

Structural, electric, and magnetic properties of Mn perovskites

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Abstract

Recently, the interesting electric or magnetic properties such as high-T_c superconductivity and colossal magnetoresistance bring forth intense interests in transition metal oxides with perovskite structure in the field. Those interesting properties originate in the strong couplings among charge, spin, orbital, and lattice degrees of freedom. More various novel and complex phase transitions can be tuned by temperature, doping, magnetic field, and pressure. This paper covers theoretical and experimental investigations on such strongly correlated systems laying stress on the manganese oxide as a good example.

I. Introduction

Although manganese oxides as one example of transition-metal oxides with perovskite structure had been considerably studied in the aspect of its magnetic properties already about fifty years ago, the recent discovery of colossal magnetoresistance (CMR) has stimulated a lot of intensive researches in these compounds. In a transition-metal oxide with perovskite structure, its spin, charge, and orbital degrees of freedom are strongly coupled, so that a variety of magnetic and electronic phases appear in response to external conditions such as temperature, chemical doping, magnetic field, and pressure. These correlations are owed to anisotropic d-orbitals of transition metal, their degeneracy splitting under the perovskite structure, and interactions between spins and charges.

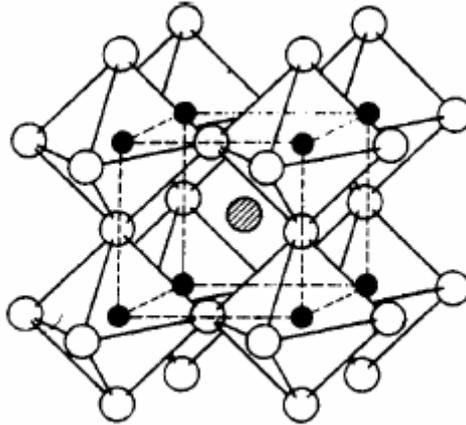


Fig. 1 The ideal cubic perovskite structure; the empty sphere: O, the filled sphere: M, and the hatched sphere: A. From **Goodenough, 2004**

The ideal cubic perovskites have the octahedron in which a transition metal is surrounded by six oxygen ions as a building block, which is stacked in the cubic structure. (Fig. 1) In the compounds of composition AMO_3 , where A denotes a cation like a rare-earth metal ion or a divalent metal ion and M denotes a transition metal, the cation A is located at the center of each octahedron. Depending on the size of ions and external conditions as pressure, each octahedron undergoes shape-deformation, tilt, and rotation, so that a whole system also deviates from a cubic structure. The degree of

deformation can be indicated by the geometric tolerance factor, $d \equiv \frac{\langle A-O \rangle}{\sqrt{2}\langle M-O \rangle}$,

where $\langle A-O \rangle$ is the bond length between a cation A and an oxygen ion and $\langle M-O \rangle$ is the bond length between a transition metal ion M and an oxygen ion. [1] In addition, the $M-O-M$ bond angle denotes the degree of tilt.

II. Background

1. Crystal Field Splitting

The degenerate five d-orbitals of transition metal lying at the center of an octahedron are split depending on Coulomb repulsion with fully occupied p-orbitals of neighboring oxygen ions. The orbitals, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ point toward six oxygen ions located at the corners of octahedron, so that their energy level is higher than the energy level of the other three orbitals, d_{xy} , d_{yz} , and d_{zx} which point between oxygen ions. The former orbitals are called e_g orbitals, while the latter orbitals are called t_{2g} orbitals. As the gap between these two energy levels becomes larger, the more electrons tend to fill low-level t_{2g} orbitals, allowing two electrons with opposite spins to occupy the same orbital. This competes with the Hund's rule which prefers to a parallel spin alignment accompanying the occupation of different orbitals. For example, in the case of $LaMnO_3$ where Mn^{3+} has four electrons in d-orbitals, the Hund's coupling is larger than the energy gap, so that all spins are aligned parallel with three electrons occupying each of three t_{2g} orbitals and one electron occupying one of two e_g orbitals.

2. Jahn-Teller Effect

Because one e_g electron has the two possible orbitals which are doubly degenerate, a compound system can gain energy and become more stable if the degeneracy is lifted.

This degeneracy lift can be achieved the displacement of the oxygen ions surrounding the transition-metal ion. For example, when an octahedron is elongated along the z-axis, the $d_{3z^2-r^2}$ orbital is less overlapped with apical oxygen orbitals; that is, the electron occupying the $d_{3z^2-r^2}$ orbital undergoes weaker repulsion than electrons occupying $d_{x^2-y^2}$ orbitals, so that $d_{3z^2-r^2}$ becomes to have a lower energy level than $d_{x^2-y^2}$ and the occupation of a lower level make the system more stable. This phenomenon is called the Jahn-Teller effect. [2]

3. Semicovalent Exchange Interaction

The cooperative ordering of this Jahn-Teller distortion results in the corresponding magnetic, i.e. spin, order in a system from the semicovalent exchange interaction by Goodenough. [3] In this interaction, the semicovalent bond is described as the bond formed by overlapping between the empty hybrid orbital of a transition metal ion and the fully occupied orbital of a neighboring oxygen ion. When two orbitals are overlapped, only the oxygen electron whose spin is parallel to the local spin of the transition-metal ion can have its share in the bond because of Hund's rule; in this case, the semicovalent bond occurs only below T_c (Curie temperature) since the local spins are aligned below T_c , and the bond becomes covalent above T_c . The coupling between the local spins of the transition metal and the spin of the oxygen ion allows the prediction of the magnetic coupling between neighboring transition metal ions separated by an oxygen ion. For example, the magnetic coupling in manganese oxide depends on whether each bond in $Mn-O-Mn$ is semicovalent or not. If both of bonds are semicovalent, two manganese ions are antiferromagnetically coupled because two spins in the full orbital of the oxygen ion are antiparallel by Pauli Exclusion Principle. In other hand, if one bond is semicovalent and the other is ionic, the local spin of Mn which has the semicovalent bonding with O is antiparallel to the other oxygen spin which is antiparallel to the local spin of the other Mn ionically bound to the oxygen by a direct exchange interaction; consequently, the spins of two manganese ions are ferromagnetically coupled. Because a covalent bond is shorter than an ionic bond, the $Mn-Mn$ separation in the antiferromagnetic spin coupling is smaller than in the ferromagnetic coupling. This interaction mediated by the semicovalent bond is called the semicovalent exchange interaction. The compound in which this interaction is

dominant behaves like an insulator because the electrons participating in the bonding are just bound to the bonding region and not itinerant.

4. Double Exchange Interaction

However, such a metallic and ferromagnetic phase as shown in doped manganese oxides, i.e. manganites, can't be explained only by the above exchange interaction. For this, Zener first proposed the double exchange interaction. [4] For the doped manganites which have the disordered mixture of Mn^{3+} and Mn^{4+} , the e_g electron makes a real hopping from Mn^{3+} to O^{2-} to Mn^{4+} depending on the alignment of the local spins of Mn^{3+} and Mn^{4+} . If the spins of Mn^{3+} and Mn^{4+} are parallel, the oxygen spin parallel to the spins of Mn^{4+} hops to Mn^{4+} followed by the hopping of the e_g spin of Mn^{3+} to the vacated spin site of the oxygen. In other hand, if the spins of Mn^{3+} and Mn^{4+} are antiparallel, the e_g spin can't hop to the oxygen because its spin is parallel to the spin remained in the oxygen. Thus, the itinerancy of electrons, i.e. conductivity, is strongly coupled with ferromagnetism based on the double exchange interaction.

Now using these backgrounds, we can examine the strong correlations between spin, charge, orbital and lattice giving various properties in manganese oxides. Among them, the characteristic of $LaMnO_3$ are first studied.

III. Experimental and Theoretical Examinations in Manganites

1. Undoped Manganese oxide - $LaMnO_3$

$LaMnO_3$ has the A-type magnetic order in which the spins are ferromagnetically aligned in planes, but antiferromagnetically aligned between planes, while the orbital ordering has the alternate alignment of the two anisotropic orbitals, $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$.

This magnetic ordering is highly correlated under the semicovalent exchange interaction and the anisotropy of the transfer integral. The orbital ordering shown in the Fig. 2 was recently observed by Murakami, Hill *et al.* with the resonant x-ray scattering [5], while the magnetic order in $LaMnO_3$ was investigated by Wollan and Koehler from neutron diffraction experiments in 1955 [6]. (Fig. 3)

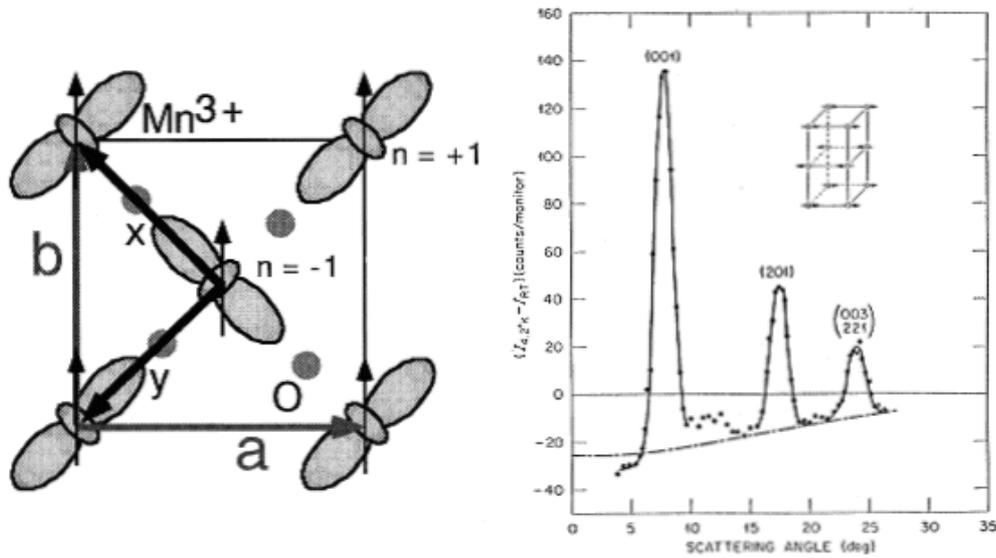


Fig. 2 (left panel) Schematic view of the orbital and spin ordering in the a-b plane of the perovskite manganite, $LaMnO_3$. The orbital ordering along the c axis is expected to repeat the same pattern. From Murikami *et al.*, 1998.

Fig. 3 (right panel) Temperature difference pattern and antiferromagnetic structure (Type A) for $LaMnO_3$. From Wollan and Koehler, 1955.

The alternating ordering of two orbitals in planes causes the alternating ordering of empty lattice orbitals; that is, the anion, O^{2-} , neighbors to two cations, Mn^{3+} , with each differently polarized empty orbital. In such a configuration, one empty d orbital points toward the full O^{2-} p orbital, i.e. strongly overlap the O^{2-} orbital, but the other empty d orbital rarely overlap the O^{2-} orbital. This makes only one $Mn-O$ bond semicovalent; thus the magnetic moments of two nearest neighboring Mn^{3+} in the plane are ferromagnetically aligned under the semicovalent exchange interactions.

This coupling between spin and orbital ordering has been theoretically studied more by Maezono *et al.* [7]. The model Hamiltonian that they introduced represents the anisotropy of the transfer integral based on the double degeneracy of the e_g orbital and the orbital ordering and the strong interactions between electrons such as the Hund interaction and the Coulomb interactions as follows. $H = H_K + H_{Hund} + H_{onsite} + H_S$. In this Hamiltonian, the first term H_K (kinetic energy of e_g electrons) depends on the electron transfer intensity, and implies the dependence of the orbital degeneracy and

anisotropy. The term H_{Hund} parameterizes the Hund's coupling between e_g and t_{2g} spins, H_{onsite} also parameterizes the on-site Coulomb interactions between e_g electrons, and H_S denotes the magnitude of the AF coupling between nearest neighboring t_{2g} spins; for the reasonable value of this coupling, J_S , we can apply the semicovalent exchange interaction method to predict the state of a system as discussed above. The estimated free energy based on this model Hamiltonian is minimized for each different magnetic order as J_S , the AF coupling, increases. In addition, each magnetic order optimizes its orbital order. Fig. 4 shows the change of the magnetic order, $F \rightarrow A \rightarrow C \rightarrow G$, accompanied with the change of the orbital order, $G \rightarrow G \rightarrow A \rightarrow A$. However, in this case the A-type AF magnetic ordered state for the reasonable values of J_S favors the G-type orbital ordering of $d_{y^2-z^2}$ and $d_{z^2-x^2}$ in which two orbitals are alternately aligned on the nearest neighboring manganese sites. This contradicts with the experimental result, i.e. the alternate ordering of $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals. It's because the Jahn-Teller coupling has not been taken into account.

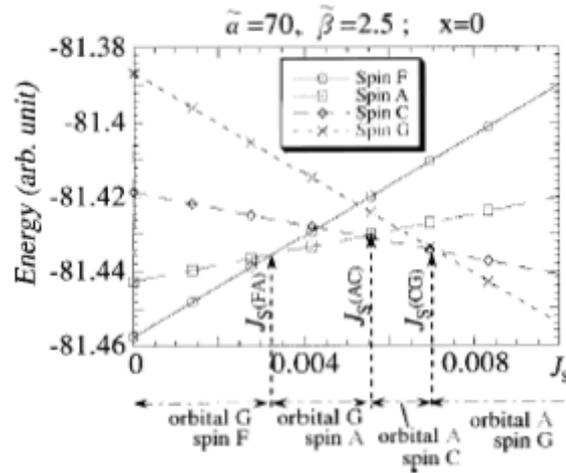


Fig. 4 Free energy for each spin alignment as a function of antiferromagnetic interaction between t_{2g} spins J_S at $x=0$. From Maezono *et al.*, 1998b

The Jahn-Teller effect causes the energy level splitting of the two degenerate e_g orbitals by which the energy gain competes with the strain energy loss by the lattice distortion. This effect can be represented by the following term; now, this modifies the model Hamiltonian referred above.

$$H_{JT} = g \sum_j \vec{Q}_j \cdot \vec{T}_j + \frac{1}{2} \sum_j \omega_0^2 \vec{Q}_j^2 + \sum_j V(\vec{Q}_j)$$

where \vec{T}_j (isospin operator) implies the orbital dependence, \vec{Q}_j (local lattice distortion) implies the lattice dependence. This JT distortion also affects the transfer integral intensity. The numerical calculation with this effect well predicts the alternate $d_{3x^2-r^2}/d_{3y^2-r^2}$ ordering rather than the $d_{y^2-z^2}/d_{z^2-x^2}$ ordering; this corresponds to the elongated octahedron along the in-plane directions observed experimentally.

2. Doped Manganese Oxide - $La_{1-x}Ca_xMnO_3$

The doped manganites are formed by replacing the trivalent rare-earth metal ions as La by the divalent metal ion as Ca in the parent compound $LaMnO_3$, and have the mixed valence of Mn^{3+} and Mn^{4+} . The Mn^{3+} ion has one e_g electron which is sensitive to the Jahn-Teller effect and can act as a mobile charge carrier in compounds, while Mn^{4+} is inactive with respect to the JT distortion and has no carrier since Mn^{4+} has the empty e_g orbitals. These properties are helpful to describe the characteristics of the doped manganites. For these compounds, the double exchange interaction plays a more important role depending on the doping level and shows a close relation between the spin and charge dynamics as the coupling with orbital degrees of freedom.

The neutron diffraction study by Wollan and Koehler also informed the magnetic order in compounds with each different doping level as well as $LaMnO_3$ referred above. [6] The compound of composition $La_{1-x}Ca_xMnO_3$ shows the A-type antiferromagnetic phase for the small x ranges, $0 \leq x \leq 0.1$. Since only a few Mn^{4+} ions replace Mn^{3+} ions, the semicovalent exchange interactions are still dominant, and it's no wonder that it remains in the same type antiferromagnetic state as the parent compound $LaMnO_3$ has. In addition, the cooperative Jahn-Teller effect is still valid, but it has the remarkable decrease with the increase of Mn^{4+} ions, so as to vanish near

$x \sim 0.15$; thus, the increase of Mn^{4+} ions also leads to the decrease of the temperature at which the long-range orbital order states melt.

As the doping progresses, the double exchange interactions become more dominant and the ferromagnetic phase occurs below the Curie temperature. For the narrow x ranges, $0.1 \leq x \leq 0.21$, the e_g^1 electrons are still localized but ferromagnetically couple the spin states of neighboring t_{2g}^3 electrons. This is, the ferromagnetic insulator phase appears, and it also shows the orbital and charge ordered state.

For $0.21 \leq x \leq 0.4$, the band formed by e_g orbital hybridization is less occupied, i.e. more holes are doped, so that the electrons become itinerant. As the result, the manganites undergo the transition from the insulator phase to the metal phase depending on the values of doping at low temperature. Since the double exchange interactions require the disorder of Mn^{3+} and Mn^{4+} ions so that $Mn^{3+} - O - Mn^{4+}$ is degenerate with $Mn^{4+} - O - Mn^{3+}$, the orbital order melts for the metallic phase. In other words, the hybridization of degenerate e_g orbitals builds up the F-type ordering. When $x \sim 0.3$, the largest number of Mn^{3+} ions have only one Mn^{4+} near neighbor respectively, and the double exchange interactions are optimized; thus, the Curie temperature and the conductivity have their own maximum values.

While the system of these doping levels at low temperature is well explained by the double exchange interactions, the insulatorlike properties above T_c need another factor for explanation. It's because the partially occupied e_g band make the system always metallic, and the double exchange interactions are not enough. Millis *et al.* introduce the small Jahn-Teller polaron, which is formed by less distorted empty e_g orbitals of Mn^{4+} than those of neighboring Mn^{3+} ions. The energy gain owe to this JT distortion makes the charge carriers locally trapped, so that the system behaves like the insulator. [8]

When doped further beyond $x \sim 0.4$, the Coulomb interactions between electrons become important and help localize electrons. In particular, the system in which the doping level is a rational fraction exhibits a charge ordered state, in which Mn^{3+} and Mn^{4+} order alternately in the crystal. This charge ordered state results from the

dominance of the nearest neighbor Coulomb repulsion. This charge ordering has an effect on the lattice parameters, i.e. the tolerance factor, and an orbital ordering is stabilized under the electron and spin interactions. Fig. 5 describes the type CE (Charge-Exchange) orbital and antiferromagnetic order at $x \sim 0.5$. The spins are ferromagnetically aligned in zigzag chains and antiferromagnetically aligned along the c-axis, while the charge and orbital ordering in the planes is stacked parallel along the c-axis. Chen and Cheng observed the evidence for this charge ordering by electron microscopy. [9]

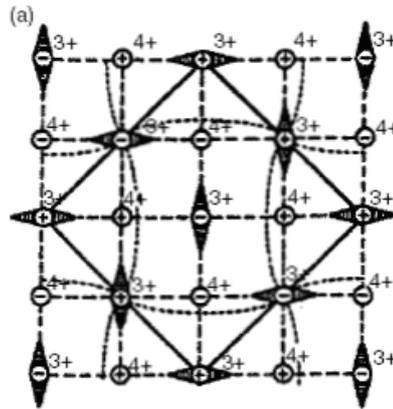


Fig. 5 Type CE orbital and antiferromagnetic order of Mn(IV) and Mn(III) in a-b planes. From Goodenough, 2004

For $0.5 < x \leq 0.75$, the system of $x = n/(n+1)$ orders in diagonal charge stripes. In this order, the slabs of $Mn^{4+} / Mn^{4+} / Mn^{4+}$ diagonal planes are inserted between the slabs of alternate $Mn^{3+} / Mn^{4+} / Mn^{3+}$ diagonal planes as shown in Fig. 6.

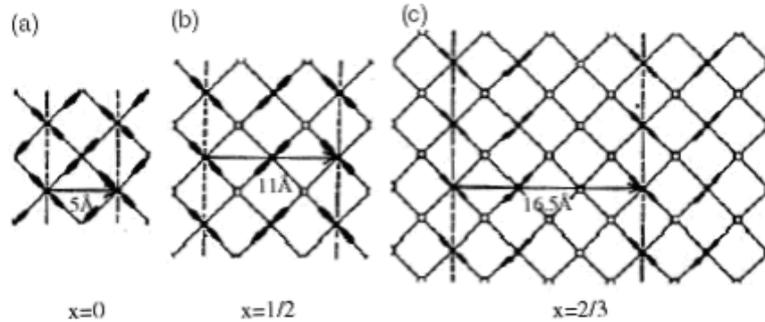


Fig. 6 Orbital ordering at Mn(III) ions in the a-b planes of $La_{1-x}Ca_xMnO_3$. From Goodenough, 2004

For $0.75 < x < 0.9$, doped manganites undergo a phase transition to a type-C antiferromagnetic state where spins form ferromagnetic chains along the c-axis and those chains are antiferromagnetically coupled with neighboring chains. This system has electrons itinerant along the chains and its structure is more cubic because the lattice distortion decreases mostly.

In the almost fully doped region, $0.9 \leq x \leq 1.0$, the G-type antiferromagnetic phase is observed, where each spin is aligned antiparallel to nearest neighboring spins. The G-type AF order of CaMnO_3 , $x=1$, is well predicted by the semicovalent exchange interactions as the case of LaMnO_3 , $x=0$. Since CaMnO_3 is composed of only Mn^{4+} ions, p orbitals of O^{2-} are strongly overlapped with empty e_g orbitals of Mn^{4+} on both sides, that is, both of $\text{Mn}-\text{O}$ bonds are covalent. Thus local spins on Mn sites are antiferromagnetically coupled to those on nearest neighboring Mn sites.

The below Fig. 7 summarizes various emergent phase for different doping levels and temperature.

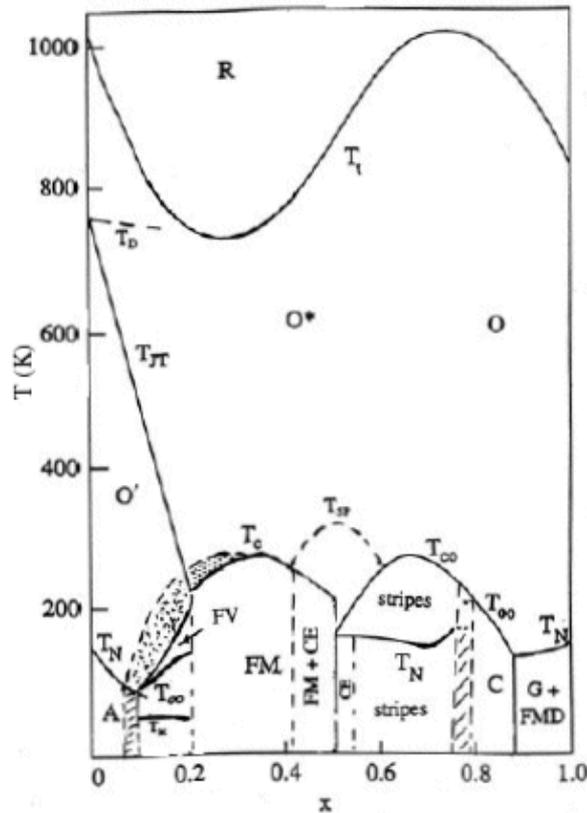


Fig. 7 Tentative temperature- x phase diagram for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. From Goodenough, 2004

IV. Exotic Phase Transition - CMR

Owing to these complicated couplings between spin, charge and orbital degrees of freedom, the strongly correlated system also has a variety of exotic phase transitions depending on the environmental conditions such as magnetic field and pressure as well as temperature and chemical doping. One of them is “Colossal Magnetoresistance.”

The negative magnetoresistance implies that there occurs the decrease in resistivity when applying the magnetic field to a material; the value is defined as $\frac{-[\rho(H) - \rho(0)]}{\rho(0)}$.

This effect is simply understood as a spin valve. From the double exchange interaction, e_g electrons can be itinerant when local spins, i.e. t_{2g} spins, are ferromagnetically coupled. Thus, the application of an external magnetic field leads to align the local spins and enhances the conductivity. When a weakly applied magnetic field brings forth a relative huge change, for example 10 times, in resistivity, it's particularly called colossal magnetoresistance (CMR). Fig 8 plainly shows this CMR effect.

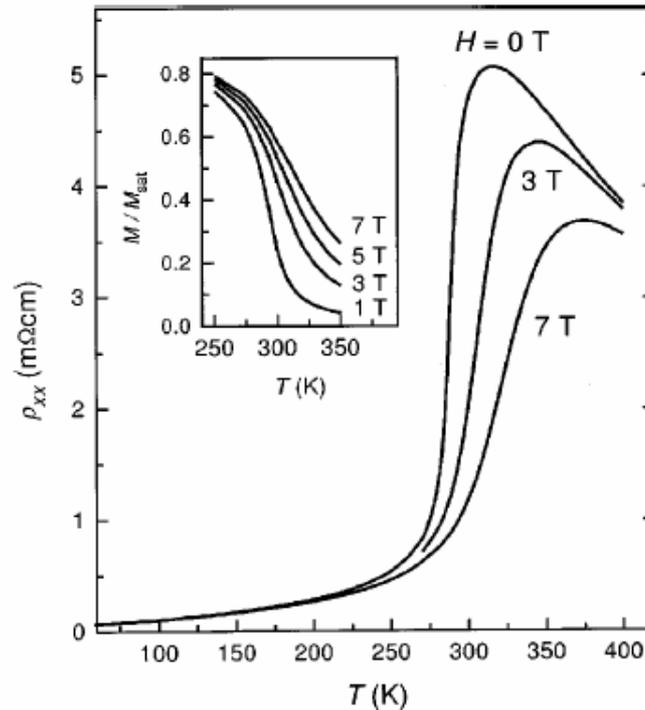


Fig. 8. Main panel: the temperature dependence of $\rho_{xx}(H, T)$ of a $La_{2/3}(Pb, Ca)_{1/3}MnO_3$ single crystal at variance fields H . Inset: $M_H(T)$ in the transition region. From Chun *et al.*, 2000

This CMR effect is based on the strong correlation between spin and charge order, but the orbital degrees of freedom also play an important role. The system which has the insulatorlike behavior near above T_c has short-range ordered e_g orbitals. This ordering is considered as “electron liquid-crystal.” [10] This is formed antiferromagnetically just above T_c , but undergoes a phase transition to a ferromagnetic state when applying an magnetic field. Concomitantly, this accompanies an insulator-metal transition.

V. Conclusion

We have examined some principles which describe the strong correlations among the degrees of freedom of spin, charge, orbital, and lattice, moreover applied them to such a real system as manganese oxides. We have confirmed that the observed phases and the transition between them are well-consistent with the predictions by those principles.

Although the recent intense investigations have been devoted to the perovskite transition-metal oxides field, there still exist a lot of states and materials which has rarely been discussed theoretically and unraveled experimentally. The high-temperature superconducting cuprates are still in the center of the most interesting systems, and the layered ruthenium oxides $Ca_{n+1}Ru_nO_{3n+1}$ have lately attracted considerable attention. The layered systems which have the Ruddlesden-Popper structure exhibits much of interesting physics and complex phases based on the 2-D systemlike properties.

The experiments for the pressure dependence of phase have been attempted as discussed above, but the magnitude of pressure applied remains low because of its delicate pressurizing process. Thus the high pressure experiment is still open to challenge. In addition, the external parameters like an electric field and light can act as a controller in the phase transition process like chemical doping, temperature, and magnetic field discussed above. In fact, it's possible that the electric field gives direct effects to the order of orbital, and concomitantly the magnetic order, if the material is a good insulator. The transitions by light also have already been observed for $Pr_{1-x}Ca_xMnO_3$. Such a control bears a big potential for some applications in the future.

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