Perovskite manganites as spin–charge–orbital coupled systems

J. Inoue

Phil. Trans. R. Soc. Lond. A 1998 **356**, 1481-1491
doi: 10.1098/rsta.1998.0231

Perovskite manganites as spin–charge–orbital coupled systems

By J. Inoue

Department of Applied Physics, Nagoya University, Nagoya 464-01, Japan

Perovskite manganites have attracted much interest in the fields of both basic science and technological applications due to so-called colossal magnetoresistance (CMR). It is known that the electron–electron interaction and electron–lattice interaction are strong in the manganites. The former interaction brings about a strong coupling between spin, charge and orbital degrees of freedom. In this article, we present a brief review for magnetic states in the manganites with emphasis on the role of orbitals. The complicated magnetic states in the manganites could be related to the CMR effect observed in the charge-ordered phase. Charge dynamics of a hole introduced into the orbital ordered state will be briefly explained.

Keywords: colossal magnetoresistance; manganites; spin–orbit coupling; orbital ordering; charge dynamics; magnetization process

1. Introduction

Recently, the colossal magnetoresistance (CMR) in perovskite manganites has attracted much interest in the field of both basic science and technological applications. Although a large MR effect has already been reported for polycrystalline bulk samples (Matsumoto 1970; Kusters *et al*. 1989; Chahara *et al*. 1993; von Helmolt *et al*. 1993), the observation of the CMR, an order of $10^3\%$ MR ratio, in thin films of $La_{2/3}Ca_{1/3}MnO_3$ has accelerated research into CMR (Jin *et al*. 1994). Detailed study of the CMR has been performed for single crystalline samples with fine tuning of composition (Tokura *et al*. 1994; Urushibara *et al*. 1995; Schiffer *et al*. 1995). So far, three types of lattice structure have been reported to exist in perovskite manganites: a cubic-type perovskite $LaMnO_3$, a single-layer-type La_2MnO_4 and a double-layer-type $La_3Mn_2O_7$ (Moritomo *et al*. 1996). The double-layer-type manganites show CMR (Moritomo *et al*. 1996; Kimura *et al*. 1996), but the single-layer-type manganites are always insulating.

Phase diagrams obtained from resistivity measurements have been reported for $La_{1-x}Sr_xMnO_3$, $La_{1-x}Ca_xMnO_3$, $Pr_{1-x}Sr_xMnO_3$ and $Pr_{1-x}Ca_xMnO_3$ (Urushibara *et al*. 1995; Schiffer *et al*. 1995; Tomioka *et al*. 1995; Tokura *et al*. 1996; Kuwahara *et al*. 1996). In the former two manganites, the CMR is most pronounced near the ferromagnetic (F) Curie temperature T_C with composition $x \sim 0.3$. By applying the external magnetic field, the paramagnetic insulator phase just above T_C changes to a F metal phase. A characteristic of $Pr_{1-x}Sr_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ is existence of a charge-ordered (CO) antiferromagnetic (AF) phase at $x = 0.5$. The CO phase extends down to $x \sim 0.3$ in $Pr_{1-x}Ca_xMnO_3$. The appearance of the CO phase is related to the ionic radius of La, Pr, Ca and Sr (Hwang *et al*. 1995). Tokura and others (Tomioka *et al*. 1995; Tokura *et al*. 1996; Kuwahara *et al*. 1996) have shown

Phil. Trans. R. Soc. Lond. A (1998) **356**, 1481–1491
Printed in Great Britain

that the AF-CO state of $Pr_{1-x}Sr_xMnO_3$ and $Pr_{1-x}Ca_xMnO_3$ can be changed to the F metal state by the external magnetic field. This is nothing but an insulator–metal transition driven by the external magnetic fields. Thus, the CMR is realized as transitions from the paramagnetic insulators to F metals (first type) and from AF-CO insulators to F metals (second type). So, the important issues may be how the insulating phases are realized, and how they change to the F metal phase.

In addition to the CMR effect, the manganites show strong lattice distortion and complicated spin ordering (Wollan & Koehler 1955; Jirák *et al*. 1985). The undoped manganite, $LaMnO_3$, is an AF insulator with a layered spin structure which is called A-type AF. The F metal phase appears in the region of $0.1 < x \lesssim 0.5$. In the region of $0.5 \lesssim x \leqslant 1.0$, various types of AF ordering, such as, the stripe-type AF (C-type AF), usual alternate-type AF (G-type AF), and a complicated spin and charge-ordered phase, CE-type AF appear. These complicated spin orderings have been argued in terms of coupling between spin and orbital which is caused by strong Coulomb interaction between electrons (Goodenough 1955; Kanamori 1959; Kugel' & Khomskiĭ 1972).

So far two possible mechanisms have been proposed (Furukawa 1994; Millis *et al*. 1995); one is based on the so-called double-exchange (DE) interaction (Zener 1951; Anderson & Hasegawa 1955; de Gennes 1960) and the other is based upon the dynamical Jahn–Teller effect combined with the DE interaction. Inoue & Maekawa (1995) have also shown that the DE interaction may enhance the MR effect. The dynamical Jahn–Teller model with DE interaction may well account for the first type of CMR in La–$SrMnO_3$, however, the second type of CMR, change from AF-CO insulators to F metals, has not yet been well understood. It may not be unnatural to consider that the second type of CMR can be related to the complicated spin orderings in manganites.

In this paper, we will present a brief review of our work on the spin and orbital orderings in manganites. Because the Coulomb interaction has the largest energy scale (Saitoh *et al*. 1995), we first treat it properly and derive the coupling between spin and orbital in manganites (Ishihara *et al*. 1996, 1997). The spin and orbital degrees of freedom are treated on equal footing by using the exact diagonalization (ED) method with emphasis on the role of the orbitals on magnetic states of $LaMnO_3$ and 50% doped CO manganite (Koshibae *et al*. 1997, 1998). We will compare the results obtained with some new experimental ones. Next, we study the carrier dynamics of a single hole introduced into the orbital ordered state to get insight on how the A-AF state changes to the F metal state. In § 2, the basic features of the electronic state of the manganites and the model used in our work will be explained. In § 3, the effect of the orbitals on the magnetic states studied in the ED will be reviewed. The carrier dynamics in the orbital ordered state will be briefly described in § 4, followed by a short summary of the paper.

2. Electronic state and model

Because of the cubic symmetry of the octahedron of oxygen ions surrounding the Mn ion, the 3d levels of the Mn ion split into doubly degenerate e_g and triply degenerate t_{2g} states. Four 3d electrons of Mn^{3+} of $LaMnO_3$ occupy the 3d levels in accordance with the Hund rule coupling. The overlap between the t_{2g} and oxygen p-wave functions is rather weak and then the t_{2g} electrons behave as localized spins with

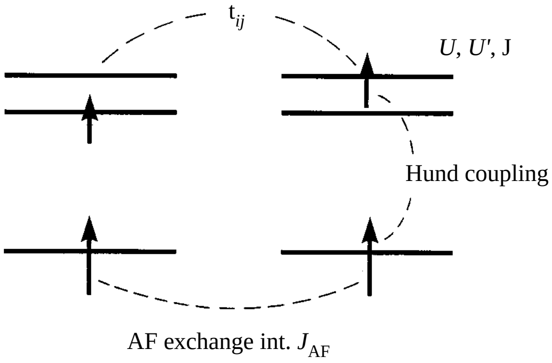

Figure 1. Schematic representation of the electronic states of Mn ions as the starting model of the present work.

$S = 3/2$. These t_{2g} spins, however, interact with each other due to virtual hopping onto the oxygen sites, resulting in a superexchange AF interaction.

On the other hand, the e_g orbitals intermix with the p-orbitals of oxygen and e_g electrons can be mobile. However, the hopping of e_g electrons is prohibited in $LaMnO_3$ due to the strong Coulomb repulsion and the Hund coupling. This leads to the AF insulator phase of $LaMnO_3$. In the case where there is only one electron per degenerate e_g state, the lattice usually tends to distort to lift the degeneracy and lower the electron energy (Jahn–Teller distortion). In the doped manganites, Mn^{4+} ions with vacant e_g states are introduced and the e_g electrons of Mn^{3+} ions become mobile so long as the Hund coupling is not violated. When the t_{2g} spins of Mn^{3+} and $Mn^{4+}$are parallel, the hopping of e_g electrons does not violate the Hund coupling, but there is a loss in the AF interaction energy between t_{2g} spins. With an increasing number of Mn^{4+} ions, the gain in the kinetic energy of e_g electrons by hopping overcomes the loss in the AF interaction energy and then the doped manganites become F metals (DE interaction).

Thus, the characteristic features of the electronic states of Mn ions are the strong Hund coupling, the degeneracy of the e_g orbitals, the hopping of e_g electrons, the AF superexchange interaction between t_{2g} spins, and the Coulomb repulsion between e_g electrons. When the double occupancy of the e_g state is prohibited by the strong Coulomb repulsion between e_g electrons, there appears an internal degree of freedom for e_g electrons to occupy either the $x^2 - y^2$ or $3z^2 - r^2$ orbital of the e_g state. In the doped manganites, there is a charge degree of freedom for e_g sites. Therefore, in manganites, the e_g electrons have three internal degrees of freedom: the spin, orbital and charge.

A naive explanation of the CMR effect may be given in terms of the DE interaction. In the paramagnetic state without the external magnetic field, the direction of the t_{2g} spins is random and the e_g electrons hardly hop to the vacant e_g state because of the strong Hund coupling. By applying a strong enough magnetic field, the spins become parallel and the e_g electrons can hop easily without violating the Hund coupling. Therefore, the mobility of e_g electrons increases, resulting in the MR effect. Recently, the dynamical Jahn–Teller lattice distortion has been added to the double-exchange interaction to obtain the quantitative explanation of the CMR effect (Millis *et al*. 1995).

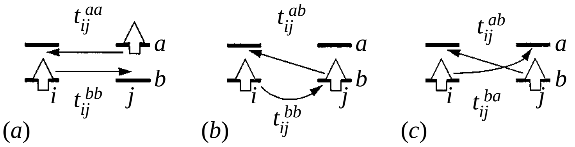

Figure 2. Typical examples of the exchange process to get the effective Hamiltonian.

Our starting model consists of the following terms (see figure 1): hopping integrals between e_g (x^2-y^2 and $3z^2-r^2$) orbitals on nearest neighbour (NN) Mn ions, the Hund coupling between itinerant e_g and localized t_{2g} spins, on-site Coulomb interaction between e_g electrons, i.e. intra-, inter-orbital Coulomb and inter-orbital exchange interactions U, U' and J, respectively, and the AF interaction between localized t_{2g} spins. Here, we consider the purely electronic part, excluding the lattice degree of freedom. As U, U' and J have the largest energy scale, we eliminate them in the second-order perturbation and obtain an effective Hamiltonian for e_g electrons which is characterized by an interaction constant $\tilde{J}$ (Ishihara *et al*. 1996, 1997). Some typical exchange processes are shown in figure 2. The effective Hamiltonian shows the strong coupling between spins and orbitals. In a limiting case where there is no hopping integral between x^2-y^2 and $3z^2-r^2$ orbitals, and that between x^2-y^2 oribitals is the same as that between $3z^2-r^2$ orbitals, the effective Hamiltonian is given as (Inagaki 1975)

$$H_{\text{eff}} = -\tilde{J}\sum_{\langle ij\rangle}(\tfrac{3}{4}n_i n_j + \boldsymbol{S}_i\cdot\boldsymbol{S}_j)(\tfrac{1}{4} - \boldsymbol{T}_i\cdot\boldsymbol{T}_j), \tag{2.1}$$

with $\tilde{J} = 4t_0^2/(U'-J)$, where t_0 is the overlap between x^2-y^2 orbitals along the x-direction. Here, n_i, $\boldsymbol{S}_i$ and $\boldsymbol{T}_i$ are the number operator, spin operator and pseudo-spin (orbital) operator for the e_g electron on site i, respectively. The coupling is F in the spin space but AF in the orbital space. This can be seen in figure 2*a* where the intermediate state is the most favourable due to the inter-orbital exchange interaction J within the e_g state.

Without the simplification to derive equation (2.1), the H_{eff} is more complicated (Ishihara *et al*. 1996, 1997) and the interaction is anisotropic because of the character of the d-orbitals. This anisotropic F interaction between e_g spins competes with the isotropic AF interaction J_{AF} between t_{2g} spins via the strong Hund coupling. In the doped manganites, the e_g electrons are mobile, which produces a double exchange-type F interaction. This F interaction is also anisotropic because the hopping of e_g electrons depends on the orbitals. Thus, the isotropic AF exchange interaction between t_{2g} spins competes with the anisotropic F interaction between e_g spins also in the doped manganites. These competitions between the anisotropic F and isotropic AF interactions are the source of the variety of the magnetic states discussed below (Ishihara *et al*. 1996, 1997; Koshibae *et al*. 1997, 1998).

3. Spin and orbital coupling

We use the ED method in order to treat the spin and orbital degrees of freedom on equal footing. We deal with three-dimensional 8-site ($2\times2\times2$) clusters with the periodic boundary condition. One should note that the proper symmetry of the system is retained only when the three dimensions are taken into account. We further

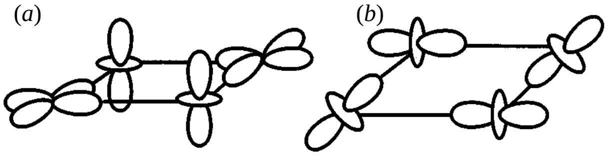

Figure 3. Orbital ordered states: (*a*) $(x^2-y^2,3z^2-r^2)$ ordering and (*b*) $(3y^2-r^2,3x^2-r^2)$ ordering.

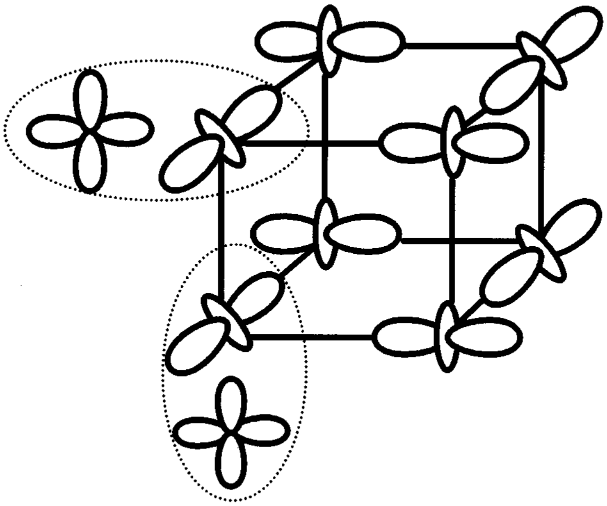

Figure 4. Orbital ordering in the A-type antiferromagnetic state. Some of the unoccupied orbitals are also shown.

make some simplifications for the effective Hamiltonian to make the ED method tractable (Koshibae *et al*. 1997). In the following, we show the calculated results and the interpretation for (i) the ground state of the insulating $\mathrm{LaMnO_3}$, (ii) the ground state of 50% doped CO phase, and (iii) the magnetization process of the latter.

The spin and orbital orderings in $\mathrm{LaMnO_3}$ have been studied by calculating the spin correlation functions $S(\boldsymbol{Q})$ with a wave vector $\boldsymbol{Q}$ and the orbital correlation functions. Types of spin ordering can be identified by the $\boldsymbol{Q}$ vector at which $S(\boldsymbol{Q})$ is maximum. As the $\boldsymbol{Q}$ vector changes from $\boldsymbol{Q}=(0,0,0),(0,0,\pi),(0,\pi,\pi)$ to (π,π,π) with increasing $J_{\mathrm{AF}}/\tilde{J}$, the spin ordering changes in order of F, A-, C-, and G-type AF.

Type of the orbital ordering can be identified by calculating the orbital correlations. In F, C- and G-type AF states, orbitals align antiferromagnetically, that is, the x^2-y^2 and $3z^2-r^2$ orbitals are occupied alternately, as shown in figure 3*a*, which is denoted as $(x^2-y^2,3z^2-r^2)$ ordering, hereafter. In the $(x^2-y^2,3z^2-r^2)$ ordering, the F coupling along the z-axis is stronger than that within the basal $(x-y)$ plane. This can be easily seen in the following way. Let us consider a situation where an x^2-y^2 orbital in the basal plane is occupied. The unoccupied orbital is then $3z^2-r^2$, which overlaps more strongly with the occupied $3z^2-r^2$ orbitals on the NN sites along the z-direction than with those within the basal plane. Therefore, the effective F interaction along the z-direction is stronger than that within the basal plane. Then, the F state naturally changes to C- and G-type AF states with increasing $J_{\mathrm{AF}}/\tilde{J}$.

In this orbital ordering, however, the A-type AF does not appear. The A-type AF occurs when the orbital ordering is rearranged to $(3y^2 - r^2, 3x^2 - r^2)$ ordering, as shown in figure 3*b*. In this orbital ordering the F interaction along the z-axis is weaker than that in the basal plane (see figure 4). Let us consider the occupied $3y^2 - r^2$ orbital. Because the unoccupied counterpart of this orbital overlaps strongly with the NN $3x^2 - r^2$ orbitals within the basal plane, the effective F interaction becomes large within the plane. In contrast, the overlap between the occupied and unoccupied orbitals along the z-direction is weak, as can be seen in figure 4. Therefore, for a relatively weak AF interaction J_{AF}, the net interaction becomes F within the basal plane, but remains AF along the z-direction. In the calculation, the orbital correlation of this ordering has actually been found to develop in the parameter region where the A-type AF is realized. In other words, the orbitals adjust themselves to lower the ground state energy by realizing four F bonds and two AF bonds in the A-type AF for small values of $J_{\mathrm{AF}}/\tilde{J}$. Thus we can conclude that these various magnetic states at zero doping may appear as a result of competition between the anisotropic F exchange interaction and the isotropic AF exchange interaction originated from the strong Coulomb interaction and the anisotropy of the 3d wave functions. Taking suitable parameter values, we can explain the A-type AF in $\mathrm{LaMnO_3}$.

Similar results have been obtained in a mean-field study for the original Hamiltonian including U, U' and J (Maezono *et al.* 1998). The orbital ordering in the A-type AF obtained, however, is not the $(3y^2 - r^2, 3x^2 - r^2)$ ordering, but an ordering of the following two orbitals,

$$\Psi_{\pm} = (|x^2 - y^2\rangle \pm |3z^2 - r^2\rangle)/\sqrt{2}. \tag{3.1}$$

In spite of the difference between these results, the interpretation for the occurrence of A-AF is unchanged.

Next, we show the results of the ground state of the 50% doped CO phase. Here, a large NN Coulomb interaction V has been introduced to realize the CO state and the value of S of t_{2g} spins is taken to be 1/2 in order to make the ED study for $2 \times 2 \times 2$ possible. With fixed values of V and t_0, the maximum value of total S_z has been calculated, from which the spin orderings have been identified. The spin ordering changes in order of F, A-AF, C-AF and G-AF(Ferri) with increasing J_{AF}. The result is similar to that obtained for $\mathrm{LaMnO_3}$.

It is interesting to note that the A-type AF structure has been observed near 50% doped manganites, for example, $(\mathrm{Nd\text{-}La})_{0.5}\mathrm{Sr}_{0.5}\mathrm{MnO_3}$ (Moritomo *et al.* 1997), $\mathrm{Nd}_{0.45}\mathrm{Sr}_{0.55}\mathrm{MnO_3}$, $\mathrm{Pr}_{0.5}\mathrm{Sr}_{0.5}\mathrm{MnO_3}$ (Kawano *et al.* 1997) and $\mathrm{Nd}_{1-x}\mathrm{Sr}_x\mathrm{MnO_3}$ (Kuwahara 1998). In $\mathrm{Nd}_{1-x}\mathrm{Sr}_x\mathrm{MnO_3}$, the F metal state for $x < 0.48$ changes to the AF-CO state at $x = 0.5$ and becomes A-AF around $x = 0.55$. For $x > 0.6$, $\mathrm{Nd}_{1-x}\mathrm{Sr}_x\mathrm{MnO_3}$ are C-AF insulators. In the A-AF state, the resistivity is quite anisotropic, i.e. the resistivity within the basal plane is much smaller than that along the z-direction. This metallic behaviour within the basal plane might be related to the orbital ordering (Kuwahara 1998).

The calculated values of S_z, that is, the magnetization, is plotted in figure 5 as a function of magnetic field H/J_{AF}. We find that there are several intermediate states in the magnetization process. The appearance of various intermediate states is due to the change in the orbital ordering. This result has been confirmed by an analysis of an Ising model for this system (Koshibae *et al.* 1998). Thus we can say that the role of the orbital is important also in the doped case. It should be noted that the

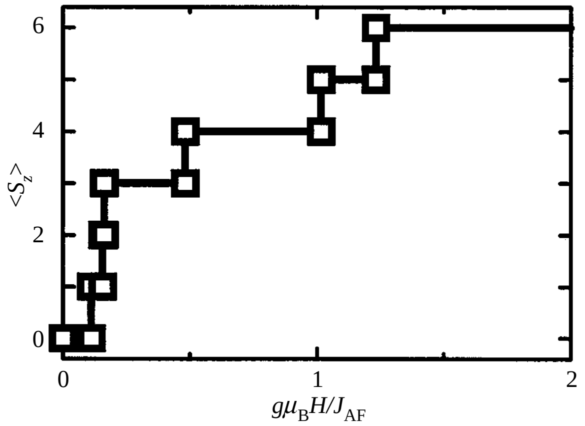

Figure 5. Calculated results of the magnetization process.

competing interactions are the AF superexchange interaction between t_{2g} spins and the DE-type anisotropic F interaction between e_g electrons. The superexchange type F interaction, which is important in $LaMnO_3$, is much weaker in the CO phase. As the DE-type F interaction comes from the motion of the e_g electrons, the magnetic states can be related to the metalicity of the system.

The magnetization process has been measured for both $Sm_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ (Tokunaga 1998). In these magnetization processes, there exist stepwise structures. At this present stage, however, we can not say whether the appearance of the intermediate state may or may not be related to the change in the orbital states. Further investigation will be interesting.

4. Carrier dynamics in the orbital ordered state

In $La_{1-x}Sr_xMnO_3$, the insulating A-AF changes to metallic F with increasing x. This change has been explained in terms of the DE interaction (Zener 1951; Anderson & Hasegawa 1955; de Gennes 1960). However, the metallic state appears only for $x >$ 0.1. Because the spins are parallel within the plane, the doped holes, i.e. the vacant e_g states, can easily travel within the planes and the manganites become metallic easily. The real situation is far from this picture. There may be several reasons for this discrepancy, for example, existence of lattice distortion and/or impurity potentials. Here, we study the effect of the orbital ordering on the dynamics of the doped hole.

We consider a single hole, a vacant e_g state, introduced into the orbital ordered state of the A-AF state with a constraint that double occupancy of e_g electrons on the same site is prohibited. The orbital ordering of the A-AF state is shown in figure 3*b*. We restrict ourselves to a motion of the hole within the basal plane for simplicity. In this case, we can eliminate the spin degree of freedom because the spins within the plane are all parallel. This kind of problem is similar to that of the t–J model. In this case, the model is a t–J model for the orbital pseudo-spins.

We use a variational method to treat the strong correlation between pseudo-spins of orbitals (Inoue & Maekawa 1990). The variational function is a Bloch function composed of a linear combination of various basis functions representing the position of the hole and orbital states surrounding it. By solving the secular equation, we obtain the energy-momentum relation $E(\boldsymbol{k})$ of the hole within the two-dimensional Brillouin zone. There are many branches in $E(\boldsymbol{k})$ because of the correlation effect between the hole motion and orbital states. We are interested in the lowest energy branch because we are dealing with the single hole problem. The lowest energy state appears at the momentum $\boldsymbol{k} = (0, 0)$. Because of the sublattice structure of the orbital ordering, the states with $\boldsymbol{k} = (0, 0)$ and (π, π) are degenerate. The bandwidth of the band is about t_0, which is narrower compared to that of $8t_0$ in the usual tight-binding model. However, it is still wider than that in the t–J model. In the t–J model, the bandwidth is of order of J. The relatively wideband width in the present model is due to the interband hopping. By this interband hopping, the hole can travel in the plane without disturbing the orbital ordering. The interesting point is that $E(\boldsymbol{k})$ depends on the type of orbital ordering. When we take an AF $(x^2 - y^2, 3z^2 - r^2)$ orbital ordering, the $E(\boldsymbol{k})$ is different from that for the A-AF orbital ordering. In this case, the lowest energy state appears at $\boldsymbol{k} = (\pi, 0)$.

The appearance of the metallic ferromagnetism in the doped manganites is still a controversial issue. The double-exchange interaction is believed to be essential for it; however, the effects of polarons and impurities have not yet been clarified. As the bandwidth of the hole in the orbital ordered state is rather narrow, as shown above, the motion of the hole can be strongly influenced by other effects, e.g. lattice polarons and imperfections. The change in the orbital state around the hole may also change the interlayer coupling between spins. Further study along this line is needed.

5. Summary

In this paper, we have reported a brief review on the role of orbitals on the magnetic state in manganites. In the insulating $LaMnO_3$ phase, the strong Coulomb interaction brings about an effective Hamiltonian which includes a coupling between spin and orbital degrees of freedom. The coupling is ferromagnetic in spin space and antiferromagnetic in orbital space. Because of the anisotropy of the 3d orbitals, the ferromagnetic interaction is anisotropic. This anisotropic interaction competes with the isotropic antiferromagnetic interaction between t_{2g} spins, which leads to occurrence of various types of spin ordering.

In the 50% doped charge-ordered phase, the double-exchange-type interaction brings about the anisotropic ferromagnetic interaction between e_g electrons, which competes with the isotropic antiferromagnetic interaction between t_{2g} spins. The competition also causes a variety of magnetic states at the ground state and in the magnetization process. Thus the orbital is crucial to the magnetic state in the manganites, and might be related to the CMR effect in a sense that many magnetic states may be realized within a rather narrow energy window.

Finally, we have studied the effect of orbital ordering on the motion of a single hole. The bandwidth of the lowest energy excitation is determined by the inter-orbital hopping and is narrower than that of the one-particle tight-banding model.

The work has been done in collaboration with S. Maekawa, S. Ishihara, W. Koshibae Y. Kawamura and S. Okamoto, and was supported by a Grant-in Aid for Scientific Research on Priority-Areas from the Ministry of Education, Science, Culture and Sport of Japan.

References

Anderson, P. W. & Hasegawa, H. 1955 *Phys. Rev.* **100**, 675.

Chahara, K., Ohno, T., Kasai, M., Kanke, Y. & Kozono, Y. 1993 *Appl. Phys. Lett.* **62**, 780.

de Gennes, P.-G. 1960 *Phys. Rev.* **118**, 141.

Furukawa, N. 1994 *J. Phys. Soc. Jpn* **63**, 3214.

Goodenough, J. B. 1955 *Phys. Rev.* **100**, 564.

Hwang, H. Y., Cheong, S.-W., Radaelli, P. G., Marezio, M. & Batlogg, B. 1995 *Phys. Rev. Lett.* **75**, 914.

Inagaki, S. 1975 *J. Phys. Soc. Jpn* **39**, 596.

Inoue, J. & Maekawa, S. 1990 *J. Phys. Soc. Jpn* **59**, 2110.

Inoue, J. & Maekawa, S. 1995 *Phys. Rev. Lett.* **74**, 3407.

Ishihara, S., Inoue, J. & Maekawa, S. 1996 *Physica* C **263**, 130.

Ishihara, S., Inoue, J. & Maekawa, S. 1997 *Phys. Rev.* B **55**, 8280.

Jin, S., Tiefel, T. H., McCormack, M., Fastnacht, R. A., Ramesh, R. & Chen, L. H. 1994 *Science* **264**, 413.

Jirák, Z., Krupička, S., Šimša, Z., Ddouhá, M. & Vratislov, S. 1985 *J. Magn. Magn. Mater.* **53**, 153.

Kanamori, J. 1959 *J. Phys. Chem. Solids* **10**, 87.

Kawano, H., Kajimoto, R., Yoshizawa, H., Tomioka, Y., Kuwahara, H. & Tokura, Y. 1997 *Phys. Rev. Lett.* **78**, 4253.

Kimura, T., Tomioka, Y., Kuwahara, H., Asamitsu, A., Tamura, M. & Tokura, Y. 1996 *Science* **274**, 1698.

Koshibae, W., Kawamura, Y., Ishihara, S., Okamoto, S., Inoue, J. & Maekawa, S. 1997 *J. Phys. Soc. Jpn* **66**, 957.

Koshibae, W., Kawamura, Y., Inoue, J. & Maekawa, S. 1998 *J. Phys. Soc. Jpn* **66**, 2985.

Kugel', K. I. & Khomskiĭ, D. I. 1972 *JETP Lett.* **15**, 446.

Kusters, R. M., Singleton, J., Keen, D. A., McGreevy, R. & Hayes, W. 1989 *Physica* B **155**, 362.

Kuwahara, H. 1998 (In the press.)

Kuwahara, H., Tomioka, Y., Moritomo, Y., Asamitsu, A., Kasai, M., Kumai, R. & Tokura, Y. 1996 *Science* **272**, 80.

Maezono, R., Ishihara, S. & Nagaosa, N. 1998 (In the press.)

Matsumoto, G. 1970 *J. Phys. Soc. Jpn* **29**, 606.

Millis, A. J., Littlewood, P. B. & Shraiman, B. I. 1995 *Phys. Rev. Lett.* **74**, 5144.

Moritomo, Y., Asamitsu, A., Kuwahara, H. & Tokura, Y. 1996 *Nature* **380**, 141.

Moritomo, Y., Kuwahara, H., Tomioka, Y. & Tokura, Y. 1997 *Phys. Rev.* B **55**, 7549.

Saitoh, S., Bocquet, A. E., Mizokawa, T., Namatame, H., Fujimori, A., Abbate, M., Takeda, Y. & Takano, M. 1995 *Phys. Rev.* B **51**, 13 942.

Schiffer, P., Ramirez, A. P., Bao, W. & Cheong, S.-W. 1995 *Phys. Rev. Lett.* **75**, 3336.

Tokunaga, M., Miura, N., Tomioka, Y. & Tokura, Y. 1998 *Phys. Rev.* B **57**, 5259.

Tokura, Y., Urushibara, A., Moritomo, Y., Arima, T., Asamitsu, A., Kido, G. & Furukawa, N. 1994 *J. Phys. Soc. Jpn* **63**, 3931.

Tokura, Y., Tomioka, Y., Kuwabara, H., Asamitsu, A., Moritomo, Y. & Kasai, M. 1996 *Physica* C **263**, 544.

Tomioka, Y., Asamitsu, A., Moritomo, Y., Kuwahara, H. & Tokura, Y. 1995 *Phys. Rev. Lett.* **74**, 5108.

Urushibara, A., Moritomo, Y., Arima, T., Asamitsu, A., Kido, G. & Tokura, Y. 1995 *Phys. Rev.* B **31**, 219.

von Helmolt, R., Wecker, J., Holzapfel, B., Schultz, L. & Samwer, K. 1993 *Phys. Rev. Lett.* **71**, 2331.

Wollan, E. O. & Koehler, W. C. 1955 *Phys. Rev.* **100**, 545.

Zener, C. 1951 *Phys. Rev.* **82**, 403.

Discussion

A. J. Millis (*Johns Hopkins University, USA*). What is seen in the phase diagram is that we have in the far left of the phase diagram a good ferromagnetic metal at low temperature, lanthanum strontium manganite. The lanthanum strontium manganite goes to a good metal from a very highly resistive state. The 50% doped material goes to an insulator from a high-temperature state which has apparently a rather lower resistance. In the half-half compound the resistivity above the charge-ordering transition temperature is small, of the order of $10^{-3}\,\Omega\,\text{cm}$, and dropping, and yet it becomes insulating at zero temperature. Whereas with the other material, the resistivity is high and increasing and yet it becomes metallic: why?

In particular, why does a low resistance state give you an insulator and a high resistance state give you a metal. The insulating phase in the praseodymium compound emerges out of an apparently metallic phase whereas the metallic phase of the lanthanum strontium material emerges out of an insulating phase. Why is it that a thing which starts out as a metal 'wants' to become an insulator at low temperature, and a thing which starts out as an insulator 'wants' to become a metal at low temperature? In other words, what is the physics that gives me charge ordering for $x > 0.5$ but no charge ordering for $x < 0.5$?

J. Inoue. That is related to the spin ordering and the hopping matrix element. In this case the bond angle of manganese–oxygen–manganese is a little bit larger as compared to this one, so that because of a subtle balance of the hopping integral this charge-ordered state appears within a very small range of concentration.

A. J. Millis. But I thought that at all $x > 0.5$ was basically a charge-ordered insulator?

J. Inoue. In this case yes it is almost always charge ordered, because the hopping integral is much smaller than, say, other interacting parameters.

D. M. Edwards (*Imperial College, London, UK*). Andy Millis asks why the material is a ferromagnetic metal for $x < 0.5$ and a charge-ordered insulator for $x > 0.5$. In the simple double-exchange model even with infinite Hund d-rule exchange J, we have shown variationally (and therefore rigorously) for local spin $S = 1/2$, the ferromagnetic state is unstable against spin reversal for 0.55, x, 0.85. For $s = 3/2$ there is a tendency to instability in a similar range, and instability does occur for smaller J. This indicates how ferromagnetism is lost but I cannot comment on charge ordering.

J. Evetts (*University of Cambridge, UK*). In the AF(A) antiferromagnetic metal, is the metallic phase highly anisotropic, almost two dimensional?

J. Inoue. Yes, it has been measured, and I think the resistivity perpendicular to the plane is 100 times larger than the resistivity along the plane.

T. Venkatesan (*University of Maryland, USA*). Following on from the previous question, in NdSrMnO, what are the lowest resistivity values in the antiferromagnetic metal phase?

J. Inoue. I cannot remember the exact values, but I think the order was 10^{-3}–$10^{-4}\,\Omega\,\text{cm}$.

P. B. Littlewood (*University of Cambridge, UK*). What might be the effect of including lattice-mediated interactions, perhaps longer-range Coulomb interactions for example, in stabilizing more complex structures or striped incommensurate phases, and how might that appear in some of these?

J. Inoue. It is quite difficult to get a complicated charge-ordered phase and the problem is, what is the long-range Coulomb interaction? To get a complicated structure it may not be sufficient to include only the long-range Coulomb interaction, or, say, some particular electron–phonon coupling. Maybe this kind of structure is eventually determined by Jahn–Teller distortions, which is quite possible, but for the moment we do not do anything.

G. A. Gehring (*University of Sheffield, UK*). Can the superposition of ferromagnetic and antiferromagnetic phases together be considered as having been seen in some of the experiments? Something which has a superposition—say a canted ferromagnet?

J. Inoue. I think the C-type structure observed so far is always insulating so there is no canted state in the C-type structure for the moment. Is that sufficient?

G. A. Gehring. There has been some neutron scattering which has seen both antiferromagnetic response and antiferromagnetic spin waves, and short-range ferromagnetic response and ferromagnetic spin waves coexisting.

J. Inoue. In this manganite the canted state is observed. I do not know if there is a report for higher temperatures where the C-type is realized.

D. Edwards. Is there any direct evidence for orbital ordering? Is it seen possibly in neutron scattering?

J. Inoue. Yes, there is an observation of the ordering in this complex structure but it is not a three-dimensional case, only a one-dimensional case using a special kind of X-ray diffraction. They observed a four-fold symmetry in the experiment and they conclude that there should be some orbital ordering, but they could not identify the type of orbital which orders.