroys he stability of the charge ordering and induces the DE. The effect of the Sr substitution on the charge ordered state of Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ is equivalent to the application of magnetic field on Pr$_{0.65}$Ca$_{0.35}$MnO$_3$.

This competition also compels the system to have some interesting phenomena like magnetic and thermal hysteresis of resistivity and magnetization. From the magnetoresistance of the polycrystalline of Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0-0.35) series for cooling and warming processes shown in Fig.4-27 to 33, we can find that the MI transition occurs accompanied with the happening of hysteresis. The hysteresis loop is decreased with the increase of magnetic filed and disappears when the magnetic field is high enough to induce the DE ferromagnetic state. Figure 4-36 and 37 show the thermal hysteresis loop in M of x=0 and 0.05. We can see the hysteresis loop appears at the temperature below T$_{CO}$. The origin of thermal hysteresis in M is the field-induced structural change,$^{12,13}$ and a clearly hysteresis is observed during the increase and decrease of an external magnetic field at a fixed temperature. In the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ sample, the hysteresis field region is observed to depend critically on the temperature and drastically expand with decrease of temperature. The critical
field decreases with the increasing of Sr-concentration. With advanced study in $\rho$ and $M$ of the \textit{Pr}$_{0.65}$\textit{Ca}$_{0.35}$\textit{MnO}_3 sample at 10K (Fig.4-39), there is a sharp fall of resistivity (over 6 orders of magnitude) around 6T (where the threshold in $M$ is observed) during sweeping up the magnetic field and is not increased from the minimum value with the sweeping down of it confirming the irreversible turn out of canted AFM spins to FM ones in \textit{Pr}$_{0.65}$\textit{Ca}$_{0.33}$\textit{MnO}_3 polycrystals. The transport mechanism in it may be somewhat different from that of \textit{Pr}$_{0.65}$\textit{Ca}$_{0.25}$\textit{Sr}$_{0.1}$\textit{MnO}_3 (Fig.4-41). Actually the $\rho$ and $M$ at 10K (Fig.4-40) of the \textit{Pr}$_{0.65}$\textit{Ca}$_{0.3}$\textit{Sr}$_{0.05}$\textit{MnO}_3 sample reveals the same thing. This once more signifies the electronic and magnetic instability in this \textit{Pr}$_{0.65}$\textit{Ca}$_{0.25}$\textit{Sr}$_{0.1}$\textit{MnO}_3 sample below $T_{MI}$ at low magnetic fields.

5.1 \textit{Pr}$_{0.65}$\textit{Ca}$_{0.25}$\textit{Sr}$_{0.1}$\textit{MnO}_3 :

Special interest is focused on the sample of $x=0.1$ where a first order MI transition is confirmed at 80 K from hysteresis cure despite the charge ordering taking place at a higher temperature around 200K. Actually the observation of both the CO and MI transition at the zero field is rather unusual.

Temperature profiles of $\rho$ for \textit{Pr}$_{0.65}$\textit{Ca}$_{0.25}$\textit{Sr}$_{0.1}$\textit{MnO}_3 at different magnetic fields (H) are shown in Fig. 4-23. The resistivity decreases with the increase of magnetic fields. The MI transition becomes broader and the $T_{MI}$ moves to higher temperatures with the increase of H. The CO state is observed (as indicated by $T_{CO}$ in Fig. 4-23) up to a magnetic field of 2.5T. In fact, the temperature profile of resistivity of $x=0.1$ sample without magnetic field (Fig. 4-23) is similar to that of $x=0$ with the magnetic field of 5T (Fig. 4-20). Variation of $M$ with temperature at different magnetic fields (0.01-8T) for \textit{Pr}$_{0.65}$\textit{Ca}$_{0.25}$\textit{Sr}$_{0.1}$\textit{MnO}_3 sample is shown in Fig. 4-44. The ferromagnetic transition temperature ($T_C$), defined as the temperature where $M$ is saturated, rises with the
increase of magnetic fields. Situation at 2T is very typical and different from others where M has started to increase at T ~ 200K, and exhibits a shoulder at around 175K, then increases and finally becomes saturated at T ~ 80K though these transitions are not so vivid from temperature variation of $\rho$ at 2T (Fig. 4-23).

The temperature dependence of C generally accounts for the anomalies corresponding to different thermodynamic phase transitions. It is a bulk property and shows rather a small anomaly due to minor impurity or short range or meta-stable ordering phases. Figure 4-47 illustrates the temperature distinction of C for Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ sample at diverse magnetic fields (0-8T) wherever anomalies owing to AFM, CO and FM transitions are noticed respectively at $T_N$, $T_{CO}$ and $T_C$. AFM and CO anomalies are clearly observed up to 2.5T and the FM anomalies detected from 3 to 8T are in accordance with those illustrated in Figs. 4-23 and 44. However, also from the plot of its C vs. T at different magnetic fields (Fig. 4-47), we cannot successfully resolve its specific heat anomaly for FM transition, which should be normally accompanied by the MI transition at $T_{MI}$ ~ 80K of Fig. 4-16 (for details, see Figs. 4-17 and 49). Thus we speculate that the ferromagnetic metallic (FMM) state at low magnetic fields and low temperatures (below $T_{MI}$) in this sample is very unusual and denoted as FM$^*$M. Depending on the results of Figs.4-16 to 18, T-H phase diagram is sketched for the Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ manganite in Fig. 5-5. It obviously indicates the PMI, COI, AFMI, FMM and metal-insulator transition (M) regions. The shaded area denotes the unusual ferromagnetic metallic (FM$^*$M) state which may be due to electronic and magnetic instability of the sample below $T_{MI}$ at low magnetic fields. In the following paragraphs, we present more detailed data and further discuss these phenomena.

Figure 5-51 shows the hydrostatic pressure (P) dependent ac magnetic
susceptibility ($\chi_{ac}$) for $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$ measured in warming temperature (T) from 80 to 280K. At ambient pressure, there is a very small anomaly at 200K owing to CO transition. With the increase of P, the temperature dependent $\chi_{ac}$ profile becomes very similar to that of temperature dependent magnetization in various magnetic fields (Fig. 4-44). The low temperature FM$^*$ ordering signal at ambient pressure (not seen in Fig.5-51 as the temperature is not low enough) is dramatically enhanced by applying external pressure. The behavior for pressure of 7.4 kbar on ac susceptibility is almost the same as that of magnetic field of 2T on magnetization shown in Fig. 4-44. A sharp transition due to FM ordering is observed with $T_C \sim 200K$ for the pressure of 9.9 kbar. Basically, the external pressure can stabilize the structure (reduce the distortion) and suppress the spin fluctuations in perovskite manganites. Therefore; it is reasonable to see the increase of $T_C$ and the melting of CO state with the increase of pressure. This also designates the electronic and magnetic instability in this sample due to spin fluctuations below $T_{MI}$.

To corroborate this electronic and magnetic instability, the magnetic field dependent thermal hysteresis of resistivity for $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.1}\text{MnO}_3$ is shown in Fig.4-30. The hysteresis loop is decreased with the increase of magnetic field and almost disappears at 3T. MI transition takes place at lower temperatures during cooling compared to those in the course of heating at low magnetic fields. The difference of $T_{MI}$ during cooling and warming is about 50K at zero field. It is interesting that the low temperature end of the hysteresis loop starts at nearly $T_C \sim 45K$ at 0T and moves in the direction of higher temperature being around $T_{MI} \sim 80K$ at 2T. Though the high temperature end of the hysteresis loop is far below the CO transition temperature ($T_{CO}$) at 0T, it approaches to $T_{CO} \sim 200K$ at 2T. At zero magnetic field, the resistivity becomes the minimum at $T_C$ during cooling while it
starts increasing from the minimum value at much higher temperature in warming. The FM* spins, responsible for metallic state via DE interaction, are randomly
oriented at zero magnetic field due to spin fluctuations between T_{MI} and T_{C} and considerable irreversibility of the spins during warming causes the large hysteresis loop. With the increase of magnetic field, the FM* spins become more aligned as their fluctuations decrease and long range order is achieved with the decrease of irreversibility. Thus the hysteresis loop is reduced along with the shift of high temperature end of hysteresis loop up to T_{CO} \sim 200K as the CO states are more melted. These again suggest the electronic and magnetic instability owing to spin fluctuations in Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_{3} at low magnetic fields below T_{MI}.

Temperature variation of zero field cooled (ZFC) and field cooled (FC) magnetization (M) of Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_{3} is shown in Fig. 4-45. It should be recorded that for ZFC magnetization measurement, the sample was first cooled from room temperature (~300K) to the lowest measured temperature (~10K) without field, then H=100 Oe was applied and the ZFC magnetization data were collected on warming temperature up to 300K. Subsequently, the FC magnetization data were taken on cooling temperature. The ZFC magnetization starts increasing with the increase of temperature, remains almost constant between T_{C} \sim 45K and T_{MI} \sim 80K, then decreases up to 110K and becomes nearly constant with slight decrease at T_{CO} \sim 200K. Though the FC magnetization follows the same path from room temperature to 110K, it has a stiff enhancement starting around T_{MI} \sim 80K and finally turns out to be saturated approximately at T_{C} \sim 45K. Even if the nature of FC magnetization curve is similar to Fig. 4-44, that of ZFC magnetization is quite unusual. For the Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_{3} sample, there is a sharp MI transition observed at T_{MI} \sim 80K in the absence of magnetic fields (Fig. 4-16). From resistivity and magnetization curves
(Figs. 4-16 and 18), we also distinguish that it is FM metallic below MI transition temperature ($T_{MI}$) at zero magnetic field. The mechanism for the behavior of FC and ZFC magnetization in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ (may be due to spin fluctuations) is unusual. This once more designates the electronic and magnetic instability in this sample below $T_{MI}$ at low magnetic fields. For comparison, we performed the profiles of M vs. T for $H_{DC}=0$Oe, $H_{AC}=1$Oe and the frequency is 500Hz (Fig. 4-46). The cures of M for cooling and warming processes are really unusual as the ZFC magnetization. This strange behavior of M appears at very low field or ZFC process again suggests the electronic and magnetic instability owing to spin fluctuations in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ at low magnetic field below $T_{MI}$.

Figure 4-41 displays the magnetic hysteresis of $\rho$ and M of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ at a fixed temperature (10K). Here, the sample was first cooled down to 10K at zero magnetic field, then the resistivity and magnetization measurements were taken by sweeping the magnetic field first up and then down. The resistivity is decreased with increasing magnetic fields. It slightly increases from the minimum value in the course of decreasing magnetic fields and the irreversibility occurs at around $H \sim 3$T. Magnetization curves also show similar irreversible performance at a lower magnetic field $\sim 2$T. In the absence of magnetic field, the FM$^*$ spins may be canted or meta-stable or fluctuating in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ sample. So M is small as H is small (near 0T) during increasing and decreasing of magnetic fields. But the FM$^*$ spins are better aligned, spin fluctuations decrease and perhaps long range order is achieved above $\sim 2$T confirming the saturation of magnetization and resistivity. Hence it is once more specified that the canted or meta-stable FM$^*$ spins are stabilized above 2T and long range FM ordering is achieved. It is noticed that both $\rho$ and M curves exhibit a threshold at a magnetic field of approximately 1T in its sweeping up mode. In our
sample the threshold of resistivity is detected at 1T (where the threshold in M is also observed) and the ρ slightly increases with the sweeping down of magnetic field implying that the transport mechanism in it possibly due to electronic and magnetic instability induced by spin fluctuations.

The final verification on the electronic and magnetic instability in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ below T$_{MI}$ at low magnetic fields is attained from the C/T vs. T curves (Fig. 4-49). It is well established$^{11}$ that the CO insulating state is unstable under high magnetic fields and a MI transition may take place due to the melting of CO insulating states resulting in a ferromagnetic metallic (FMM) one. Generally, the FM transition temperature (T$_C$) and the MI transition temperature (T$_{MI}$) are close to each other. Comprehensible anomalies should be observed in C because of stable FM phase transitions.$^{35}$ Within this scenario, the absence of anomaly in C at T$_{MI}$, the presence of small specific heat anomaly at T$_C$ and substantial difference between T$_{MI}$ and T$_C$ would specify the instability of the FM state below T$_{MI}$. Figure 4-49 shows no anomaly at T$_{MI}$ ~ 80K corresponding to MI transition (observed from Figs.4-16 and 23), but demonstrates rather a smaller than expected one at T$_C$ ~ 45K (shown by arrow in Fig. 4-49) at low magnetic fields (≤1T). The C data for zero magnetic field are collected during cooling and warming which illustrate the anomalies at same temperature (T$_C$) without resolvable hysteresis. The inset of Fig.4-49 shows the absolute values (taken by HPTR calorimeter) of discrete C/T data of the sample at zero magnetic field in which the anomaly around 45K is further confirmed. The approximate magnitude of jump seen in the specific heat (∆C) estimated from the inset of Fig.4-49 at T$_C$ ~ 45K is only about 0.85 J/mol K whereas that for its CO transition at zero field (Fig. 4-47) is about 19 J/mol K. The ∆C associated with FM transition of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ (Fig. 4-49) at T$_C$ ~ 45K is much smaller than that
of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ (26.2 J/mol K) at $T_C \sim 280$K (Fig. 4-17) and of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ (30.4 J/mol K) at $T_C \sim 200$K and $H=3T$ (Fig. 4-47). In addition, this small anomaly due to FM transition (0.85 J/mol K) in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ is also smeared at $H=1\sim2T$ (Figs. 4-47 and 49) but resume at $T_C \sim 200$K and $H=3T$ (Fig. 4-47). Thus we speculate that the unusual ferromagnetic metallic (FM$^*$M) state in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ below $T_{MI} \sim 80$K at low magnetic fields is different from that of a typical FMM state. Moreover, the existence of unusual (FM$^*$M) state in this sample below its $T_{MI} \sim 80$K reflects the electronic and magnetic instability in it and is of short range ordered in nature due to spin fluctuations.
Fig. 5-1. The phase diagram of $T$ vs. $x$ for the $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_x\text{MnO}_3$ series.
Fig. 5-2. The cures of $\text{MRR}_{\text{max}}$ vs. $x$ of the $\text{Pr}_{0.65}\text{Ca}_{0.35-x}\text{Sr}_{x}\text{MnO}_3$ for $H=0.1$, 0.2, and 0.5T.
Fig. 5-3. $\rho(H)/\rho(0)$ vs. H bellows 0.1 Tesla of the x=0.1 sample at 70K and the x=0.35 sample at 295K.
Fig. 5-4. MR vs. T of the Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0, 0.05, and 0.1) samples for 0T≤H≤8T.
Fig. 5-5. The H-T phase diagram of the Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ sample.
Chapter Six: Conclusion

In summary, we have studied the resistivity, magnetoresistance, magnetization and specific heat of polycrystalline Pr$_{0.65}$Ca$_{0.35-x}$Sr$_x$MnO$_3$ (x=0-0.35) perovskite manganites in various temperatures (10-300K) and magnetic fields (0-8T). We have following conclusion.

The sample with x ~ 0.1 shows unusual ferromagnetic metallic (FM$^*$M) state below metal-insulator transition temperatures (T$_{MI}$) and at low magnetic fields. There is a dramatic enhancement of MRR near T$_{MI}$ at low magnetic fields induced by the rapidly increasing T$_{MI}$ for Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ but the electronic and magnetic instability causes the processes irreversible. The thermal and magnetic hysteresis is observed around T$_{MI}$ in resistivity and magnetization but not on the specific heat of Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$. The specific heat anomaly for FM$^*$ state is observed at T$_C$ ~ 45K, which is about 35K lower than T$_{MI}$ ~ 80K indicating that there is strong spin fluctuations between T$_C$ and T$_{MI}$. An unexpectedly small specific heat anomaly without thermal hysteresis for Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ at T$_C$ ~ 45K smears at H=1-2T and resumes again at H=3T around T$_C$ ~ 200K signifies its unusual FM$^*$M state. All of these data imply that the FM$^*$M state in Pr$_{0.65}$Ca$_{0.25}$Sr$_{0.1}$MnO$_3$ between its T$_{MI}$ and T$_C$ at low magnetic fields is subjected to an unstable or a short range magnetic ordering induced by spin fluctuations and resulted from the interplay of CO/AFM insulating and FM metallic states.
References:


