Colossal magnetoresistance and quenched disorder in manganese oxides

Nobuo Furukawa\textsuperscript{1*} and Yukitoshi Motome\textsuperscript{2}

\textsuperscript{1}Department of Physics, Aoyama Gakuin University, Kanagawa 299-8558, Japan
\textsuperscript{2}RIKEN (The Institute of Physical and Chemical Research), Saitama 351-0198, Japan

We give an overview on several recent topics of colossal magnetoresistive manganites in both experiments and theories, focusing on the effect of quenched disorder. The disorder is intrinsically involved since the compounds are solid solutions, and its importance has been pointed out in several experiments of transport and magnetic properties. Recent progress in the experimental control of the strength of disorder is also reviewed. Theoretically, the effect of the disorder has been explored within the framework of the double-exchange mechanism. Several efforts to understand the phase diagram and the electronic properties are reviewed. We also briefly discuss a recent topic on the effect of disorder on competing phases and the origin of colossal magnetoresistance.

KEYWORDS: colossal magnetoresistive manganites, quenched disorder, double-exchange model, competing orders

1. Introduction

Colossal magnetoresistance (CMR) in perovskite manganese oxides has been one of the central issues in condensed matter physics.\textsuperscript{1–5} CMR is a gigantic response of the electrical resistivity to the external magnetic field; the resistivity sharply decreases even on the order of $10^{-1} - 10^{6}$ by applying the magnetic field of only a few Tesla. Besides fundamental understanding of the mechanism of CMR, possibilities of technological applications have motivated this field.

CMR manganites exhibit a variety of physical properties such as ferromagnetism, antiferromagnetism, metal-insulator transition, charge ordering and orbital ordering. The most universal phenomenon is the transition from the high-temperature paramagnetic phase to the low-temperature ferromagnetic metallic phase.\textsuperscript{6,7} This transition is basically understood by the double-exchange (DE) mechanism.\textsuperscript{8–11} There, $S = 3/2$ localized spins in $t_{2g}$ orbitals and itinerant electrons in $e_{g}$ orbitals are strongly coupled by the ferromagnetic Hund’s-rule coupling, which gives rise to the intimate interplay between the electron conductivity and the magnetism. However, it is obvious that the DE mechanism is insufficient to understand the rich phenomena in the CMR manganites comprehensively. Therefore, the key issue is how to explain the various properties and what kind of extension is necessary to the simple DE picture.

In these CMR manganites, whose chemical formula is generally given by $\text{AMnO}_3$, electronic properties strongly depend on A-site cations. That is, one may control the physical properties by substituting the A-site cations. There are two types of the substitution: One is the substitution with different ionic valences, which is usually called the valence control and the ionic-radius control. Fine tuning of these controls and the ionic-radius control is that these substitutions inevitably introduce quenched disorder as well since the systems are solid solution compounds. Random distribution of different A-site cations leads to structural and electronic disorder. In the long survey of the manganites, the disorder effect has not attracted much attention, and has been considered as a secondary effect to the doping or bandwidth controls. However, this hidden effect has been reconsidered in recent experimental and theoretical efforts, and revealed to play a crucial role in the physics of manganites.

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In this contribution, we give an overview of the investigation on the disorder effect in CMR manganites. This is not a comprehensive review but may be a (biased) summary of recent trends in this field. This paper is organized as follows. In the next section 2, we will give short survey of experimental indications for the importance of the disorder. In Sec. 3, several theoretical efforts are introduced to explain the disorder effects in manganites. Section 4 is devoted to discussion on a possible mechanism of CMR with emphasis on the role of quenched disorder.

2. Experimental

In this section, we show several experimental studies which indicate the importance of the quenched disorder in CMR manganites.
2.1 Residual resistivity
Disorder effect is apparently found in the residual resistivity, i.e., the value of the electrical resistivity as the temperature approaches zero. Coey et al. reported the transport properties of $A_{0.7}A'_{0.3}$MnO$_3$ for various combinations of $A^{3+}$ and $A'^{2+}$ cations, and found that the residual resistivity largely depends on the combination of $(A, A')$. Temperature dependences of the resistivity are schematically shown in Fig. 1. These substitutions of the $(A, A')$ cations correspond to the ionic-radius control and do not change the doping concentration. At the same time, the effective mass, which is estimated by the specific heat measurement, does not show any significant enhancement. Hence, the change of the residual resistivity demonstrates that different ionic radii of the $A$-site cations indeed introduce the quenched disorder in the system, which scatters itinerant electrons at low temperatures and changes the lifetime of quasi-particles.

The increase of the residual resistivity appears to correlate with the decrease of the Curie temperature $T_C$, as schematically indicated in Fig. 1. This correlation has been systematically explored, and will be discussed in the next section.

At the same time, as the residual resistivity increases, the system becomes more insulating above $T_C$, and exhibits larger sudden drop of the resistivity at $T_C$ as shown in Fig. 1. The larger drop leads to more sensitive response to the external magnetic field, i.e., the larger CMR effect. Thus, the insulating behavior above $T_C$ is crucial to consider the mechanism of CMR. This issue will be discussed in Sec. 4.

2.2 Curie temperature
In the simple DE scenario, the Curie temperature $T_C$ scales to the effective bandwidth. Radaelli et al. pointed out that this scaling no longer hold in the series of the ionic-radius control in $A_{0.7}A'_{0.3}$MnO$_3$. They found that the change of $T_C$ is much larger than that of the bandwidth. For instance, from $(A, A') = (La, Sr)$ to $(La, Ca)$, $T_C$ decreases by about 30% while the bandwidth estimated from the structural data decreases by less than 2%. This implies a hidden mechanism to suppress the kinetics of electrons in this substitution of the ionic-radius control.

More direct evidence was revealed by Rodriguez-Martinez and Attfield. They measured $T_C$ for $A_{0.7}A'_{0.3}$MnO$_3$ with the same average ionic radius of the $A$ sites, i.e., the same effective bandwidth. They found that even for the same bandwidth, $T_C$ varies according to the combinations of $(A, A')$ and well scales to the variance of the $A$-site ionic radius: $T_C$ decreases for larger variance. This scaling strongly indicates that the disorder due to the random distribution of $A$-site cations with different ionic radii suppresses the motion of itinerant electrons.

2.3 Spin excitation anomalies
Another indication, which is rather indirect, is found in the spin excitation spectrum. Hwang et al. reported that the magnon dispersion shows softening and broadening near the Brillouin zone boundaries. Dai et al. confirmed that these anomalous behaviors appear universally in compounds showing rather low $T_C$. On the contrary, in compounds showing higher $T_C$ such as $La_{0.7}Pr_{0.3}$MnO$_3$, the magnon dispersion does not show the anomalies and obeys a cosine-like form, which is well explained by the simple DE model. These results suggest a hidden mechanism beyond DE in the low-$T_C$ compounds.

Recently, it has been pointed out that these anomalies can be explained simply by introducing quenched disorder to the DE model. This scenario will be discussed in Sec. 3.5.

2.4 A-site order/disorder materials
A big progress for understanding the disorder effect has been made recently. Millange et al. demonstrated that it is possible to synthesize mixed valence compounds $A_{0.5}A'_{0.3}$MnO$_3$ in which the $A^{3+}$ and $A'^{2+}$ cations order periodically in lattice structure. These special compounds, which are called the $A$-site ordered manganites, exhibit distinct properties from the materials with random configuration of $A$-site cations. We can compare the ‘clean’ systems (A-site ordered) and the ‘dirty’ systems (A-site disordered) both of which have the same chemical formula.

One of the most appealing aspects of these $A$-site ordered materials is multiferroic behavior between the ferromagnetic metallic phase and the charge and orbital ordered insulating phase, as pointed out by Nakajima et al. and Akahoshi et al. When the disorder is introduced, the charge/orbital ordered phase becomes unstable and replaced by some glassy phase, and therefore, the multiferroic phase is strongly suppressed down to much lower temperature. These drastic and asymmetric changes of the phase diagram are depicted in Fig. 2 schematically. More interestingly, in the multiferroic region, the system shows a disorder-induced insulator-to-metal transition. In the disordered compounds, charge-order (CO) fluctuations are surprisingly enhanced above $T_C$, and a typical CMR behavior is observed. These results indicate that the competing orders and the quenched disorder play an
important role in the CMR phenomena.

3. Theoretical

Here we pick up several theoretical efforts to understand the disorder effect in CMR manganites.

3.1 Green’s function technique and transfer matrix method

In an early stage, the effect of the quenched disorder was examined by using some Green’s function technique. Allub and Alascio studied by using the renormalized perturbation expansion, and discussed the localization of the electrons.\textsuperscript{28} Mazzaferro \textit{et al.} applied the equation-of-motion method and calculated the energy difference between ferromagnetic state and paramagnetic state.\textsuperscript{29}

The localization-delocalization phenomenon has also been examined by the transfer matrix method.\textsuperscript{30–32} By including the quenched disorder and the random hoppings of itinerant electrons under the influence of the local magnetic field by localized spins, the phase diagram as well as transport properties are explored.

3.2 First-principle calculation

Pickett and Singh examined the effect of disorder due to the $A$-site substitution by using the first-principle local density functional method with a virtual-crystal approximation.\textsuperscript{33} An important result is the distribution of screened Coulomb energy at Mn sites. They showed that the potential energy is indeed disordered and its distribution has the width of the order of 0.1 eV. This energy scale is comparable to the transfer integrals of itinerant electrons, and hence cannot be neglected.

3.3 Dynamical mean-field study

Several studies have been done by using the dynamical mean-field theory (DMFT).\textsuperscript{34–37} The DMFT for the DE model in the absence of the disorder has successfully reproduced the CMR phenomena in rather ‘clean’ systems.\textsuperscript{38–40} The calculations have been extended to the cases with the disorder. The density of states, $T_C$, and transport properties have been calculated as functions of the strength of disorder, the doping concentration, and temperature. The disorder effect on the ferromagnetic metal transition is qualitatively explained by the series of the DMFT studies.

An important effect which is missed in the DMFT is spatial fluctuation, while it fully includes the thermal fluctuations.\textsuperscript{41} In real materials, itinerant electrons move around with feeling the effect of disorder which are randomly distributed in space. The spatial fluctuation may be relevant for more quantitative argument. This is indeed the case as we will show in the next section.

3.4 Monte Carlo study

Monte Carlo (MC) simulation has also been performed for the DE model with the quenched disorder.\textsuperscript{32, 43} In this technique, both thermal and spatial fluctuations are included and essentially exact results are obtained numerically for finite-size clusters. It is necessary to perform a large scale simulation in order to take many random averages and examine the finite-size effect by using the finite-size scaling analysis. The authors have developed a new MC algorithm which drastically reduces the computational cost.\textsuperscript{44, 45}

The comparison between the DMFT results and the MC results is shown in Fig. 3. The MC estimates of $T_C$ are significantly lower than those by the DMFT, which suggests that the spatial fluctuations substantially suppress $T_C$.\textsuperscript{43, 46} The result clearly indicates the importance of the spatial fluctuations.

It is explicitly shown that $T_C$ scales to the kinetic energy of electrons, which decreases with the square of the strength of disorder in the weak disorder regime.\textsuperscript{43} It is also indicated that MC results well reproduce the large
reduction of $T_C$ mentioned in Sec. 2.2 by taking into account the strength of disorder estimated by the first-principle calculation (Sec. 3.2).

3.5 Spin excitation anomalies

The authors pointed out that the spin excitation anomalies described in Sec. 2.3 can be explained by the DE model with the quenched disorder.\cite{20-22} The disorder induces broadening, branching (softening of the lower branch), and gap-opening at around the Fermi wave number $k_F$ of the itinerant electrons. A typical result is shown in Fig. 4. The origin of the anomalies is the Friedel oscillation: The itinerant electrons tend to screen the quenched disorder, which induces the $2k_F$ charge density oscillation. This charge density oscillation is equivalent to the spin density oscillation because the system is in the half metallic state, i.e., the perfectly spin-polarized state. Thus, the nonmagnetic disorder couples with the magnetic excitation, and induces the anomalies at $k_F$. This novel effect has been recently confirmed in perturbative approaches.\cite{47,48}

Although the disorder scenario appears to give a comprehensive understanding of the various properties of CMR manganites, several other mechanisms have also been proposed for the spin excitation anomalies, for instance, antiferromagnetic superexchange interactions between the localized spins,\cite{49} orbital degree of freedom in the $e_g$ bands,\cite{50} the electron-lattice coupling,\cite{51} and the electron-electron correlation.\cite{52-54} The microscopic origin is still controversial among these scenarios. Further experiments are desired to settle this controversy.

3.6 Competing phases and disorder-induced insulator-to-metal transition

The multicritical behavior in the A-site order/disorder manganites (Sec. 2.4) has also been studied theoretically by explicitly taking account of the quenched disorder.\cite{55-57} Here, to describe the competition between the ferromagnetic metal and the CO insulator, an extended DE model has been studied by incorporating the coupling to lattice distortions. MC calculation has been applied to include large fluctuation effects in this competing disordered system.

MC results well reproduce the asymmetric response of the phase diagram to the quenched disorder. The ferromagnetic metallic phase remains robust though $T_C$ is reduced. On the contrary, the CO phase is surprisingly fragile against the disorder. As a consequence, the multicritical point shifts to the CO regime and strongly suppressed down to lower temperature. Numerical results also reproduce the disorder-induced insulator-to-metal transition as observed in experiments.\cite{55,57} In this regime, it is clarified that the CO fluctuation, i.e., a remnant of the long-range CO which is destroyed by the disorder is enhanced toward $T_C$ as temperature decreases as observed in experiments.\cite{55} This leads to insulating behavior of the resistivity, which is a key aspect for the typical CMR effect.

These results reveal that the quenched disorder plays a crucial role to induce the CMR in the phase competing regime. This gives a clue to enhance the CMR effect and open a way of applications in future.

4. Discussion

One of the key issues concerning the CMR phenomena in manganites is to clarify why insulating state appears at higher temperatures while metallic state exists at lowest temperatures, as mentioned in Sec. 2.1. Experimentally, charge localizations in manganites are closely related to CO fluctuations in such a way that enhancements of CO fluctuations above $T_C$ suddenly disappear below $T_C$.\cite{58,59} In order to investigate the mechanism of the CMR phenomena, it is crucial to clarify why energetically unstable charge localized states arise in the higher temperature range.

Various theories based on polaron mechanisms claim that localized polarons are formed above $T_C$ to gain energies through electron-lattice couplings, while polarons are deformed to gain kinetic energies in the FM phase below $T_C$.\cite{60-62} These scenarios do not explain why a reentrant transition from CO fluctuating region to FM phase appears in wide range of the phase diagrams where CMR is observed.

In order to understand this phenomena, the authors have proposed a scenario where the reentrant behaviors are driven by the entropy gain due to the random pinning potentials.\cite{63}

Let us consider a system where the CO phase competes with the FM phase. By adding quenched disorder, phase of the CO order parameter couples with the local pinning potentials. Since the pinning potentials are randomly distributed, phase mismatches create the domain structures. In other words, random pinning potentials introduce frustrations to the phase of the CO order parameter. Effects of the frustration is i) a destruction of the CO long range order, ii) an increase of the energy of the CO state, and iii) an increase of the entropy of the CO state.

At the same time, phase of the FM order parameter does not couple with the local pinning potentials. In the presence of the CO-FM competition, introduction of the pinning potential destroys the CO phase and replaces it with the FM phase at lower temperature range. On the other hand, at higher temperature range, the CO fluctuations is stabilized by its large entropy. This results in an entropy-driven reentrant behavior of CO fluctuations relevant to CMR, which also explains the phase diagrams of the A-site ordered/disordered manganites.

Let us now discuss from the viewpoint of designing a new material which exhibits CMR. We consider that it is necessary to introduce an insulating phase which couples with random pinning potentials in such a way that frustrations are introduced to the phase of the order parameter. Although the order parameter of the insulating phase could be anything, it is favorable if the ordering
temperature scale is high enough so that the CMR phenomena are observed from higher temperatures.

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